03 Surface Chemistry

Introduction :

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas.

Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces.

Adsorption :

The tendency of accumulation of molecular species at the surface than in the bulk of a solid (or liquid) is termed as adsorption. The molecular species or substance, which concentrates or accumulates at the surface is termed as adsorbate and the material on whose surface the adsorption has taken place is called adsorbent.

Example of Adsorbents :

(a) Silica gel : It acts as a good adsorbent and is prepared by mixing sodium silicate with 10% hydrochloric acid at 50° C.

(b) Metals : Metals act as good adsorbents and are being used for contact catalysis. These are prepared by the reduction of their oxides or of the salts under suitable experimental conditions. Examples are Ni, Cu, Ag, Pt and Pd.

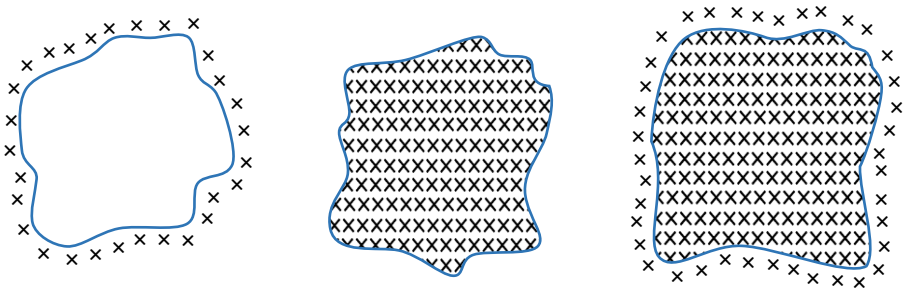
(c) Colloids : As colloids possess high surface per unit mass due to their small size, they act as good adsorbents.

Examples of Adsorbates: There are various gases (He, Ne, O_2, N_2, SO_2, NH_3 etc.) and substances in solution (NaCl, KCl) which can be adsorbed by suitable adsorbents.

Distinction between adsorption and absorption:

In adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.

Sorption : The process in which both adsorption and absorption take place simultaneously is generally termed as sorption.



Adsorption Absorption Sorption

(i) In adsorption, the composition of final sample at surface & bulk will differ largely, while in absorption, the composition will be nearly same.
(ii) The rate of adsorption decreases with time but absorption occurs at nearly constant rate.
(iii) Adsorption is always exothermic but absorption may be endothermic or exothermic.

Examples for adsorption and absorption :

(i) Water vapour is absorbed by anhydrous calcium chloride while it is adsorbed by silica gel.
(ii) Ammonia is adsorbed by charcoal while it is absorbed by water to form ammonium hydroxide.
$NH_3 + H_2O \rightarrow NH_4OH$
(iii) Decolourisation of sugar solution by activated charcoal is another example of adsorption. In this example, charcoal adsorbs the colouring material and thus decolourises the solution.
(iv) The colour of the lake test for aluminium ions is due to adsorption of dye (litmus) on the freshly precipitated aluminium hydroxide.
(v) Case of adsorption of water vapour on the surface of a crucible.
(vi) When sponge is put into water, it takes up water. It is example of absorption.

Mechanism of Adsorption :

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

Characteristics of adsorption :

The various characteristics of adsorption are as follows :

(i) Adsorption is a spontaneous process and takes place in no time.
(ii) The phenomenon of adsorption can occur at all surfaces and five types of interfaces can exist : gas-solid, liquid-solid, liquid-liquid, solid-solid and gas-liquid. The gas-solid interface has probably received the most attention in the literature and is best understood. The liquid-solid interface is now receiving much attention because of its importance in many electrochemical and biological systems.
(iii) It is accompanied by a decrease in the free energy of the system, i.e. ΔG. The adsorption will continue to such an extent that ΔG continues to be negative.
(iv) As the process of adsorption involves loss of degree of freedom of the gas in passing from the free gas to the adsorbed film there is a decrease in the entropy of the system.
It follows from the Gibbs-Helmholtz equation
$\mathbf{\Delta G = \Delta H - T\Delta S}$
Where ΔG is the change in free energy, ΔH is the change in heat content, ΔS is the change in entropy, and T is the temperature of the system. As the entropy and free energy decrease in adsorption, the value of H decreases. This decrease in heat content (H) appears as heat. Hence the adsorption process must always be exothermic.

Illustration 1:

A vessel of capacity 8.21 L contains NH_3 gas at 1.5 atm and 27°C. Now, 5 gm charcoal is added in the vessel and left for sufficient time. After sufficient time, the pressure of gas decreased to 1.2 atm. Calculate the mass of NH_3 gas adsorbed per gram of charcoal. Neglect the volume of charcoal.

Solution:

Mass of NH_3 gas adsorbed = $\frac{\Delta P.V.M}{RT} = \frac{0.3 \times 8.21 \times 17}{0.0821 \times 300}$ = 1.7 gm

$\therefore$ Mass of NH_3 gas adsorbed per gm of charcoal = $\frac{1.7}{5}$ = 0.34 gm

Types of Adsorption :

There are two main types of adsorption of gases on solids.

(i) Physical adsorption or physisorption :

In this adsorption, accumulation of gas on the surface of a solid occurs on account of weak Vander Waals' forces.

(ii) Chemical adsorption or chemisorption :

The gas molecules or atoms are held to the solid surface by chemical bonds (covalent or ionic) in nature. Chemisorption has high energy of activation and is, therefore, often referred to as activated adsorption.

Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption.

Note :

A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, hydrogen is first adsorbed on nickel by van der Waals' force. Molecules of hydrogen then dissociate and hydrogen atoms are held on the surface by chemisorption.

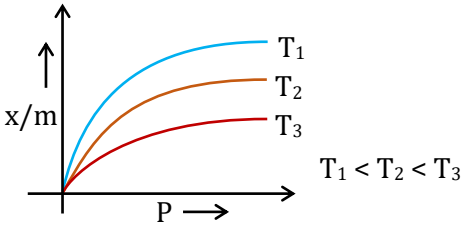
Comparison of Characteristics of Physisorption and Chemisorption

	PHYSICAL ADSORPTION	CHEMICAL ADSORPTION
1	It is caused by weak forces.	It is caused by chemical bond formation.
2	It is not specific.	It is highly specific (Bond formation is necessary).
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 from compounds with the adsorbent exhibit chemisorption.
5	Enthalpy of adsorption is low (20-40 kJ mol^{-1}).	Enthalpy of adsorption is high (80-240 kJ mol^{-1}).
6	Low temperature is favourable. It decreases with increase of temperature.	High temperature is favourable. It increases with the increase in temperature upto certain limit.
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 forms multilayers on adsorbent surface under high pressure.	It forms unimolecular layer.

Illustration 2:
The heat of physisorption lie in the range of
(A) 1 – 10 kJ mol^{-1} (B) 20 – 40 kJ mol^{-1}
(C) 40 – 200 kJ mol^{-1} (D) 200 – 400 kJ mol^{-1}
Ans. (B)
Solution:
Enthalpy of adsorption in physisorption is low and lie in range of 20 – 40 kJ mol^{-1}.
Illustration 3:
The nature of bonding forces in chemisorption
(A) purely physical such as Vander Waal's forces
(B) purely chemical
(C) both chemical and physical simultaneously.
(D) none of these
Ans. (B)
Solution:
In chemisorption adsorbate and adsorbent are linked through pure chemical bonds.
Illustration 4:
Which statements is/are correct ?
(A) Physical adsorption is multilayer, non-directional and non-specific.
(B) Chemical adsorption is generally monolayer and specific in nature.
(C) Chemical adsorption is due to free valence electrons of atoms.
(D) Chemical adsorption is stronger than physical adsorption.
Ans. (A,B,D)

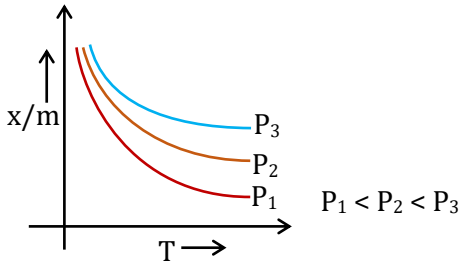
Factors affecting adsorption of gases on solids :

(i) Nature of gas : Easily liquefiable gases (having higher critical temperature) gets adsorbed to the greater extent.
(ii) Nature of adsorbate: Charcoal, silica gel, alumina gel, colloids are good adsorbents.
(iii) Surface area : Adsorption increases on increasing the surface area.
(iv) Pressure : Adsorption of gas at solid surface (increases due to) decrease in volume of system & hence extent of adsorption increases on increasing pressure.



Adsorption isotherms

(v) Temperature : T↑ Physisorption↓ Chemisorption↑



Adsorption isobars

Illustration 5:

Which gas will be adsorbed on a solid to greater extent.

(A) A gas having non-polar molecule.

(B) A gas having highest critical temperature (T_C).

(C) A gas having lowest critical temperature.

(D) A gas having highest critical pressure.

Ans. (B)

Solution:

Gas having higher critical temperature (T_C) are adsorbed to greater extent on solid surfaces.

Freundlich adsorption isotherm:

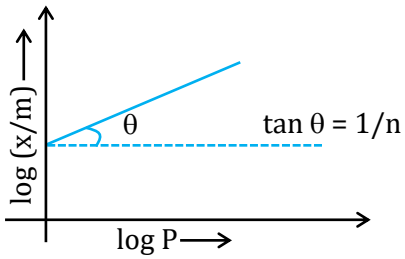
Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed (x) by unit mass of solid adsorbent (m) and pressure at a particular temperature. The relationship can be expressed by the following equation:

$$\frac{x}{m} = k.p^{1/n} \quad (n > 1)$$

where k & n are constant, depending on nature of gas, solid & temperature.

For any combination of gas, solid & temperature, the values of k & n may be determined graphically.

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log P$$



Freundlich isotherm is straight line. Freundlich isotherm fails at high pressure.

Langmuir's adsorption isotherm:

He derived the condition of equilibrium theoretically assuming that adsorption is

(a) monolayer

(b) uniform at solid surface

(c) adsorbate particles do not interact each other at the surface.

$$M(s) + X(g) \underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftharpoons}} M - X(s)$$

At any instant :

Rate of adsorption, $r_a \propto P$

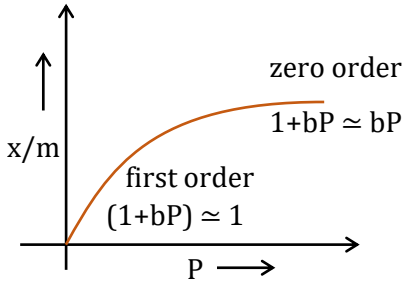
$\propto (1 - \theta)$

$\therefore \quad r_a = K_aP(1 - \theta)$

Where, θ = Fraction of surface area already occupied by adsorbate particles and

Rate of desorption, $r_d \propto \theta \Rightarrow r_d = K_d.\theta$

At equilibrium $r_a = r_d$



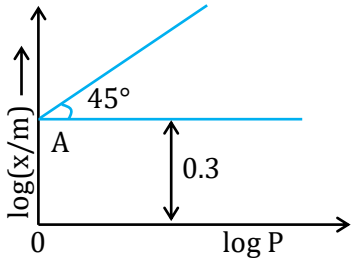
$$\theta = \frac{K_aP}{K_d + K_aP} = \frac{K_a/K_d\ P}{1 + K_a/K_d\ P} = \frac{K_{eq}P}{1+K_{eq}P}$$

Now, $\frac{x}{m} \propto \theta$

$$\frac{x}{m} = K\theta = K\frac{K_{eq}P}{1+K_{eq}P} = \frac{aP}{1+b.P}$$ (where a, b = constants)

Illustration 6:

Graph between $\log\left(\frac{x}{m}\right)$ vs log P is provided for adsorption of NH_3 gas on metal surface. Calculate weight of NH_3 gas adsorbed by 50 gm of metal surface at 2 atm pressure.



Solution:

From Freundlich's adsorption isotherm $\frac{1}{1}\frac{x}{m} = kP^{1/n}$

Taking log on both sides : $\log\frac{x}{m} = \frac{1}{n}\log P + \log k$ (y = mx + c form)

Slope = tan 45° = $\frac{1}{n} \Rightarrow n = 1$

Intercept = log k = 0.3 = log 2

k = 2

So, equation will be :

$\frac{x}{m} = 2p^1$

Given, m = 50 g & P = 2 atm

$\Rightarrow \frac{x}{m} = 2x^2$ x = 200 g

So, amount of NH_3 adsorbed on surface is 200 g.

Adsorption from solution phase :

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. Similarly, the litmus solution when shaken with charcoal becomes colourless. The following observations have been made in the case of adsorption from solution phase:

(i) The extent of adsorption decreases with an increase in temperature.

(ii) The extent of adsorption increases with an increase of surface area of the adsorbent.

(iii) The extent of adsorption depends on the concentration of the solute in solution.

(iv) The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure, concentration of the solution is taken into account, i.e., $\frac{x}{m} = kC^{1/n}$

(C is the equilibrium concentration, i.e., when adsorption is complete).

Applications of Adsorption :

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

(i) Production of high vacuum:

The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.

(ii) Gas masks:

Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

(iii) Control of humidity:

Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

(iv) Removal of colouring matter from solutions:

Animal charcoal removes colours of solutions by adsorbing coloured impurities.

(v) Heterogeneous catalysis:

Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

(vi) Separation of inert gases:

Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

(vii) In curing diseases:

A number of drugs are used to kill germs by getting adsorbed on them.

(viii) Froth floatation process:

A low-grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent.

(ix) Adsorption indicators:

Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.

(x) Chromatographic analysis:

Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

Berzelius in 1835 used the word "catalyst" for the first time for some substance, which alter rate of chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction and the phenomenon is known as catalysis.

Example : Potassium chlorate when heated at 653K to 873K, it gives O_2, When MnO_2 is used in this reaction, the O_2 is formed quickly at the low temperature hence MnO_2 is a catalyst.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

Types of catalysts :

On the basis of phases of catalyst and reactants.

(A) Homogeneous Catalysis :

When catalysts and reactants are in same phase then the process is said to be homogeneous catalysis and

Example : (i) $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

(ii) $CH_3COOCH_3(\ell) + H_2O(\ell) \xrightarrow{HCl(\ell)} CH_3COOH(aq) + CH_3OH(aq.)$

(iii) $C_{12}H_{22}O_{11}(aq.) + H_2O(\ell) \xrightarrow{H_2SO_4(\ell)} \underset{\text{Glucose}}{C_6H_{12}O_6(aq.)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq.)}$

(B) Heterogeneous Catalysis :

When catalysts and reactants are in different phases, then process is known as heterogeneous catalysis and catalyst is called heterogeneous catalyst.

Example:

(i) $2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

(ii) $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$

(iii) $4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$

(iv) Vegetable oils $(\ell) + H_2(g) \xrightarrow{Ni(s)}$ Vegetable ghee (s).

Types of Catalysis :

On the basis of the ways, they alter the rate of chemical reaction.

(A) Positive Catalysis :

A substance which increase the rate of chemical reaction is called positive catalyst and this process is called positive catalysis.

(i) $2SO_2(g) + O_2(g) \xrightarrow[\text{(positive catalyst)}]{Pt(s)} 2SO_3(g)$

(ii) $N_2(g) + 3H_2(g) \xrightarrow[\text{(positive catalyst)}]{Fe(s)} 2NH_3(g)$

(B) Negative Catalysis :

A substance which decrease the rate of chemical reaction is called negative catalyst and this process is called negative catalysis.

Example:

(i) $2H_2O_2 \xrightarrow[\text{(negative catalyst)}]{H_3PO_4 \text{ or glycerol}} 2H_2O + O_2$

(ii) Rate of decomposition of chloroform decreases in the presence of 1% ethyl alcohol.

$$CHCl_3 + \frac{1}{2}O_2 \xrightarrow[\text{(negative catalyst)}]{\text{1\% ethyl alcohol}} COCl_2 + HCl$$

(iii) T.E.L. is used as negative catalyst in petrol which reduces knocking.

(iv) $2H_2SO_3 + O_2 \xrightarrow[\text{(negative catalyst)}]{\text{phenol}} 2H_2SO_4$

(v) $2C_6H_5CHO + O_2 \xrightarrow[\text{(negative catalyst)}]{\text{quinol}} 2C_6H_5COOH$

(C) Auto-catalysis :

When one of the reaction products behave as catalyst for that reaction and increase the rate of reaction then the phenomenon is called auto-catalysis.

Auto-catalytic reactions are slow in the beginning but become increasingly rapid as the reaction proceeds.

Example :

(i) $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH$ (Auto-catalyst) + C_2H_5OH

(ii) $2KMnO_4 + 5\begin{matrix}COOH\\|\\COOH\end{matrix} + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4$ (Auto-catalyst) + $8H_2O + 10CO_2$

(iii) $2\ AsH_3 \rightarrow 2As$ (Auto-catalyst) $+3H_2O$

(D) Induced Catalyst :

When one reaction catalyse another reaction than the phenomenon is called induced catalysis and that reaction is called induced catalyst. eg :

(i) Sodium sulphite (Na_2SO_3) is oxidised to Na_2SO_4 in atmosphere but sodium arsenite (Na_3AsO_3) does not oxidises to Na_3AsO_4 in air. When both are kept together both are oxidised in air. Here oxidation of Na_2SO_3 catalyse the oxidation of Na_3AsO_3. Hence oxidation reaction of Na_2SO_3 act as an induced catalyst for oxidation reaction of Na_3AsO_3.

(ii) Similarly, reduction of $HgCl_2$ to Hg_2Cl_2 by oxalic acid is very slow while that of $KMnO_4$ is fast but mixture of $HgCl_2$ and $KMnO_4$ is reduced rapidly by oxalic acid.

Promoters/Activators :

Substance which themselves are not catalyst but its presence can increase the catalytic activity of catalyst. A promoter increases the number of active sites on the surface.

E.g. :

(i) $N_2 + 3H_2 \xrightarrow[\text{Mo (promoter)}]{\text{Fe (catalyst)}} 2NH_3$

(ii) Vegetable Oil + $H_2 \xrightarrow[\text{Cu (promoter)}]{\text{Ni (catalyst)}}$ Vegetable ghee.

(iii) $CO + 2H_2 \xrightarrow[Cr_2O_2\text{ (promoter)}]{\text{ZnO (catalyst)}} CH_3OH$

Catalytic Poisons/ Anti-catalysts/ Catalyst Inhibitor :

Substance which themselves are not catalyst but whose presence decrease the activity of the catalyst. Poisoning is due to preferential adsorption of poison on the surface of the catalyst.

(i) $N_2 + 3H_2 \xrightarrow[CO/H_2S(\text{catalytic poisons})]{Fe(\text{catalyst})} 2NH_3$

(ii) $2SO_2 + O_2 \xrightarrow[As_2S_3(\text{catalytic poisons})]{\text{Platinised asbestos (catalyst)}} 2SO_3$

(iii) Rosemond's Reactions : $RCOCl + H_2 \xrightarrow[BaSO_4(\text{poisons catalyst})]{Pd(\text{catalyst})} RCHO + HCl$

(iv) $C_2H_4 + H_2 \xrightarrow[CO \text{ or } Ag \text{ vapours(poisons catalyst)}]{Ni(\text{catalyst})} C_2H_6$

(v) $2H_2O_2 \xrightarrow[HCN(\text{poisons catalyst})]{\text{colloidal Pt(catalyst)}} 2H_2O + \frac{1}{2}O_2$

Characteristics of Catalysis :

(i) A Catalyst remains unchanged in mass and chemical compositions at the end of reactions. However, its physical state can be changed.

Example : Granular MnO_2 during decomposition of $KClO_3$ is left as powder at the end of the reaction.

(ii) Finely divided state of catalyst is more efficient for the reactions because surface area increases and more adsorption take place.

(iii) A small amount of catalyst is generally sufficient to catalyse almost unlimited reaction but in some cases the rate of reaction depends on amount of catalyst.

Example :

(A) In Friedel Craft reaction more amount of catalyst is required.

(B) In hydrolysis of ester in acidic and alkaline medium, rate of reaction is proportional to concentration of $H^{\oplus}$ or $OH^{\ominus}$ ions.

(iv) A catalyst cannot initiate the reaction. But sometimes the activation energy is so large that practically a reaction may not start until a catalyst lowers the activation energy significantly. For example, mixture of hydrogen and oxygen do not react at room temperature but the reaction occurs very rapid in presence of Pt black.

$H_2 + O_2 \xrightarrow{\text{room temperature}} \text{No reaction}$

$H_2 + \frac{1}{2}O_2 \xrightarrow{\text{Pt black}} H_2O$

(v) Catalysts are generally specific in nature. A substance which acts as a catalyst in a particular reaction, fails to catalyse other reaction.

(vi) Catalyst cannot change equilibrium state but it helps to attain equilibrium quickly.

(vii) A catalyst does not change the enthalpy, entropy and free energy of a reaction.

(viii) Optimum temperature : There is a particular temperature at which the efficiency of a catalyst is maximum this temperature is known as optimum temperature.

Adsorption Theory of Heterogeneous Catalyst :

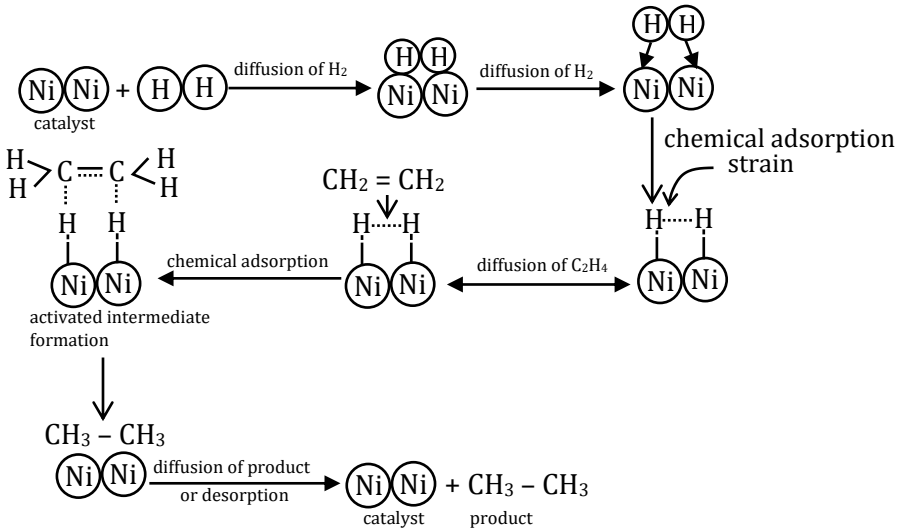
This theory explains the mechanism of heterogeneous catalyst. This theory is combination of two theories, intermediate compound formation theory and the old adsorption theory, the catalytic activity is localised on the surface on the catalyst. The mechanism involves 5 steps.

(i) Diffusion of reactant to the surface of the catalyst.

(ii) Adsorption of reactant molecules on the surface of the catalyst.
(iii) Formation of activated intermediate.
(iv) Formation of product on the catalyst surface.
(v) Diffusion of product from the catalyst surface or desorption.

Examples :

Let us consider addition of H_2 gas to ethylene in presence of Ni catalyst, the reaction takes place as follows.

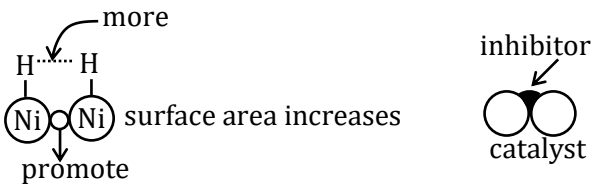


Note :

The surface of catalyst unlike the inner part of bulk, has free valency which provides the sheet for chemical forces of attraction.

Factors Supporting Theory :

(i) This theory explains the role of active centre, more free valency which provide the more space for the more adsorption and concentration increases as a result increase in rate of reaction.
(ii) Rough surface has more active pores, there will be more free valency so more will be rate of reaction.
(iii) The theory explains centre action of promoters which occupied inertial void as a result surface area for the adsorption increases and therefore rate of reaction increases.



(iv) The theory explains of function of poisons or inhibitors. In poisoning, preferential adsorption of poisons take place on the catalyst, surface area for the adsorption on the catalyst decreases hence rate of reaction decreases.

Enzyme catalysis :

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water. They are very effective catalysts which catalyse numerous reactions, especially those connected with natural processes. The enzymes are, thus, termed as biochemical catalysts and the phenomenon is known as biochemical catalysis.

Some Enzymatic Reactions

Enzyme	Source	Enzymatic reaction
Invertase	Yeast	Sucrose → Glucose and fructose
Zymase	Yeast	Glucose → Ethyl alcohol and carbon dioxide
Diastase	Malt	Starch → Maltose
Maltase	Yeast	Maltose → Glucose
Urease	Soyabean	Urea → Ammonia and carbon dioxide
Pepsin	Stomach	Proteins → Amino acids

Characteristics of enzyme catalysis :

(1) Most highly efficient : One molecule of an enzyme may transform one million molecules of the reactant per minute.

(2) 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. It does not catalyse hydrolysis of any other amide.

(3) Highly active under optimum temperature : The optimum temperature range for enzymatic activity is 298-310 K. Human body temperature being 310 K is suited for enzyme-catalysed reactions.

(4) Highly active under optimum pH: The rate of an enzyme-catalysed reaction is maximum at a particular pH called optimum pH, which is between pH value 5-7.

(5) Increasing activity in presence of activators and co-enzymes: It has been observed that when a small non-protein (vitamin) is present along an enzyme, the catalytic activity is enhanced considerably. Activators are generally metal ions such as $Na^{\oplus}$, $Co^{2\oplus}$, $Cu^{2\oplus}$, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity.

(6) Influence of inhibitors and poisons: Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances.

Mechanism of enzyme catalysis :

The enzyme catalysed reactions may be considered to proceed in two steps.

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

$$E + S \longrightarrow ES^{\#}$$

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

$$ES^{\#} \longrightarrow E + P$$

Where, E = Enzyme

S = Substrate,

$ES^{\#}$ = Enzyme-substrate Complex, (Disclaimer : # is a symbol used to show an activated complex)

P = product

Illustration 7:

Which of the following is incorrect for a catalyst?

(A) Bio-chemical reactions are mostly catalysed by enzymes

(B) Catalyst does not start a reaction

(C) Catalyst changes the equilibrium constant of a reaction

(D) Co-enzymes increase the activity of an enzyme

Ans. (C)

Illustration 8:

What is the effect of enzymes on the rate of biochemical reactions?

(A) The rate increases (B) It does not change

(C) The rate decreases (D) either (B) or (C)

Ans. (A)

Illustration 9:

In heterogenous catalysis of a gaseous reactants over solid catalyst

(A) Reaction occurs on the surface of catalyst

(B) Reaction occurs when gases diffuse towards the surface of catalyst

(C) Reaction starts when gases are about to desorb from the catalyst surface

(D) Reaction occurs before adsorption of reactants

Ans. (A)

Solution:

The reactant gases get adsorbed on the surface of the catalyst and reaction occurs on the surface itself.

Illustration 10:

Which of the following is the best example of shape selective catalysis?

(A) finely divided nickel (B) zeolites

(C) palladium (D) platinum

Ans. (B)

Solution:

The catalytic reaction that depends upon the structure of pores 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 structure.

Illustration 11:

Why are enzymes highly specific?

(A) They are nitrogenous material (B) They have active site on their surface

(C) They are biological catalyst (D) They are very active

Ans. (B)

Solution:

Enzymes are highly selective catalysts, meaning that each enzyme only speeds up a specific reaction. The molecules that an enzyme works with are called substrates. The substrates bind to a region on the enzyme called the active site.

Thomas Graham classified the soluble substances into two categories depending upon the rate of their diffusion through animal and vegetable membranes or parchment paper.

Crystalloids :

They diffuse rapidly in solution and can rapidly pass through animal or vegetable membranes, e.g. urea, sugar, salts and other crystalline substances.

Colloids :

They diffuse very slowly in solution and cannot pass through animal or vegetable membranes, e.g. starch, gelatin, silicic acid, proteins etc. Since this class of substances generally exist in amorphous or gelatinous condition and hence the name colloid meaning **"glue form".**

Note :

Actually, every substance irrespective of its nature can be crystalloid or colloid under suitable conditions. For example:

(i) NaCl, though a crystalloid in water behaves like a colloid in benzene.

(ii) Soap is a colloid in water, while it behaves like a crystalloid in benzene.

Therefore, "A substance is said to be in the colloidal state, when it is dispersed in another medium in the form of very small particles having diameter between 10^{-4} cm to 10^{-7}cm".

S.No.	Property	Suspension	Colloidal solution	True solution
1	Particle size	>10^{-4} cm or 10^{4} Å	10^{-7} cm to 10^{-4} cm or 10 Å to 10^{4} Å	<10^{-7} cm or 10 Å
2	Visibility	Visible with naked eye.	Visible with ultra microscope.	Not visible with any of the optical means.
3	Diffusion	Does not diffuse	Diffuse very slowly	Diffuse rapidly
4	Settling	Settles under gravity	Does not settle but it may settle under centrifuge	Does not settle
5	Nature	Heterogeneous	Heterogeneous	Homogeneous
6	Appearance	Opaque	Generally clear	Clear

Colloidal solutions :

They are considered as a heterogeneous system consisting of the following three components:

1. **Dispersed phase (discontinuous or inner phase) :** It consists of discrete particles significantly larger than ordinary molecules and this small particles of solute is diffused in solvent.
2. **Dispersion medium (continuous phase Or outer phase) :** It is the medium in which dispersed phase is present. This consists of continuously interlinked molecules.
3. **Stabilising agent:** This is a substance which tends to keep the colloidal particles apart. Some colloids are self stabilizers.

Dispersed phase + Dispersion medium = Dispersion system (Colloidal solution)

Each of the two phases constituting a colloidal system may be a gas, a liquid or a solid. For example, in milk, the fat globules are dispersed in water. Hence fat globules form a dispersed phase and water is the dispersion medium.

Classification of colloids :

1. **Depending upon the physical state of the dispersed phase and that of dispersion medium :**

The colloidal solutions are divided into the following eight categories:

1	Solid	Solid	Solid sol	Some coloured glasses, gem stone
2	Solid	Liquid	Sol	Paints, inks, white of eggs
3	Solid	Gas	Aerosol	Smoke, dust
4	Liquid	Solid	Gel	Curds, pudding cheese, jellies
5	Liquid	Liquid	Emulsion	Milk, cream, oil in water
6	Liquid	Gas	Liquid Aerosol	Clouds, mist, fog (water in air)
7	Gas	Solid	Liquid foam	Cake, bread, lava, pumice stone
8	Gas	Liquid	Solid foam	Soap lather, froth, whipped cream

Note :

Since the two gases are completely miscible in each other, they always form a true solution.

2. Depending upon the appearance of colloids :

On this basis, colloids are divided into the following two main categories :

(A) Sol : When a colloidal solution appears as fluids, it is termed as Sol. Sols are named after dispersion medium. For example, when dispersion medium is water, they are called hydrosols when the dispersion medium is alcohol they are called alcosols and so on.

(B) Gels : When a colloid has a solid-like appearance, it is termed as gel. The rigidity of gel varies from substance to substance.

3. Depending upon the interaction of the two phases (i.e. dispersed phase and dispersion medium)

According to Perrin and Freundlich, colloids may be classified into lyophobic and lyophilic

(A) Lyphobic or solvent-hating : When the dispersed phase has less affinity for the dispersion medium, the colloids are termed as lyophobic. But when the dispersion medium is water, they are given the name hydrophobic. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes or by heating or by shaking & hence are not stable.

(B) Lyophilic or solvent loving: When dispersed phase has a greater affinity for the dispersion medium, the colloids are termed as lyophilic and when the dispersion medium is water, they are given the name hydrophilic. "they are also called natural colloids, substances like proteins, starch and rubber etc. are grouped under this category

S.No.	Property	Lyophilic	Lyophobic (Extrinsic Sol)
1	Preparation	They are easy to prepare. Only contact with the dispersion medium is needed to Stabilise.	They are difficult to prepare. Special methods are used. Addition of stabilizers is essential for their stability.
2	Size of particles	The particles are just bigger molecules	The particles are aggregates of thousands of molecules
3	Nature	Reversible; once precipitated easily pass back into the colloidal state by contact with dispersion medium	Irreversible, once precipitated does not easily pass into colloidal state
4	Conductivity	With lyophilic salts high conductivities can generally be measured	Owing to their sensitivity in electrolytes the conductivity of lyophobic sol can rarely be ensured over a considerable range of concentration
5	Tyndall effect	Less distinct	More distinct
6	Viscosity	Higher than that of water	Almost same as that of water
7	Surface Tension	Lower than that of water	almost same as that of water
8	Hydration	Particles are heavily hydrated	Particles are poorly hydrated

9	Stability	Very stable, coagulated with difficulty	Less stable, coagulated easily
10	Charge	Depends on the pH of the medium. It can be even zero.	Have characteristic charge (Positive or negative)
11	Concentration of the dispersed phase	Higher concentrations of dispersed phase are possible	Only low concentrations of the dispersed phase are possible
12	Example	Albumin, Glycogen, Rubber, Silicic acid etc.	Au, Ag, some emulsions etc.

4. Depending upon the electrical charge on the dispersed phase:

On this basis the colloids may be divided into the following two main categories :

(A) Positive Colloids : The dispersed phase carries the positive charge. The particles of sol in Water are positively charged. Examples of this type are methylene blue and TiO_2 sols.

(B) Negative Colloids: This dispersed phase carries the negative charge. For example, the particles of As_2S_3 sol in water are negatively charged. The other examples are copper or gold sol and certain dye-stuffs like eosin. Congo red etc.

5. Depending on the structure of colloid particles :

According to Lumie and others, colloids can also be classified into molecular and micellar colloids. The particles of molecular colloids are single macromolecules and their Structure is similar to that of small molecules. Particles of micellar colloids are aggregates of many molecules or groups of atoms which are held together by cohesive or Vander Waal's forces. The examples of molecular colloids are albumin, silicons, rubber etc. while that of micellar colloids or Sulphur, gold, soap detergents etc.

(A) Multimolecular colloids : The multimolecular colloidal particles consists of aggregate of atoms of small molecules with diameter less than 10^{-10} 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_8 molecules. These particles are hold together by Vander Waal's forces. These are usually lyophobic sols.

(B) Macromolecular colloids : The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varying from thousand to millions. These substances are generally polymers. Naturally occurring macromolecules such as starch, cellulose and proteins. Artificial macromolecules such as polyethylene, nylon, polystyrene, Dacron, synthetic rubber, plastics, etc. The size of these molecules is comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resembles true solutions in some respect.

(C) Associated colloids or micelles : these colloids behave as normal electrolytes at low concentrations but colloids at higher concentrations. This is because at higher concentrations, they form aggregated (associated) particles called miscellas. Soap and synthetic detergents are examples of associated colloids. They furnish ions which may have colloidal dimensions.

$$RCOONa \rightarrow RCOO^{\ominus} + Na^{\oplus}$$

Sodium Stearate soap ($R = C_{17}H_{35}$)

The long-chain $RCOO^{\ominus}$ ions associate or aggregate at higher concentrations and for 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. It gives $Na^{\oplus}$ and stearate ions. These ions associate to form micelles of colloidal size.

In general, lyophilic sols are more stable than lyophobic sols. The additional stability is due to the presence of an envelope of the solvent (say water) around the colloidal particle. The process is known as hydration. To coagulate a hydrophilic sol, we have to add a dehydrating agent in addition to an electrolyte.

Note :

Sometimes the names Emulsoids and Suspensoids are also used for hydrophilic and hydrophobic colloids respectively.

Preparation of sols :

Preparation of lyophilic Sols : Preparation of lyophilic Sols : Many organic substances like gelatine, starch, agar-agar, egg albumin, glycogen etc. dissolve readily in water either in cold or on warming to give colloidal solutions directly. These are the lyophilic colloids. For example, sots of egg albumin or glycogen can be prepared by dissolving 1-2 g of the finely divided substance in 100 mL of distilled water and then allowing it to stand for two hours after constant stirring. After two hours, the solutions are filtered.

Preparation of lyophohic Sols: Such Sols can be prepared by the two general way :

(i) By dispersion of coarse particles (Dispersion method). Here we start with bigger particles and break them down to the colloidal size.

(ii) By inducing molecular particles to form large aggregates (condensation method). Here we start with particles of molecular dimensions and condense them to the colloidal dimensions.

Dispersion methods :

(A) Mechanical dispersion : Here the substance is first finely powdered and a coarse suspension is made by shaking the powdered substance with the dispersion medium. This suspension is then passed through a colloid mill consisting of two discs, moving in opposite directions at a very high speed (Fig. I) The particles of the suspension are subjected to a great shearing force and break down to the colloidal dimension. The space between the two discs controls the size of the colloidal particles to be obtained. Rubber, ink, paints and varnishes are prepared by this method.

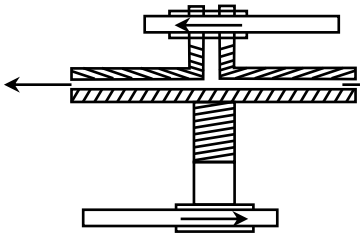


Fig-I

(B) Electrical Dispersion- Bredig's arc methods :

This is commonly used method for preparing the colloidal solutions of metals. An electric arc is struck between two metallic rods kept under the liquid (dispersion medium). A current of 10 amperes and a voltage of 100 to 300 volts is generally employed. The liquid is kept cooled by surrounding it with a cooling mixture. Tiny particles of the metal break away from the rods and disperse in the liquid. Gold, platinum, silver, copper and such other metals can thus be obtained in the colloidal form. (Fig. II)

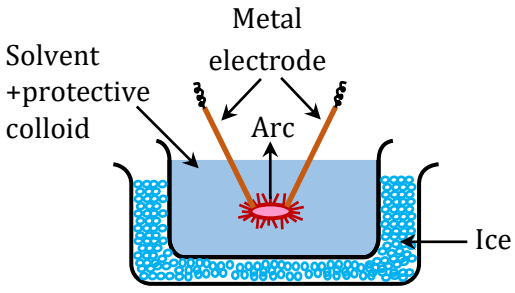


Fig-II

(C) Peptization : The process of bringing a precipitated substance back into the colloidal state is known as peptization. It is carried out by the addition of an electrolyte. The electrolyte added is termed as peptizing or dispersing agent. It involves the adsorption of a suitable ion supplied by the electrolyte added by the particles of the precipitate. Peptization may be carried out by the following ways :

(i) By electrolyte : Freshly prepared precipitate of $Fe(OH)_3$ can be changed into colloidal state when precipitate is treated with a small amount of $FeCl_3$ solution. The sol obtained is positively charged due to the preferential adsorption of $Fe^{3\oplus}$ ions (from $FeCl_3$) on sol particles of $Fe(OH)_3$ as $[Fe(OH)_3]Fe^{3\oplus}$. It should be noted that only freshly prepared precipitates can be peptized.

(ii) By washing a precipitate : Peptization sometimes can be brought about by repeated washings of a precipitate. For example, if the precipitate of $BaSO_4$, is washed continuously, a state is reached when the washings carry some of the particles of the substances in the form of colloidal solution.

Chemical methods :

All chemical changes giving rise to insoluble reaction product can be used for the formation of sols, particularly when suitable stabilizers are also present.

(A) Oxidation : Sols of some non-metals are obtained by oxidation. For example. Sulphur is obtained in colloidal form by passing H_2S gas through bromine water of HNO_3 solution.

$H_2S + Br_2 \rightarrow HBr + S$
Colloidal

Similarly, sol iodine is obtained by oxidising hydroiodic acid with iodic acid as
$HIO_3 + 5HI \rightarrow 3H_2O + 3I_2$, it can be made stable by adding a small amount of gelatin.

(B) Reduction : Sols of some metals are obtained by the reduction of their salts. Gold sols are made by reduction Of $HAuCl_4$ solution with reducing agents like tannic acid, HCHO, H_2O_2, phosphorus, hydrazine etc. Carey Lee's silver sol is obtained by reducing solution of $AgNO_3$ containing alkaline dextrin as stabilizer with variety of reducing agents. Stabilised colloidal suspension of graphite in water is known as aquadag and one in oil is known as oildag.

(C) Hydrolysis : This method is generally employed for the preparation of sols of number of a hydroxides and hydrous oxides. $Fe(OH)_3$, $Al(OH)_3$ and sols are obtained by boiling solution of the corresponding chlorides.

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

A beautiful red sol of ferric hydroxide is prepared by boiling ferric acetate in a beaker having distilled water (500 mL).

$$(CH_3COO)_3\,Fe + 3H_2O \rightarrow Fe(OH)_3 + 3CH_3COOH$$

The excess of ferric acetate may be removed by electrodialysis because its presence renders the sol unstable.

Organic esters of silicon, such as ethyl silicate, will hydrolyze in water to form colloidal silicic acid, $Si(OH)_4$ and alcohol.

(D) Double decomposition : This is the usual way of forming sols of insoluble salts. If the solutions containing the component ions of an insoluble substance are mixed, a precipitate will result. If the substance has low solubility, the precipitate will be colloidal. Colloidal sol of Prussian blue may be prepared by mixing very dilute solutions of $FeCl_3$ and $K_4[Fe(CN)_6]$.

$$3K_4[Fe(CN)_6] + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12\ KCl$$

Sols of arsenious sulphide and mercuric sulphide are obtained by passing H_2S into the saturated solutions of corresponding soluble salts of their oxides,

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

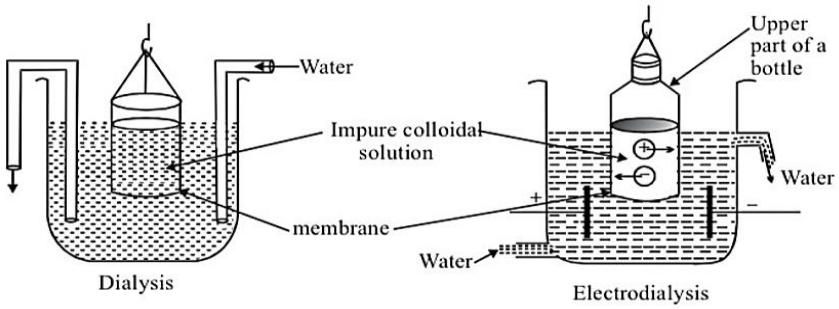
$$Hg(CN)_2 + H_2S \rightarrow HgS + 2HCN$$

(E) Oxidation-reduction methods : Many colloidal sols are prepared by oxidation- reduction reactions. An example of this method is the preparation of the colloidal molybdenic oxide which may be prepared by the reduction of ammonium molybdate with hydrogen sulphide. The sol of hydrated MnO_2 can be prepared by the reduction of 0.01 M $KMnO_4$ with ammonia. This sol can be made stable by adding a definite quantity of gelatin.

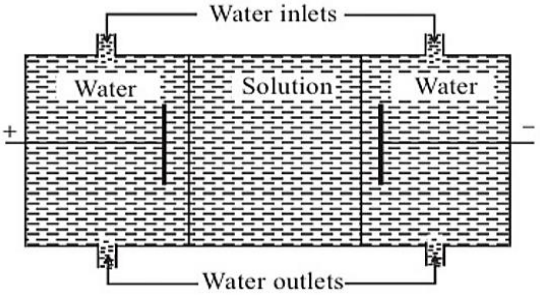
Purification of sols :

Excessive quantities of electrolytes and some other soluble impurities remain in a sol as a result of the method selected for preparation, particularly in chemical condensation Methods.

1. **Dialysis :** This method is based on the fact that colloidal particles are retained by animal membrane or a parchment paper while electrolytes pass through them. The sol is taken in a parchment or cellophane bag, which itself is placed in running water in a trough. Gradually, the soluble impurities diffuse out leaving a pure sol behind. Dialysis is a slow process and it takes several hours and sometimes even days for complete purification.



2. **Electrodialysis :** Dialysis can be fastened by applying an electric field if the substance in true solution is an electrolyte. This process is then called electrodialysis. By means of electrodialysis, it is possible to get a colloid in pure state in short time, although the electric current does not affect non-conducting impurities such as alcohol, sugar, etc.



3. **Ultra filtration :** This is a method not only for purification of the sol but also for concentrating the sol. The pores of the ordinary filter paper are large enough (1030 mg) for the colloidal particles (203 mg) to pass through. But if the pores are made smaller the colloidal particles may be retained on the filter paper. This is known as ultra-filtration.

4. **Ultra-centrifugation :** The colloidal particles share the motion of the molecules of the dispersion medium and are in a state of continuous zig-zag motion called Brownian movement. Sol particles are prevented from settling by this continuous haphazard zigzag motion. The sol is kept in a high-speed centrifuging machine revolving at a very high speed (about 15000 revolutions per minute) so that the colloidal particles settle quickly, the slime can be suspended in water so as to get a sol.

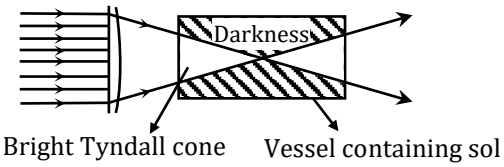
Properties of colloids :

General properties of colloids may be studied under several heads.

1. **Heterogeneous nature :** Colloidal solutions are heterogeneous in nature consisting of two distinct phases viz. the dispersed phase and the dispersion medium. Experiments like dialysis, ultrafiltration and ultra-centrifuging, clearly indicate the heterogeneous character of colloidal system.
2. **Non-settling nature:** Colloidal solutions are quite stable. The suspended colloidal particles remain suspended in the dispersion medium indefinitely. In other words, there is no effect of gravity on the colloidal particles.
3. **Filtrability :** Colloidal particles readily pass through ordinary filter papers because the size of the pores of the filter paper is larger than that of the colloidal particles.
4. **Size of the particles of the dispersed phase :** Colloidal dispersions generally range in particle size from 1 nm to 1μ in diameter. properties which distinguish them from true solution are mainly due to their large size.
5. **Diffusibility :** Colloidal suspensions unlike true solutions do not readily diffuse through fine membranes and have a little power of diffusion. This is due to the large size of the colloidal particles as compared to ordinary solute particles.
6. **Colour :** The colour of the sol is not always the colour of the substance in the bulk. The colour of the colloidal solution changes as the sign and shape of the particles change. It may exhibit different colours when seen by reflected and transmitted light. For example, diluted milk gives a blue colour in reflected light and red colour in transmitted light.
7. **Shape of the colloidal particles :** Different sol particles have different shapes, for example, red gold sol, silver sol, platinum sol. As_2S_3 sol has particles $Fe(OH)_3$ sol and gold sol have disc or platelet like particles. Rod-like particles appear in V_2O_5 sol, tungstic acid sol etc.
8. **Visibility :** Most of the sols appear to true solutions with a naked eye, but the colloidal particle can be seen through an ultramicroscopy
9. **Colligative properties :** Sol particles because of their free suspensions amongst the molecules of the medium, share kinetic energy with them in the same manner as molecules of regular solutes do. This gives rise to colligative properties like osmotic pressure lowering, depression of freezing point and elevation of boiling point. Of these, the osmotic pressure alone has measurable values and its measurement has been used for finding average particle weight in colloidal suspensions. The reason for this may be put as follows:

As colloidal particles are not simple molecules and are bigger particles (i.e. physical aggregation of about 1000 molecules) their number in the colloidal solutions are comparatively small. As the magnitude of colligative properties depends upon the number of solute particles present in the solvent, their values are smaller.

10. Tyndall Effect : Scattering of light by the colloidal particles present in a colloidal solution is known as Tyndall effect and is mainly caused by the scattering of blue part of light by the colloidal particles. If a strong beam of light is passed through a colloidal solution placed in a dark place, the path of the beam gets illuminated. The illuminated path of beam is called Tyndall Cone.



The scattering is caused if the size of particles is of the order of wavelength of light. The same effect is not observed when the light is passed through a true solution as the size of solution particles is too small to cause any scattering.

(a) The diameter of the dispersed particles is not much smaller than the wavelength of the light used.

(b) The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude. This condition is satisfied by lyophobic sols. The lyophilic sols show little or no Tyndall effect as there is very small difference in the refractive indices of the dispersed phase and dispersion medium.

Application of Tyndall effect : Tyndall effect has been used by Zsigmondy and Siedentop for making an ultra-microscope. Ultra-microscope is a microscope arranged so that light illuminates the object from the side instead from below. In ultra-microscope, incident light does not strike the eye of the observer and thus observes the scattering produced by the sol particle against a dark background. An actual image formation is not obtained but the presence of particle can be seen.

11. Brownian movement : The colloidal particles of a colloidal solution when viewed through an ultra-microscope show a constant zig-zag motion. This type of motion was first observed by Robert Brown and hence known as Brownian movement. It is caused by the uneven impacts of the particles of the dispersion medium on the colloidal particles. As the size of the particles increases, the probability of uneven impacts decreases and the Brownian movement becomes slow. When the dispersed particles acquire the dimensions of suspension, no Brownian movement is observed.

This motion is independent of the nature of the colloid but depends on the size of the particles and the viscosity of solution. Smaller the size and lesser the viscosity, faster is the motion. The motion becomes intense at high temperature.

Importance of Brownian motion :

(a) Brownian movement provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.

(b) It counters the force of gravity acting on colloidal particles and hence helps in providing stability to colloidal sols by not allowing them to settle down.

Electrical properties of colloids :

Electric Double Layer Theory or Helm-holtz Electric double layer :

The surface of colloid particles acquires a positive or negative charge by the selective (preferential) adsorptions of common ions carrying positive or negative charge respectively to form first layer. This layer attracts counter ions from dispersion medium and form a second layer. The combination of two layers of opposite charge around the colloidal particle is called Helm-holtz electric double layer. The first layer of ions is firmly held and is termed as fixed layer while the second layer is mobile which is termed as diffused layer. The charge of opposite ions of fixed and diffused layer double layer results in a difference in potential between two opposite charge layers is called the electro-kinetic potential or zeta potential which can be given by

$$Z = \frac{4\pi\eta\mu}{D}$$

Where η = viscosity coefficient, D = dielectric constant of medium.

μ = velocity of colloidal particles when an electric field is applied.

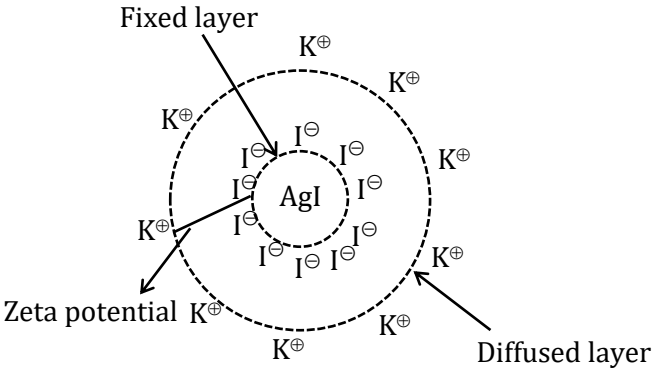
Example :

When silver nitrate solution is added to KI solution, the precipitation of AgI adsorb iodide ions from the D.M with the formation of fixed layer and negatively charged colloidal solution form, however when KI solution is added to $AgNO_3$ solution positive charge sol result due to the adsorbs of $Ag^{\oplus}$ ions from D.M.

$AgI/I^{\ominus}$ $AgI/AI^{\oplus}$

Negative charged Positively charged.

This fixed layer attracts counter ions from the medium forming a second layer.



Electro-kinetic effects :

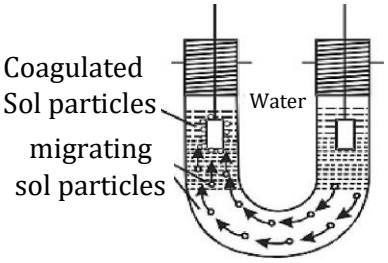
Colloid particles carry electric charge. When the sols are placed in the electric field, certain special effects are noticed, which are termed as electro-kinetic effect. Such effects involve the relationship between the movement of one phase with respect to another in the exhibition of some electrical properties.

(1) Electrophoresis or catephoresis

(2) Electro osmosis or Electroendosmosis

(1) Electrophoresis or Catephoresis : The colloidal particles carry an electric charge. The colloidal solution is taken in a U-shaped tube and two platinum electrodes are dipped in the sol as shown in the figure. The current is then switched on. On closing the circuit, it is found that colloid particles move to the oppositely charged electrode and on reaching that electrode they get discharged. As soon as the charge of the particles is neutralized, they aggregate and settle down. This movement of colloid

particles in electric field is known as electrophoresis in case of the true solutions. Since the current in the colloidal solution must be carried by both positive and negative particles, ions of the diffused layer must be moving in a direction opposite to the direction of the movement of colloid particles. In a $Fe(OH)_3$, sol which is positively charged, the sol particles move to the negative electrode where their charge is neutralised and they aggregate and finally precipitate out. Thus, the entire colloidal matter settles down at the bottom.



Catapictesis

Importance : This phenomenon of electrophoresis is used in the following ways :

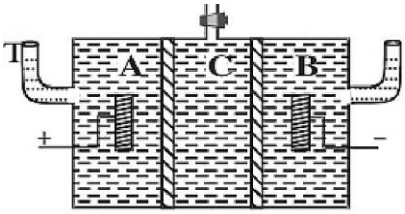
(i) Determining the charge on the colloidal particles : direction of movement of the colloidal particles in the electric field shows the charge on them.

(ii) It can also be used to determine the rate at which colloidal particles migrate under the influence of an electric field.

(iii) It is also used in the identification and determination of homogeneity.

(iv) It is of great importance for the preparative separations of the colloidal substances.

(2) Electro osmosis : It is also known as electro-endosmosis, in the above experiment, a partition is made by animal membrane or parchment paper in between two electrodes, so that only the dispersion medium can move through it and not the colloidal particles. When potential difference is set up between the electrodes, then the dispersion medium is seen to move in a direction opposite to the direction of movement of the colloidal particles. This movement of the dispersion medium relative to the dispersed phase under the influence of the electric field is known as electro-osomosis. This is indicated by the rise of water level in one limb of the U-tube.

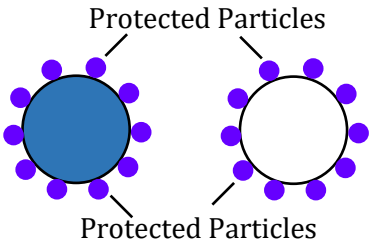


Measurement of electro-osmosis

Protection of colloids :

Protection :

When certain hydrophilic colloids such as gum, gelatin, agar-agar etc. are added to a hydrophobic colloid, the stability of the latter is markedly increased. Now the addition of the small amounts of electrolytes does not cause the precipitation of the hydrophobic colloid. This action of the hydrophilic colloids to prevent precipitation of the hydrophobic colloid by the electrolytes is called protection and the hydrophilic colloid is called protective colloid. It is further observed that the protective colloid not only increase the stability of the hydrophobic colloid but the latter can be evaporated to dryness and the dry mass peptised by simply shaking with water. Thus, the protective colloid converses an irreversible (hydrophobic) colloid into a reversible colloid.



Formation of protective colloids

Some examples of protective colloids are :

(i) Soluble substance like $Ca_3(PO_4)_2$ are held as colloids in blood due to protective action of protein in blood.

(ii) To prevent clogging in pens; superior pen inks contain some protective colloids

(iii) Casein in human milk is better protected than in the cow's milk. It is because of this that cow's milk is more easily coagulated.

(iv) Protargol and Argyrol powders are the protected forms of colloidal silver.

Explanation :

The particles of the protected colloid get adsorbed on the particles of the hydrophobic colloid, thereby forming as protective layer around it. 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 hydrophobic colloid is due to the mutual adsorption of the hydrophilic and hydrophobic colloids. It is immaterial which is adsorbed on which. In fact, the smaller particles whether of the protective colloid or of the hydrophobic colloid are adsorbed on the bigger particles.

Gold Number :

The power of the hydrophilic colloid to prevent the precipitation of a lyophobic colloid by addition of an electrolyte depends upon the nature of the substance. The protective character of various hydrophilic substances can be expressed quantitatively by gold number. The gold number according to Zsigmondy may be defined as: "The number of milligrams of the protective colloid which must be added to 10 cc of a given gold sol so as to just prevent its precipitation by addition of 1 cc of 10% NaCl solution."

Smaller the gold number, higher the protective power of a colloid. Gold numbers of some protective colloids are given below :

S.No.	Protective Colloid	Gold number
1	Gelatin	0.005 - 0.01
2	Hemoglobin	0.03
3	Gum arabic	0.15
4	Egg albumin	0.08 - 0.10
5	Potato starch	25
6	Sodium oleate	0-4
7	Gum tragacanth	2
8	Starch	25 - 50

The protective power was also measured by **Ostwald** in terms of **Congo-Rubin number.** It is the amount of a protective colloid in mg which prevents colour change in 100 mL. of 0.01% Congo-Rubin dye solution to which 0.16 g equivalent of KCl is added when observed after 10-15 minutes.

Coagulation or flocculation :

The colloidal sols are stable by the presence of electric charges on the colloidal particles. Because of the electric repulsion the particles do not come close to one another and coalesce. The removal of charge by any means will lead to the aggregation of particles and hence precipitation immediately. The process by means of which the particles of the dispersed phase in a sol are precipitated is known as coagulation or flocculation.

Electric charges on lyophobic particles can be removed by the application of an electric field as is used in electrophoresis. But a common method of producing precipitation is by the addition of electrolytes.

The precipitate after being coagulated is known as coagulum.

Methods for coagulating a sol :

There are several methods employed for coagulating a sol. Some of them are noted below :

(1) By addition of electrolytes : When excess of an electrolyte is added. The colloidal particles are precipitated. The reason is that colloidal particles taken up ions carrying charged opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for neutralisation of charge on the particles is called the flocculating ion.

It has been observed that, generally, the greater the valency of the flocculating ion added, the greater is its power to cause precipitation. This is known as **Hardy-Schulze Rule.**

(a) The ions carrying charge opposite to that of sol particles are effective in carrying the coagulation of the sol.

(b) Coagulation power of an electrolyte is directly proportional to the fourth power of the valency of the ions causing coagulation.

In the coagulation of a negative sol, the flocculating power of $Na^{\oplus}$, $Ba^{2\oplus}$ and $Al^{3\oplus}$ ions is in the order of $Al^{3\oplus} > Ba^{2\oplus} > Na^{\oplus}$

Similarly, in the coagulation of a positive sol, the flocculation power of $Cl^{\ominus}$, $SO_4^{2\ominus}$, $PO_4^{3\ominus}$, $[Fe(CN)_6]^{4\ominus}$ is in the order of $[Fe(CN)_6]^{4\ominus} > PO_4^{3\ominus} > SO_4^{2\ominus} > Cl^{\ominus}$

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

S.No.	Arsenious sulphide sol		Ferric hydroxide sol	
	Electrolyte	Coagulation value milli moles/litre	Electrolyte	Coagulation value (milli moles/litre)
1	NaCl	52	KCI	132
2	KCl	51	K_2CrO_3	0225
3	$BaCl_2$	0.69	K_2SO_4	0.21
4	$MgSO_4$	0.22	$K_3[Fe(CN)_6]$	0.096
5	$AICI_3$	0.093	$K_4[Fe(CN)_6]$	0.085

(2) Physical methods : The coagulation of some sols can be carried out by (a) mechanical treatment, (b) heating or cooling, (c) irradiation, (d) vigorous shaking, (e) treatment with electric current etc.

(3) By continuous dialysis : We know that traces of electrolytes are present in the colloidal system which are necessary for the stability. If the sol is subjected to continuous dialyser the colloidal system becomes unstable.

(4) Salting out : Coagulation of lyophilic sol can be made by the addition of sufficient high concentrations of certain ions. Thus, salting out of lyophilic colloids is due to the tendency of ions to become solvated, causing the removal of adsorbed water from the dispersed particles.

Emulsions :

Emulsion is a colloidal system consisting of immiscible liquids. e.g. milk is an emulsion in which particles of liquid fat are dispersed in water. In common occurrence, however, one of the liquids is water and the other, and oily substance insoluble in it. The suspended droplets are larger than the particles of the cols: it is because of the density differences between the phases being small. Emulsion droplets can be observed under an ordinary microscope and sometimes even with a magnifying lens.

An emulsion is a heterogeneous system consisting of more than one immiscible liquids dispersed in one another in form of droplets whose diameter, in general, exceeds 0.1μ. Such systems possess an extremely small stability which is made by the addition of surface-active agents, finely divided solids, etc.

Type of Emulsions :

Emulsions are of two types :

(i) Oil in water (o/w) type : In these emulsions oil forms the dispersed phase and water, the dispersion medium. For example, milk, vanishing cream, etc. These are also called aqueous emulsions.

(ii) Water in oil (w/o) type : In these emulsions water is in the dispersed phase and oil in the dispersion medium. For example, butter, cold cream etc. are also called oil emulsions.

In addition to above there is one usual type known as multiple emulsion. As the name indicates, a multiple emulsion is one in which both types of emulsion exist simultaneously. It can be denoted as w/o/w emulsion.

Factors determining the type of emulsions :

When two liquids, say oil in water are shaken to form an emulsion, the type of emulsion formed, (i.e. oil in water or water in oil) depends upon the following factors :

(A) Relative proportion of the two liquids : As a general rule the liquid present in excess forms the dispersion medium. For example, to obtain an emulsion of oil in water, water is taken in excess and to obtain water in oil emulsion, oil is taken in excess.

(B) Surface tension of the two liquids : The liquid with greater tendency to form spherical drops and hence the dispersed phase. Thus, if the surface tension of an oil in is greater than that of water, it will form an oil in water type emulsion.

Preparation of emulsions : Emulsions are usually obtained by spraying mixtures of phases through narrow nozzles or in counter-rotary agitators.

A condensation method given by Summer has been employed in preparation of concentrated o/w emulsions.

Note :

Emulsifying agents or stabilizers are used to form stable emulsions.

Characteristic of emulsions:

(i) Concentration and particles size : In the case of emulsions the amount of one liquid dispersed in another is relatively much greater as compared to the soles. The maximum amount of one liquid which can dispersed in another cannot exceed 74% of the total volume available. Emulsions more concentrated than 74% have also been found. The diameter of droplets in case of emulsions is of the order of 0.001 – 0.05 mm.

(ii) Optical properties : A relationship between optical properties and particle size and also between light scattering with the properties of suspensions have been reported. The interfacial areas in emulsions by optical measurements have been determined by Langlois and other's in 1954.

(iii) Viscosity : The property of viscosity (resistance to flow) is quite important both for practical and theoretical purposes. It provides some information about the structure of emulsions.

(iv) Electrical Conductivity : This property is useful in distinguishing between o/w and w/o type of emulsions. The emulsion in which water is the dispersion medium possesses high conductivity than the emulsion having oil as dispersion medium.

Emulsifiers :

In order to prepare stable emulsions, it is important to add a third component known as emulsifier or emulsifying agent in suitable amounts. Several types of emulsifiers are known.

(i) Long chain compounds with polar groups such as soap, sulphonic acid, sulphates etc.

(ii) Most of the lyophilic colloids also act as emulsifiers such as glue, gelatin etc.

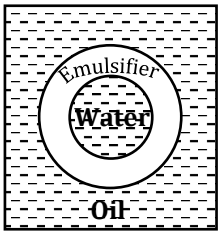
(iii) Certain insoluble powders as clay, lamp, black etc.

(iv) Soluble substances like iodine also act as emulsifiers.

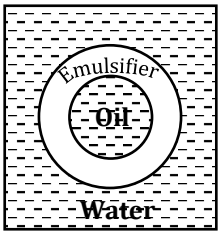
Role of an emulsifier : An emulsifier may act in two ways :

(1) It may be more soluble in one liquid than in the other: In this case it will form a sort of protective film around the drops of this liquid in which it is less soluble and thus prevents them from coming together (fig-a)] For example neutral soaps which are more soluble in water than in olive oil is water type emulsion [Fig.-b]. Acidic soaps which are more soluble in oils than in water, give water in oil type emulsion [fig-c]

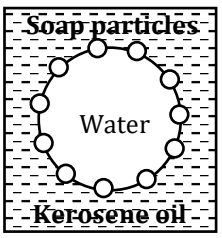
(2) The emulsifiers may be insoluble in both the liquids but not unequally wetted by the two.



Emulsification of oil and water by an acid soap [Fig-a]



Emulsification of oil and water by neutral soap [Fig-b]



Emulsification of water and kerosene by soot particles [Fig-c]

Importance of Emulsions :

Emulsions find manifold applications in various fields.

(i) Medicine - Numerous medicines and pharmaceutical preparations are emulsions. In such forms they have been found to be more effective. Cod-liver oil, caster oil, petroleum oil are used in medicines and are emulsions.

(ii) Articles of daily use- Milk is an emulsion of fat dispersed in water stabilised by casein. Ice cream is an emulsion. Butter, coffee, fruit jellies etc., are all emulsions in nature.

(iii) Cosmetics : The skin penetrating vanishing creams o/w type emulsions and hair creams, cold creams are w/o type emulsions. The lotions, creams and ointments are stabilized by lanoline.

(iv) Industry : The latex obtained form the sap of certain trees is an emulsion of negatively charged rubber particles dispersed in water.

During the concentration of sulphide ores, froth floatation process is employed. In the process, oil emulsion is added to the finely divided ore and foam produced by passing ore contains most of the particles of the ore.

Emulsion of oils and fats have been employed in leather industry for making soft leather and water proof. Asphalt emulsified in water is used for building roads, with the necessity of melting the Asphalt. Emulsions are also employed in oil and fat industry, paints and varnishes, cellulose and paper industry etc. Furthermore, spraying liquids in the form of emulsions are used in agriculture.

Surfactants :

Surfactants are substances which get preferentially adsorbed at the air-water, oil-water and solid-water interfaces, forming an oriented monolayer where in the hydrophilic groups point towards the aqueous phase and hydrocarbon chains point towards the air or the oil phase. The surfactants can be cationic, anionic on non-ionogenic.

Sodium salts of higher fatty acids such as sodium palmitate ($C_{15}H_{31}COONa$), sodium stearate ($C_{17}H_{35}COONa$) and sodium oleate ($C_{17}H_{33}COONa$) are anionic surfactants. The salts of sulphonic acids of high molar mass and general formula ($C_nH_{2n+1}SO_3M$, alkyl sulphonates) or ($C_nH_{2n+1}C_6H_4SO_3M$, alkyl and aryl sulphonates) where $M^{\oplus}$ is $Na^{\oplus}$, $K^{\oplus}$, $NH_4^{\oplus}$, are other anionic surfactants.

Cationic surfactants are those which dissociate in water to yield positively charged ions. Some example are octadecyl ammonium chloride, Cetyl trimethyl ammonium chloride, Cetyl pyridium chloride etc.

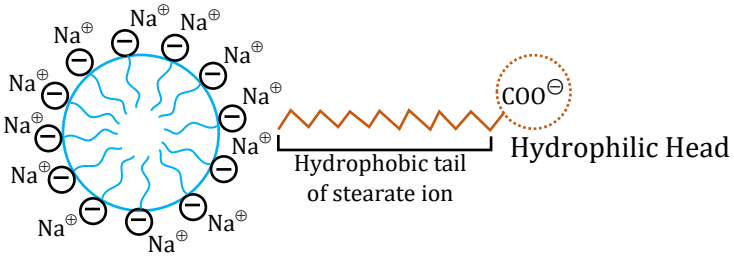
Non-ionogenic surfactants are those whose molecules cannot undergo dissociation. When an alcohol having a high molar mass reacts with several molecules of ethylene oxide, a non-ionogenic surfactant is produced.

The hydrophilic nature of hydroxy ethylated surfactants can be controlled during their synthesis by varying not only the number of carbon atoms in a hydrophobic chain but also the number of hydroxy ethylene groups. These surfactants are soluble even in hard water. Hydrophobic surfaces become hydrophilic when non-ionogenic surfactants are adsorbed from aqueous solutions.

Micelles :

When the surfactant molecules in the water-air interface become so packed in the monolayer that no more molecules can be accommodated with ease, they aggregate in the bulk of the solution leading to the formation of associated colloids also called micelles.

The formation of micelles takes place only above a particular temperature called **Kraft temperature** (T_k) and above a particular concentration called **critical micelle concentration** (CMC). On dilution, these colloids revert back to individual ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is 10^{-4} to 10^{-3} mol L^{-1}.



A Spherical micelle

Mechanism of micelle formation :

Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as $RCOO^{\ominus}Na^{\oplus}$. (example: sodium stearate $CH_3(CH_2)_{16}COO^{\ominus}Na^{\oplus}$. When dissolved in water, it dissociates into $RCOO^{\ominus}$ and $Na^{\oplus}$ ions. The $RCOO^{\ominus}$ ions, however, consist of two parts - a long hydrocarbon chain R which is hydrophobic and a polar group $COO^{\ominus}$ which is hydrophilic.

The $RCOO^{\ominus}$ ions are, therefore, present on the surface with their $COO^{\ominus}$ groups in water and the hydrocarbon chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with $COO^{\ominus}$ part remaining outward on the surface of the sphere. An aggregate thus formed is known as 'ionic micelle'.

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

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

Cleansing action of soaps :

The cleansing action of soap is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles. Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus, soap helps in emulsification and washing away of oils and fats. The negativity charged sheath around the globules prevents them from coming together and forming aggregates.

(a) Grease on cloth

(b) Stearate ions arranging around the grease droplet and

(c) Grease droplet surrounded by stearate ions (micelle formed)

Gels :

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium are called gels. The common examples are boot polishes, jelly, gum Arabic, agar agar, processed cheese and silicic acid. When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids with accumulate on its surface. This action of gels is known as **Syneresis 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 behavior 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 placed in it with simultaneous swelling. This phenomenon is called imbibition.	They do not exhibit imbibition.

Consider the following pairs

S.No.	Dispersed Phase	Dispersing Medium	Type
1	Liquid	Gas	Aerosol
2	Gas	Liquid	Foam
3	Liquid	Liquid	Emulsion
4	Liquid	Solid	Solid Sol

Illustration 12:

Which of the following will show Tyndall effect?

(A) Aqueous solution of soap below critical micelle concentration

(B) Aqueous solution of soap above critical micelle concentration

(C) Aqueous solution of Sodium Chloride

(D) Aqueous solution of Sugar

Ans. (B)

Solution:

Aqueous solution of soap above critical temperature show Tyndall effect.

Illustration 13:

Given below are statements regarding colloids. Identify the correct statement.

(A) Based on the nature of the interaction between the dispersed phase and dispersed medium, the colloids are classified into multimolecular colloids, macromolecular colloids, and associated colloids.

(B) In multimolecular colloids, the particles have the size in the colloidal range of diameter >1

(C) Starch, cellulose, etc. are examples of naturally occurring macromolecular colloids.

(D) Bredig's arc method is one of the chemical methods to prepare colloids.

Ans. (C)

Solution:

Starch, cellulose, etc. are examples of naturally occurring macromolecular colloids

Illustration 14:

Identify the INCORRECT statement regarding colloids.

(A) Cheese is an example of Gel in which dispersed phase is liquid and dispersion medium is solid.

(B) A colloid is a homogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

(C) The lyophobic colloids are also termed as irreversible sols.

(D) The formation of associated colloids takes place above Kraft temperature.

Ans. (B)

Solution:

A colloid is a homogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium

Illustration 15:

Which property of colloids is applied in rubber plating & sewage disposal?

(A) Peptization (B) Brownian movement

(C) Tyndall effect (D) Electrophoresis

Ans. (D)

Solution:

Electrophoresis movement of colloidal particles towards an electrode, when they are subjected to an electrical field.

Illustration 16:

Ferric hydroxide is a negative sol, which of the following electrolyte will coagulate it most:

(A) $FeCl_3$ (B) $CaCO_3$ (C) $BaSO_4$ (D) NaCl

Ans. (A)

Solution:

If $FeCl_3$ is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of $Fe^{3\oplus}$ ions.

Ferric hydroxide is a negative sol, $FeCl_3$ electrolyte will coagulate the most.