Chapter 5

Surface Chemistry

Adsorption Isotherms, Adsorption from Solution Phase & Catalysis

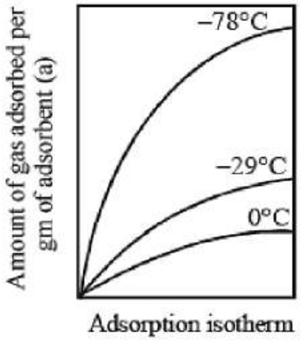
What is Adsorption Isotherm?

The variation of adsorption with pressure at a constant temperature is called adsorption isotherm. Adsorption is usually described by isotherms. It is due to the fact that temperature plays an important role or that it has a great effect on the whole process.

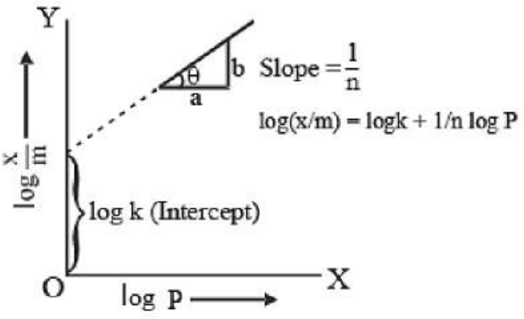
Different Isotherm Models

1. Freundlich adsorption isotherm

Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation.



Adsorption isotherm



At constant temperature $\mathbf{x/m = k \cdot P^{1/n}}$
where `x' is the mass of the gas adsorbed on a mass `m' of the adsorbent at a pressure P. k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.
At low pressure, the amount of the gas adsorbed per unit quantity of adsorbent is proportional to the pressure. At high pressure, the amount of adsorbed gas is independent of pressure. At intermediate pressures, Freundlich adsorption isotherm is expected to hold

2. Langmuir Adsorption Isotherm

According to Langmuir —

(a) There is adsorption of gas molecules on the surface of the solid.
(b) There is desorption of the adsorbed molecules from the surface of the solid.
(c) There is formation of unimolecular layer and thus it is chemisorption
(e) A dynamic equilibrium is attained when rate of adsorption = rate of desorption.
(f) Based on the above facts, langmuir adsorption isotherm is represented as

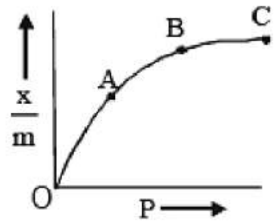
$\theta = \frac{aP}{1+bP}$, (where θ is fractional coverage)

Case-I At very high pressure

$bp >>> 1$, hence $1 + bp \approx bp$
$\therefore \theta = \frac{ap}{bp} = \frac{a}{b}$ = constant

Case-II At very low pressure

$bp <<< 1$
$1 + bp \approx 1$
$\theta = ap$,
$\theta \propto p$
This is shown along OA



3. BET theory (after Brunauer, Emmett, and Teller)

The BET theory was proposed by Brunauer, Emmett and Teller in the year 1938. This theory explains the formation of multilayer adsorption during physisorption. This theory also talks about the uniformity in the sites of adsorption of solid surfaces. It assumes that when adsorption occurs at one site it will not affect adsorption at neighbouring sites.

Adsorption from Solution Phase

Solid surfaces can also adsorb solutes from solutions.
A few examples are:

- When the litmus solution is shaken with charcoal, it becomes colourless because the dye of the litmus solution is adsorbed by charcoal.
- When the colourless Mg $(OH)_2$ is precipitated in the presence of magneson reagent (a blue coloured dye). it acquires blue colour because the dye is adsorbed on the solid precipitate. The extent of adsorption from the solution depends upon the concentration of the solute in the solution and can be expressed by the **Freundlich isotherm.** The Freundlich adsorption isotherm for the adsorption from solution is, xm = $kc^{1/n}$ where x is the mass of the solute adsorbed, m is the mass of the solid adsorbent, c is the equilibrium concentration of the solute in the solution, n is a constant having value greater than one. k is the proportionality constant, (The value of k depends upon the nature of solid, its particle size, temperature, and the nature of solute and solvent etc.) The plot of x/m against c is similar to that of the Freundlich adsorption isotherm.

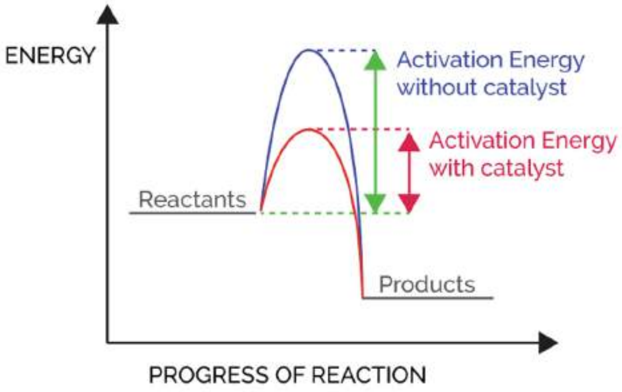
  The above equations may be written in the following form:

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

where c, is the equilibrium concentration of the solute in the solution.

Catalysis

- All reactants need to overcome certain energy, better known as activation energy in order to form products.
- This activation energy is the difference between the energy of the transition state and the reactant species. Some reactant molecules have enough kinetic energy to overcome this energy barrier whereas others don’t.
- Hence, not all reactions happen at the same rate in general conditions. Therefore, certain reagents are added which lower the required activation energy for the conversion of reactants to products.
- These reagents are known as catalysts and this process of lowering the activation energy is known as catalysis.



- Catalysis of chemical reactions increases the rate of chemical reaction with the help of a catalyst.
- Catalysts increase the rate of a reaction without undergoing any chemical or physical change.
- As discussed above, catalysts just decrease the energy barrier for the conversion of reactants to products.

Types of Catalysis

Catalysis of chemical reactions is generally divided into two categories:

- **Homogeneous Catalysis:** Homogeneous catalysis of chemical reactions is a process where the reactants involved in the reaction and the catalyst are in the same phase. For example hydrolysis of sugar in the presence of sulphuric acid.
- **Heterogeneous Catalysis:** Heterogeneous catalysis of chemical reactions is a process where the reactants involved in the reaction and the catalyst are in different phases. For example reaction of hydrogen and nitrogen in the presence of finely divided iron to form ammonia.

Mechanism of Heterogeneous Catalysis of Chemical Reactions:

The modern theory of adsorption proposed a five-step mechanism for the catalysis of chemical reactions. These steps are:

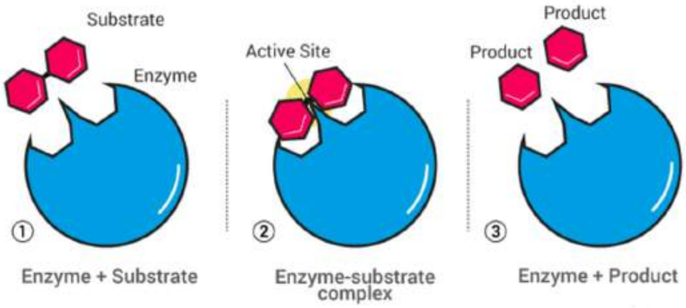
- Introduction and diffusion of reactant molecules on the catalytic surface.
- Adsorption of molecules of reactants on the catalytic surface.
- Formation of intermediate on a catalytic surface by a chemical reaction between the reactant molecules.
- Desorption of product molecules from the catalytic.

- Diffusion of product molecules away from the catalytic surface to form final products.

Mechanism of Enzyme Catalysis

- The mechanisms of enzyme catalysis usually vary in different processes. However, they are quite similar in principle to other types of chemical catalysis.
- There is a reduction of energy barrier(s), therefore, separating the reactants from the products. With reduced activation energy the fraction of reactant molecules that can overcome this barrier increases and the product is formed.
- An important factor that we need to consider is that enzymes can catalyze reactions in both directions but cannot take a reaction forward nor change the equilibrium position. The enzyme is not changed or consumed during the reaction and it can perform many catalyses repeatedly.
- Meanwhile, the most common mechanism that explains the activity of enzymatic catalysis is the lock and key mechanism.

Important concepts of lock and key mechanism:



- This mechanism exactly explains the action of an enzyme.
- The enzyme surface exactly like a key.
- Its surface has so many active centres with many fructose groups.
- Substrate molecule has a shape exactly like a lock, this enzyme fits into the substrate molecule where the exchange of functional groups takes place.
- This leads to the formation of an enzyme-substrate complex which transforms into an enzyme product complex.
- This enzyme product complex dissociates into enzyme and products.

FAQs:

1. Adsorption of gas on a solid is always exothermic explain?

Adsorption of gas on a solid is a spontaneous process. When a gas adsorbs on the solid, due to molecular interaction process, the entropy of gas molecules decreases. To make the process spontaneous, adsorption must be exothermic.

2. Among SO2, CH4, H2 gases which gas adsorbs more on the charcoal and why?
Sulphur dioxide adsorbs more than methane and hydrogen since the critical temperature of sulphur dioxide is higher than methane and hydrogen.

3. What do you mean by critical temperature? What is the relation of critical temperature and the gas adsorbed?

The temperature above which a gas cannot be liquefied even by the application of high pressure is known as critical temperature. Greater is the critical temperature (To) more in the gas adsorbed on the surface.

4. What are the factors of effective adsorption of gases on solids?

Nature of gases: Ease is liquefication more is gas adsorbed.
The surface area of adsorbent: More the surface area more gas is adsorbed.
Temperature: Physisorption increases with a decrease in temperature while chemisorption increases with an increase in temperature.
Pressure: It affects only physisorption if pressure increase amount of gas adsorbs also increase.

5. Define activation.

When adsorbents are heated in a vacuum from 573 – 623 K, the surface area is increased and it is known as activation.

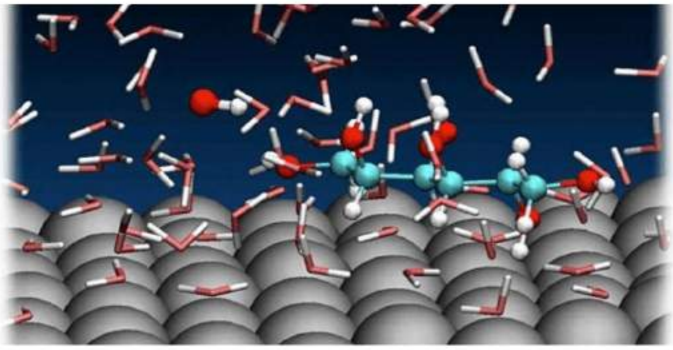
6. Write about adsorption from solutions?

Charcoal pieces are added to the acetic acid solution. Some of the acetic acid molecules adsorb on charcoal. This depends upon,

- Nature of adsorbate
- The surface area of the adsorbent
- Temperature
- Concentration

Surface chemistry is referred to as the study of the phenomenon occurring on the surfaces of substances. This is very applicable in industries and day to day lives. In other words, surface chemistry deals with all types of surface phenomenon.

What is Surface Chemistry?



It is the study of the chemical phenomena that occur at the interface of two surfaces which can be solid-liquid, solid-gas, solid-vacuum, liquid-gas, etc. Some applications of surface chemistry are known as surface engineering. There are various phenomena taking place on the surface of substances and some of them are:

- Adsorption
- Heterogeneous Catalysis
- Corrosion
- Crystallization

Applications of Surface Chemistry

In a wider perspective, surface chemistry deals with the interaction of surfaces of one system with that of the other system. Some phenomena work on this principle such as:

- Catalysis
- Colloid Formation
- Electrode Reactions
- Chromatography

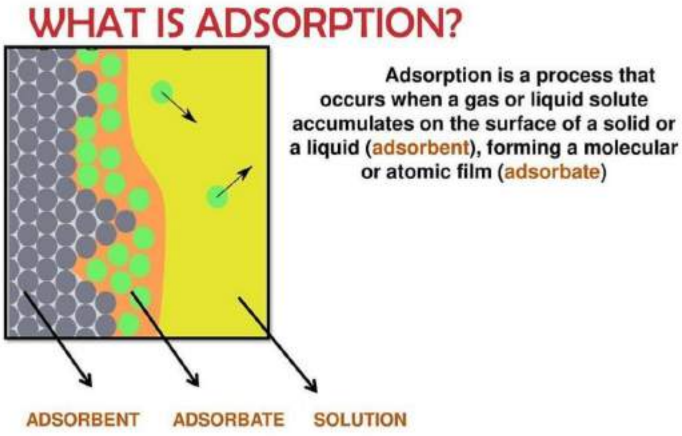
Surface Chemistry has a major role in various chemical processes such as:

- Enzymatic reactions at the biological interfaces found in the cell walls and membranes.
- In the electronics industry, they are used in the surface and interface of microchips found in computers.

- In automobile exhausts, the heterogeneous catalysts found in the catalytic converter for cleaning emissions.

Role of Adsorption in Surface Chemistry

Accumulation of species on higher concentration on the surface of a substance due to intermolecular force is known as adsorption. For Example, gases such as H_2, O_2, N_2 adsorbs on the surface of activated charcoal.



Enthalpy of Adsorption: The amount of heat energy liberated when one mole of gas is adsorbed on the unit surface area of adsorbent is known as enthalpy of adsorption.

Types of Adsorption

Due to the force of interaction between adsorbate and adsorbent, adsorption in surface chemistry is classified into two types.

1. Physical Adsorption or Physisorption

There exists a weak van der Waals force between adsorbate and adsorbent.
Characteristics:

- Nature of forces: weak van der Waals forces
- Specificity: It is not specific in nature
- Reversibility: The process is reversible
- Layer: It is a multi-layered process
- Enthalpy of adsorption: Low enthalpy of adsorption [20 – 40 KJ/mole]
- The energy of activation: Very low
- Desorption: Very easy

- Factors affecting: Surface area of adsorbent nature of adsorbate, pressure, temperature.

2. Chemical Adsorption or Chemisorption

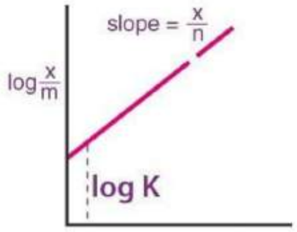
It is due to strong chemical forces between adsorbate and adsorbent.
Characteristics:

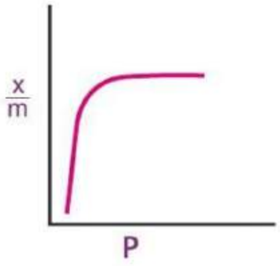
- Nature of forces: Strong chemical forces
- Specificity: Highly specific nature
- Reversibility: It is irreversible
- Layer: It is a single-layered process
- Enthalpy of adsorption: High enthalpy of adsorption [40 – 400 KJ/mole]
- The energy of activation: Very high
- Desorption: Very difficult
- Factors affecting: Surface area of adsorbent, nature of adsorbate Temperature.

Effects of Pressure and Temperature on Adsorption

1. Effect of Pressure

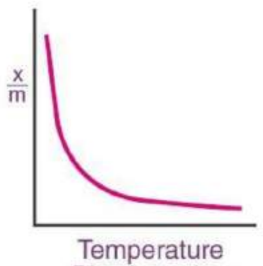
The fraction of gas adsorbed is proportional to the pressure of the gas. Adsorption increase with pressure reaches the maximum and becomes constant.



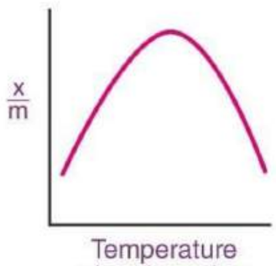


2. Effect of Temperature

- Adsorption of gases on solid is always exothermic.
- Physical adsorption follows the Lechatlier Principle, the amount of gas adsorbed decrease with the increase of temperature.
- Chemisorption increases with an increase in temperature. It reaches the maximum and then decreases.
- The curve obtained by plotting fraction of gas adsorbed and temperature at constant pressure is adsorption isobars.



Physisorption



chemisorption

Different Adsorption Isotherm Models

1. Freundlich Adsorption Isotherm

$x/m = \mathrm{K}\,[\mathrm{P}^\wedge(1/n)]$

'x' is the mass of adsorbate on the mass of adsorbent

$\Rightarrow \log \mathrm{K}/m = 1/n\,(\log \mathrm{P} + \log \mathrm{K})$

It does not apply to the adsorption of gases on solids at a higher pressure

2. Langmuir Adsorption Isotherm

- The layer of gas adsorbed on the solid adsorbent is one molecule thick.
- The adsorbed layer is uniform all over the adsorbent.
- There is no interaction between the adjacent adsorbed molecules.

Emulsions in Surface Chemistry

The colloidal solutions in which both dispersed phase and dispersion medium are liquids are called Emulsions.
Example: Paints, dyes, milk, vanishing cream. On the basis of dispersion medium emulsions in surface chemistry are classified into two types:

Oil in Water Emulsions

In this, the oil or fat droplets are dispersed in water. Example: Milk.

Water in Oil Emulsions

In this, the water droplets are dispersed in oil. Example: Vanishing cream. Emulsions are unstable, to increase the stability another substance called emulsifiers are added. Example: Milk contains natural emulsion casein.

Applications of Emulsions

- These are used in syrups

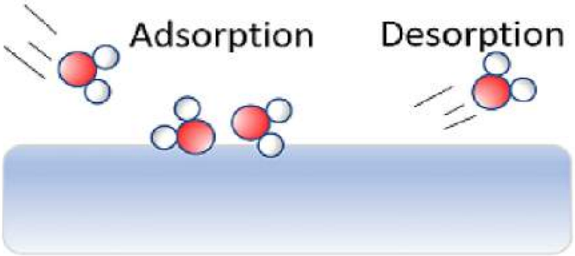
- Paints
- Toothpaste
- Digestion of fats
- Pigment and dye

Adsorption: Types, Factors & Applications

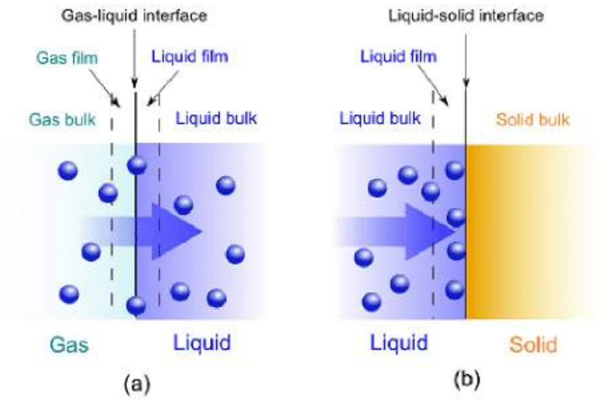
The term adsorption was first coined in 1881 by a German physicist named Heinrich Kayser. Adsorption is often described as a surface phenomenon where particles are attached to the top layer of material. It normally involves the molecules, atoms or even ions of a gas, liquid or solid in a dissolved state that is attached to the surface. Adsorption is mainly a consequence of surface energy. Generally, the surface particles which can be exposed partially tend to attract other particles to their site. Interestingly, adsorption is present in many physical, natural, biological and chemical systems and finds its use in many industrial applications.

Adsorption

- There are several examples that reveal the fact that the surface of a solid (or liquid) has a tendency to attract and retain the molecules of another immiscible phase with which it is brought into contact. These molecules remain only at the surface and do not go deeper into the bulk.
- This tendency of accumulation of molecular species at the surface than in the bulk of a solid (or liquid) is termed **adsorption**. The molecular species or substance which concentrates or accumulates at the surface is termed **adsorbate** and the material on whose surface the adsorption has taken place is called **adsorbent.**
- The reverse process i.e. removal of an adsorbed substance from the surface is called **desorption**.



- The adsorption of gases on the surface of metals is called **occlusion**.
- The term **sorption** is employed when adsorption, as well as absorption, take place simultaneously.



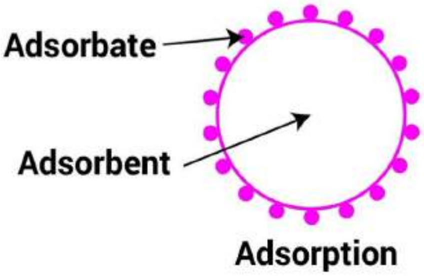
Gas-liquid absorption (a) and liquid-solid adsorption (b) mechanism. Blue spheres are solute molecules.

Adsorption is a process which involves the accumulation of a substance in molecular species in higher concentration on the surface. If we look at Hydrogen, Nitrogen and Oxygen, these gases adsorb on activated charcoal. Meanwhile, we have to note that adsorption is different from absorption. The two processes involve totally different mechanisms.

For the adsorption process, two components are required,

1. Adsorbate: Substance that is deposited on the surface of another substance. For example, H2, N2 and O2 gases.

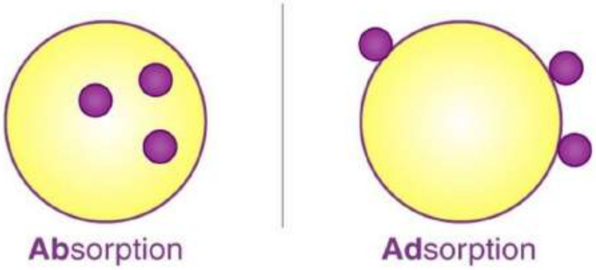
2. Adsorbent: Surface of a substance on which adsorbate adsorbs. For example, Charcoal, Silica gel, Alumina.



Distinction Between Adsorption And Absorption

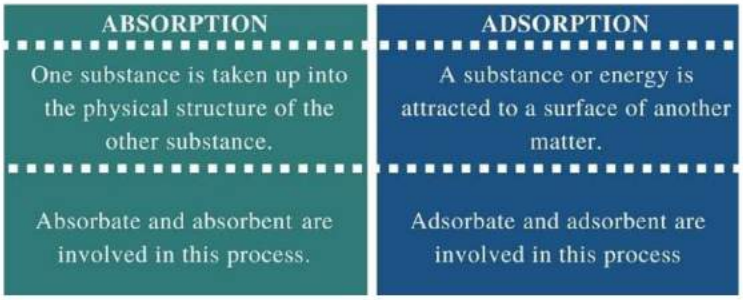
- In adsorption, the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid
- Adsorption is due to the fact that the surface particles of the adsorbent are in a different state than the particles inside the bulk. Inside the

adsorbent, all the force acting between the particles are mutually balanced but on the surface, the particles are not surrounded by atoms or molecules of their kind on all sides and hence they possess unbalanced or residual attractive forces.



- These forces of the adsorbent are responsible for attracting the adsorbate particle on its surface.
- Adsorption is a surface phenomenon, whereas absorption is a bulk phenomenon.
- Adsorption occurs only at the surface of the adsorbent, whereas absorption occurs throughout the body of the material.

Table: Difference between Adsorption and Absorption



ABSORPTION	ADSORPTION
One substance is taken up into the physical structure of the other substance.	A substance or energy is attracted to a surface of another matter.
Absorbate and absorbent are involved in this process.	Adsorbate and adsorbent are involved in this process

Mechanism of Adsorption

It is an exothermic process which means that energy is liberated during this process. The amount of heat that gets evolved when one mole of the adsorbate is adsorbed on the adsorbent is known as enthalpy. The change in enthalpy is denoted to be negative. The reason behind this is that when adsorbate molecules are adsorbed on the surface, the freedom of movement of molecules become restricted and this results in a decrease in entropy. At constant temperature and pressure, adsorption occurs spontaneously.

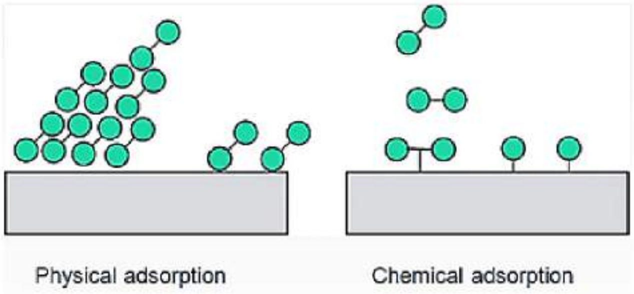
Types of Adsorption

(A) Positive and Negative Adsorption

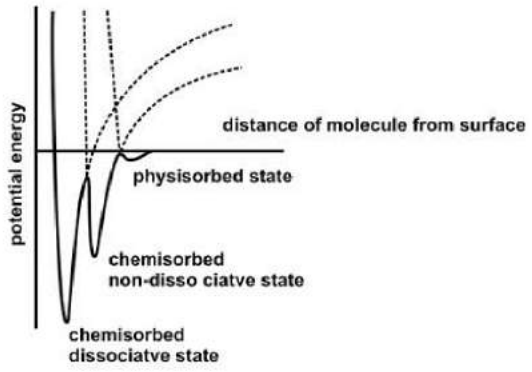
- When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is called positive adsorption.
- When the concentration of the adsorbate is less relative to its concentration in the bulk, it is called negative adsorption.

(B) Physisorption and Chemisorption

- When a gas is adsorbed at the surface of a solid by week forces (Van der Waal's forces), it is called **physical adsorption**.
- When a gas is held on the surface of a solid by forces similar to those of a chemical bond, it is called **chemical adsorption or chemiosorption.** The chemical bonds may be covalent or ionic in nature. Chemisorption has a rather high energy of activation and is, therefore, often referred to as activated adsorption.

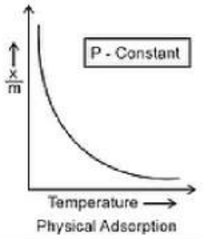
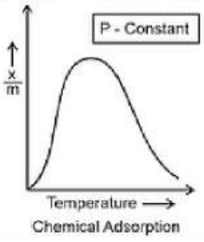


- Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption.
- Physical adsorption at low temperature may pass into chemisorption as the temperature is increased.
- For example, hydrogen is first adsorbed on nickel by van der Walls' force. Molecules of hydrogen then dissociate and hydrogen atoms are held on the surface by chemisorption.



Potential energy map of Physisorption and Chemisorption

Table: Comparison of Physisorption and Chemisorption

Physical Adsorption	Chemical Adsorption
1. It is caused by intermolecular van der Walls' 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. It depends on the nature of gas. More easily form com liquefiable gases are adsorbed readily.	It depends on the nature of gas. Gases which pounds with the adsorbent exhibit chemisorption.
5. Heat of adsorption is low.	Heat of adsorption is high.
6. Low temperature is favourable. It decreases with increase of temperature 	High temperature is favourable. It increases with increase of temperature. 
7. No appreciable activation energy is involved.	High activation energy is involved.
8. High pressure is favourable. does pressure causes desorption.	Decrease of High pressure is favourable. Decrease of pressure not cause desorption.
9. It depends on the surface area. It increases with increase of surface area.	It also depends on the surface area. It increases with increase of surface area.
10. It forms multilayers on adsorbent surface under high pressure.	It forms unimolecular layer.

Characteristics of Adsorption

1. Molecules at the surface of a solid, a metal, or a liquid experience in net inward force of attraction with free valencies.
2. Adsorption is accompanied by the evolution of heat. The amount of heat evolved when one mole of a gas is adsorbed on a solid, is known as molar heat of adsorption. Its magnitude depends upon the nature of the gas.
3. The magnitude of gaseous adsorption depends upon temperature, pressure, nature of the gas and the nature of the adsorbent.
4. Adsorption decreases with an increase in temperature since it is accompanied by the evolution of heat.
5. The adsorption increases with an increase in pressure since adsorption of gas leads to a decrease in pressure.
6. More readily soluble and easily liquefiable gases HCl, Cl_2 , SO_2 and NH_3 are adsorbed more than the so-called permanent gases such as H_2 , O_2 , N_2 etc. because Vander Waal's forces involved in adsorption are much predominant in the former gases than the latter category of gases.

Factors that affect the extent of adsorption on a solid surface

Nature of the adsorbate (gas) and adsorbent (solid)

- Porous and finely powdered solid e.g. charcoal, fullers earth, adsorb more as compared to the hard non-porous materials. Due to this property powdered charcoal is used in gas masks used in coal mines.
- Gases with high critical temperature are ads or bed at higher extent as compared to gases with lower critical temperatures.

Table: Volumes of gases at N.T.P., adsorbed by 1g of charcoal at 288 K

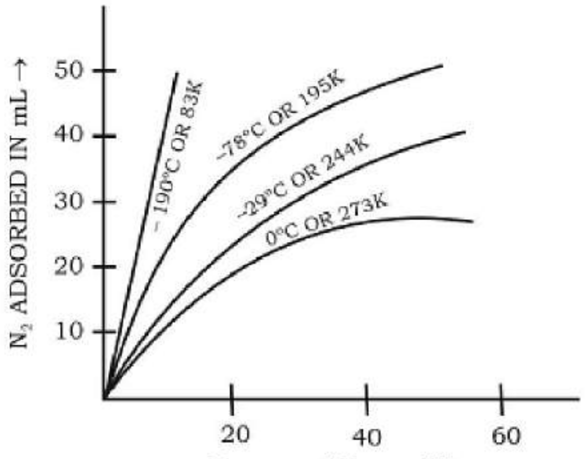
Gas	H_2	N_2	CO	CH_4	CO_2	HCl	NH_3	SO_2
Volume adsorbed (mL)	4.7	8.0	9.3	16.2	48	72	181	380
Critical temp (K)	33	126	134	190	304	324	406	430
	Critical temperature increases → **Ease of liquefaction increases →** **Adsorption increases →**							

The Surface area of the Solid Adsorbent

- The extent of adsorption depends directly upon the surface area of the adsorbent, i.e. larger the surface area of the adsorbent, the greater is the extent of adsorption.

Effect of pressure on the adsorbate gas

- An increase in the pressure of the adsorbate gas increases the extent of adsorption.
- At low temperature, the extent of adsorption increases rapidly with pressure.
- At low pressure, the extent of adsorption is found to be directly proportional to the pressure.
- At high pressure (closer to the saturation vapour pressure of the gas), the adsorption tends to achieve a limiting value.



Variation of adsorption of N_2 on charcoal with pressure at different constant temperatures

Effect of Temperature

- As adsorption is accompanied by the evolution of heat, so according to **Le-Chatelier's principle,** the magnitude of adsorption should decrease with rising in temperature.
- The amount of heat when one mole of the gas is adsorbed on the adsorbent is called the **heat of adsorption.**

Effect of adsorption from solution

- The adsorption from solutions by solid adsorbents is found to depend upon the following factors:
  (i) Nature of the adsorbate and the adsorbent.
  (ii) The adsorption decreases with **temperature.**
  (iii) Greater the **surface area of the adsorbent** greater is the adsorption.
  (iv) Concentration of the solute in the solution.

Applications of Adsorption

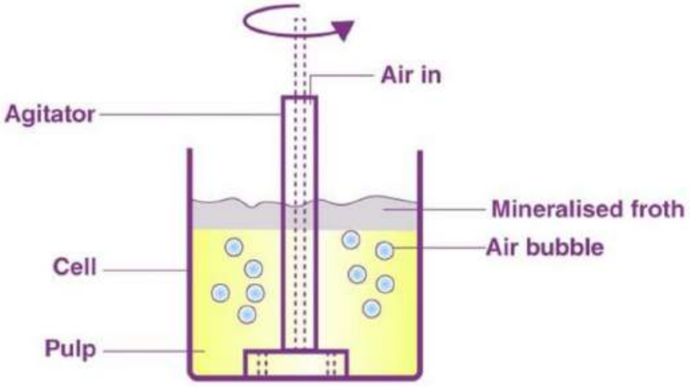
The phenomenon of adsorption finds a number of applications. Important applications are given as follows:

- **Production of high vacuum:** A bulk of charcoal cooled in liquid air is connected to a vessel that has already been exhausted as for as possible by a vacuum pump. The remaining traces of air are adsorbed by the charcoal to produce a very high vacuum.
- **In Gas masks:** It is a device that consists of activated charcoal or a mixture of adsorbents. This apparatus is used to adsorb poisonous gases (e.g. Cl_2, CO, oxide of sulphur etc.) and thus purify the air for breathing is coal mines.
- **For desiccation or dehumidification:** Certain substances have a strong tendency to absorb water such as silica and alumina (Al_2O_3). These substances can be used to reduce/remove water vapours or moisture present in the air. Silica gel is also used for dehumidification in electronic equipment.
- **Removal of colouring matter from solution:** Animal charcoal removes colours of solutions by adsorbing coloured impurities. It is also used as a decolouriser in the manufacture of cane sugar.
- **Heterogeneous catalysis:** Mostly heterogeneous catalytic reactions proceed through the adsorption of gaseous reactants on the solid catalyst.

  Examples:
  (i) Finely powdered nickel is used for the hydrogenation of oils.
  (ii) Finely divided vanadium pentaoxide (V_2O_5) is used in the contact process for the manufacture of sulphuric acid.
  (iii) Pt, Pd are used in many industrial processes as catalyst.
  (iv) Manufacture of ammonia using iron as a catalyst.
- **Separation of inert gases**
  Due to the difference in the degree of adsorption of gases by charcoal, a

mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

- **Softening of hard water**
  The hard water is made to pass through a column packed with zeolite (sodium aluminium silicate)
- **De-ionisation of water**
  For softening, water can be de-ionised by removing all dissolved salts with the help of cation and anion-exchanger resin.
- **In curing diseases**
  A number of drugs are adsorbed on the germs and kill them or these are adsorbed on the tissues and heat them.
- **Cleaning agents**
  Soap and detergents get adsorbed on the interface and thus reduce the surface tension between dirt and cloth, subsequently, the dirt is removed from the cloth.
- **Froth floatation process**

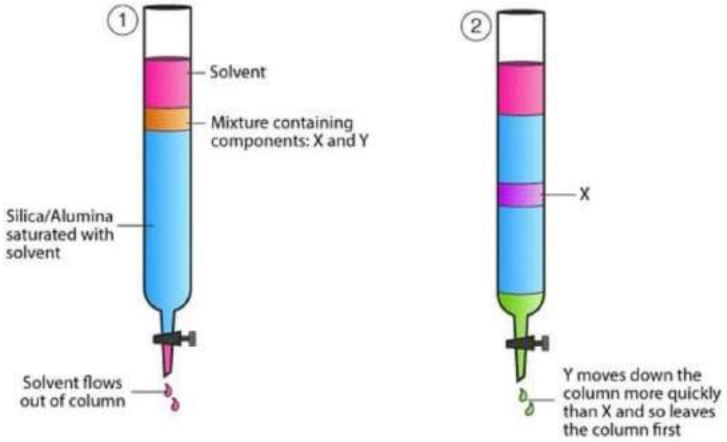


- **(i)** A low-grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method.
  (ii) The finely divided ore is added to water containing pine oil and foaming agent.
  (iii) The air is bubbled through the mixture.
  (iv) The foam formed rises to the surface on which mineral particles wetted with oil are adsorbed while earthy matter settles down at the bottom.
- **In adsorption indicators**
  The surface of certain precipitates such as silver halide has the property of adsorbing some dyes like eosin, fluorescein etc. In this case of

precipitation titrations (for example $AgNO_3$ Versus NaCl) the indicator is adsorbed at the endpoint producing a characteristic colour on the precipitate.

- **Chromatographic analysis**

  The phenomenon of adsorption has given an excellent technique of analysis known as chromatographic analysis. The technique finds a number of applications in analytical and industrial fields. The chromatographic technique is based on differential adsorption of different constituents of a mixture.



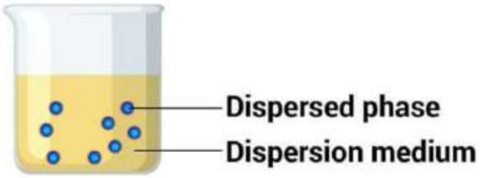
Absorption Chromatography

- **In dyeing**

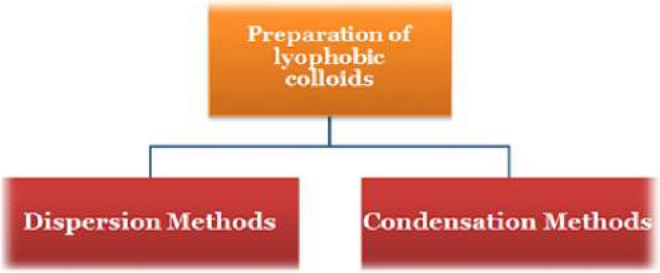
  Many dyes get adsorbed on the cloth either directly or by the use of mordants. "Catalyst is a substance which speeds up and speeds down a chemical reaction without itself being used up at the end of the reaction and the phenomenon is known as catalysis.

Preparation, Purification & Properties of Colloidal Solutions

Stable colloids are also known as lyophilic sols, in these strong forces of interaction exist between the dispersed phase and the dispersion medium. These are prepared by the following suitable methods.



Thus, there are two ways by which the lyophobic sols can be prepared:



(i) Condensation methods: By splitting coarse aggregates of a substance into colloidal size.

(ii) Dispersion methods: By aggregating very small particles (atoms, ions or molecules) into colloidal size.

Dispersion methods	Condensation methods
1. Mechanical dispersion	1. Exchange of solvents
2. Electro-dispersion state	2. Change of physical
3. Ultrasonic dispersion	3. Chemical methods:
4. Peptisation	(i) Double decomposition (ii) Oxidation (iii) Reduction (iv) Hydrolysis

Condensation Methods

1. By Exchange of Solvents

- If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility of sulphur or phosphorus is obtained due to low solubility in water.
- Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.

2. By change of physical state

Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabilizer (an ammonium salt or citrate)

3. Chemical methods

The chemical methods involve chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of supersaturation is produced but the actual precipitation is avoided.

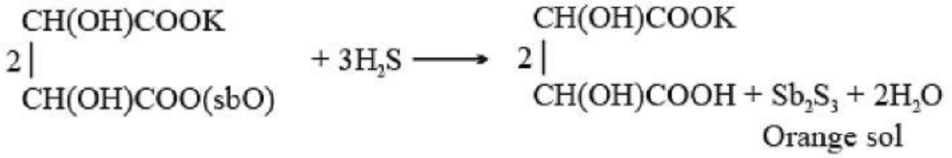
Some familiar reactions used are:

Double decomposition

(i) Arsenious sulphide sol: A 1% solution of arsenious oxide is prepared is hot water. The solution is cooled, filtered and is then gradually in hot water saturated with hydrogen sulphide. This is continued till an intense yellow-coloured solution is obtained. Excess of H_2S is removed by bubbling hydrogen through the solution.

$$As_2O_3 + 3H_2S \longrightarrow \underset{\text{Yellow sol}}{As_2S_3} + 3H_2O$$

(ii) Antimony sulphide sol: A 0.5% solution of potassium antimonyl tartrate is added drop by drop to water saturated with H_2S, whilst H2S is being passed through the solution. Orange coloured solution of antimony sulphide is obtained.



$$2\begin{array}{l}CH(OH)COOK\\|\\CH(OH)COO(sbO)\end{array} + 3H_2S \longrightarrow 2\begin{array}{l}CH(OH)COOK\\|\\CH(OH)COOH\end{array} + \underset{\text{Orange sol}}{Sb_2S_3} + 2H_2O$$

Oxidation

A colloidal solution of sulphur is obtained by passing H2O into a solution of sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

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

Reduction

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

$2AuCl_3 + 3SnCl_2 \longrightarrow 3SnCl_4 + 2Au$

Organic reducing agents such as **formaldehyde, phenylhydrazine, tannic acid**, etc., can also be used.

$AgNO_3$ + tannic acid ⟶ Silver sol

$AuCl_3$ + tannic acid ⟶ Gold sol

Hydrolysis

Colloidal solutions of some salts can be prepared by hydrolysis. A colloidal solution of ferric hydroxide is obtained by boiling a dilute solution of ferric chloride.

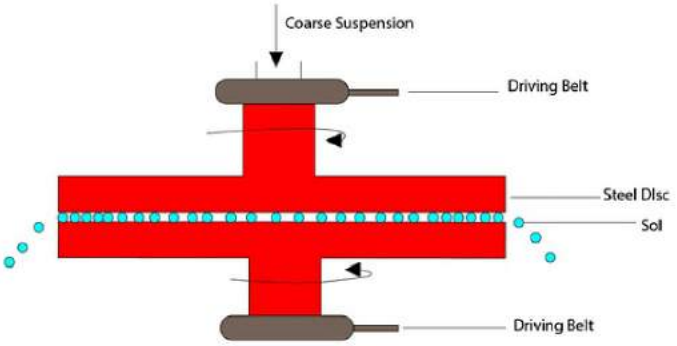
$FeCl_3 + 3H_2O \longrightarrow \underset{\text{Red sol}}{Fe\ (OH)_3} + 3HCl$

The colloidal solution of silicic acid is also obtained by hydrolysis of a dilute solution of sodium silicate with 4N hydrochloric acid which is added drop by drop with constant stirring.

Dispersion Methods

Mechanical Dispersion

- The solid material is first finely ground by usual methods. It is then mixed with a dispersion medium which gives a coarse suspension.
- The suspension is now introduced into the colloid mill. The simplest form of colloid mill consists 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.

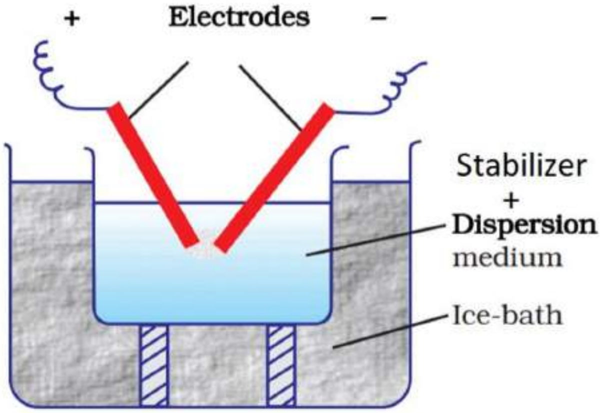


Mechanical Dispersion

- The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution.
- **Colloidal graphite** (a lubricant) and **printing ink**, are made by this method. **Tannin** is used as a stabilizer in the preparation of colloidal graphite and gum arabic in **lampblack colloidal solution** (Indian ink).

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 agents such as a track of KOH.
- The water is cooled by immersing the container in an ice bath. The intense heat of the arc vaporises some of the metal which condenses under cold water.



Note:

- This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.
- This method comprises both dispersion and condensation.

Ultrasonic Dispersion

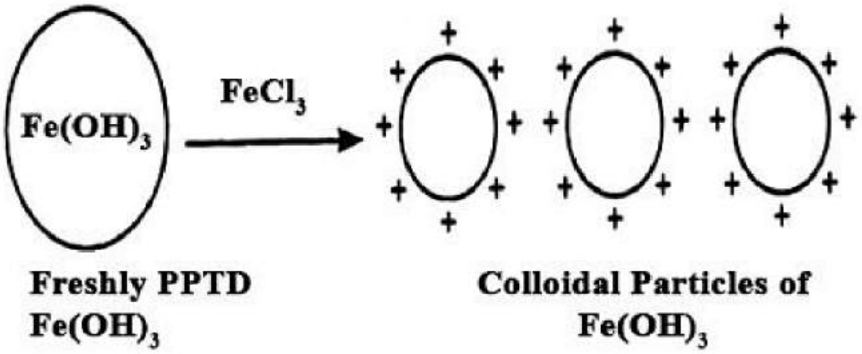
- The sound waves of high frequency are usually called **ultrasonic waves**. These waves can be produced when quartz crystal discs are connected with a high-frequency generator.

- The application of ultrasonic waves for the preparation of colloidal solutions was first introduced by **wood and Loom is, in 1927**. Various substances like oils, mercury, sulphur, sulphides and oxides of metals can be dispersed into a colloidal state very easily with the help of ultrasonic waves.

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.**
A few examples of sols obtained by peptization are:

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



Peptization

- Freshly prepared stannic oxide on treatment with a small amount of dilute hydrochloric acid forms a stable colloidal solution of stannic oxide.
- Freshly precipitated silver chloride can be converted into a colloidal solution by a small amount of hydrochloric acid.
- Cadmium sulphide can be peptized with the help of hydrogen sulphide.

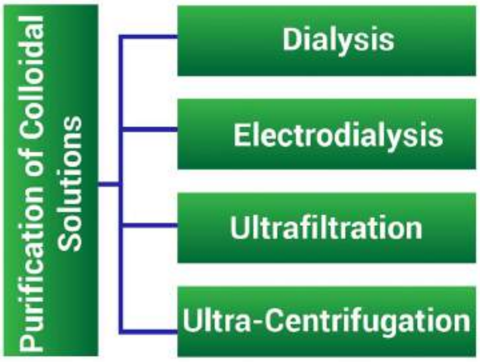
The process of peptization thus involves the adsorption of suitable ions (supplied by the electrolyte added -- particularly a common ion) and electrically charged particles then split from the precipitate as colloidal particles.

Important peptizing agents: Sugar, Gum, Gelatin & Electrolytes.

Example: Freshly prepared ferric hydroxide can be converted into a colloidal state by shaking it with water containing Fe^{3+} or OH^- or $FeCl_3$

$Fe(OH)_3 + xFe^{3+} \xrightarrow{\quad} Fe(OH)_3.xFe^{3+}$
Precipitate Peptizing agent colloid

Purification of Colloidal Solutions

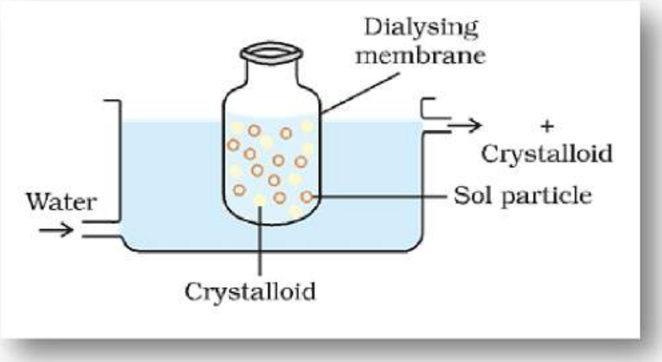


- Colloidal solutions when prepared, generally contain an excessive amount of electrolytes and some other soluble impurities.
- While the presence of traces of electrolyte is essential for the stability of the colloidal solution, larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum.
- The process used for reducing the number of impurities to a requisite minimum is known as the **purification of colloidal solution**.

The purification of the colloidal solution is carried out by the following methods:

Dialysis

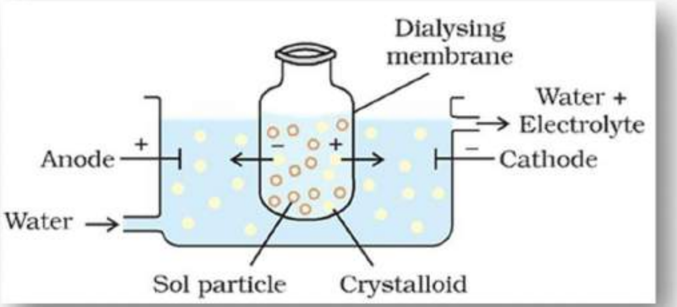
- It is a process of removing a dissolved substance from a colloidal solution **by means of diffusion** through a suitable membrane.
- Since particles (ions or smaller molecules) in a true solution can pass through animal membrane (bladder) or parchment paper or cellophane sheet but not the colloidal particles, the membrane can be used for dialysis.
- The apparatus used for this purpose is called dialyser. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing (Fig.)



- The molecules and ions diffuse through the membrane into the outer water and the pure colloidal solution is left behind.

Electro-Dialysis

- Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte.
- The process is then named **electrodialysis**. The colloidal solution is placed in a bag of the suitable membrane while pure water is taken outside. Electrodes are fitted in the compartment as shown in Fig.



- The ions present in the colloidal solution migrate out to the oppositely charged electrodes.

Ultrafiltration

- Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by **specially**

prepared filters, which are permeable to all substances except the colloidal particles.

- Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with collodion solution to stop the flow of colloidal particles.
- The usual collodion is a **4% solution of nitrocellulose** in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a collodion solution, hardening by formaldehyde and then finally drying it. Thus, by using ultra-filter paper, the colloidal particles are separated from the rest of the materials.
- Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied. The colloidal particles left on the ultra-filter paper are then stirred with a fresh dispersion medium (solvent) to get a pure colloidal solution.

Properties of Colloidal Solutions

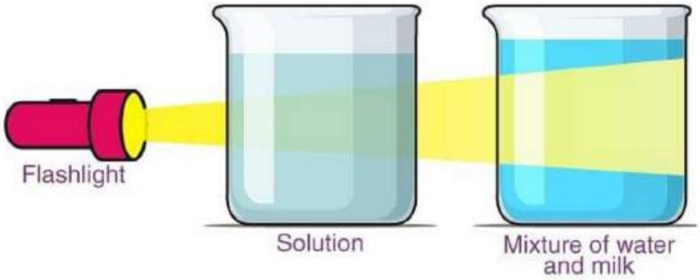
Various properties exhibited by the colloidal solutions are described below:

Colligative Properties

- Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a **true solution**.
- Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at the same concentrations.

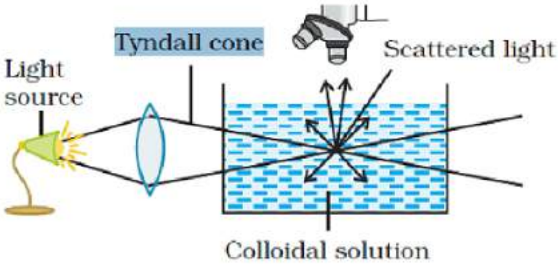
Tyndall effect

- If a homogeneous solution placed in dark is observed in the direction of light, it appears clear and, if it is observed from a direction at right angles to the direction of the light beam, it appears perfectly dark.
- Colloidal solutions viewed in the same way may also appear reasonably clear or translucent by the transmitted light but they show a mild to strong **opalescence** when viewed at right angles to the passage of light, i.e., the path of the beam is illuminated by a bluish light.



Light scattering by particles in a colloid

- This effect was first observed by **Faraday** and later studied in detail by Tyndall and is termed as the Tyndall effect. The bright cone of the light is called the Tyndall cone (Fig.).



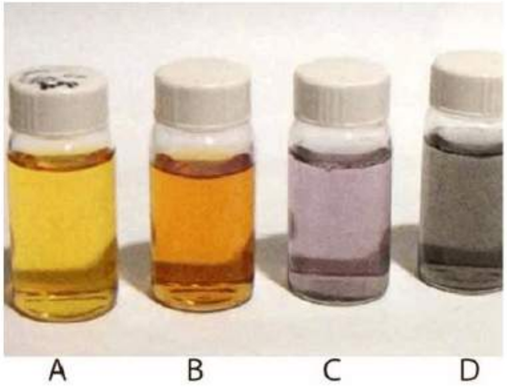
- The Tyndall effect is due to the fact that colloidal particles scatter light in all directions in space. This scattering of light illuminates the path of the beam in the colloidal dispersion.
- Tyndall effect can be observed during the projection of pictures in the cinema hall due to the scattering of light by dust and smoke particles present there.
- 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 the light used.

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

Colour

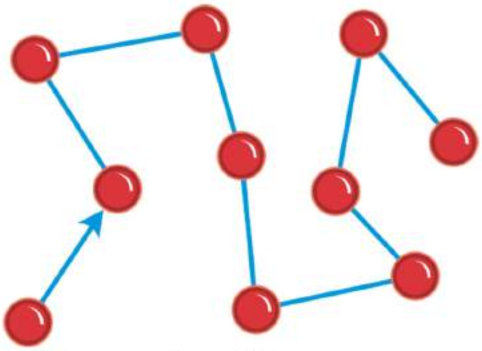
- The colour of the colloidal solution depends on the wavelength of light scattered by the dispersed particles.
- The wavelength of light further depends on the size and nature of the particles. The colour of the colloidal solution also changes with the manner in which the observer receives the light.



- For example, a mixture of milk and water appears blue when viewed by the reflected light and red when viewed by the transmitted light. The finest gold sol is red in colour; as the size of particles increases, it appears purple, then blue and finally golden.

Brownian Movement

- When colloidal solutions are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view.
- This motion was first observed by the **British botanist, Robert Brown**, and is known as **the Brownian movement** (Fig.).



Brownian Movement of a Particle

- This motion is independent of the nature of the colloid but depends on the **size of the particles** and the **viscosity of the solution**. The smaller the size and lesser the viscosity, the faster is the motion.
- The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium.

- The Brownian movement has a stirring effect that does not permit the particles to settle and thus, is responsible for the stability of sols.

Charge on Colloidal Particles

- Colloidal particles always carry an electric charge.
- The nature of this charge is the same on all the particles in a given colloidal solution and may be either positive or negative.
- A list of some common sols with the nature of a charge on their particles is given below:

Positively charged sols	Negatively charged sols
Hydrated metallic oxides, e.g., $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ and $Fe_2O_3.xH_2O$, etc. Basic dye stuffs, e.g., methylene blue sol. Haemoglobin (blood) Oxides, e.g., TiO2 sol.	Metals, e.g., copper, silver, gold sols. Metallic sulphides, e.g., As_2S_3, Sb_2S_3, CdS sols. Acid dyestuffs, e.g., eosin, congo red sols. Sols of starch, gum, gelatin, clay, charcoal, etc.

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

  AgI/I^- AgI/Ag^+
  Negatively charged Positively charged

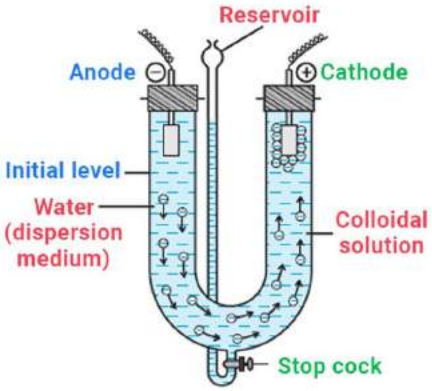
  (b) If $FeCl_3$ is added to an excess hot water, a positively charged sol of hydrated ferric oxide is formed due to the adsorption of Fe^{3+} ions. However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of OH- ions

  $Fe_2O_3.xH_2O/Fe^{3+}$ $Fe_2O_3.xH_2O/OH^-$
  Positively charged Negatively charged

- 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.
  $AgI/I^- K^+$ $AgI/Ag^+ I^-$
- The combination of the two layers of opposite charges around the colloidal particle is called Helmholtz electrical double layer. According to modern views, the first layer of ions is firmly held and is termed the fixed layer while the second layer is mobile which is termed diffused layer.
- Since the separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer result in a difference in potential between these layers. 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 particles is largely responsible in providing stability to the colloidal solution because the repulsive forces between charged particles having the same charge prevent them from coalescing or aggregating when they come closer to one another.

Electrophoresis

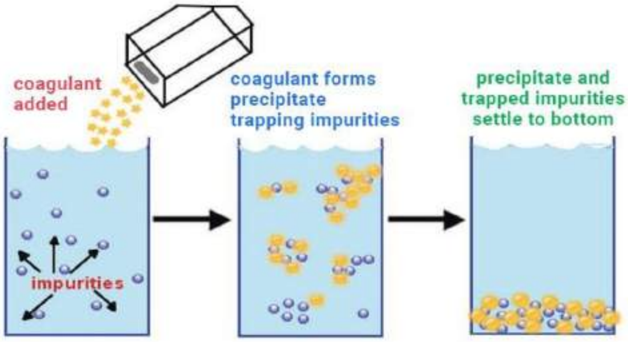
- The existence of charge on colloidal particles is confirmed by the **electrophoresis** experiment. When an electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode.
- The movement of colloidal particles under an applied electric potential is called **electrophoresis**. Positively charged particles move towards the cathode while negatively charged particles move towards the anode. This can be demonstrated by the following experimental setup (Fig.).



- When electrophoresis, i.e., movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed **electroosmosis**.

Coagulation or Precipitation

- The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If somehow, the charge is removed, the particles will come nearer to each other to form aggregates (or coagulate) and settle down under the force of gravity.
- The process of settling colloidal particles is called coagulation or precipitation of the sol.



The coagulation of the lyophobic sols can be carried out in the following ways:

(i) By electrophoresis: The colloidal particles move towards oppositely charged electrodes, get discharged and precipitated.

(ii) By mixing two oppositely charged sols: Oppositely charged sols when mixed in almost equal proportions, neutralise their charges and get partially or completely precipitated. Mixing of hydrated ferric oxide (+ve sol) and arsenious sulphide (–ve sol) bring them in the precipitated forms. This type of coagulation is called mutual coagulation.

(iii) By boiling: When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of the dispersion medium. This reduces the charge on the particles and ultimately lead to settling down in the form of a precipitate.

(iv) By persistent dialysis: On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.

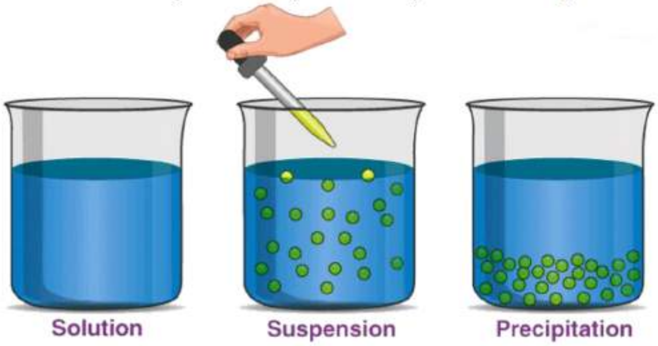
(v) By the addition of electrolytes: When an excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for the neutralisation of charge on the particles is called the coagulating ion. A negative ion causes the precipitation of positively charged sol and vice versa.
It has been observed that, generally, the greater the valence of the flocculating ion added, the greater is its power to cause precipitation. This is known as the Hardy-Schulze rule. In the coagulation of a negative sol, the flocculating power is in the order: $Al^{3+} > Ba^{2+} > Na^{+}$
Similarly, in the coagulation of a positive sol, the flocculating power is in the order: $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$
The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value. The smaller the quantity needed, the higher will be the coagulating power of an ion.

Colloids & Its Classification

What is Colloid?

A colloid is primarily a heterogeneous mixture in which the minute particles of one substance are dispersed in another substance, called the dispersion medium.

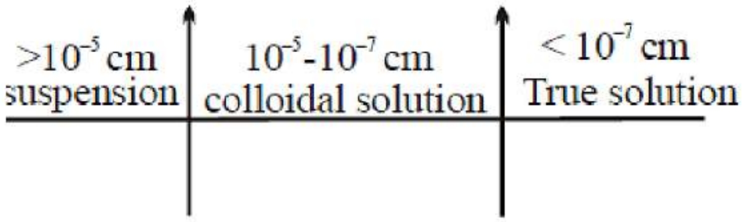
The minute particles here are 1 to 1000 nanometers in diameter but they still remain suspended and do not settle at the bottom of the mixture. They are visible under an optical or an electron (smaller particles) microscope.



The distinction between True Solution, Colloidal Solution & Suspension

Name of property	True solution	Colloidal solution	suspension
1. Particle size	$< 10^{-7}$ cm	10^{-7} to 10^{-5} cm	$> 10^{-5}$ cm
2. Visibility	Not visible with any of the optical means	Images are visible under an Ultra microscope	visible with the naked eye
3. Separation with filter	Not possible	Not possible	Possible
4. Diffusion	Diffuses readily	Diffuse very slowly	Does not diffuse
5. Nature	Homogeneous	Heterogeneous	Heterogeneous
6. Setting	Does not settle	Settle under centrifuge	Settles under influence of gravity
7. Tyndall effect	Does not show	Shows	May or may not show
8. Brownian movement	Does not show	Shows	may show

Particle size:

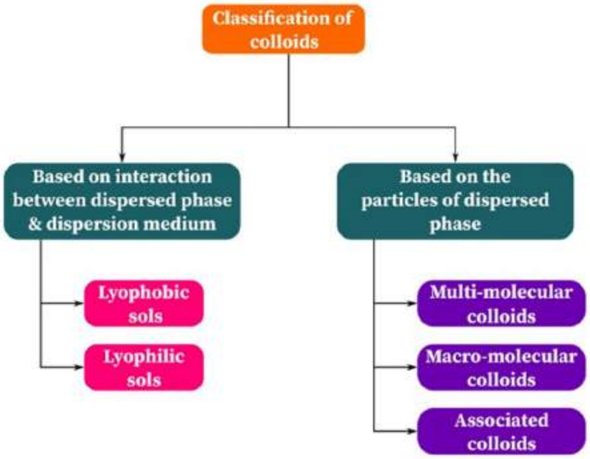


Dispersed Phase and Dispersion Medium

A colloidal system is heterogeneous in character. It consists of two phases, namely a dispersed phase and a dispersion medium.
(a) **Dispersed Phase (DP):** It is the component present in small proportion and is just like a solute in a true solution. For example, in the colloidal state of sulphur in the water, the former acts as a dispersed phase.
(b) **Dispersion Medium (DM):** It is normally the component present in excess and is just like a solvent in a solution.
The particles of the dispersed phase are scattered in the dispersion medium in a colloidal system.

Classification of Colloids

Colloids can be classified in a number of ways based upon some of their important characteristics.



Based on Interaction between Dispersed Phase and Dispersion Medium:

On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types :

1. Lyophobic colloids: The colloidal system in which the dispersed phase has no affinity for the dispersion medium are called lyophobic (solvent hating) colloids. They are easily precipitated (or coagulated) on the addition of small amounts of the electrolyte, by heating or by shaking. They are less stable and irreversible. When the dispersion medium is water, these are known as hydrophobic colloids. Examples of lyophobic colloids include sols of metals and their insoluble compounds like sulphides and oxides.
The essential differences between the lyophilic and lyophobic colloids are summarised in the table.

2. Lyophilic Colloids: The colloidal system in which the particle of dispersed phase has great affinity for the dispersion medium, are called lyophilic (solvent-loving) colloids. In such colloids, the dispersed phase does not get easily precipitated and the sols are more stable. Such colloidal systems, even if precipitated, may be reconverted to the colloidal state by simply agitating them with the dispersion medium. Hence lyophilic colloids are reversible. When the dispersion medium is water, these are called hydrophilic colloids. Some common examples of lyophilic colloids are gum, gelatin, starch, rubber, proteins, etc.

Difference between Lyophilic and Lyophobic Sols

	Property	*Lyophilic sols/hydrophilic*	*Lyophobic/hydrophobic sols*
1.	Nature	Reversible	Irreversible
2.	Preparation	They are prepared very easily by shaking or warming the substance with dispersion medium. They do not required any electrolyte or stabilization.	They are difficult to prepare, Special methods are used. Addition of stabiliser is essential for their stability.
3.	Stability	They are very stable and are not easily coagulated by electrolytes.	They are generally unstable and get easily coagulated on addition of electrolytes.
4.	Charge	Particles carry no or very little charge depending upon the pH of the medium.	Colloidal particles have characteristic charge (positive or negative)
5.	Viscosity	Viscosity is much higher than that of the medium.	Viscosity is nearly the same as that of the medium
6.	Surface Tension	Surface tension is usually less than that of the medium.	Surface tension is nearly the same as that of the medium.
7.	Migration in electric field	The particles may or may not migrate in an electric field.	The colloidal particles migrate either towards cathode or anode in an electric field
8.	Solvation	Particles are heavily solvated.	Particles are not solvated.
9.	Visibility	The particles cannot be seen under ultra microscope.	The particles though invisible, can be seen under ultra microscope.
10.	Tyndall effect	Less distinct.	More distinct.
11.	Action of electrolyte	Large amount of electrolyte is required to cause coagulation.	Small amount of electrolyte is sufficient to cause coagulation.
12.	Examples	Mostly organic substances e.g. starch, gums, proteins, gelatin, rubber etc.	Generally inorganic substance e.g., metal sols, sulphides and oxides sols.

Based on the type of particles of the Dispersed Phase

Depending upon the molecular size, the colloidal system has been classified into three classes:

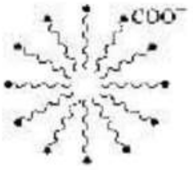
1. Multimolecular colloids: The multimolecular colloidal particles consists of an aggregate of atoms of small molecules with diameters less than 10^{-9} m or 1 nm.
For example, a sol. of gold contains particles of various sizes having several atoms. A sol. of sulphur consists of particles containing a thousand or so S_2 molecules. These particles are held together by Vander Waal's forces. These are usually lyophobic sols for example gold sol.

2. Macromolecular colloids: The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varying from thousands to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose, and proteins. Artificial macromolecules are such as polyethylene, nylon, polysyrene, dacron, synthetic rubber, plastics, etc. The size of these molecules is comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resembles true solutions in some respects. For example - Starch, cellulose, proteins, and enzymes.

3. Associated colloids or micelles: These colloids behave as normal electrolytes at low concentrations but colloids at higher concentrations. This is because, at higher concentrations, they form aggregated (associated) particles called miscelles. Soap and synthetic detergents are examples of associated colloids. They furnish ions that may have colloidal dimensions.
$RCOONa$ - $RCOO^{-}$ Na
Sod. Stearate soap $= (R = C_{17}H_{35})$
The long-chain $RCOO^{-}$ ions associate or aggregate at higher concentrations and form miscelles and behave as colloids. They may contain 100 or more molecules. Sodium stearate $C_{17}H_{35}COONa$ is an example of an associated colloid. In water, it gives Na and sterate, $C_{17}H_{35}COO^{-}$ ions. These ions associate to form miscelles of colloidal size.
Colloids that behave as normal electrolytes at low concentration, but exhibit colloidal properties at higher concentration due to the formation of aggregated particles called micelles are referred to as associated colloids. The micelles are formed by the association of dispersed particles above a certain concentration and a certain minimum concentration is required for the process of aggregation to take place. The minimum concentration required for micelle formation is called micellisation concentration (CMC) and its value depends upon the nature of the dispersed phase. For soaps, CMC is 10^{-3} - 10^{-4} M.

Mechanism of Micelle Formation

Micelles are formed by surface-active molecules called surfactants such as soaps and detergents. These molecules have the lyophilic group at one end and a lyphobic group at the other end. Let us take the example of a soap (say sodium oleate, $C_{17}H_{33}COO^{-}Na$). The long hydrocarbon part of oleate radical ($C_{17}H_{33}$ -) is lyophobic end while COO^{-} part is the lyophilic end. When the concentration of the solution is below its CMC, sodium oleate behaves like a normal electrolyte and ionizes to give $C_{17}H_{33}COO^{-}$ and Na ions. When the concentration exceeds CMC, the lyophobic part starts receding away from the solvent and tends to approach each other. However, the polar COO^{-} ends tend to interact with the solvent (water). This finally leads to the formation of bigger molecules having the dimensions of colloidal particles. Thus 100 or more oleate ions are grouped together in a spherical way keeping their hydrocarbon parts inside and the -COO^{-} part remains projected in water.



Based on Physical state of Dispersed Phase & Dispersion Medium

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids, or gaseous, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and not a colloidal system. Typical examples of various types along with their characteristic names are given in the table.

Common Colloidal System

DP	*DM*	*Colloidal system*	*Examples*
Gas	Liquid	Foam or froth	Soap sols, lemonade froth, whipped cream.
Gas	Solid	Solid foam	Pumice stone, styrene, foam, foam rubber.
Liquid	Gas	Aerosols of Liquids	Fog, clouds, fine insecticide spray, mist.
Liquid	Liquid	Emulsions	Milk, hair cream
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies, curd.

Solid	Gas	Aerosols of Solid	Smoke, dust
Solid	Liquid	Sols	Most paint, starch dispersed in water, gold sol, muddy water, cell fluids, inks.
Solid	Solid	Solid sols	Ruby glass, some gem stones.

Based on Dispersion Medium

1. Water: Hydrosols
2. Alcohol: Alcohols
3. Gases: Aerosols
4. Benzene: Benzosol
5. Solid: Gel

Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperatures and low concentrations of gelatin, the colloid is a hydrosol. But at low temperature and high gelatin concentration, the hydrosol can change into a gel.

Examples of Colloids

Examples of Colloid Solutions

The use of colloids vs crystalloids is still very specifically controversial. A colloid preferred by a physician or basically a plasma expander may work better if colloids are present instead of crystalloids. Many of the colloids might contain albumin which has osmotically equal to plasma and 25% of solutions.

Colloids help in pulling fluid into the bloodstream. Their effects last several days if the lining of the capillaries is found to be normal.

Most of these colloid solutions have the following characteristics.

- Thermal kinetic energy helping the mobility
- The inertial effect's absence from fluids
- Now or negligible gravitational effects
- The type of interactions due to electromagnetic radiation
- Closer at home we get to see milk which is considered to be the best example of colloid, the shampoo that we get to use, liquid hand wash we use and moreover, the liquid metal polisher we usually use at home.

Examples of Colloids in Chemistry

Foam

Milk

Smoke

Detergents

Gel

Blood

Paint

Cosmetics

The properties of colloidal dispersions are closely linked to the high surface area of the dispersed phase and the chemistry of these interfaces. This natural combination of colloid and surface chemistry represent a major research space and we get to see a variety of categories of colloids based on these basic properties.

Examples: fog, smog, and sprays

- The dispersed phase for the above examples is liquid and a dispersion medium of gas. These are usually termed as liquid aerosol.

Examples: smoke and dust in the air

- The dispersed phase for the above-mentioned examples is solid and the dispersion medium is gas. This is termed a solid aerosol.

Examples: milk and mayonnaise

- The dispersed phase for the above-mentioned examples is liquid and the dispersion medium is liquid as well. The term used for these is emulsion.

Examples: pigmented plastics

- The dispersed phase for the above-mentioned example is solid and the dispersion medium is solid as well. The term used for such a mix is solid suspension.

Examples: silver iodide sol, toothpaste, and Au sol

- The dispersed phase for the above-mentioned examples is solid and the dispersion medium being liquid. The term used for such colloidal solution paste at high temperature is sol.

The huge difference in surface area of colloids and surface of attachments follows the natural fact that particulate matter has a high surface area to mass ratio. This leads to one of the properties of the surface as a factor for colloidal solutions.
For example, the molecules of organic dye or pollutants can possibly be removed effectively from water by the method of adsorption onto particulate activated charcoal. This is because of the coal's high surface area. This property and process are widely used for water purification and all kinds of oral treatments.
Molecules in the bulk of liquid can interact via attractive forces with many nearest neighbors than those at the surface. The molecules at the surface must have higher energy than those in bulk as they are partially freed from bonding with neighboring molecules.
Work must be done to take fully interacting molecules from the bulk of liquid to create any new surface. This gives rise to surface energy or tension of a liquid and hence stronger the molecular force between liquid molecules the greater will be the work done.

Types of Colloids and Examples

Colloids are classified according to the state of the dispersed phase and the dispersion medium.

- Any colloid with water as the dispersing medium can be classified as hydrophobic or hydrophilic.
- A hydrophobic colloid is one in which only weak attractive forces exist between the water and the surface of the colloidal particles.
- The best example would the precipitation of silver chloride and the result ends up as colloidal dispersion. The precipitation reaction occurs too rapidly for ions to gather from long distances and make large crystals. The ions aggregate to form small particles that remain suspended in the liquid.
- A stable hydrophobic colloid can be made to coagulate by introducing ions into the dispersing medium.
- For example, the milk which contains a colloidal suspension of protein-rich casein micelles with a hydrophobic core. When milk ferments the lactose is converted to lactates and hydrogen ions. The protective charge on the surface of the colloidal particles are overcome and the milk coagulates forming clumps of curds.

- Similarly, soil particles are often carried by water in rivers and streams as hydrophobic colloids. Finally, when the river meets the seawater which has a high concentration of salts the particles coagulate to form silt at the basin of the river.
- Even the municipality water treatment plants often add salts such as aluminium sulphate to clarify water, where aluminium ions hydrated cations neutralize the charge on hydrophobic colloidal soil particles causing these particles to aggregate and settle out.
- In all of these specific cases, the liquid is strongly absorbed on to the surface of particle which makes the interface between particle and liquid similar to the interface between liquid and itself. This makes the system intrinsically stable as there is a reduction in Gibbs free energy when the particles are dispersed.

Examples of Colloids in Daily Life

There is a huge number of products that we get to use either directly or indirectly on a daily basis. Some of these products are quite relevant to our life. Rest are although used in some way or other, we never get to see them in our immediate surroundings.
The examples of colloids that we usually find around us are as follows.

1. Liquid aerosol

- The aerosol sprays that we either use as personal perfumatory products usually contain aerosol
- The various types of insecticide spray or repellents we use against mosquitoes and other insects
- Smog or the smoke and fog combination creates a thick slowly moving colloidal material. Naturally occurring fog and clouds

2. Solid aerosol

- The naturally occurring smoke or man-made fire smoke carries suspended particles in the air
- Dust storm or simply dust in the atmosphere

3. Foam

- The shaving cream lather used for shaving purpose
- The whipped cream we get to see in cream batter

4. Emulsion

- Various types of cosmetic lotions we use on a daily basis
- Mayonnaise we use as bread spread
- Naturally occurring milk

5. Gels

- The butter that we usually use as bread spread
- Jelly products that we use as various spreads

6. Sols

- Man-made paints
- Ink and other products which are basically combination made at a high temperature

7. Solid sols

- Various products made from Styrofoam, insulation, and other cushion materials
- Apart from the above-mentioned list, there are many bio colloids which we get to see on a daily basis like medicines and injectables

Examples of Colloids in Medicine

- Colloids are considered as very good intravascular volume expanders. These are fluids containing high molecular weight substances that usually do not pass through capillary membranes.
- The colloid osmotic pressure these materials exert is related to the size of the molecule. Smaller the size of molecule, higher is the initial oncotic pressure as smaller molecules fit in a volume of fluid than larger molecules.
- As the molecules become larger it lasts longer. For example, synthetic products like dextran and hydroxyethyl starches and haemoglobin based oxygen-carrying solutions along with natural colloids like plasma, whole blood and human serum, etc.
- Usually, the colloids used in the medicinal field are isosmolar and have the potential to cause allergic reactions in body but clinically these appear to have limited exposure to such synthetic ones.
- Daltons are considered to be potent colloids but are not long-lasting. They have no direct effects on the coagulation of platelets. Dextrans are polysaccharides produced by the bacterium in sucrose media. Due to many particles per unit volume, Dex 40 has a better oncotic pull than Dex 70.

- Hydroxyethyl starch is made from maize or sorghum which is primarily amylopectin and can expand almost 1. 4 times the volume infused and is hence used for anti-inflammatory uses and for better capillary permeability.
- The infusion of synthetic colloids begins when a patient has gone through acute hemorrhage or loss of albumin. Synthetic colloids are given as slow intravenous push as patients in shock require sustained intravascular volume expansion.

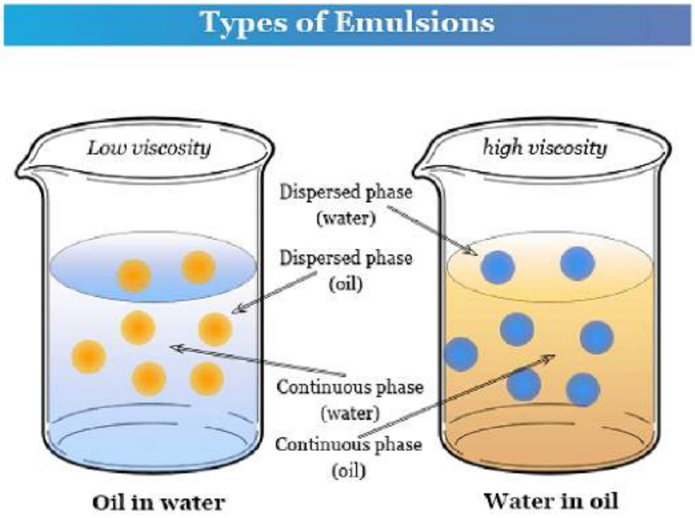
Emulsions & Colloids Around Us

Emulsions

An emulsion is a colloidal solution of a liquid. It may be defined as a heterogeneous system consisting of more than one immiscible liquids dispersed in one another in the form of droplets whose diameter, in general, exceeds 0.1 m.

For example, milk is an emulsion in which small drops of liquid fat are dispersed in aqueous medium. Cod liver oil is an emulsion in which the water drops are dispersed in the oil. This means in most of the emulsions one of the liquid is water and the other liquid is oil. Here the term 'oil' is used to represent all organic substances which are soluble in water.

Types of Emulsions



(1) **Oil in water type emulsion (O/W)***:* In this emulsion, oil is the dispersed phase and water is the dispersion medium. It is denoted by O/W or O in W. For example, milk (liquid fat dispersed in water), vanishing cream, etc.

(2) **Water in oil type:** In this emulsion, water is the dispersed phase and oil is the dispersion medium. It is denoted by W/O or W in O. For example, butter, cod liver oil, cold cream, etc.

The type of emulsion obtained by agitating two immiscible liquids depends upon the relative amounts of two components liquids. The liquid that is in excess forms the dispersion medium. Thus, the two types of emulsions can be inter-converted into each other by changing the concentration of one of the liquids.

The distinction between two types of Emulsions

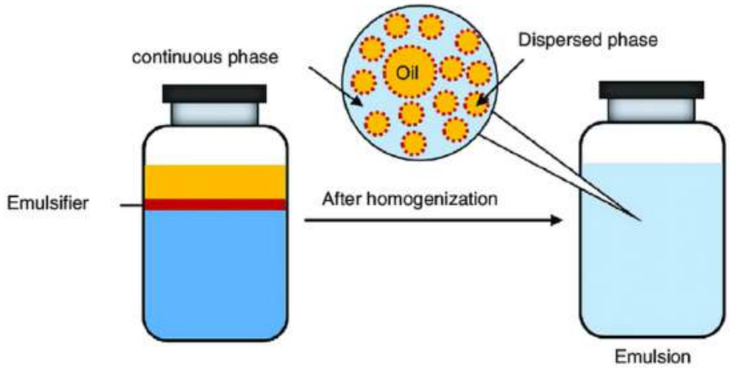
The two types of emulsions may be distinguished from each other in a number of ways.

(1) **Dye test:** It involves the addition of oil soluble dye to the emulsion under experiment. If the emulsion acquires the colour of the dye readily, it is water-in-oil type emulsion and it the emulsion remains colourless, it is oil-in-water type emulsion.

(2) **Conductivity test :** It involves the addition of electrolyte to the emulsion under experiment. If the conductivity of the emulsion increases appreciably with the addition of electrolyte, it is
oil-in-water type emulsion and it conductivity is very small, it is water-in-oil type emulsion.

(3) ***Dilution test:*** As a general rule, an emulsion can be diluted with the dispersion medium while the addition of the dispersed phase forms a separate layer. Thus, if an emulsion can be diluted with oil, it is a water-in-oil type.

Preparation of emulsion (Emulsification)



Emulsification is the process which involves the preparation of emulsion. Generally, an emulsion is prepared by subjecting a mixture of the immiscible liquid to a distinct layers upon standing. The oil globules rise to form an upper layer while aqueous medium forms lower layers. To prevent the separation of layers and to get the stable emulsion, a small quantity of the third substance is added. This substance that stabilizes the emulsion is called *emulsifier* or *emulsifying agent*. The commonly used emulsifying agents are soaps, detergents and lyophilic colloids. Casein, a lyophilic colloid present in milk, acts as an emulsifier as it forms a protective layer around fat molecules dispersed in water. Hence milk is a fairly stable emulsion.

Function of Emulsifier

The main function of emulsifier or emulsifying agents is to lower the interfacial tension between oil and water and thus helps the intermixing of two liquids. For example, a molecule of a soap or detergent (emulsifier) gets concentrated at the interface between oil and water. The polar end of the emulsifier is in water and non-polar end is in oil as shown in figure.

In a soap, RCOONa, R is the non-polar end, whereas COO^{-} Na is the polar end.

Properties of Emulsion

(i) The size of particles of the dispersed phase of an emulsion is usually larger than in sols.

(ii) Like colloidal particles, emulsions exhibit properties such as Tyndall effect, Brownian movement (provided the particles are not too large), electrophoresis, coagulation, etc.

Demulsification

The process which involves the breaking of an emulsion into two separate liquid layers is called demulsification. The following methods may be used to bring demulsification:

(1) **Chemical Methods***:* An emulsion may be demulsified by adding a chemical substance whose action on the dispersed phase and the dispersion medium is opposite to that of the original emulsifying agent used to produce the stable emulsion.

(2) **Centrifugation***:* Cream is separated from milk by the centrifugal method.

(3) **Cooling***:* Fat can be removed from milk by keeping it in a refrigerator for a few hours.

Demulsification

Besides the above noted methods of demulsification, the following methods have also been developed:

(i) Suitable centrifugal action-milk cream is separated from milk by centrifugation.

(ii) Application of electric field-electrophoresis.

(iii) Addition of an electrolyte having multivalent opposite charge than that on the dispersed phase.

(iv) Chemical destruction of stabiliser.

(v) Distilling off of one of the components, usually water.

(vi) Addition of demulsifiers like alcohol, phenol etc.

Use of Emulsions

(1) Many pharmaceutical preparations-medicines, ointments, creams and various lotions are emulsions. It is believed that medicines are more effective and easily assimilated by the body tissues when they are in colloidal form i.e., emulsion.

(2) All paints are emulsions.

(3) The digestion of fat in the intestines is helped by emulsification. A little of the fat forms a medium soap (emulsifier) with the alkaline solution of the intestine and this soap emulsifier the rest of the fats, thus making it easier for the digestive enzymes to do their metabolic functions.

(4) Soaps and detergents remove dust and dirt from the dirty piece of cloth by making an oil in water emulsion.

(5) Milk is an emulsion of liquid fats in water.

(6) In the process of metallurgy, one of the important steps is the concentration of ore which is usually done by froth floatation process in which an oil is added to the finely-divided ore taken in water. The particles of ore go on the surface due to formation of foams while the other impurities are left at the bottom of the vessel.

(7) The emulsion of asphalt in water is used in road making and building.

Gels

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium are called gels. The common examples are : boot polishes, jelly, gum arabic, agar agar, processed cheese and silicic acid.

When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids with accumulate on its surface. This action of gels is known as Synresis or Weeping. Some gels such as silica, gelatin and ferric hydroxide liquify on shaking and reset on allowing to stand. This phenomenon of Sol-gel transformation is called thixotropy.

Gels are divided into two categories i.e. elastic gels and non elastic gels. The two categories differ from their behaviour towards dehydration and rehydration as under.

Elastic gels	Non-elastic gels
1. They change to solid mass on dehydration which can be changed back to original form by addition of water followed by warming.	1. They change to solid mass on dehydration which cannot be changed back to original form with water.
2. They absorb water when placed in it with simultaneous swelling. This phenomenon is	2. They do not exhibit imbibation called imbibation.

Colloids around Us

Application of Colloids

(1) **Medicines:** The medicines containing gold, silver or calcium etc. in colloidal form are more effective and easily assimilated by the human systems.

(2) **Dyes:** In dyeing, mordants colloidal substances are used in textile dyeing industry to fasten dyes.

(3) **Rubber industry:** Latex is a colloidal solution of negatively charged particles. The article to be rubber plated is made the anode. Under the influence of electric field the rubber particles get deposited on the anode and the article gets rubber plated.

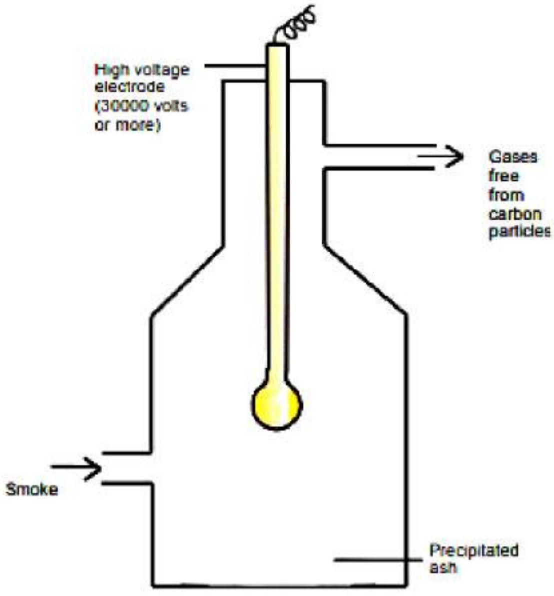
(4) **Smoke screens:** Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage.

(5) **Formation of delta:** The river waver carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.

(6) **Purification of water:** The turbidity in water is due to the presence of negatively charged clay particles. The addition of potash alum, i.e., Al^3 ions neutralizes the negative charge on the colloidal particles and thus causes their coagulation. The coagulated matter settles down and thus becomes clear.

(7) **Artificial rain:** Artificial rain can be caused by throwing electrified sand on clouds which are colloidal solutions or charged particles of water in air.

(8) **Smoke precipitation:** Smoke coming out of the chimney is industrial area is a nuisance and health hazard. It is a colloidal particles are charged particles and thus they are removed from fuel gases by electrical precipitation (Cottrell Precipitator).



Cottrell smoke precipitator

In, the smoke is made to pass through chambers fitted with highly electrically charged plates which precipitate the carbon and dust particles leaving in the gases to escape through chimney (figure).

(9) **Sewage disposal:** Sewage water consists of particles of dirt, rubbish, mud, etc., which are of colloidal dimensions and carry an electric charge and thus do not settle down easily. These particles can thus be removed by cataphoresis. A system of two tanks fitted with metallic electrodes is used for this purpose. When electric field is created, then the dust particles are coagulated on he oppositely charged electrodes. The deposit may be utilized as a manure.

(10) **Cleansing action of soap and detergent:** Soap solution may be used to wash off the dirt sticking to the fabric, in the presence

(i) If forms a collodial solution in water forms (miscelles), removes dirt by simple adsorption of oily substance and thus washes away.

(ii) It decreases the interfacial tension between water and grease, and it causes the emulsification of grease in water. By mechanical action such as rubbing, the dirt particles are also detached along with the only material.

(11) **In Photography:** Various colloidal system are used in photographic process. In the preparation of photographic plates, the silver bromide in gelatin is coated

on thin glass plates. In developing and fixation, various colloidal substances are used. In different kinds of colour printing, gelatin and other colloidal mixtures are used.

(12) **Blue colour of the sky:** Colloidal particles scatter only blue light and the rest of is absorbed. In sky there are a number of dust and water particles. They scatter blue light and, therefore, sky looks bluish. If there were no scattering, the sky would have appeared totally dark.