

Surface Chemistry

1. Colloidal Solution

The foundation of colloid chemistry was Laid by an english scientist, Thomas Graham in 1861.

Table : Comparision of suspensions colloids and true solutions.

S.No.	Property	Suspension	Colloid	True Solution or Crystalloidal
(i)	Particle size	$>10^{-5}$ cm or 10^3Å ⁰ or 100 m μ .	10^{-7} to 10^{-5} cm or 10Å to 10^3Å or 1m μ to 100 mm	$<10^{-7}$ cm or 10Å or 1 m μ
(ii)	Visibility	Visible with naked eye	Visible with ultramicroscope	Not visible with any of the optical means
(iii)	Seperation (a) with filter paper	Possible	Not possible	Not possible
	(b) with membranes	Possible	possible	Not possible
(iv)	Diffusion	Does not diffuse	Diffuse very slowly	Diffuses rapidly
(v)	Settling	Settles under gravity	Does not settle but it may settle under Centrifuge	Does not settle
(vi)	Nature	Heterogeneous	Heterogeneous	Homogeneous
(vii)	Tyndal effect Brownian moment	May or may not show	Clear shows	not show

2. Types of Colloidal solutions

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

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

Type of colloidal Solution	Dispersed Phase	Dispersion Medium	Example
Foam	gas	liquid	Whipped Cream, Shaving Cream, Soda water
Solid Foam	gas	solid	Cork, pumice stone, Foam rubber
Uquid Aerosol	liquid	gas	Fog, mist, clouds
Emulsion	liquid	liquid	milk, hair cream
Gel	liquid	solid	butter, cheese curd, Jellies, boot polish
Smoke (aerosol)	solid	gas	dust, soot in air
Sol (liquid)	solid	liquid	ink, colloidal gold
Solid sol	solid'	solid	Ruby glass (gold dispersed in glass), allys

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

We restrict our study mainly to colloidal systems which consist of a solid substance dispersed in a liquid. These are frequently referred to as sols or colloidal solutions, The colloidal solutions in water ~ as the dispersion medium are termed hydrosols or Aquasols. When the dispersion medium is alcohol or benzene, the sols are referred to as Alcosols and Benzosols respectively.

3. LYOPHILIC AND LYOPHOBIC SOLS

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

Colloidal solutions in which the dispersed phase has no affinity or attraction for the medium or for the solvent are called Lyophobic colloidal (Solvent heating) solutions.

	Property	Lyophobic sol (Suspensoid)	Lyophilic sol (Emulsoid)
1.	Preparation	Can not be prepared easily Special methods are required	Can be easily prepared by Shaking or warming the Substance with solvent
2.	Stability	are less stable	are more stable
3.	Reversibility	are irreversible	are reversible
4.	viscosity	viscosity is nearly same as that of the solvent	viscosity is much higher than that of solvent
5.	Surface tension	Surface tension is almost same as that of solvent	surface tension is usually low
6.	Hydration or solvation	These are less solvated as the particles have less affinity for the solvent	These are highly solvated as the particles have great affinity for solvent
7.	Charge	The particles carry a characteristic charge either positive or negative	The particles have little charge or no charge at all
8.	Visibility	Particles can be seen under microscope	Particles can not be seen under microscope
9.	Coagulation or precipitation	Precipitated by low concentration of electrolytes	Precipitated by high concentration of electrolytes
10.	Tyndal effect	More Scattering	Less Scattering
11.	Migration in electric field	migrate towards anode or cathode as these particles	may or may not migrate carry charge
12.	General Example	Mostly of Inorganic nature	Mostly of organic nature

4. Methods of Preparation

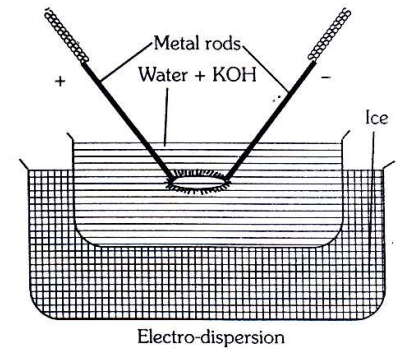
Lyophilic sols may be prepared by simply warming the solid with liquid dispersion medium eg. starch with water. On the other hand lyophobic sols have to be prepared by special methods. These methods fall into two categories

- Dispersion Methods in which larger macro sized particles are broken down to colloidal size.
- Condensation methods in which colloidal sized particles are built up by aggregating single ions or molecules. This method is also known as condensation method.

Dispersion method	Aggregation or condensation method
1. Mechanical dispersion	1. Exchange of solvents
2. Electro-dispersion	2. Change of physical state
3. Ultrasonic dispersion	3. Chemical methods
4. Peptization	(a) double decomposition (b) Oxidation (c) Reduction (d) Hydrolysis

5. Electro-Dispersion (Bredig's arc method)

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



Note:

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

6. 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 :

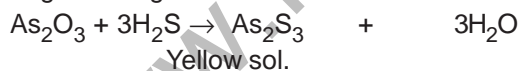
- (i) Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution once forms a dark reddish brown solution. Ferric chloride acts as a peptizing agent.
- (ii) Freshly prepared stannic oxide on treatment with a small amount of dilute hydrochloric acid forms a stable colloidal solution of stannic oxide.
- (iii) Freshly precipitated silver chloride can be converted into a colloidal solution by adding a small amount of hydrochloric acid.
- (iv) 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 that split from the precipitate as colloidal particles.

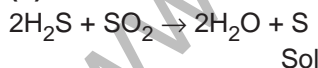
Chemical method: The chemical method involves chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of super-saturation is produced but the actual precipitation is avoided. Some familiar reactions used are:

(a) Double decomposition (i) Arsenious sulphide sol: A 1% solution of arsenious oxide is prepared in hot water. The solution is cooled, filtered and is then gradually added to water saturated with hydrogen sulphide, whilst a stream of H_2S is being passed through the solution

This is continued till an intense yellow coloured solution is obtained. Excess of H_2S is removed by bubbling hydrogen through the solution.

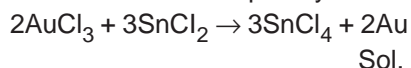


(b) Oxidation - A colloidal solution of sulphur is obtained by passing H_2S into a solution of sulphur dioxide.



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

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



7. PROPERTIES OF COLLOIDAL SOLUTIONS -

1. **Heterogeneous** - Colloidal particles in a solution differ in sizes and are not homogeneously distributed throughout the solution.
2. **Visibility** - Colloidal particles can not be seen with naked eyes or with the help of microscope. It is a well known fact no particle is visible if its diameter is less than half the wavelength of light used. The visible light has greater wavelength than the size of colloidal particle. .

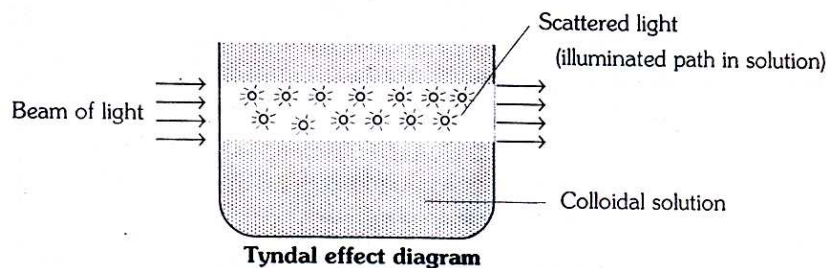
3. **Filterability** - Colloidal particles pass through an ordinary filter paper but do not pass through parchment and other fine membranes.
4. **Surface tension and viscosity** - For Lyophobic sols, surface tension and viscosity are not very different from those of the medium, as there is very slight interaction between the suspended particles and the medium. On the other hand Lyophilic sols show a high degree of solvation of the particles and therefore, the properties of the medium are modified. Thus the viscosity is much higher for the sol than for the medium. Furthermore the surface tension of the sol is lower than that of pure medium.
5. **Colour** - The colour 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. For example the colour of silver sol changes with the particle (suspended) diameter in solution.

Colour of Ag sol	particle diameter
orange yellow	6×10^{-5} mm
orange - Red	9×10^{-5} mm
purple	13×10^{-5} mm
violet	15×10^{-5} mm

6. **Colligative properties** - These properties depend on the number of solute particles in solution. In case of colloidal solutions., colloidal particles are the aggregates of many ions or smaller molecules and when compared to true solutions or normal solutions, the total no. of particles of solute in solution are ve'ry less and hence these solutions exhibit colligative properties to lesser extent.

7. **Optical properties** - Sols exhibit tyndal effect

When a beam of light is passed through a sol and viewed at right angles, the path of the light shows up as a hazy beam of cone (limited path by bluish light). This was first observed by Farraday and later by Tyndal and in known as Tyndal effect. The bright cone of the light is called 'Tyndal cone". The tyndal effect-is due to the fact that the colloidal particles absorb light and scatter in all directions in space. The scatterise of light illuminates the path of the beam in the colloidal dispersion.



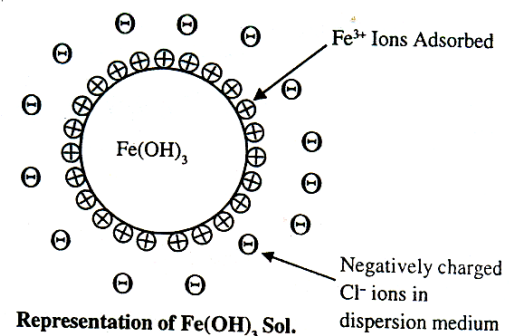
SOME EXAMPLES OF TYNDAL EFFECT ARE

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

8. **Kinetic properties** - When a sol is examined with an ultramicroscope, the suspended particles are seen as shining specks of light. By following an individual particle, it is observed that the particle is in a state of continuous motion in zig-zag directions. The continuous rapid zig-zag motion of a colloidal particle in the dispersion medium is called "Brownian movement or mottion (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

9. **Charge on colloidalparticales** - Colloidal particles always carry an electric charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the sol. A list of common sols with the type of change on their particles is given ahead.

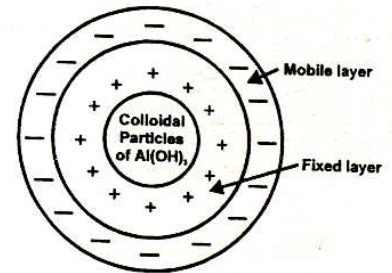


Positively charged	Negatively charged
1. Metallic hydroxides e.g. $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ & $\text{Fe}(\text{OH})_3$ 2. Basic dye stuff example Methylene blue sol 3. Proteins in acidic medium	Metallic sulphides like As_2S_3 , Sb_2S_3 , Cds Acid dye stuff example - Congoed sols Proteins in basic medium Sols of starch, gum, geatin, clay & cgarcoal

8. ELECTRICAL DOUBLE LAYER

The surface of a colloidal particle acquires a +ve by selective adsorption of a layer of positive ions around it. This layer attracts counter ions from the medium which form a second layer of -ve charges. The combination of the two layers of +ve and -ve charges around the sol particle was called Helmholtz double layer. According to modern view, the first layer of ions is firmly held and is termed fixed layer while the second layer is mobile which is termed as diffused layer.

The combination of the compact and diffused layer is referred as the stern double layer. The diffused layer is only loosely attached to the particle surface and moves in the opposite direction under an applied electric field. The potential difference between the fixed layer and the diffused layer of opposite charge is called electrokinetic potential or zeta potential.



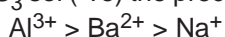
9. **Electrophoresis** - If electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode, due to charge them, The movement of sol particles under an applied electric potential is called "Electrophoresis", Depending upon the direction of movement of particles towards cathode, or anode electrophoresis can be called "cataphoresis" or "Anaphoresis". Electrophoresis provides an experimental proof to show that the colloidal particles are charged particles.
10. **Electro osmosis** - The medium will move in opposite direction to the dispersed phase under the influence of applied electric potential. The movement of dispersion medium under the influence of applied potential is known as 'Electro - osmosis'.
11. **Coagulation or Precipitation** - We know that the stability of a lyophobic sol is due to the adsorption of positive or negative ions by the dispersed particles. The repulsion forces between the charged particles do not allow them to settle. If somehow, the charge is removed there is nothing to keep the particles apart from each other. In such cases they aggregate or flocculate and settle down under the action of gravity. The flocculation and settling down of the discharged sol particles is called coagulation or the precipitation can be brought about in four ways
- By addition of electrolyte.
 - By electrophoresis.
 - By mixing two oppositely charged sols.
 - By boiling.

(a) By addition of electrolytes

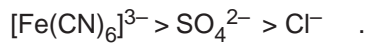
When an electrolyte is added in excess to a sol, then the electrolyte furnishes both the type of ions in solution. The oppositely charged ions get adsorbed on the surface of colloidal particles this causes neutralisation and thereby the size and mass of colloidal particle increases and it becomes a suspension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

Hardy Schulze Rule - states that the precipitating effect of an ion on dispersed phase of opposite charge increases with the valence of the ion.

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



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



The minimum concentration of an electrolyte in milli moles per litre required to cause precipitation of a sol in 2 hours is called FLOCCULATION VALUE. The smaller the flocculating value, the higher will be the coagulating power of the ion.

(d) **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 neutral coagulation of two sols of opposite charge can be effected by mixing them.. For eg $\text{Fe}(\text{OH})_3$ (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 removes the adsorbed charged layer from the sol and therefore the sol particles settle down.

12. **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 occur. Under this condition a small quantity of electrolyte can bring about coagulation.

13. **Protection or Protective action.**

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

The property of Lyophilic sols to prevent the precipitation or coagulation of a lyophobic salt is called protection.

The Lyophilic sol used to protect a lyophobic sol from precipitation is referred to as a protective colloid. Lyophilic sols form a thin layer around lyophobic sol or around the ions furnished by electrolyte and therefore the coagulation can not take place (as the size does not increase much). Gelatin, Albumen, Gum Arabia, Potato Starch are some of the examples of protective colloids.

The Lyophilic colloids differ in their protective power. The protective power is measured in terms of "Gold number" introduced by Zsigmondy.

The number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of gold sol on addition of 1 ml of 10% NaCl solution is known as gold number of that protector (Lyophilic colloid)

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

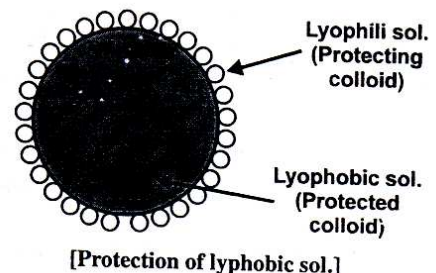
The smaller the gold number of a protective Lyophilic colloid, greater is its protection power.

Gold Number of some hydrophilic colloids

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

$$\text{Protection Capacity} \propto \frac{1}{\text{Protection Number}}$$

Gelatin and starch have the maximum and minimum protective powers.



14. EMULSIONS

These are liquid-liquid colloidal systems i.e.

There are two types Emulsions

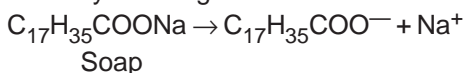
- (i) Oil dispersed in water (o/w types)
- (ii) Water dispersed in oil (w/o types)

In the first type water acts dispersion medium examples of this type of emulsions are milk and vanishing cream. In milk, liquid fat is dispersed in water. In the second system oil acts as dispersion medium common examples of this type are butter and cream.

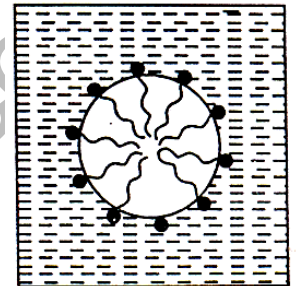
Emulsions of oil and water are unstable and sometimes they separate into two layers on standing. For stabilisation of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agent form an interfacial film between suspended particles and the medium. The Principal agent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

15. Associated Colloids [Micelles]

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



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

**16. GELS**

A gel is a jelly like colloidal system in which a liquid is dispersed in a solid medium.

Gels may be classified into two types

- (a) **Elastic gels** - These are those which possesses the property of elasticity. They change their shape on applying force and return to original shape when the force is removed. Gelatin, starch and soaps are examples substances which form elastic gels.
- (b) **Non - elastic gels** - These are the gels which are rigid e.g. Silica gel. These are prepared by appropriate chemical action. Thus silica gel is produced by adding concentrated hydrochloric acid to sodium silicate solution of the correct concentration.

Multi Moleuclar	Macro Molecular	Associated colloidal
Formation by aggregation a large number of atoms or Smaller molecules of substance.	Formation by aggregation of big size molecules These are polymer & with atomic mass	Ex. → Soap & Detergents
Ex. → Gold, Sol, Sulphur sol (A ₄)	Ex. → Starch, Cellulose, Protein Etc.	

17. APPLICATIONS OF COLLOIDS

Colloids play an important role in our daily life and industry. Some of the important applications of colloids are listed below -

1. Food.
2. Medicines.
3. Paints.
4. Electrical precipitation of smoke.
5. Purification of sewage water.
6. Formation of Delta
7. Purification of blood .

8. **Adsorption Indicators.** Indicators like fluorescein function by adsorption of ions on to sol particles. When silver nitrate solution is run into a solution of sodium chloride containing a fluorescein a white ppt of AgCl is first formed. At the end point the white ppt turns sharply pink.
9. **Tanning.** Animal leather (skin) is soft due to the presence of very fine globules oils and fats in the pores of skin. These globules are of colloidal in nature. When this soft leather (skin) is placed in salt water, these globules of oils and fats coagulate and settle down in water. Now when the animal hides are dried they become hard. This process of making soft leather to hard leather by dipping it in salt water is called tanning usually chromium salts are used for tanning.
10. **Clearing action of soaps and detergents.** Dust and dirt particles on clothes are colloidal in nature soaps being sodium salts of higher fatty acids coagulates them which become suspension particles called micelle and roll out due to greater volume and greater mass.
11. **Industrial products.** Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc are all colloidal solutions.
12. Colloidal solution of graphite in water is called "Aqua dag" while that in Oil is called oil dag.
18. **ADSORPTION & CATALYSIS**

Adsorption

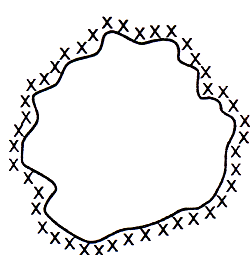
Adsorption:- The phenomenon of increase in concentration at the surface due to molecular surface force is known as adsorption.

Adsorbent:- The solid substance on the surface of which adsorption takes place is called adsorbent. Examples of adsorbents are activated charcoal, Pt, Pd, Ni etc.

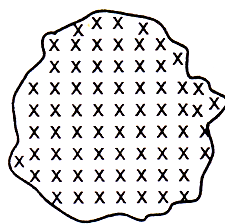
Adsorbate:- The substances, gases or-liquids which are adsorbed on the surface of adsorbent are called adsorbate.

Sorption:- It may be defined as the process in which both adsorption and absorption take place simultaneously.

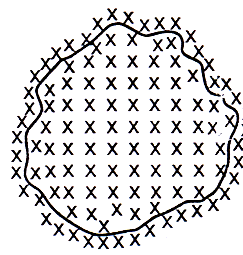
Absorption:- When a substance is uniformly distributed throughout the body of a solid or liquid, the phenomenon is called absorption.



Adsorption



Absorption



Sorption

18.1 MECHANISM OF ADSORPTION

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

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

Comparison of physical adsorption and Chemical adsorption

	Physical Adsorption	Chemical Adsorption
1.	It is caused by intermolecular van der Waals forces	It is caused by chemical bond formation.
2.	It is not specific	It is highly specific.
3.	It is reversible	It is irreversible.
4.	Heat of adsorption is low. -20 to -40 KJ/mol^{-1}	Heat of adsorption is high. -200 to 400 KJ/mol^{-1}
5.	No appreciable activation energy is involved.	High activation energy is involved.
6.	It forms multilayers on adsorbent surface under high pressure.	It forms unimolecular layer.

- (i) **Nature of adsorbate:-** Readily liquefiable gases such as HCl, SO₂, CO₂, CH₄, NH₃ etc. are more easily adsorbed by and adsorbent than the permanent gases H₂, N₂ etc.
- (ii) **Nature of adsorbent:-** Activated charcoal is a better adsorbent than transitional metals.
- (iii) **Specific area of adsorbent:-** The greater the specific area of adsorbent the greater will be the extent of adsorption.
Extent of adsorption state of sub-division of adsorbent.
- (iv) **Pressure:-** Extent of physical adsorption increases as the pressure of the gas increases, till a saturation point is reached.

Freundlich gave the following relationship between extent of adsorption $\frac{x}{m} = K \frac{1}{P^n}$

Where:

X = mass of adsorbate, m = mass of adsorbent and pressure P:

K and n are constants, depends upon the nature of adsorbate as well as adsorbent

(a) At low pressure: $\frac{x}{m}$ is directly proportional to the pressure

$$\text{i.e. } \frac{x}{m} \propto P^1$$

(b) At high pressure:- 'The extent of adsorption,

$$\frac{x}{m} \text{ becomes independent of pressure i.e. } \frac{x}{m} \propto P^0$$

(c) At intermediate pressure:- $\frac{x}{m}$ will depend upon the power of pressure which lies between 0 and 1 i.e.

$$\frac{x}{m} \propto P^{\frac{1}{n}} \text{ where } n > 1$$

$$\text{or } \frac{x}{m} = K P^{\frac{1}{n}} \dots\dots\dots (i)$$

On taking logarithm on both sides of

(i) We get

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P \dots\dots\dots (ii)$$

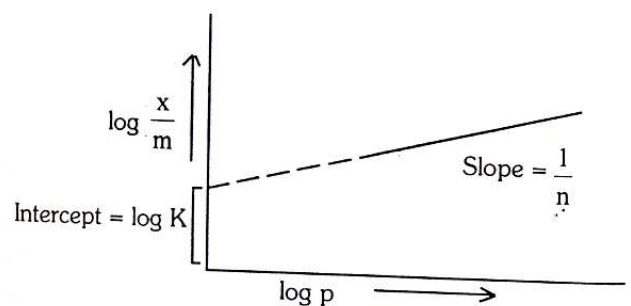
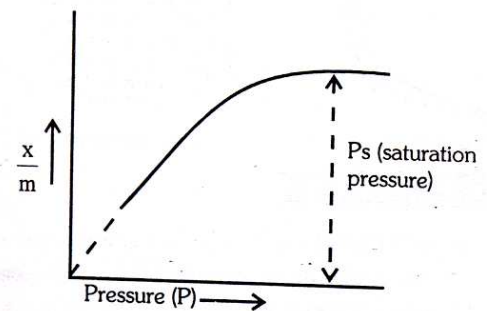
Expression (i) and (ii) are called Freundlich adsorption isotherm.

Expression (ii) represents a straight line. The slope of the line will be $\frac{1}{n}$ while its intercept on the log

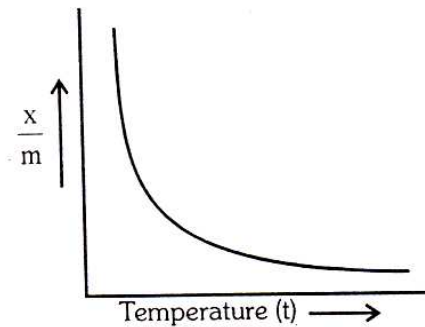
$\frac{x}{m}$ axis will be logK

- (v) **Temperature:-** Adsorption is accompanied by evolution of heat i.e. H is negative, so the rate of adsorption should decrease with rise in temperature. It is found to be so in case of physical adsorption. The effect of temperature is represented by an adsorption isobar.
- (vi) **Activation of adsorbent:-** An adsorbent can be activated either by heating or by bringing it in finely divided state, or by making its surface rough by rubbing. For example charcoal is activated by heating it in vacuum at 1000°C.

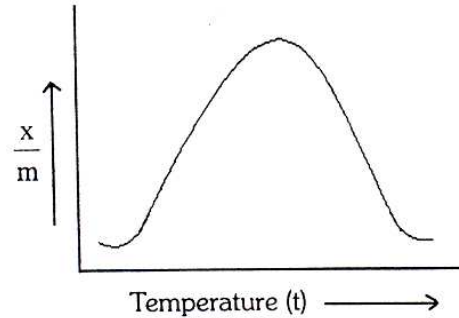
Adsorption isobar - A graph between the amount of adsorbate adsorbed per gram of adsorbent and the temperature (t) at a constant pressure is called adsorption isobar.



Adsorption isobar for physical adsorption



Adsorption isobar for chemical adsorption

**Applications of adsorption :**

- | | |
|-------------------------------|---|
| (1) Production of high vacuum | (2) Gas masks |
| (3) Humidity control | (4) Removal of colouring matter from solution |
| (5) Heterogeneous catalysis | (6) Separation of inert gases |
| (7) Softening of hard water | (8) Deionisation of water |
| (9) In curing diseases | (10) Cleaning agents |
| (11) Froth floatation process | (12) Adsorption indicators |
| (13) Chromatographic analysis | |

19. CATALYSIS

The phenomena in which the rate of a reaction is altered (increased or decrease) by the presence of a substance (Catalyst) is known as catalysis.

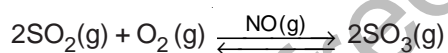
Catalytic reactions are divided into two types.

(a) Homogeneous catalysis :

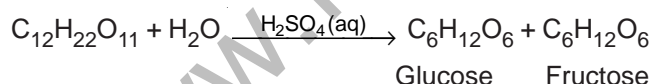
(b) Heterogeneous catalysis

Homogeneous catalysis:- When the reactants and the catalyst are in the same physical state, i.e. in the same phase, it is called homogeneous catalysis. For example.

- (i) Lead chamber process:- In this process for the manufacture of sulphuric acid (H_2SO_4) NO (gas) is used as a catalyst.

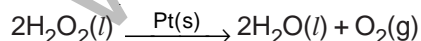


- (ii) Inversion of cane sugar:- In aqueous solution is catalysed by dilute acid (Hydrogen ions)



- (b) **Heterogeneous catalysis**:- When the catalyst and the reactants are not in the same physical state i.e. not in the same phase, it is called heterogeneous catalysis. For example.

- (i) Decomposition of $\text{H}_2\text{O}_2(\text{l})$:



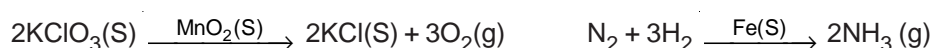
- (ii) Haber process for NH_3

**19.1 TYPES OF CATALYSIS**

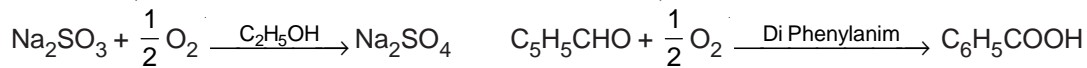
Catalysts are divided into four types.

- | | |
|------------------------|-------------------------|
| (i) Positive catalysts | (ii) Negative catalysts |
| (iii) Autocatalysts | (iv) Induced catalyst |

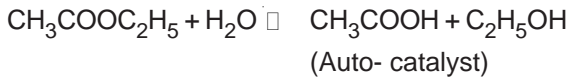
- (i) **Positive catalysts**:- The substance which increases the rate of a reaction is known as a positive catalyst. It decreases the energy of activation for the reaction. For example:



- (ii) **Negative catalysts:-** The substance which decreases the rate of chemical reaction is called negative catalyst or inhibitor. It increase the activation energy for the reaction. For example.

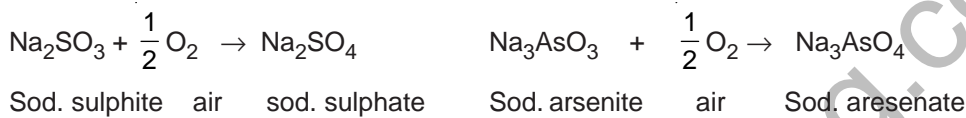


- (iii) **Autocatalysts:-** When one of the products of the reaction begins to act as a catalyst, it is called auto- catalyst. for example. In the initial stages the reaction is slow but as soon as the products come into existence the reaction rate increases



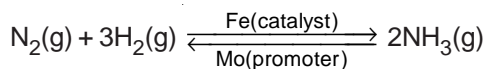
- (iv) **Induced catalyst:-** When a chemical reaction enhances the rate of another chemical reaction it is called induced catalysis. For example:-

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



Promoters:- Those substance which do not themselves act as catalysts but their presence increases the activity of a catalyst are called catalytic promoters or catalyst for a catalyst. Example:

In the Haber process for the synthesis of ammonia, Fe is the catalyst while molybdenum (Mo) acts as a promoter.

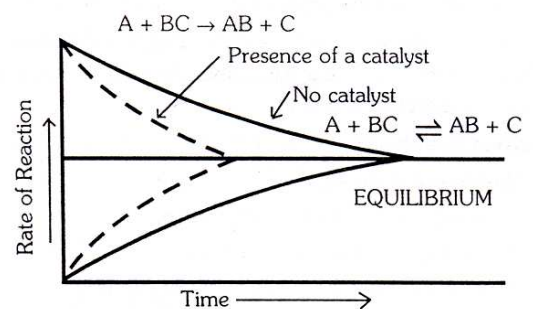


Catalytic Poison:- The substance whose presence decreases or destroy the activity of a catalyst is called catalytic poison. For example:- Carbon monoxide or H_2S in hydrogen gas, acts as a poison for Fe catalyst in the Haber process for NH_3 , As_2O_3 acts as poison for Pt asbestos in contact process for H_2SO_4

Inhibitors:- Those substances which retard rate of a chemical reaction are known as inhibitor. For example: H_3PO_4 , glycerol or acetamide decrease the rate of decomposition of hydrogen peroxide.

General characteristics of catalysts:

- (i) A catalyst remains unchanged in mass and chemical composition but change their physical state.
- (ii) Only a very small amount of catalyst is sufficient to catalyze a reaction.
- (iii) A catalyst does not initiate a reaction & does not controlled on chemical Rxn.
- (iv) When a catalyst is a solid, it is usually more efficient when used in finely divided form.
- (v) Generally catalyst does not change the nature of products.
- (vi) A catalysts does not change the equilibrium state of a reversible reaction but help to time achive of equilibrium state. or position of equilibrium.
- (vii) The catalysts is generally specific in nature.
- (viii) Change rate constant of Rxn.
- (ix) does not change free energy of Rxn.



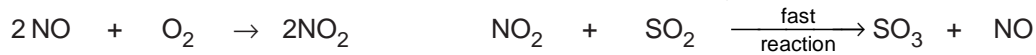
THEORIES OF CATALYSIS

Intermediate compound formation theory:- This theory is 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 SO_3 is explained as follows.



catalyst reactant Intermediate intermediate reactant product catalyst regenerated

Adsorption theory:- This theory explains 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 absorbed on the surface of the catalyst at adjacent points. Adsorption leads to higher concentration of the adsorbed reactant on the surface of a catalyst.
- (ii) As adsorption is an exothermic process, the heat of adsorption provides the necessary activation energy for the chemical reaction to proceed.
- (iii) The adsorbed reactant molecules are tied on the solid surface of the catalyst. The bonds between the atoms of chemisorbed reactant molecules are weakened. The reactant molecules of sufficient energy combine together and with the surface of the catalyst to form a surface activated complex. This adsorbed activated complex is decomposed to form products at a definite faster rate.
- (iv) The product molecules rapidly leave the catalyst surface to make room for the other reactant molecules to get absorbed. Thus the chemical combination between reactant molecules goes on at the surface of the catalyst at a much faster rate.

Catalysts in Industry:- Some of the important processes and their catalysts are given in below.

Industrial process	Catalyst used
Preparation of O_2 from KClO_3 (Hetero)	MnO_2
Haber's process for ammonia (Hetero)	Fe; Mo as promoter
Ostwald's process for HNO_3 from NH_3 (Hetero)	Pt Gauge
Chamber process for H_2SO_4 (Hetero)	Nitric oxide (NO) gas
Contact process for H_2SO_4 (Hetero)	V_2O_5
Deacon's process for manufacture of Cl_2 (Hetero)	CuCl_2
Bosch process for H_2 (Hetero)	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$
Manufacture of vegetable ghee (Hetero)	Ni, Cu as promoter
Hydrolysis of ester (Homo)	aq H_2SO_4
Aldol condensation of aldehyde (Homo)	-OH
Enolisation of ketone (Homo)	H^+ or -OH
Cracking of hydrocarbon (Hetero)	Zeolites