

SURFACE CHEMISTRY

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting into a higher concentration of molecules on the surface is called *adsorption*. The substance adsorbed on the surface is called *adsorbate* and the substance on which it is adsorbed is called *adsorbent*. The surface where the process takes place is known as *interface*.

Examples :

1. Dyes get adsorbed on cotton fibres, activated carbon, etc.
2. Ammonia gas placed in contact with charcoal gets adsorbed on it.
3. Oxalic acid placed in contact with activated carbon gets adsorbed on it.

Positive and Negative Adsorption

Positive adsorption : In case of adsorption by solids from the solutions, mostly the solute is adsorbed on the surface of the solid adsorbent so that the concentration of solute on the surface of the adsorbent is greater than in the bulk. This is known as positive adsorption. Hence when the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is known as positive adsorption.

Negative adsorption: In some cases, the solvent from the solution may be adsorbed by the adsorbent so that the concentration of the solution increases than the initial concentration. This is called negative adsorption. Hence if the concentration of the adsorbate is less on the surface of the adsorbent than in the bulk, it is known as negative adsorption.

Factors Affecting Adsorption

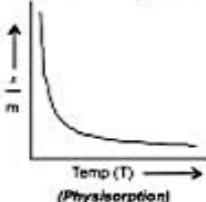
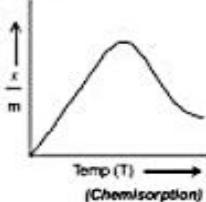
1. **Nature and surface area of the adsorbent :** If the surface is polar or activated, that is, some active groups are present at the surface, it is favourable for adsorption. Similarly, if the surface area of the adsorbent is large, the amount of adsorption would be more. That is why finely divided substances have a larger adsorption power than when they are present in a compact form.
2. **Nature of adsorbate :** Whether the adsorbent is a gas or a solute present in a solution, factors like structure and dimensions of the molecule and presence of some polar group affect adsorption.
3. **Temperature :** Normally, adsorption decreases with an increase in temperature; however, it can be vice versa as well.
4. **Concentration/Pressure:** At constant temperature, adsorption increases with an increase in concentration or pressure of the adsorbate.

There are two main types of adsorption

1. Physical adsorption/ van der Waal's adsorption/ Physisorption. When molecules are held at the surface by van der Waal's forces (which are weak intermolecular forces of attraction) without resulting in the formation of any chemical bond between the adsorbate and adsorbent, it is called physical adsorption. It is a reversible process. Also, a decrease in temperature increases the adsorption.
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2. Chemical adsorption/Chemisorption. When the adsorbate molecule is held on the surface of a solid by forces similar to those of a chemical bond, the type of adsorption is called chemical adsorption or chemisorption. The heat released during chemisorption is high and the process is normally irreversible. Another important aspect is that physical adsorption is non-specific in nature whereas chemical adsorption is specific in nature and occurs when there is a tendency towards the formation of some sort of bond between the adsorbate and adsorbent molecule.

COMPARISON OF PHYSI-SORPTION AND CHEMISORPTION

S.No.	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 liquefiable gases are adsorbed readily.	It depends on the nature of gas. Gases which form compounds with the adsorbent exhibit chemi-sorption.
5.	Heat of adsorption is low due to weak forces (4-40 kJ/mole)	Heat of adsorption is high due to strong attractive forces (40-400 kJ/mole)
6.	Low temperature is favourable. It decreases with increase of temperature.	High temperature is favourable. It increases with increase of temperature.
	 <i>(Physical adsorption)</i>	 <i>(Chemisorption)</i>
7.	No appreciable activation energy is involved.	High activation energy is involved.
8.	High pressure is favourable. Decrease of pressure causes desorption.	High pressure is favourable. Decrease of pressure does 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. x/m , that is, amount adsorbed per gram of adsorbent (x = amount adsorbed and m = amount of adsorbent) depends on the chemical nature of both the adsorbent and adsorbate and also on their physical state.
2. x/m depends on the equilibrium concentration or pressure of the adsorbate and temperature.
3. Adsorption can be reversible or irreversible.
4. Adsorption is generally followed by a decrease in enthalpy and entropy both.
5. Adsorption can be selective and specific or non-specific.

Thermodynamics of Adsorption :

Adsorption is spontaneous process, so for the process ΔG is negative. According to Gibbs equation.

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

For adsorption ΔS (Change in entropy) is always negative because adsorption of molecules on the surface lowers the disorder. So, for value of ΔG to be negative, ΔH must necessarily be negative and $|\Delta H| > |T \Delta S|$. The process is exothermic because it involves forces of attraction between adsorbate and adsorbent.

As the process of adsorption proceeds further ΔH becomes less and less after certain time period. When ΔH becomes equal to $T\Delta S$, $\Delta G = 0$ and system attains equilibrium. At equilibrium,

$$\text{Rate of adsorption} = \text{Rate of desorption}$$

Illustration

1. 50 mL of 1 M oxalic acid (molecular mass = 126) is shaken with 0.5 g of wood charcoal. The final concentration of the solution after adsorption is 0.5 M. Calculate the amount of oxalic acid adsorbed per gram of charcoal

Sol. Calculation of initial amount of oxalic acid in 50 mL solution. 1 M oxalic acid solution means 1 mole of oxalic acid (126 g) present in 1000 mL solution.

$$\therefore 50 \text{ mL of } 1 \text{ M solution will contain oxalic acid} = \frac{126}{1000} \times 50 = 6.6 \text{ g}$$

Calculation of amount of oxalic acid in 50 mL solution after adsorption. Concentration of solution after adsorption = 0.5 M. Thus, 1000 mL of the solution contain oxalic acid = 0.5 mol = 63 g

$$\therefore 50 \text{ mL of the solution will contain oxalic acid} = \frac{63}{1000} \times 50 = 3.15 \text{ g}$$

Calculation of amount adsorbed per gram

$$\text{Amount of oxalic acid adsorbed by } 0.5 \text{ g charcoal} = 6.30 - 3.15 \text{ g} = 3.15 \text{ g}$$

$$\therefore \text{amount of oxalic acid adsorbed per gram of charcoal} = 6.30 \text{ g}$$

Exercise

1. The following data were obtained for the adsorption of CO on 3 g of charcoal at 0°C

$$\text{Pressure, P (mm)} : 180 \quad 540$$

$$\text{Volume of gas adsorbed, } x (\text{cc}) \text{ reduced to S.T.P.} : 16.5 \quad 38.1$$

Calculate the values of the constants k and n used in Freundlich equation.

Ans. $0.1044 \text{ cm}^3 \text{ g}^{-1}$ (when pressure is in mm)

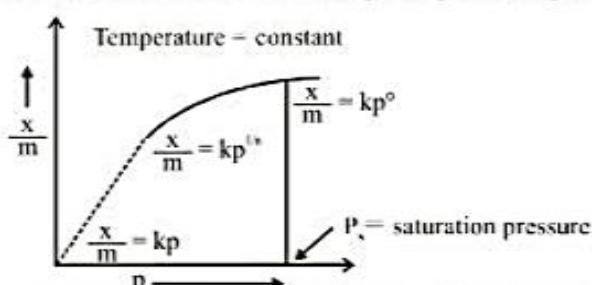
ADSORPTION ISOTHERMS

A relation between x/m (amount adsorbed per unit weight of adsorbent) and the equilibrium concentration or pressure at a fixed temperature is called *adsorption isotherm*. This is experimentally obtained by determining x/m as a function of 'c' or 'p'. Two such isotherms (empirical relation) are given below.

1. **Freundlich Adsorption Isotherm :** It is represented as

$$\frac{x}{m} = k C^{1/n} \text{ or } \frac{x}{m} = kP^{1/n}, \text{ depending on whether the adsorbate is a solution or a gas.}$$

Where x = amount of adsorbate, m = amount of adsorbent P = pressure, k and n are constants which depend on the nature of the adsorbent and the gas at given temperature.



The graph obtained gives following information about extent of adsorption.

(a) **At very low pressure :** At very low pressures, the graph is nearly straight line and at these pressures.

$$\frac{x}{m} \propto P \text{ or } \frac{x}{m} = k.P$$

(b) **At intermediate range of pressure :** At these pressures graph is curved and

$$\frac{x}{m} \propto P^{1/n} \text{ or } \frac{x}{m} = k.P^{1/n} \quad (\text{probable 'n' value is } 0.1 - 0.5)$$

(c) **At very high pressure :** The graph becomes parallel to x-axis which indicates that extent of adsorption is independent to the pressure i.e.,

$$\frac{x}{m} \propto P^0 \text{ or } \frac{x}{m} = k$$

2. Langmuir adsorption isotherm :

Another isotherm derived by Langmuir considers the formation of only a mono-molecular layer of adsorbate on adsorbent. It is known as *Langmuir adsorption isotherm* and is based on the following points:

- (a) It takes place on the surface of solids till a unimolecular layer is formed.
- (b) Adsorption is a result of condensation of adsorbate molecules on solid surface and their evaporation.
- (c) At equilibrium, the rate of condensation becomes equal to the rate of evaporation.

Based on these aspects, Langmuir derived the expression given below:

$$\frac{x}{m} = \frac{ap}{1+bp}$$

The values of constants 'a' and 'b' depend upon the nature of adsorbate, nature of solid adsorbent, and temperature. 'p' is equilibrium pressure.

Langmuir theory has limitations. This theory of unimolecular adsorption is valid only at a low pressure and high temperature. As the pressure is increased or temperature is lowered, additional layers start forming. This leads to multilayer adsorption.

Applications of Adsorption :

1. **In making gas masks :** In gas masks, activated charcoal preferentially adsorbs the harmful gases like, CH_4 , CO , Cl_2 etc.
2. **In decolorisation processes :** for decolorisation of sugar cane juice, it is passed over activated animal charcoal, where colouring matter gets adsorbed on the surface of charcoal.

3. **In making moisture free atmosphere :** Silica gel, alumina etc are used to remove moisture as they adsorb water. That is why, small packets of silica gel are kept with delicate instruments.
4. **In production of high vacuum :** In an evacuated vessel, an adsorbent is added to remove small amounts of gases and this produces high vacuum.
5. **Chromatography :** A technique used for separation of substances is based on adsorption process.
6. **In purification of water :** Ions from water may be removed by ion-exchange resins and the process involves adsorption.
7. **In the extraction of metals :** Froth floatation process used for the concentration of ores is based on preferential adsorption of ore particles.
8. **Adsorption indicators :** Some dyes like, eosin, fluorescein etc. get adsorbed on the surface of precipitates and this property serves as basis for adsorption indicators.

Illustration

1. Applying Freundlich adsorption isotherm, calculate the amount of acetic acid adsorbed by 1 kg of blood charcoal at 25° C from a 5% vinegar solution (mass/volume). Given that if the concentration is expressed in molarity (mol dm^{-3}), x/m is mass of the solute adsorbed per gram of adsorbent, then $k = 0.160$ and $n = 2.32$.

Sol. According to Freundlich adsorption isotherm, $\frac{x}{m} = k C^{1/n}$ (i)

5% vinegar (acetic acid solution) means 5 g of acetic acid are present in 100 mL of the solution
Molar mass of acetic acid (CH_3COOH) = 60 g mol^{-1}

$$\therefore 5 \text{ g of acetic acid} = \frac{5}{60} \text{ mol}$$

$$\therefore 1000 \text{ mL of the solution will contain acetic acid} = \frac{5}{60} \times \frac{1}{100} \times 1000 = 0.837 \text{ mol.}$$

i.e. Concentration of the solution (C) = 0.837 mol L^{-1}

$$\frac{x}{m} = 0.160 \times (0.837)^{1/2.32}$$

$$\therefore \log \frac{x}{m} = \log (0.160) + \frac{1}{2.32} \log (0.837) = -0.7959 + 0.435 (-0.0773) = -0.8295$$

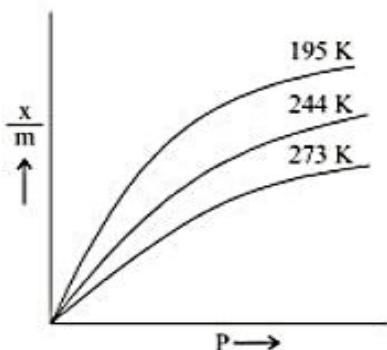
$$\therefore \frac{x}{m} = \text{Antilog} (-0.8295) = 0.1481 \text{ g (g charcoal)}^{-1}$$

$$\therefore \text{Amount adsorbed by 1 kg (1000 g) of charcoal} = 148.1 \text{ g}$$

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Exercise

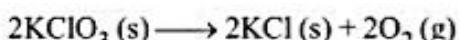
1. Consider the adsorption isotherms given on the side and interpret the variation in the extent of adsorption (x/m) when



- Ans.**
- (a) (i) temperature increases at constant pressure
(ii) pressure increases at constant temperature
 - (b) Name the catalyst and the promoter used in Haber's process for manufacture of ammonia
- (a) (i) As temperature increases at constant pressure, adsorption (x/m) decreases
(ii) As pressure increases at constant temperature, first adsorption increases upto a particular pressure and then it remains constant, i.e., becomes independent of pressure.
- (b) Finely divided iron is used as catalyst and molybdenum is used as promoter

CATALYSIS

Potassium chlorate, when heated strongly (380°C - 600°C), decomposes slowly as



However, when a small amount of manganese dioxide (MnO_2) is added, the decomposition takes place at a considerably lower temperature range (200°C - 360°C) and at a much considerable rate. The added MnO_2 remain unchanged with respect to its mass and composition.

The systematic study of the effect of different foreign substances on the rates of chemical reactions was made by Berzelins, in 1835. He named these foreign substances as **catalyst**.

Substances, which alter the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as **catalysts** and the phenomenon is known as **catalysis**.

CHARACTERISTICS OF CATALYTIC REACTIONS

- (i) The catalyst remains unchanged in amount and chemical composition at the end of the reaction.
However, it may undergo considerable change in physical properties like physical state, colour etc..
- (ii) A small quantity of the catalyst is normally capable of producing the desired effect. However, in some reactions, the rate depends on the amount of catalyst. For example, the rate of inversion of cane sugar catalysed by H^+ ion changes with the change in H^+ ion concentration.

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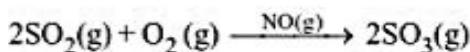
- (iii) The catalyst is generally specific in its action. For example, the decomposition of KClO_3 is catalysed by MnO_2 but not by platinum. On the other hand, MnO_2 can catalyse the decomposition of KClO_3 but not KClO_4 or KNO_3 .
- (iv) The catalyst does not initiate a reaction; it merely accelerates the reaction that is already occurring.
- (v) A catalyst does not alter the final state of equilibrium in a reversible reaction.

TYPES OF CATALYSIS

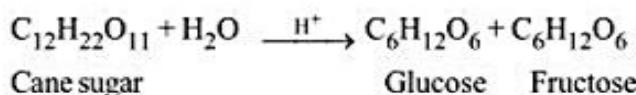
(a) Homogeneous Catalysis :

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, NO(g) is used as a catalyst.

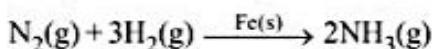


- (ii) Inversion of cane sugar:-** Inversion (hydrolysis) of sugar is catalysed by H^+ ions.

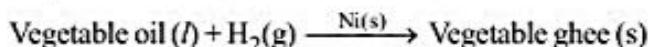


(b) Heterogeneous catalysis: When the catalyst and the reactants are not in the same physical state i.e. not in the same phase, it is called heterogeneous catalysis. for example,

- (i) Haber's process for NH_3 formation:**

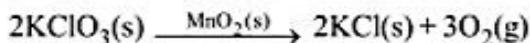


- (ii) Hydrogenation of vegetable oils** in the presence of finely divided nickel as catalyst.

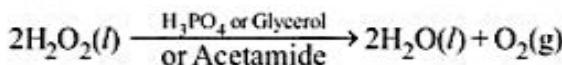
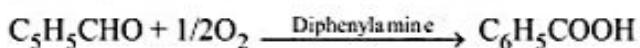
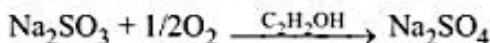


TYPES OF CATALYSTS

- (i) Positive catalyst (or catalyst):-** The substance which increases the rate of a reaction is known as a positive catalyst. Normally the term catalyst is used for positive catalyst. For example:

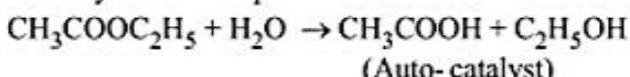


- (ii) Negative catalyst (or inhibitor) :-** The substance which decreases the rate of chemical reaction is called negative catalyst or inhibitor. For example:



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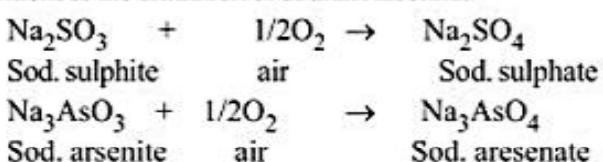
(iii) Autocatalysts:- When one of the products of the reaction begins to act as a catalyst, it is called auto-catalyst. For example:



In the initial stages, the reaction is slow but as soon as the products come into existence, the reaction rate increases.

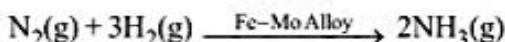
(iv) Induced catalyst:- When a chemical reaction enhances the rate of another chemical reaction, it is called induced catalysis. For example :

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



Promoters:- Those substances 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. For 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 destroys 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 .



THEORIES OF CATALYSIS

It is not possible to give a uniform explanation of the mechanism of the phenomenon of catalysis, as catalytic reactions are of various nature. However, the following are two basic theories of catalysis.

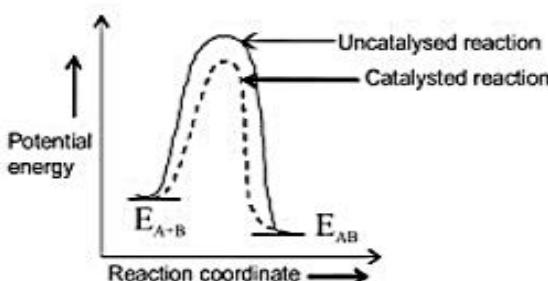
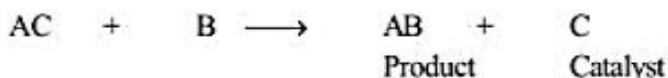
(i) Intermediate compound formation theory

According to this theory, the catalyst first forms an intermediate compound with one of the reactants. The intermediate compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.

Consider, a reaction of the type $\text{A} + \text{B} \xrightarrow{\text{C}} \text{AB}$ which occurs in presence of a catalyst C, may take place as

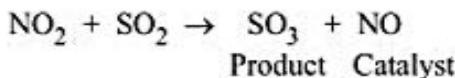
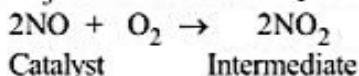


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Thus, a catalyst increases the rate of a reaction by providing a pathway whose activation energy is lower than the activation energy of the uncatalyzed reaction.

Many catalytic reactions can be explained on the basis of this theory. Consider the catalytic oxidation of SO_2 to SO_3 in the lead chamber process (NO is taken as catalyst). This occurs as follows



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

(ii) Adsorption Theory

This theory explains the mechanism of heterogeneous catalysis. The old point of view was that when the catalyst is in solid state and the reactants are in gaseous state or in solutions, the molecules of the reactants are adsorbed on the surface of the catalyst. The increased concentration of the reactants on the surface influences the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is taken up by the surface of the catalyst, which is utilised in enhancing the chemical activity of the reacting molecules. The view does not explain the specificity of a catalyst.

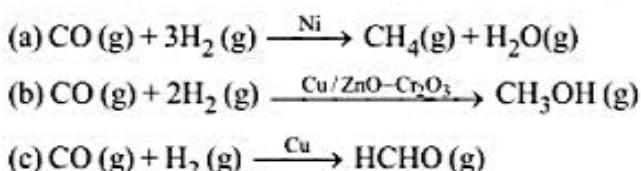
The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst. The mechanism involves five steps:

- Diffusion of reactants to the surface of the catalyst.
- Adsorption of reactant molecules on the surface of the catalyst.
- Occurrence of chemical reaction on the catalyst surface, through formation of an intermediate.
- Desorption of reaction products away from the catalyst surface.
- Diffusion of reaction products away from the catalyst surface.

IMPORTANT FEATURES OF SOLID CATALYSIS :

- Activity :** The activity of a catalyst depends upon the strength of chemisorption. The reactants must get adsorbed reasonably strongly on the catalyst to become active but not so strongly that they become immobile at the surface and do not desorb from the surface. Due to need of such behaviour in solid catalyst, transition metals are normally better catalyst (specially metals of group 7 to 9.)

(ii) Selectivity: Sometimes, the change in catalyst may change the reaction product. The selectivity of a catalyst is its ability to direct a reaction to yield a particular product. For example,



Can you predict the reason behind different action of different catalyst?

SHAPE-SELECTIVE CATALYSIS BY ZEOLITES:

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

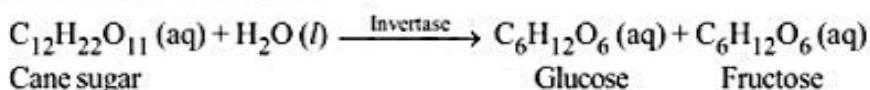
Zeolites are good shape-selective catalysts because of their honey comb-like structures. They are microporous aluminosilicates of general formula, $M_{x/n} [AlO_2]_x \cdot [SiO_2]_y \cdot m H_2O$, with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al-O-Si framework. They are found in nature as well as synthesised for catalytic selectivity. Zeolites, before using as catalysts, are heated in vacuum. When the trapped water molecules come out, zeolite becomes porous, i.e., the cavities in the cage-like structure, which were occupied by water molecules, becomes vacant. The size of the pores generally varies between 260 pm to 740 pm. Thus, only those molecules can be adsorbed in these pores whose size is small enough to enter these cavities and also leave easily. Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in petroleum industry is ZSM-5, which converts alcohol directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

ENZYME CATALYSIS:

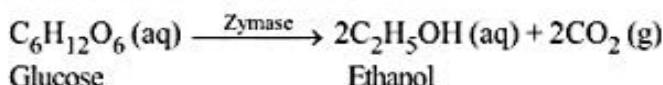
Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are protein molecules of high molecular masses (ranging from 15000 to 1000000 gm/mol) and form colloidal solutions in water.

Enzymes are incredibly efficient catalysts. They catalyse large number of reactions, especially the natural processes. Most of the reactions occurring in the bodies of animals and plants to maintain the life process are catalysed by enzymes. This is why, enzymes are also called **biochemical catalysts** and the phenomenon is known as **biochemical catalysis**. Some of the enzyme catalysed reactions are:

(i) Inversion of cane sugar:

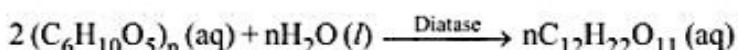


(ii) Conversion of glucose into ethanol:

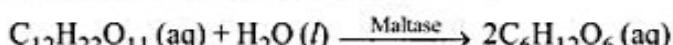


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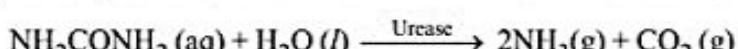
(iii) **Conversion of starch into maltose :**



(iv) **Conversion of Maltose into Glucose:**



(v) **Decomposition of urea into ammonia and carbon dioxide :**



(vi) **Conversion of milk into curd :**

The enzyme lactobacilli helps in the conversion of milk into curd.

CHARACTERISTICS OF ENZYME CATALYSIS:

(i) **Most highly efficient :** One molecule of an enzyme may transform million molecules of the reactant into product, per minute.

(ii) **Highly specific nature :** Each enzyme is specific for a given reaction, i.e., one catalyst cannot catalyse more than one reaction. For example the enzyme urease catalyses the hydrolysis of urea only.

(iii) **Highly active at optimum temperature :** The rate of an enzyme catalysed reaction becomes maximum at a certain temperature called **optimum temperature**. For most of the enzyme, the optimum temperature is 298-310K.



Can you predict whether our body temperature is suitable for the maximum catalytic activity of enzymes or not?

(iv) **Highly active at optimum pH :** The rate of an enzyme catalysed reaction becomes maximum at a particular pH, called optimum pH. For most of the enzyme, the optimum pH is 5-7.

(v) **Influence of activators and coenzymes :** It is observed that when a small non-protein (vitamin) is present with an enzyme, the catalytic activity of enzyme enhances considerably. Such substances are called co-enzymes.

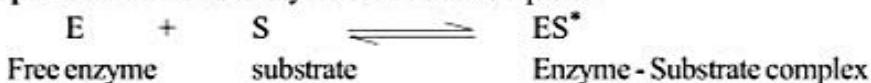
Similarly, the metal ions like Na^+ , Mn^{2+} , Co^{2+} , Cu^{2+} etc, when weakly bonded to enzyme molecules, increases the catalytic activity of enzymes. These metal ions are called activators.

(vi) **Influence of inhibitors and poisons :** The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes.

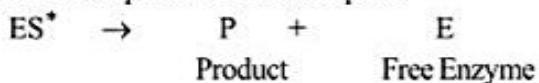
MECHANISM OF ENZYME CATALYSIS : There are a large number of cavities present at the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as $-NH_2$, $-COOH$, $-OH$, etc. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. Due to the presence of active groups on the surface of catalyst, an activated complex is first formed, which then, decomposes to yield the products and enzyme molecules.

Such mechanism (key and lock model) was first proposed in 1913, by the biochemists Michaelis and Menten. It may be expressed kinetically as :

Step-I : Formation of enzyme - substrate complex :



Step-II : Decomposition of the complex



CATALYSTS IN INDUSTRY :

Some of the important processes and their catalyst are given in below.

<i>Industrial process</i>	<i>Catalyst used</i>
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 ₂ SO ₄ (Hetero)	Nitric oxide (NO) gas
Contact process for H ₂ SO ₄ (Hetero)	V ₂ O ₅
Deacon's process for manufacture of Cl ₂ (Hetero)	CuCl ₂
Bosch process for H ₂ (Hetero)	Fe ₂ O ₃ + Cr ₂ O ₃
Manufacture of vegetable ghee (Hetero)	Ni, Cu as promoter
Hydrolysis of ester (Homo)	aq H ₂ SO ₄
Cracking of hydrocarbon (Hetero)	Zeolites

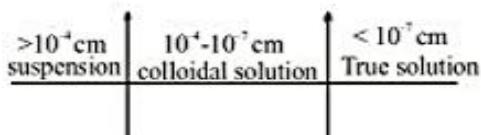
COLLOIDS

Graham classified substances into crystalloids and colloids, but this classification is not totally valid now as many crystalloids under certain conditions behave as colloids.

A colloidal state of matter may be defined as a state in which the size of the particles is such that they can pass through filter paper but not through a vegetable or animal membrane.

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Particle size



Phase of colloids :

A colloidal system is heterogeneous in character. It consists of two phases, namely a dispersed phase and a dispersion medium.

- (a) **Dispersed Phase :** 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 water, the former acts as a dispersed phase.
- (b) **Dispersion Medium :** 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.

(1) *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 system are possible. A gas mixed with another gas forms a homogeneous mixture and not a colloidal system. Typical examples of various type alongwith their characteristic names are given in table.

COMMON COLLOIDAL SYSTEM

<i>Dispersed Phase</i>	<i>Dispersion medium</i>	<i>Colloidal system</i>	<i>Examples</i>
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 sprays.
Liquid	Liquid	Emulsions	Milk
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies, curd.
Solid	Gas	Aerosols of Solid	Smoke, dust
Solid	Liquid	Sols	Must paint, starch dispersed in water, gold sol, muddy water, inks.
Solid	Solid	Solid sols	Ruby glass, some gem stones.

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A colloidal system in which the dispersion medium is a liquid or gas are called sols. They are called hydrosols or aqua sols, if the dispersion medium is water. When the dispersion medium is alcohol or benzene, they are accordingly called alcohols or benzosol.

Colloidal systems in which the dispersion medium is a gas are called aerosols.



Solutions can be classified into 9 types whereas colloids can be classified into 8 can you predict the reason?

Colloids in which the dispersion medium is a solid are called gels, e.g. cheese etc. They have a more rigid structure. Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosol. But at low temperature and high gelatin concentration, the hydrosol can change into a gel.

(2) ***Based on interaction or affinity of phases :*** On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types :

- (i) **Lyophilic Colloids :** The colloidal system in which the particles of dispersed phase have 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.
- (ii) **Lyophobic colloids :** The colloidal system in which the dispersed phase have 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 table.

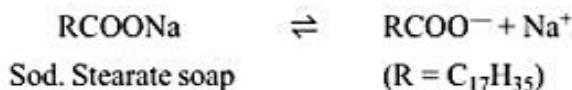
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DIFFERENCE BETWEEN LYOPHILIC AND LYOPHOBIC SOLS

	Property	<i>Lyophilic sols</i>	<i>Lyophobic sols</i>
1.	Nature	Reversible	Irreversible
2.	Preparation	They are prepared very easily by shaking or warming the substance with dispersion medium. They do not require any electrolyte for 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 seen	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 etc.	Generally inorganic substance e.g., metal sols, sulphides and oxides sols.

- (3) ***Based on type of particles of the dispersed phase :*** Depending upon the molecular size, the colloidal system has been classified into three classes :
- (i) ***Multimolecular colloids :*** The multimolecular colloidal particles consists of 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.

- (ii) **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, polystyrene, dacron, synthetic rubber, plastics, etc. The size of these molecules are comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resemble true solutions in some respects.
 - (iii) **The associated colloids or miscelles :** 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 which may have colloidal dimensions.



The long-chain RCOO^- ions associate or aggregate at higher concentrations and form micelles and behave as colloids. They may contain 100 or more molecules.

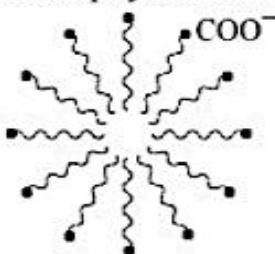
Sodium stearate $C_{17}H_{35}COONa$ is an example of an associated colloid. In water it gives Na^+ and stearate, $C_{17}H_{35}COO^-$ ions. These ions associate to form micelles of colloidal size.



Colloids which 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 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} mole L⁻¹.

Mechanism of Micelle Formation :

Micelles are formed by surface active molecules called surfactants such as soaps and detergents. These molecules have lyophilic group at one end and a lyophobic 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 lyophilic end. When the concentration of the solution is below its CMC, sodium oleate behaves as a normal electrolyte and ionises 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 tends 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.



LIST OF SURFACTANTS AND THEIR CRITICAL MICELLE CONCENTRATION (CMC)

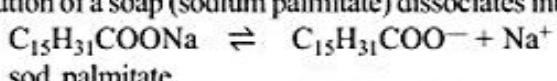
Surfactant	CMC (g/l)	Temp.(°C)
<i>Anionic</i>		
CH ₃ (CH ₂) ₆ COONa	6.5 × 10 ¹	20
CH ₃ (CH ₂) ₁₀ COONa	5.6	20–70
CH ₃ (CH ₂) ₇ OSO ₃ Na	3.0 × 10 ¹	25–50
CH ₃ (CH ₂) ₁₁ OSO ₃ Na	2.6	25–60
CH ₃ (CH ₂) ₅ C ₆ H ₄ SO ₃ Na	9.8	75
CH ₃ (CH ₂) ₁₁ C ₆ H ₄ SO ₃ Na	4.0 × 10 ⁻¹	50–75
<i>Cationic</i>		
CH ₃ (CH ₂) ₉ NH ₂ ·HCl	8.5	25
CH ₃ (CH ₂) ₁₁ NH ₂ ·HCl	2.7	30–50
CH ₃ (CH ₂) ₇ N(CH ₃) ₃ Br	7.8 × 10 ¹	25
CH ₃ (CH ₂) ₁₁ N(CH ₃) ₃ Br	5.4	25
<i>Non-ionic</i>		
CH ₃ (CH ₂) ₇ C ₆ H ₁₁ O ₆	7.3	25
C ₁₂ H ₂₀ O ₉ (C ₁₆ H ₃₁ O ₂) ₂	1.1 × 10 ⁻²	20
CH ₃ (CH ₂) ₁₀ COOC ₁₂ H ₂₁ O ₁₀	7.1 × 10 ⁻³	50



Can you observe some trend in CMC value.

Origin of charge : Various reasons have been given regarding the origin of charge on the colloidal particles. These are given below :

- (i) **Frictional electrification :** It is believed to be frictional due to the rubbing of the dispersed phase particles with medium molecules.
- (ii) **Dissociation of the surface molecules :** It leads to electric charge on colloidal particles. For example, an aqueous solution of a soap (sodium palmitate) dissociates into ions.



The Na⁺ ions pass into the solution while C₁₅H₃₁COO⁻ ions have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains. Thus, the anions which are of colloidal size bear negative charge.

- (iii) **Preferential adsorption of ions from solution :** The charge on the colloidal particles is generally acquired by preferentially adsorbing positive or negative ions from the electrolyte. Thus AgCl particles can adsorb Cl⁻ ions from chloride solutions and Ag⁺ ions from excess Ag⁺ ions solutions; the sol. will be negatively charged in the first case and positively charged in the second case.
- (iv) **Capture of electron :** It is from air during preparation of sol. by Bredig's arc method.

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- (v) **Dissociation of molecular electrolytes on the surface of particles :** H_2S molecules get adsorbed on sulphides during precipitation. By dissociation of H_2S , H^+ ions are lost and colloidal particles become negatively charged.

Electrical charged sols

S.No.	Positively charged sols	Negatively charged sols
1.	Ferric hydroxide, aluminium hydroxide	Metals such as Pt, Au, Ag, Metals sulphides, e.g. arsenius sulphide.
2.	Basic dyes such as methylene blue	Starch, clay, silicic acid.
3.	Haemoglobin	Acid dyes, such as eosin.

Preparation of colloidal solutions

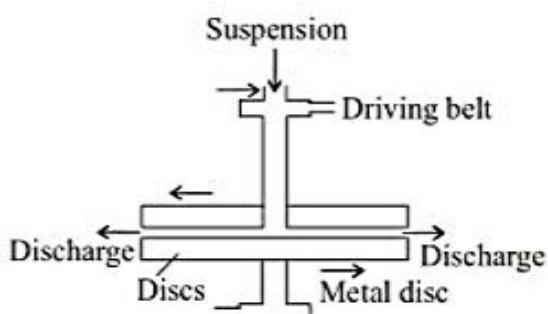
- (1) **Preparation of lyophilic sols :** The colloidal solutions of lyophilic colloids like starch, glue, gelatin etc., can be readily prepared by dissolving these substances in water either in cold or on warming. Solutions of colloidal electrolytes such as soaps and dye stuffs can also be prepared similarly.
- (2) **Preparation of lyophobic sols :** To get a substance in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension (1\AA to 10^3\AA) or increasing the size of molecular particles as to form larger aggregates. In some cases, a third substance as to form larger aggregates. In some cases, a third substance is usually added to increase the stability of the sol. These substances are called stabilizers. Thus, there are two ways by which the lyophobic sols can be prepared :
- (i) **Dispersion methods :** By splitting coarse aggregates of a substance into colloidal size.
 - (ii) **Condensation methods :** By aggregating very small particles (atoms, ions or molecules) into colloidal size.

S. No.	Dispersion methods	Condensation methods
1.	Mechanical dispersion	Exchange of solvents
2.	Electro-dispersion	Change of physical state
3.	Ultrasonic dispersion	Chemical methods : (i) Double decomposition (ii) Oxidation (iii) Reduction (iv) Hydrolysis

Dispersion Methods

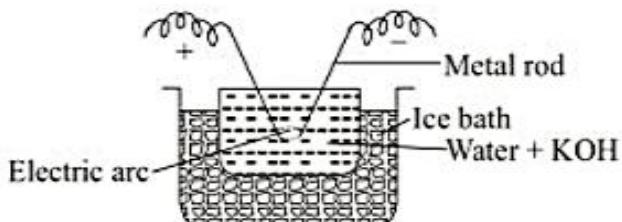
- (1) **Mechanical dispersion :** Solid material is first finely ground by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the colloid mill. The simplest form of colloid mill consists of two metal discs held at a small distance apart from one another and capable of revolving at a very high speed (about 7000 revolutions per minute) in opposite directions. 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

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are made by this method. Tannin is used as a stabilizer in the preparation of colloidal graphite and gum arabic in lamp black colloidal solution (Indian ink).

- (2) **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 trace 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 : (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.

- (3) **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 Loomis, in 1927. Various substances like oils, mercury, sulphur, sulphides and oxides of metals can be dispersed into colloidal state very easily with the help of ultrasonic waves.

- (4) **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 :

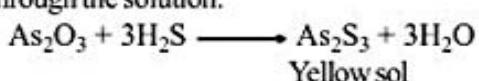
- (i) Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution at once forms a dark reddish brown solution. Ferric chloride acts as a peptizing agent.
- (ii) Freshly prepared stannic oxide on treatment with a small amount of dilute hydrochloric acid forms a stable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

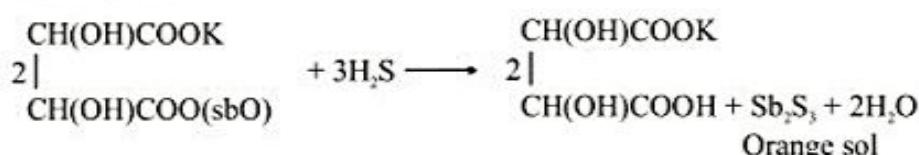
Condensation Methods

- (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 a 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 :

(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 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.



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



(b) Oxidation : A colloidal solution of sulphur is obtained by passing H_2O into a solution of sulphur dioxide.

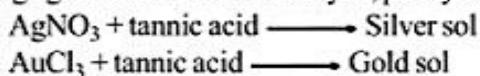


Sulphur sol can also be obtained when H_2S is bubbled through an oxidising agent (bromine water or nitric acid).

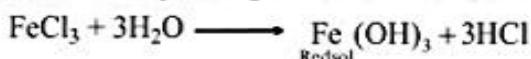
(c) Reduction : Colloidal solutions of metals like gold, silver, platinum, lead, etc., can be obtained when their salts solutions are acted upon by reducing agents.



Organic reducing agents such as formaldehyde, phenyl hydrazine, tannic acid, etc., can also be used.



(d) **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.]

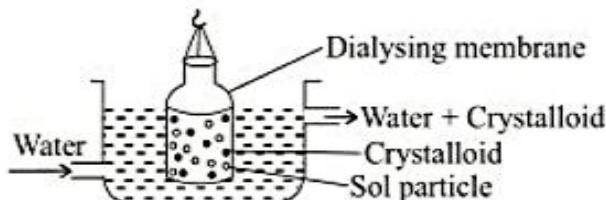


The colloidal solution of silicic acid is also obtained by hydrolysis of dilute solution of sodium silicate with 4N hydrochloric acid which is added drop by drop with constant stirring.

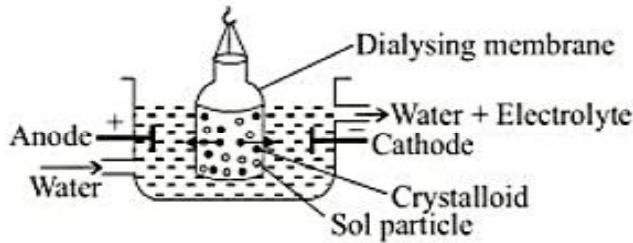
Purification of Colloidal Solution

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but 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 of these impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods.

- (i) **Dialysis*** : It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Since, particles in true solution (ions or smaller molecules) can pass through animal membranes (bladder) or parchment paper or cellophane sheet but colloidal particles do not, the above 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 flown figure. The molecules and ions diffuse through the membrane into the outer water and pure colloidal solution is left behind.



- (ii) **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 electrolyte. The process is then named electro-dialysis. The colloidal solution is placed between two electrodes while pure water is taken in a compartment on each side. Electrodes are fitted in the compartment as shown in figure the ions present in the colloidal solution migrate out to the oppositely charged electrodes.



- (iii) **Ultrafiltration** : Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by especially 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 and subsequently hardened by soaking in formaldehyde. The usual colloidion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultrafilter paper may be prepared by soaking the filter paper in a colloidion solution and hardened by formaldehyde and finally drying it. Thus, by using ultrafilter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is used.

The colloidal particles left on the ultrafilter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

Properties of Colloidal Solutions :

(1) Physical properties :

(i) Heterogeneity : Colloidal solutions are heterogeneous in nature consisting of two phases viz, the dispersed phase and the dispersion medium. Experiments like dialysis and ultra filtration clearly indicate the heterogeneous character of colloidal system. Recent investigations however, shown that colloidal solutions are neither obviously homogeneous nor obviously heterogeneous.

(ii) Filterability : Colloidal particles readily pass through ordinary filter papers. It is because the size of the pores of the filter paper is larger than that of the colloidal particles.

(iii) Non-settling nature : Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitely. Thus there is no effect of gravity on the colloidal particles.

(iv) Colour : The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors :

(a) Size and shape of colloidal particles.

(b) Wavelength of the source of light.

(c) Method of preparation of the colloidal solution.

(d) Nature of the colloidal solution.

(e) The way an observer receives the light, i.e., whether by reflection or by transmission.

(f) Stability : Colloidal solutions are quite stable. Only a few solutions of larger particles may settle but very slowly.

Examples :

(i) Finest gold is red in colour. As the size of particles increases, it becomes purple.

(ii) Dilute milk gives a bluish tinge in reflected light whereas reddish tinge in transmitted light.

(2) Mechanical Properties :

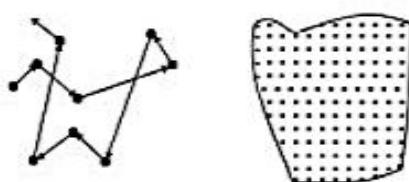
(a) Brownian movement : Colloids particles exhibit a ceaseless random and swarming motion. This kinetic activity of particles suspended in the liquid is called Brownina movement.

Robert Brown first observed this motion with pollen grains suspended in water.

Cause of movement : Brownian movement is due to bombardment of the dispersed particles by molecules of the medium. The Brownian movement (figure) depends upon the size of sol. particles. With the increase in the size of the particle, the chance of unequal bombardment decrease, and the Brownian movement too disappears. It is due to the fact that the suspension fails to exhibit this phe-nomenon.

It should be noted that Brownian movement does not change with time but changes with temperatures.

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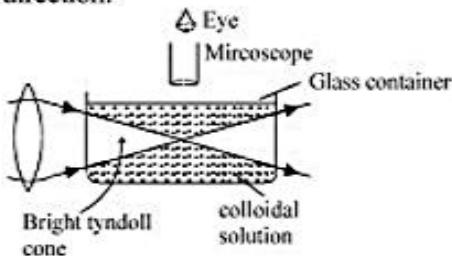
Importance :

- (i) Brownian movement is a direct demonstration of the assumption that the molecules in a gas or solution are in a state of constant ceaseless motion. Thus it confirms kinetic theory.
 - (ii) Brownian movement does not allow the colloidal particles to settle down due to gravity and thus is responsible for their stability.
 - (iii) Brownian movement helps to calculate the Avogadro's number (Detail beyond the scope of the book).
- (b) Sedimentation :** Heavier sol. particle tend to settle down very slowly under the influence of gravity. This phenomenon is called sedimentation.

(3) Optical Properties (Tyndall Effect) :

When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light (figure). This effect is called Tyndall effect. The light is observed as a bluish cone which is called Tyndall cone.

The Tyndall effect is due to scattering of light by the colloidal particles. The scattering of light cannot be due to simple reflection, because the size of the particles is smaller than the wave length of the visible light and they are unable to reflect light waves. In fact, colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles as a light of shorter wavelength. Since maximum scattering of light takes place at right angles to the place of incident light, it becomes visible when seen from that direction.



The Tyndall effect is observed under the following conditions :

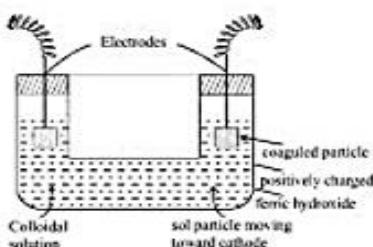
- (i) The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.
- (ii) The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids.

It is important to note that Tyndall effect is not shown by true solutions as their particles are too small to cause scattering. Tyndall effect has been used in devising ultramicroscope and in determining the number of colloidal particles in a colloidal solution.

(4) Electrical Properties : The two electrical properties of colloidal solutions are :

- (a) Electrophoresis or Cataphoresis and
- (b) Electro-osmosis

(a) Electrophoresis or Cataphoresis : In a colloidal solution, the colloidal particles are electrically charged and the dispersion medium has equal but opposite charge. Thus colloidal solution on the whole is electrically neutral. When an electric current is passed through a colloidal solution, the charged particles move towards the oppositely charged electrode where coagulate due to loss of charge.



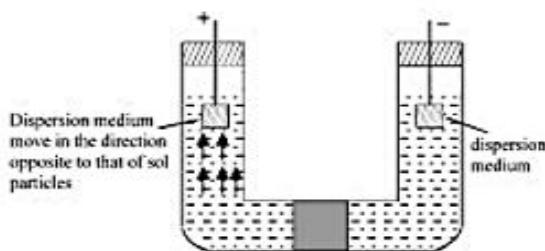
The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode, is called electrophoresis or cataphoresis.

This phenomenon is used to determine the charge on the colloidal particles. For example, when a sol. of ferric hydroxide is taken in a U-tube and subjected to electric field, the ferric hydroxide (sol.) particles get accumulated near the cathode (figure). This shows that ferric hydroxide sol. particles are positively charged.

The sol. particles of metals and their sulphides are found to be negatively charged while those of metal hydroxides are positively charged. Basic dyes such as methylene blue haemoglobin are positively charged while acid dyes like are negatively charged.

(b) Electro-osmosis : The phenomenon involving the migration of the dispersion medium and not the colloidal particles under the influence of an electric field is electro-osmosis.

Take the pure solvent (dispersion medium) in two limbs of U-tube. In the lower middle portion of U-tube, a porous diaphragm containing the colloidal system is present which divides the U-tube in two sections. In each section of U-tube, an electrode is present, as shown in figure. When the electrode potential is applied to the electrodes, the solid phase of sol. (colloidal system) cannot move but the solvent (dispersion medium) moves through the porous diaphragm towards one of the electrodes. The direction of migration of dispersion medium due to electro-osmosis determines the charge on sol. particles e.g., if the dispersion medium moves towards the cathode (negative electrode), the sol. particles are also negatively charged because the dispersion medium is positively charged as on the whole colloidal solution is neutral.



(c) Coagulation : the colloidal sols are stable due to the presence of electric charges on the colloidal particles. Because of the electrical repulsion, the particles do not come close to one another to form precipitates. The removal of charge by any means will lead to the aggregation of particles and hence precipitation will occur immediately.

This process by means of which the particles of the dispersed phase in a sol. are precipitated is known as *coagulation*.

If the coagulated particles instead of settling at the bottom of the container, float on the surface of the dispersion medium, the coagulation is called *flocculation*.

Most of the sols are coagulated by adding an electrolyte of opposite sign. This is due to the fact that the colloidal particles take up the ions of electrolyte whose charges are opposite to that on colloidal particles with the result that charge on the colloidal particles is neutralized. Thus coagulation takes place. For example, arsenic sulphide sol. (negatively charged) precipitated by adding barium chloride solution. It is due to the fact that the negatively charged particles of the sol. take up barium ions and get neutralized which lower the stability. As a result precipitation takes place.

It is observed that different amounts of different electrolytes are required to bring coagulation of a particular solution.

The minimum amount of an electrolyte required to cause precipitation of one litre of a colloidal solution is called coagulation value or flocculation value of the electrolyte for the sol. The reciprocal of coagulation value is regarded as the coagulating power.



For example, the coagulation values of NaCl , BaCl_2 and AlCl_3 for arsenic sulphide sol. are 51, 0.69 and 0.093 millimoles/litre respectively. Thus their coagulating powers are $\frac{1}{51}$, $\frac{1}{0.69}$ and $\frac{1}{0.093}$ i.e., 0.0196, 1.449 and 10.75 respectively.

The coagulation values of a few electrolytes for negatively charged arsenic sulphide and positively charged ferric hydroxide sol. are given in table given below. The valency of the coagulation ion (the ion whose charge is opposite to that of the colloidal particles) is also given.

COAGULATION VALUES OF DIFFERENT ELECTROLYTES

Arsenic sulphide sol.			Ferric hydroxide sol.		
Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)	Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)
K_2SO_4	1	63	KBr	1	138
NaCl	1	51	KNO_3	1	132
KNO_3	1	50	KCl	1	103
MgSO_4	2	0.81	K_2CrO_4	2	0.320
BaCl_2	2	0.69	K_2SO_4	2	0.215
AlCl_3	3	0.093	$\text{K}_3\text{Fe}(\text{Cn})_6$	3	0.096

From the above table, it is clear that the coagulating power of Al^{3+} ions in precipitating the arsenic sulphide sol. is approximately 550 times more than that of sodium (Na^+) or potassium (K^+) ions. Again, it is observed that the negatively charged arsenic sulphide sol. is coagulated by cations while positively charged ferric hydroxide sol. is coagulated by anions.

Hardy-Schulz rules : H. Schulze (1882) and W.B. Hardy (1900) suggested the following rules to discuss the effect of electrolytes of the coagulation of the sol.

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- (1) Only the ions carrying charge opposite to the one present on the sol. particles are effective to cause coagulation, e.g., the negative charged sol. is best coagulated by cations and a positive sol. is coagulated by anions.
- (2) The charge on coagulating ion influences the coagulation of sol. In general, the coagulating power of the active ion increases with the valency of the active ion. After observing the regularities concerning the sign and valency of the active ion, a law was proposed by Hardy and Schulz which is termed as Hardy-Schulze law which is stated as follows:

"Higher is the valency of the active ion, greater will be its power to precipitate the sol."

Thus, coagulating power of cations is in the order of $\text{Al}^{3+} > \text{Ba}^{2+}$ or $\text{Mg}^{2+} > \text{Na}^+$ or K^+ .

Similarly, to coagulating the positively charged sol. the coagulating power of anion is in the order of $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

Some other methods of coagulation :

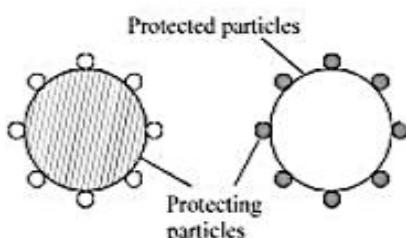
Apart from the addition of electrolyte, coagulation can also be carried out by following methods:

- (i) **By persistent dialysis :** It has been observed that traces of electrolytes are associated with the solution due to which it is stable. If the solution is subjected to prolonged dialysis, the traces of electrolytes are removed and coagulation takes place.
 - (ii) **By mutual coagulation of colloids :** When two sols of oppositely charged are mixed together in a suitable proportion, the coagulation takes place. The charge of one is neutralized by the other. For example, when negatively charged arsenic sulphide sol. is added to positively charged ferric hydroxide sol., the precipitation of both occurs simultaneously.
 - (iii) **By electrical method :** If the electrical charge of lyophobic sol. is removed by applying any electric field such as in electrophoresis, they also precipitate out.
 - (iv) By excessive cooling or by excessive heating.
-
- (5) **Colligative properties :** Colloidal solutions too exhibit colligative properties such as osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point. But the effect of colloidal particles on colligative properties except osmotic pressure is very small. This is due to the large size of colloidal particles. The number of colloidal particles produced by a given mass of colloid is much less than the number produced in a molecular solution, containing the same mass of solute. Hence the colligative effect in colloidal solutions is too less.

* PROTECTIVE COLLOIDS :

Lyophilic sols are more stable than the lyophobic sols. This is because, lyophilic colloids are extensively hydrated and these hydrated particles do not combine to form large aggregates.

Lyophobic sols are more easily coagulated by the addition of suitable electrolyte. To avoid the precipitation of lyophobic sol. by the addition of electrolyte, some lyophilic colloid is added to it. Such lyophilic colloid is called protective colloid and the action of lyophilic colloid by the electrolytes is known as protective anion. The substances commonly used as protective colloids are gelatin, albumin, gum arabic, casein, starch, glue etc. A gold sol. containing a little gelatin as protective colloid needs a very large amount of sodium chloride to coagulate the sol.



Explanation : The particles of the protective colloid get adsorbed on the particles of the lyophobic colloid, thereby forming a protective layer around it (figure). The protective layer prevents the precipitating ions from coming in contact with the colloidal particles.

According to a recent view, the increase in stability of the lyophobic colloid is due to the mutual adsorption of the lyophilic and lyophobic colloids. It is immaterial which is adsorbed on which. In fact the smaller particles, whether of the protective colloid or the lyophobic colloid, are adsorbed on the bigger particles.

Gold number of a protective colloid is a minimum weight of it in milligrams which must be added to 10 ml of a standard red gold sol so that no coagulation of the gold sol. (i.e. change of colour from red to blue) takes place when 1 ml of 10 % sodium chloride solution is rapidly added to it. Obviously, smaller the gold number of a protective colloid, the greater is the protective action.

Isoelectric Point of Colloid :

The hydrogen ion concentration at which the colloidal particles are neither positively charged nor negatively charged (i.e. uncharged) is known as isoelectric point of the colloid. At this point lyophilic colloid is expected to have minimum stability because at this point particles have no charge. The isoelectric point of gelatin is 4.7. This indicates that at pH = 4.7, gelating has no electrophoretic motion. Below 4.7, it moves towards the cathode and above 4.7 it moves towards the anode. It is not always true, e.g., silicic acid has been found to have maximum stability at the isoelectric point.

Electric double layer :

The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying +ve or -ve charges respectively. The charged layer attracts counter ions from the medium which forms a second layer. Thus, an electrical double layer is formed on the surface of the particles i.e., one due to absorbed ions and the other due to oppositely charged ions forming a diffused layer. This layer consists of ion of both the signs, but its net charge is equal and opposite to those absorbed by the colloidal particles. The existence of charges of opposite signs on the fixed and diffused parts of the double layer creates a potential between these layers. This potential difference between the fixed charge layer and diffused layer of opposite charge is called electrokinetic potential or zeta potential.

Illustration

- For the coagulation of 100 ml of arsenious sulphide sol, 5 ml of 1 M NaCl is required. What is the flocculation value of NaCl?

Sol. 5 ml of 1 M NaCl contains NaCl = $\frac{1}{1000} \times 5$ moles = 5 millimoles

Thus, 100 ml of As_2S_3 sol require NaCl for complete coagulation = 5 millimoles

\therefore 1 L, i.e., 1000 ml of the sol require NaCl for complete coagulation = 50 millimoles

\therefore By definition, flocculation value of NaCl = 50

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Exercise

1. The coagulation of 100 mL of a colloidal sol of gold is completely prevented by addition of 0.25 g of starch to it before adding 10 mL of 10% NaCl solution. Find out the gold number of starch.

Ans. 25.

Note that to test 100 mL of gold sol, 10 mL of 10% NaCl solution is required as for 10 mL of gold sol, 1 mL of 10% NaCl solution is required.

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 $0.1\ \mu$.

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.

The emulsion are classified as :

- (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 interconverted into each other by changing the concentration of one of the liquids.

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 if 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 if 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 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 which stabilizes the emulsion is called *emulsifier* or *emulsifying agent*.

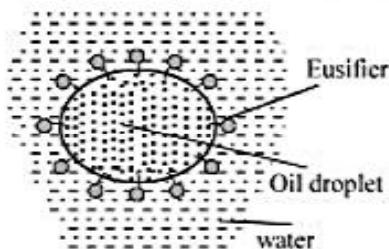
agent. The commonly used emulsifying agents are soaps, detergents and lyophilic colloids. Casein, a lyophilic colloid present in milk, acts as an emulsifier as it forms a protective layer around fat molecules dispersed in water. Hence milk is a fairly stable emulsion.

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 $\text{COO}^- \text{Na}^+$ 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.

Oil in water type emulsion (O/W) Use of emulsion :

- (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 emulsifies 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.

Illustration

1. Answer the following :

- (i) Explain demulsification.
- (ii) Can a colloidal solution conduct electricity ?
- (iii) What happens when gelatin is added to gold sol ?

Sol. (i) Breaking of an emulsion into constituent liquids
 (ii) Yes
 (iii) To increase stability

Exercise

- 1.** Classify the following into positively charged and negatively charged colloidal solutions.
- (a) Ferric hydroxide
 - (b) Arsenious sulphide
 - (c) Gold
 - (d) Stannic oxide

Ans. (a) Ferric hydroxide - positively charged
 (b) Arsenious sulphide negatively charged
 (c) Gold - negatively charged
 (d) Stannic oxide-positively charged

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.

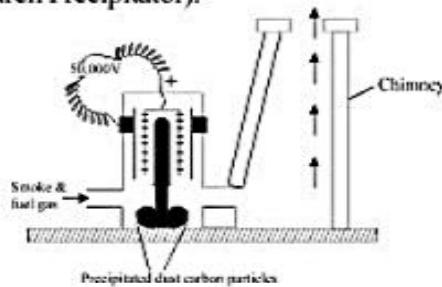
When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids which accumulate on its surface. This action of gels is known as Synesis or Weeping. Some gels such as silica, gelatin and ferric hydroxide liquify on shaking and reset on allowing to stand. This phenomenon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

S.No.	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.	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 called imbibition.	They do not exhibit imbibition.

Uses 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 in 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).



In cottrell precipitator, 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 the oppositely charged electrodes. The deposit may be utilized as a manure.

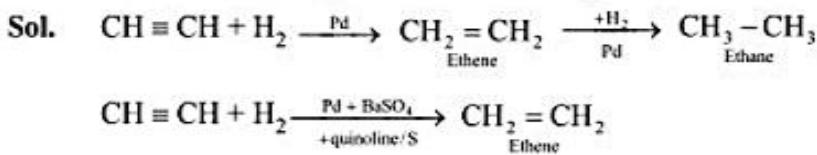
- (10) **Cleansing action of soap and detergent :** Soap solution may be used to wash off the dirt sticking to the fabric, in the presence
- If forms a colloidal solution in water forms (micelles), removes dirt by simple adsorption of oily substance and thus washes away.
 - It decreases the interfacial 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 alongwith the oil 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.

Illustration

1. Why the sun looks red at the time of setting ? Explain on the basis of colloidal properties.

Sol. At the time of setting, the sun is at the horizon. The light emitted by the sun has to travel a longer distance through the atmosphere. As a result, blue part of the light is scattered away by the dust particles in the atmosphere. Hence, the red part is visible.

2. Addition of H_2 to acetylene gives ethane in presence of palladium but if $BaSO_4$ and quinoline or sulphur are also added, the product is ethene. Why ?



$BaSO_4 + \text{quinoline/S}$ poison the catalyst. Hence, the efficiency of the catalyst decreases and the reaction stops at the first stage of reduction.

3. Explain the following observations :

- Ferric hydroxide sol gets coagulated on adding sodium chloride solution
- Cottre's smoke precipitation is fitted at the mouth of the chimney used in factories
- Physical adsorption is multilayered while chemisorption is monolayered

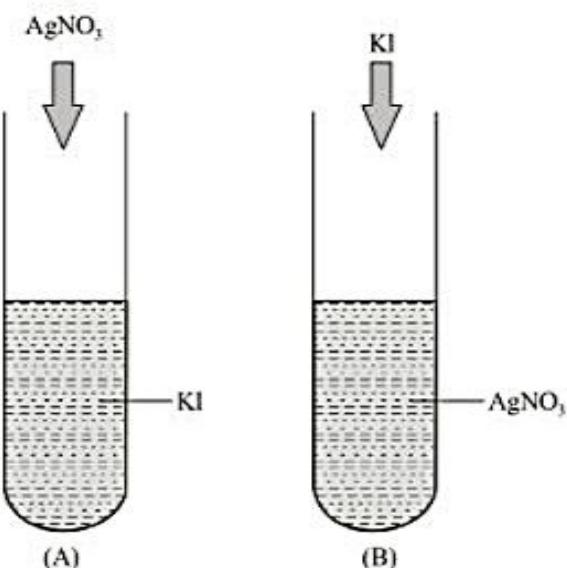
Sol.

- Ferric hydroxide is positively charged. It is coagulated by the oppositely charged Cl^- ions.
- Smoke is a colloidal dispersion containing charged carbon particles. Cottrell's precipitator attracts the charged carbon particles which are precipitated and hot air free of carbon particles escapes from the chimney.
- In physical adsorption, first layer is adsorbed on the adsorbent, second layer is adsorbed on the first layer and this continues. In chemisorption, there is reaction between adsorption and adsorbent forming a surface compound. The adsorbent is now covered and cannot react with more of adsorbate.

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Exercise

1. In an adsorption experiment, a graph between $\log(x/m)$ versus $\log P$ was found to be linear with a slope of 45° . The intercept on the $\log(x/m)$ axis was found to be 0.3010. Calculate the amount of the gas adsorbed per gram of charcoal under a pressure of 0.5 atmosphere.
- Ans.** 1.0
2. The volume of nitrogen gas v_m (measured at STP) required to cover a sample of silica gel with a monomolecular layer is $129 \text{ cm}^3 \text{ g}^{-1}$ of gel. Calculate the surface area per gram of the gel if each nitrogen molecule occupies $16.2 \times 10^{-20} \text{ m}^2$.
- Ans.** 561.8 m^2 .
3. The colloidal solution of AgI is prepared by two different methods as shown in Fig.



- (i) What is the charge on AgI colloidal particles in the two tubes (A) and (B) ?
(ii) Give reason for the origin of charge

- Ans.** (i) In tube A, as AgNO_3 is added in excess, the common Ag^+ ions are adsorbed on AgI particles. Hence, charge on the colloidal particles is positive. In tube B, as KI is added in excess, common I^- ions are adsorbed on the colloidal particles and charge is negative.
(ii) Reason for origin of charge is the preferential adsorption of common ions of the electrolyte present in excess on the colloidal particles.

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SOLVED EXAMPLES

Q.1 During adsorption, a substance

- (A) accumulates on the surface of the other substance
- (B) goes into the body of other substance
- (C) remains close to other substance
- (D) forms an aggregate with other substance

Ans. (A)

Sol. Adsorption is a surface phenomenon. The compound which is being adsorbed is known as 'adsorbate'. It concentrates on the surface of other compound known as 'adsorbent'.

Q.2 Which of the following compounds would exhibit positive adsorption when dissolved in water?

- (A) sodium sulphate
- (B) potassium nitrate
- (C) bathing soap
- (D) dyes

Ans. (C, D)

Sol. Among the compounds given above, bathing soap and dyes are capillary active substances, that is, these will rise and get concentrated at the surface of water. This is positive adsorption.

Q.3 Sorption is the term used when

- (A) adsorption takes place
- (B) absorption takes place
- (C) desorption takes place
- (D) it is not possible to differentiate between adsorption and absorption

Ans. (D)

Sol. When it is not possible to differentiate between adsorption or absorption, the term 'sorption' is used.

Q.4 Which of the following isotherms consider a multilayer formation?

- (A) Langmuir
- (B) Freundlich
- (C) B.E.T
- (D) all of these

Ans. (C)

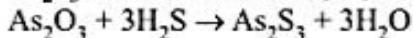
Sol. Only B.E.T considers a multilayer formation.

Q.5 As_2S_3 colloidal solution is obtained by

- (A) treating a solution of As_2O_3 with Na_2S
- (B) passing H_2S in a solution of As_2O_3
- (C) heating As and S.
- (D) reacting As_2O_3 with H_2SO_4 (dil.)

Ans. (B)

Sol. As_2S_3 colloidal solution is prepared by passing H_2S in a solution of As_2O_3 .



Q.6 Which of the following does not give a colloidal solution of sulphur?

- (A) bubbling oxygen through a solution of H_2S in water

$$2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{S}$$
- (B) passing H_2S in very dilute HNO_3 solution
- (C) solution of sulphur in alcohol is added to water
- (D) sulphur is shaken with distilled water

Ans. (D)

- Sol.** When sulphur is shaken with water, no colloidal solution is obtained. All other reactions would produce a colloidal solution.
- Q.7** Fe(OH)_3 is a positively charged colloidal solution. Which of the following would be the most effective for its coagulation?
- (A) Na_3PO_4 (B) Na_2SO_4 (C) NaCl (D) AlCl_3
- Ans.** (A)
- Sol.** According to Schulze-Hardy rule, Na_3PO_4 would be the most effective.
- Q.8** The process of passing a precipitate into colloidal solution on adding an electrolyte is called
 (A) peptisation (B) electro-osmosis (C) electrophoresis (D) dialysis
- Ans.** (A)
- Sol.** The process of throwing a fresh precipitate in a colloidal solution by shaking it with a suitable electrolyte is called peptisation.
- Q.9** Which of the following is a protective colloid?
 (A) gelatin (B) blood (C) soil (D) sulphur
- Ans.** (A)
- Sol.** Only a lyophilic colloid is a protective colloid. When added to a lyophobic colloid, it checks the coagulation of a lyophobic colloid. Gelatin is a lyophilic and so a protective colloid.
- Q.10** Gold number denotes the
 (A) flocculating value of an electrolyte
 (B) peptising power of an electrolyte
 (C) protective power of a lyophilic solution
 (D) electrophoretic movement of colloidal particles
- Ans.** (C)
- Sol.** Gold number denotes the protective power of a lyophilic colloid.
- Q.11** What is positive and negative adsorption? What type of substances exhibit positive adsorption?
Sol. If a substance is dissolved in water and it concentrates more at the surface and less in the bulk, the process is known as positive adsorption. A higher concentration of the substance in the bulk and less at the surface is negative adsorption. Substances like fatty acids, soaps, dyes, etc., show positive adsorption whereas acids, bases, and salts exhibit negative adsorption.
- Q.12** Give one example each where oxidation, reduction, and hydrolysis can be used for the preparation of a colloidal solution.
Sol. (a) A colloidal solution of gold can be produced by the reduction of AuCl_3 .
- $$2\text{AuCl}_3 + 3\text{SnCl}_2 \rightarrow 2\text{Au} + 3\text{SnCl}_4$$
- gold
sol.
- (b) Colloidal sulphur is obtained when H_2S is passed in dilute HNO_3 . (oxidation process)
- $$\text{H}_2\text{S} + 2\text{HNO}_3 \rightarrow 2\text{H}_2\text{O} + 2\text{NO}_2 + \text{S}_{\text{sol.}}$$
- (c) FeCl_3 on boiling with water gives Fe(OH)_3 solution. (Hydrolysis)
- $$\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{HCl}$$

Q.13 What is coagulation value? How can you compare the coagulating powers of two electrolytes?

Sol. The minimum amount of an electrolyte (millimoles) that must be added to one litre of a colloidal solution so as to bring about complete coagulation or flocculation is called coagulation or flocculation value of an electrolyte. Thus the smaller the flocculation value, the greater the coagulating power. As such

$$\frac{\text{Coagulating power of electrolyte I}}{\text{Coagulating power of electrolyte II}} = \frac{\text{Coagulation value of electrolyte II}}{\text{Coagulation value of electrolyte I}}$$

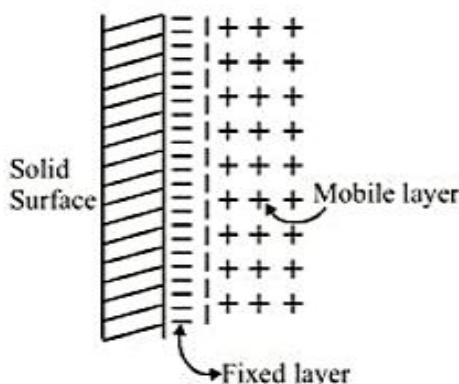
Q.14 The coagulation of 100 mL of a gold solution is completely prevented by addition of 0.25 g of starch to it before adding 1 mL of 10% NaCl solution. What is the gold number of starch?

Sol. Starch added to 100 mL of a gold solution to completely prevent its coagulation by 1 mL of 10% NaCl = 0.25 g or 250 mg.

Therefore, 25 mg of starch would be necessary to prevent coagulation of 10 mL of gold solution and, so, the gold number is 25.0.

Q.15 What is electrokinetic potential?

Sol. A colloidal particle is charged. It carries either a positive or negative charge. During the formation of a colloidal solution, the particle preferentially adsorbs one type of ion on its surface. This forms a fixed layer of charges. To counterbalance it, oppositely charged ions are attracted to form an electrical double layer. This layer is considered to be mobile as shown below.



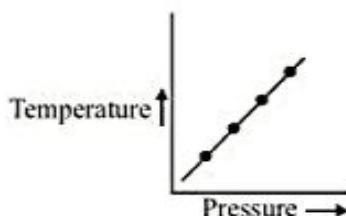
Such a double layer of charges is called Helmholtz double layer. Now it is observed that some of the compensating charges are held in the stationary liquid layer adhering to the surface. The remaining charges are distributed next to this layer in the liquid in the form of a diffuse layer. The potential difference that exists between the stationary layer of compensating charges and the diffuse layer (present in the body of solution) is called electrokinetic or zeta potential.

Q.16 What is an adsorption isostere and adsorption isobar?

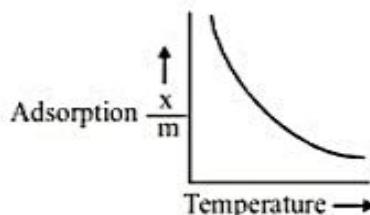
Sol. Adsorption increases with an increase in pressure and normally decreases with an increase in temperature. Thus, if temperature is increased to a certain value (so that the adsorption decreases) the pressure will have to be increased in order to have the same amount of adsorption.

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Obviously, for the same amount of adsorption, the plot between pressure vs temperature should be linear. As such, the plot between temperature vs pressure for a given amount of adsorption is called 'adsorption isostere'.



As stated above, the magnitude of adsorption should increase with a fall in temperature. This actually happens except in chemisorption, where extent of adsorption first increases and then decreases with an increase in temperature. The curve (given below) showing the effect of temperature on the extent of adsorption at a given pressure is called 'adsorption isobar'.



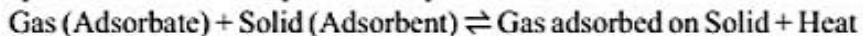
- Q.17** Adsorption of a gas on the surface of solid is generally accompanied by decrease in entropy. Still it is a spontaneous process. Explain.

Sol. Adsorption is an exothermic process, i.e., energy factor favours the process. As $\Delta G = \Delta H - T\Delta S$, in adsorption, though ΔS is -Ve but ΔH is also -Ve and $\Delta H > T\Delta S$ in magnitude so that ΔG is -Ve. Hence, the process is spontaneous.

- Q.18** Explain the following giving reasons :

- Rate of physical adsorption decreases with rise of temperature.
- Cause of Brownian moment.
- Colloidal particles scatter light

Sol. (i) Physical adsorption is an exothermic process in equilibrium



As the temperature is increased, by Le Chatelier's principle, equilibrium shifts in the backward direction, i.e., adsorption decreases.

- Q.19** A one-litre vessel contained a gas at 27°C. 6 g of charcoal was introduced into it. The pressure of the gas fell down from 700 mm to 400 mm. Calculate the volume of the gas (at STP) adsorbed per gram of charcoal. Density of charcoal sample used was 1.5 g cm^{-3} .

Sol. Volume of the vessel = 1000 cm^3

$$\text{Volume of charcoal present in the vessel} = \frac{6 \text{ g}}{1.5 \text{ g cm}^{-3}} = 4 \text{ cm}^3$$

\therefore Volume of the gas initially at 27°C , 700 mm pressure = $1000 - 4 = 996 \text{ cm}^3$

Volume of the gas at 400 mm and 27°C is again equal to the volume of the vessel excluding that of charcoal, i.e., 996 cm^3 . Let us calculate equivalent volume of the gas at 700 mm at the same temperature

$$P_1 V_1 = P_2 V_2 \text{ i.e. } 400 \times 996 = 700 \times V_2 \text{ or } V_2 = 569.1 \text{ cc}$$

\therefore Volume of the gas adsorbed at 27°C , 700 mm pressure = $996 - 569.1 = 426.9 \text{ cm}^3$

$$\therefore \text{Volume adsorbed per gram of charcoal} = \frac{426.9}{6} \text{ cm}^3 \text{ g}^{-1} = 71.1 \text{ cm}^3 \text{ g}^{-1}$$

Converting this volume to STP we get

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \text{ i.e., } \frac{700 \times 71.1}{300} = \frac{760 \times V_2}{273} \text{ or } V_2 = 59.6 \text{ cm}^3$$

- Q.20** 1 g of charcoal adsorbed 100 ml of 0.5 M CH_3COOH to form a monolayer, and thereby the molarity of CH_3COOH reduces to 0.49 M. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = $3.01 \times 10^2 \text{ m}^2 \text{ g}^{-1}$.

Sol. 100 ml of 0.5 M CH_3COOH contains $\text{CH}_3\text{COOH} = 0.05$ mole

After adsorption, CH_3COOH present = 0.049 mole

\therefore Acetic acid adsorbed by 1 g charcoal = $(0.05 - 0.049)$ mole = $0.001 = 6.02 \times 10^{20}$ molecules

$$\therefore \text{Surface area of charcoal adsorbed by each molecule} = \frac{3.01 \times 10^2 \text{ m}^2}{6.02 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$$

- Q.21** 20% of surface sites are occupied by N_2 molecules. The density of surface sites is $6.023 \times 10^{14} \text{ cm}^{-2}$ and total surface area is 1000 cm^2 . The catalyst is heated to 300 while N_2 is completely desorbed into a pressure of 0.001 atm and volume 2.46 cm^3 . Find the active sites occupied by each N_2 molecule.

Sol. **Step-I :** Calculate of total no. of surface sites

$$\text{Density of surface sites} = 6.023 \times 10^{14} \text{ cm}^{-2}$$

$$\text{Total surface area} = 1000 \text{ cm}^2 = 10^3 \text{ cm}^2$$

$$\therefore \text{Total no. of surface sites} = (6.023 \times 10^{14}) \times (10^3) = 6.023 \times 10^{17}$$

Step-II : Calculation of surface sites occupied by N_2 molecules.

$$\text{Surface sites occupied by } \text{N}_2 \text{ molecules} = \frac{20}{100} \times 6.023 \times 10^{17} = 1.2046 \times 10^{17}$$

Step-III : Calculation of total no. of N_2 molecules

$$P = 0.001 \text{ atm}, V = 2.46 \text{ cm}^3 = 2.46 \times 10^{-3} \text{ L}, T = 300 \text{ K}$$

$$PV = nRT \text{ or } n = \frac{10^{-3} \text{ atm} \times 2.46 \times 10^{-3} \text{ L}}{0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} = 10^{-7} \text{ mole}$$

$$\therefore \text{No. of molecules} = (10^{-7}) \times (6.023 \times 10^{23}) = 6.023 \times 10^{16}$$

Step-IV : Calculation of no. of sites occupied by each N_2 molecule

$$= \frac{\text{No. of sites occupied}}{\text{No. of } \text{N}_2 \text{ molecules}} = \frac{1.2046 \times 10^{17}}{6.023 \times 10^{16}} = 2$$

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