COLLOIDAL STATE & SURFACE CHEMISTRY

❑ COLLOIDAL STATE :

When water soluble substances like sodium chloride, copper sulphate, sugar etc., are put into water they dissolve and a homogeneous solution is obtained. The particles of the solute are not visible and their size is molecular size. Such mixtures are called molecular solutions or true solutions.

Now suppose we take muddy river water or an insoluble substance like lead sulphate or calcium sulphate is put into water. The particles of the solutes are visible even with the naked eye because their size is large. On keeping for some time, particles settle down. These mixtures are called suspension.

In between these two extremes, there are particles which are bigger than molecules but are too small to be seen even by a microscope. The colloidal state can thus be regarded as the intermediate state between molecules and particles of a coarse suspension.

Thomas graham (1861) classified substances into two categories on the basis of their rates of diffusion-

- **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 can not 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 colloidal state now a days may be defined as following "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} to 10^{-7} cm (100 mμ to 1 mμ).

Molecular size in true solution	Colloidal particle size	Coarse suspension particle size
10^{-7} to 10^{-8} cm	10^{-5} to 10^{-7} cm	10^{-3} to 10^{-5} cm

❑ COLLOIDAL SOLUTIONS :

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

(i) **A dispersed phase:** It is also known as discontinuous or inner phase. It consists of discrete particles significantly larger than ordinary molecules and in this small particles of solute is diffused in solvent.

(ii) **A dispersion medium or continuous phase or the outer phase** : It is the medium in which dispersed phase is present. This consists of continuously interlinked molecules.

(iii) **A 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.

- **Sol** : If dispersion of a solid in a liquid, solid or gaseous medium, the resulting solution is called sol.
- **Colloidal Solution** : If dispersion of a solid (dispersed phase) in a liquid (dispersion medium), the resulting solution is called colloidal solution.
- **Solid aerosol:** The dispersion of a solid (dispersed phase) in a gas(dispersion medium).
- **Liquid aerosol** : If the dispersed phase is a liquid and the dispersion medium is a gas, the resulting sol is called a liquid aerosol.
- **Emulsion** : When a liquid is dispersed in another liquid the resulting system is called an emulsion.

◆ **Gel** : If colloidal system becomes fairly rigid, it is termed as a gel.

❑ CLASSIFICATION OF COLLOIDS :

There are a number of basis for the classification of colloids.

(i) Depending upon the nature of the dispersed phase and that of dispersion medium the colloidal solutions are divided into the following eight categories:

S.No.	Dispersed Phase	Dispersion Medium	Name	Example
1	Solid	Solid	Solid sol	Coloured glass, gems, alloys
2	Solid	Liquid	Sol	Paints, inks, white of eggs mud
3	Solid	Gas	Aerosol	Smoke, dust
4	Liquid	Solid	Gel	Curds,pudding, cheese, jellies
5	Liquid	Liquid	Emulsion	Milk, Cream, Butter', Oil in water
6	Liquid	Gas	Liquid Aerosol	Clouds, Mist,fog (water in air)
7	Gas	Solid	Solid foam	Cake, bread, lava, pumice stone
8	Gas	Liquid	Foam	Soap lather,froth on beer, whipped cream

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

(ii) **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.

(iii) **Depending upon the interaction of the two phases.**

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. Substances like metals, etc. which have particles of size bigger than the colloidal particles or NaCl which has particles of size smaller than the colloidal size, fall in this category. Such substances are brought into colloidal state with difficulty.

(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.

(iv) Depending upon the electrical charge on the dispersed phase :

On this basis the colloids may be divided into :

(a) Positive Colloids :

The dispersed phase carries the positive charge. The particles of $Fe(OH)_3$ sol in water are positively charged. Examples of this type are also 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.

(v) Depending on the structure of colloid particles :

According to Lumiere 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. The particles of micellar colloids are aggregates of many molecules or groups of atoms which are held together by cohesive or van der 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^{-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 hold together by vandel 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 varrying from thousand to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polysyrene, dacron, synthetic rubber, plastics, etc. The size of these molecules are comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resemble true solutions in some respect.

(c) 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.

$$RCOONa \rightleftharpoons RCOO^- + Na^+$$

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

The long-chain $RCOO^-$ ions associates or aggregate at higher concentrations and form miscelles and behave as colloids. They may contains 100 or more molecules.

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

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

In general lyophilic sols are more stable than lyophobic sols. The additional stability is due to the presence of an envelop 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. Main points of differences between the two types are given in the table:

S.No.	Property	Lyophilic (Intrinsic sol.)	Lyophobhic (extrinsic sol.)
1	Preparation	They are easy to prepare. Only contact with the dispersion medium is needed to stabilise them	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 measured 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	Examples	Albumin, Glycogen, Rubber, Silicic acid etc.	Au, Ag, some emulsions etc.

☐ PREPARATION OF SOLS :

Preparation of lyophilic sols :

Many organic substances like gelatin, starch, agar, eggalbumin, glycogen etc. dissolve readily in water either in cold or on warming to give colloidal solutions directly. These are the lyophilic colloids. For example, sols of egg albumin or glycogen can be prepared by dissolving 1-2 g of the finely ground 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.

Gelatin may be regarded as a typical lyophilic linear colloid. If two grams of gelatin are placed in distilled water and kept there for several hours, it has been observed that unlike egg albumin and glycogen, gelatin does not dissolve in cold water although it does swell. The swellen gelatin may be dissolved by heating with water at 80- 90 C. If two grams of gelatin are dissolved in 400 mL of distilled water, a clear sol. is obtained on cooling.

Preparation of lyophobic sols: Such sols can be prepared by the two general ways.

(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.

A ball mill shown in fig. (II) has been employed to get a colloidal solution from a coarse suspension. Due to a high speed rotation of the mill the coarse ball-like particles roll over one another and drop down at a certain position of the mill, thereby grinding the preliminary wetted mixture. This gives rise to particles of size 6 Å. If some quantity of the dispersion medium is added, it becomes possible to get a colloidal solution.

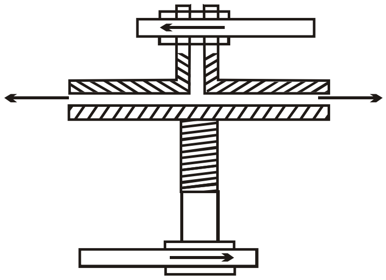


Fig-I

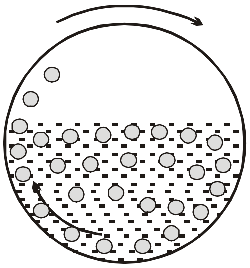


Fig-II A colloid ball mill

(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 roads and disperse in the liquid. Gold, platinum, silver, copper and such other metals can thus be obtained in the colloidal form. (Fig.III)

Svedberg modified this method and prepared sols in non-aqueous media like pentane, diethyl ether, by striking an arc with high frequency alternating current which greatly diminishes the decomposition of the liquid (fig.IV) Svedberg has shown that the electrical methods are suitable not only for preparing the hydro sols of metals like gold, silver, platinum etc., but also for sols of strongly electropositive metals, such as sodium in benzene.

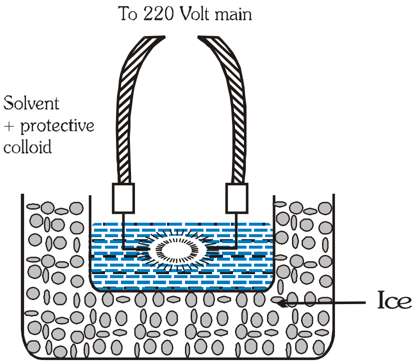


Fig-III

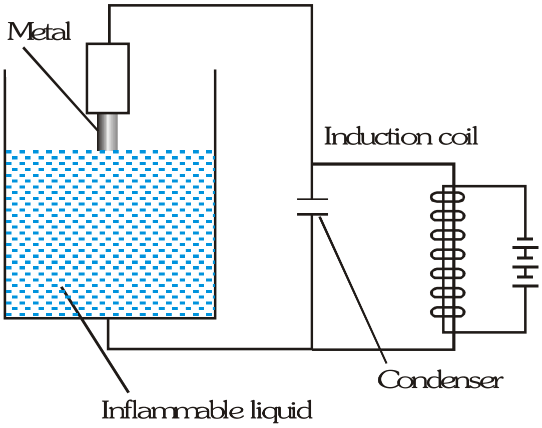


Fig-IV Svedberg's method of preparing metals sols in inflammable liquids

(c) **Peptization** : The process of bringing a precipitated substance back into the colloids state is known as peptization. It is carried out by the addition of an electrolyte. The electrolyte added is termed as peptising or dispersing agent. It involves the adsorption of a suitable ion supplied by the electrolyte added by the particles of the precipitate. Peptisation 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 thus obtained is positively charged due to the preferential adsorption of Fe^{+++} ions (from $FeCl_3$) on sol particles of $Fe(OH)_3$ as $[Fe\ (OH)_3]Fe^{+++}$.

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 products 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 dil. HNO_3 solution.

$$H_2S + Br_2 \rightarrow 2\ HBr + \underset{\text{Colloidal}}{S}$$

Similarly, sol. of iodine is obtained by oxidising hydriodic acid with iodic acid as $HIO_3+5HI\rightarrow 3\ H_2O+3I_2$, 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 Lec's silver sole 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. $Fe(OH)_3$ and $Al(OH)_3$ sols are obtained by boiling solution of the corresponding chlorides.

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

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 hydrolize 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 $K_4Fe(CN)_6$.

$$3K_4Fe(CN)_6 + 4\ FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12\ KCl$$

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

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

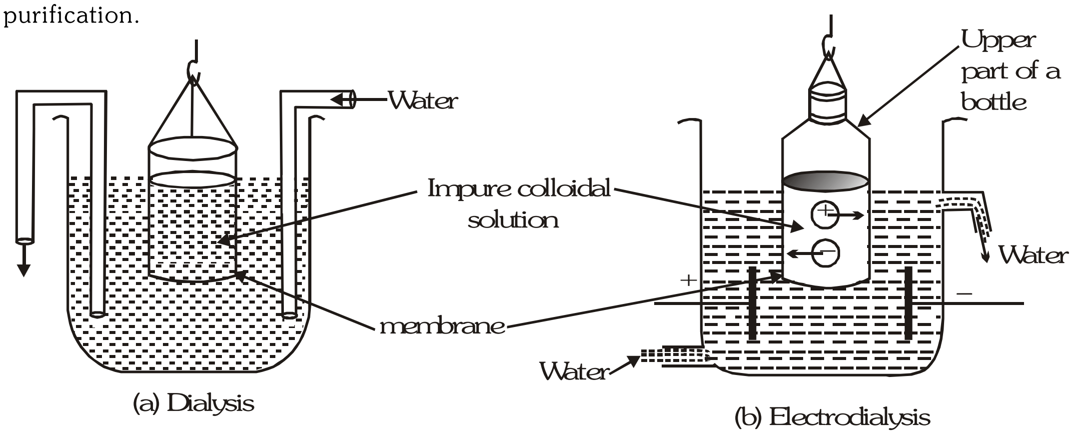
$$Hg\ (CN)_2 + H_2S \rightarrow HgS + 2\ HCN$$

(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 stabilize 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.

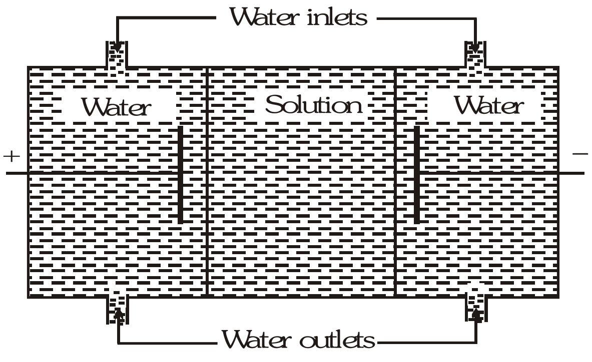
(i) **Dialysis** : This method is based on the fact that colloidal particles are retained by animal membrane or a parchment paper while electrolytes pass through them. The sol is taken in a parchment or cellophane bag, which itself is placed in running water in a trough. Gradually the soluble impurities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



(a) Dialysis

(b) Electrodialysis

(ii) **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.



(iii) **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 mμ) for the colloidal particles (203 mμ) to pass through. But if the pores are made smaller the colloidal particles may be retained on the filter paper. This process is known as ultra filtration.

(iv) **Electro decantation** : This is a method not only for purification of the sol but also for concentrating the sol. If electrodialysis is carried out without stirring the sol, the lower layer becomes more concentrated whereas the top layer becomes dilute. This process is known as electro decantation and was introduced by Pauli.

(v) **Ultracentrifuging** : The colloidal particles share the motion of the molecules of the dispersion medium and are in a state of continuous zigzag motion, called Browninan movement. Sol particles are prevented from setting by this continuous haphazard zigzag motion. The sol is kept in a high speed centrifuging machine revolving at a very high speed (about 15,00 revolutions per minute) so that the colloidal particles settle quickly, the slim can be suspended in water so as to get a sol.

☐ PROPERTIES OF COLLOIDS:

General properties of colloids may be studied under several heads.

(i) **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 ultracentrifuging, clearly indicate the heterogeneous character of colloidal system.

(ii) **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.

(iii) **Filtrability** : 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.

(iv) **Size of the particles of the dispersed phase** : Colloidal dispersions generally range in particle size from 1 mμ to 1 μ in diameter. The properties which distinguish them from true solution are mainly due to their large size.

(v) **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.

(vi) **Colour** : The colour of the sol is not always the same as the colour of the substance in the bulk. The colour of the colloidal solution changes as the size and shape of the particles change. It may exhibit different colours when seen by reflected and transmitted light. For example diluted milk gives a bluish tinge in reflected light and reddish tinges in transmitted light.

(vii) **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 spherical particles whereas $Fe(OH)_3$ sol and blue gold sol have disc or platelet like particles. Rod-like particles appear in V_2O_5 sol. tungstic acid sol, etc.

(viii) **Visibility** : Most of the sols appear to be true solutions with a naked eye, but the colloidal particle can be seen through an ultramicroscope.

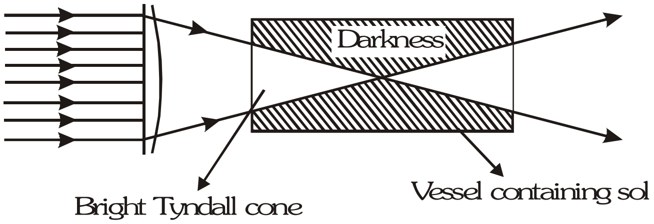
(ix) **Colligative properties** : Sol particles because of their free suspensions amongst the molecules of the medium, share kinetic energy with them in the same manner as molecules of regular solutes do. This gives rise to colligative properties like osmotic pressure lowering, depression of freezing 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.

(x) **Optical properties** : Colloidal sols exhibit the following noted optical properties:

(a) **Tyndall effect** -If a homogeneous solution is observed in the direction of light, it appears clear and when it is observed from a direction at right angles to the direction of the light beam, it appears perfectly dark. But when a beam of light passes through colloidal solutions, it is scattered, the maximum scattered intensity being in the plane at right angles to the path of light. The path beam becomes visible. The effect was first observed by Faraday but was studied in detail by Tyndall and the effect is not commonly known as Tyndall effect.

Scattering also occur in true solutions but the amount of scattering is extremely weak and there is a fundamental difference between the two types of scattering. Tyndall effect is characteristic of large particles (Rayleigh scattering) and there being no difference between the wavelengths of incident and scattered light, solutions exhibit Raman scattering which is characteristic of molecules.



The randomness of scattering of light by colloidal particles was shown by Tyndall as a bright cone of light. It is known as Tyndall cone.

◆ **Explanation :** The tyndall effect is due to scattering of light by the colloidal particles. The colloidal particles first absorb light and then a part of the absorbed light is scattered from the surface of the colloidal particles. Maximum scattereo intensity being in a plane at right angles to the plane of incident light, the path becomes visible when seen from that direction.

◆ **Application of Tyndall effect :** Tyndall effect has been used by Zsigmody and Scidentonpf for making an ultramicroscope. Ultramicroscope is a microscope arranged so that light illuminates the object from the side instead of from below. In ultramicroscope, incident light does not strike the eye of the observer and thus observes the scattering produced by the sol particle against a dark back ground. An actual image formation is not obtained but the presence of particle can be seen.

❑ ELECTRICAL PROPERTIES OF COLLOIDS :

Electro-kinetic effects : Colloid particles carry an 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. Such effects are of four types:

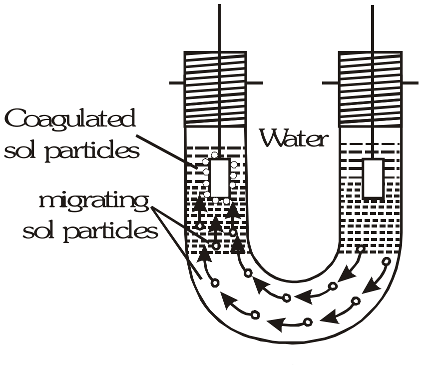
(i) Electrophoresis or catephoresis

(ii) Electro osmosis or Electroendosmosis

(iii) Streaming potential

(iv) Sedimentation potential or Dorn Effect. Let us discuss these one by one.

(i) Electrophoresis or Cataphoresis : The colloidal particles carry an electric charge. The colloidal solution is taken in a U- 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.



Cataphoresis

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.

◆ **Importance** : This phenomenon of electrophoresis is made use of in the following ways :

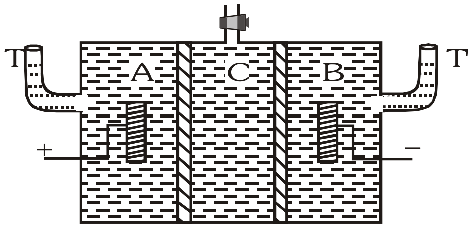
(i) Determining the charge on the colloidal particles : direction of movement of the colloidal particles in the electric field shows the charge on them.

(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.

(ii) 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.



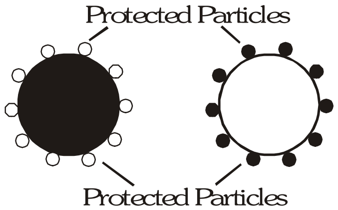
Measurement of electro-osmosis

❑ 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 charges 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 change is called electrolkinetic potential or zeta potential.

❑ 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 converse 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 a 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.

◆ **Preparation of protected colloid :** It is possible to get a protected sol by means of protective one. By means of protection, colloid in higher concentration can be obtained. Furthermore, it is important in preventing the growth of primarily precipitated particles.

◆ **Protected sol of platinum :** Paal and Amberger prepared protected sols of several metals. The platinum protected sol was obtained as follows : Chloroplatinic acid is added to sodium lysalbate (decomposition product of protein) taken in excess of water. To this NaOH is added till we get reddish-brown liquid which is then treated with hydrazine where N_2 gas evolved. This solution is kept for 6 to 7 hours and then dialysed. The black brittle and lustrous residue so obtained was dissolved in water which gives a protected platinum sol.

◆ **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 :

Protective Colloid	**Gold Number**
Heamoglobin	0.03 to 0.07
Starch	15 to 25
Gum Arabic	15 to 25
Gelatin	0.005 to 0.1

The protective power was also measured by **Ostwald** in terms of **Congo Robin number**. It is the amount of a protective colloid in mg which prevents colour change in 100 mL. of 0.01% congo robin 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 :

(i) **By the addition of electrolytes** : In this method large amount of electrolytes are added to the sols which cause precipitation. This is due to the fact the colloidal particles take up the ion whose charges are opposite to that on colloidal particles. With the result that the charge on colloidal particles is neutralised and coagulation takes place. In case of arsenious sulphide sol (negatively charged) coagulation takes place by adding $BaCl_2$. It is due to the fact that negatively charged particles of the arsenious sulphide sol take up barium ions, resulting neutralisation of the charge on the colloidal particles and hence lowering the stability of the sol.

It has been observed that generally the greater the valency of the added ion, the greater is its power to cause coagulation. An ion having an opposite charge to that of the particles of the sol is responsible for coagulation. This ion is generally called as active ion. For example calcium chloride is approximately 100 times more active than NaCl in the coagulation of a silver sol. The particles of a silver sol are stabilised by negative charges and for the coagulation the valency of the cation is effzective. Similarly for the coagulation of positive sols the valency of the anion is decisive. Further, the precipitating power of an electrolyte increases very rapidly with increase in the valency of the cation or anion, the ratios being approximately 1 : 40 : 90 for the ferric hydroxide sol and 1 : 70 : 500 for the arsenious sulphide sol.

Thus in the coagulation of ferric hydroxide sol, the coagulating power increases in the order of $Cl^- > SO_4^{--} > PO_4^{---}$ $Fe(CN)_6^{----}$, while in the coagulation of arsenious sulphide sol, the coagulating power increases in the order of $Na^+ > Ba^{++}$, Al^{+++}. This importance of valency was first recognised by Schulze (1882) and more data were obtained latter by Linder, Picton, Hardy and Freundlich. The coagulation values of NaCl, $BaCl_2$ and $La(NO_3)_3$, for the silver sol prepared by reduction of silver carbonate with tannin are 30, 0.5 and 0.003 milli/mol per/liter respectively. The coagulation or flocculation power can then be expressed as the reciprocal of these flocculation values i.e.

$$\frac{1}{30} : \frac{1}{0.5} : \frac{1}{0.003}$$

i.e. NaCl : $BaCl_2$: La $(NO_3)_3$ as 0.033 : 2 : 33. 3 or 1.60 : 10000

(ii) **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.

(iii) **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.

(iv) **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.

(v) **By hydrated ions**: Since ions can also differ in the degree of hydration or solvation, this factor also plays an important role in the precipitation of sols.

(vi) **By removal of electric charge** : Removal of electric charge on lyophobic particles by means of the application of electric field results precipitation. This is accomplished by electrophoresis.

The coagulating effect of electrolytes on hydrophobic sols was studied by Schulze, Hardy, Linder and Picton.

(a) **Hardy- Schulze Law** : According to them, the greater the valency of the active ion, greater is the power to cause coagulation. Active ion is responsible for coagulation.

Thus, in the case of positively charged sol the coagulation power of anions is in the order of

$[Fe(CN)_4]^{-4} > [PO_4]^{3-} > [SO_4]^{-2} > [Cl]^-$

In the case of negatively charged sols, the coagulation power is in order of

$Al^{+++} > Ba^{++} > Na^+$

The coagulation values of NaCl, $BaCl_2$ and $La(NO_3)_3$ for silver sol are 30, 0.5 and 0.003 millimoles/litre.

The reciprocal of coagulation value is regarded as the coagulating power or flucculating power i.e.

$$\frac{1}{30} : \frac{1}{0.5} : \frac{1}{0.003} \text{ i.e., } 1 : 60 : 1000$$

S.No.	Arsenious sulphide sol		Ferric hydroxide sol	
	Electrolyte	Coagulation value milli moles/litre	Electrolyte	Coagulation value (milli moles/litre)
1	NaCl	52	KCl	132
2	KCl	51	K_2CrO_3	0.225
3	$BaCl_2$	0.69	K_2SO_4	0.21
4	$MgSO_4$	0.22	$K_3Fe(CN)_6$	0.096
5	$AlCl_3$	0.093	$K_4Fe(CN)_6$	0.085

- 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 sols: 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 inform of droplets whose diameter, in general, exceeds 0.1 μ. 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 exists 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. The nature of the emulsifying agent determines the type of the emulsion obtained. According to Boncroft Rule :

"The phase in which the stabilizer is more insoluble becomes the external phase."

Neutral soaps which are insoluble in hydrocarbons but soluble in water give oil-in water emulsions while acid soaps which are more soluble in hydrocarbons yield water-in-oil water emulsions. Emulsions can also be prepared by using ultrasonic waves.

Emulsion is, however, also possible with stabilizers insoluble in both phases. In these cases the phase which wets the emulsifier better becomes the outer phase. Clay, glass powder, calcium carbonate, and pyrites are easily wetted by water and give rise to aqueous emulsion while lamp black, which is more easily wetted by an oil, gives oily emulsion.

A condensation method given by Summer has been employed in preparation of concentrated o/w 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. Recently stable emulsions having diameter of 0.0001 mm have also been reported.

(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 conducitivity 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.

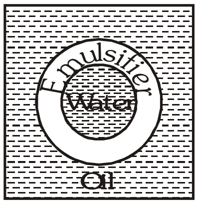
(ii) Most of the lyophilic colloids also act as emulsifiers such as glue, gelatin etc.

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

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

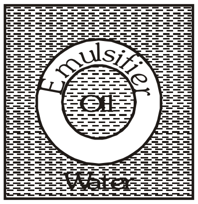
❑ **Role of an emulsifier** : An emulsifier may act in two ways :

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.



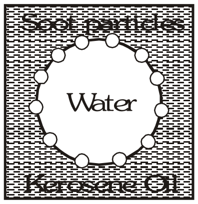
Emulsification of oil
and water by an acid soap

[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.

❑ MICELLIZATION

The diphilic nature of surfactant molecules, i.e. the presence in them of a polar (hydrophillic) and non-polar (hydrophobic) parts has been a feature of their structure imparting special properties to these molecules. The diphilic nature was characterized very well by Hartley as a "split personality". It has been exactly the diphilic nature of surfactant molecules that underlies their tendency of gathering at phase interfaces, immersing their hydrophillic part in water, and isolating their hydrophobic part from it. This tendency ascertains their surface activity i.e. their ability to be adsorbed at the water-air interface or a water-oil one, to wet the surface of hydrophobic bodies, and form structures such as soap films or lipid membranes.

With an increase in the asymmetry of the molecules (a growth in the length of the hydrophobic chain), their surface activity grows (Traube's rule) and accordingly, their special behaviour in a solution, different from that of simple salts, gets more pronounced. It manifests itself the most appreciably for long-chain surfactants with 10-20 carbon atoms in a chain that get characterized by an optimal balance of hydrophilic and hydrophobic properties. These substances, which are having many practical applications (for example, as floatation reagents, stabilizers, and detergents) have special properties in solutions that are of considerable interest.

At low concentrations these surfactants tend to form true solutions that disperse up to individual molecules (or ions). With a growth in the concentration, however, the duality of the properties of the molecules of such diphilic substances gives rise to their self-association in the solution. This results in the formation of what are called micelles.

Micelles may be defined to be aggregates of long- chain diphilic surfactant molecules or ions formed spontaneously in their solutions at a definite concentration. The latter depends on the nature of the polar group and especially on the length of the molecule chain, Micelles can be characterized by the aggregation number (the number of molecules in a micelle) and the micellar mass (the sum of the molecular masses of the molecules forming a micelle).

Micelles form by the cooperative binding of monomers to one another at concentrations exceeding a rather narrow region called the critical micellization concentration (CMC). The latter is the concentration of a surfactant at which a large number of micelles form in its solution that have been in thermodynamic equilibrium with the molecules (ions), and a number of properties of the solution sharply change.

This sharp transition to the CMC region for systems with flexible chains could be attributed to the cooperative nature of the self- association process. This makes aggregates containing many monomers considerably more stable than small particles. The CMC has been one of the most easily determined experimentally and useful quantitative characteristics of solutions of surfactants with flexible chains.

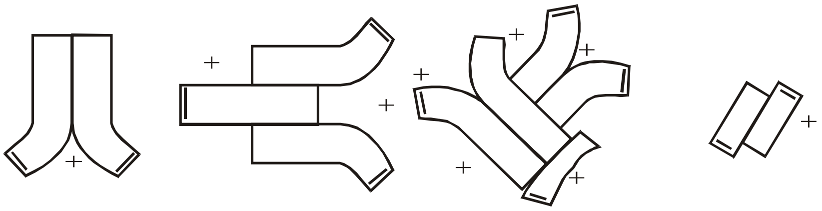
❑ IONIC MICELLES

According to McBain colloidal electrolytes cannot be regarded as macromolecules as they are individual molecules of giant size in solution. They also differ from lyophobic colloids, because the latter are unstable. Large size anions, e.g., $C_{17}H_{33}.\ COO^-$, RSO_3 etc. and cations like $RH(CH_3)_3^+$, aggregate to form ionic micelles of colloidal dimensions containing number of ions together containing appreciable water molecules. So the ionic micelles are the aggregates formed in solution by colloidal electrolytes.

The formation of micelles can also take place from neutral or non-ionic molecules, e.g. polythelene oxide.

- **Ionic micelles of sodium oleate :** The formation of micelle by sodium oleate, $C_{17}H_{33}COO^-Na^+$ is a striking example of colloidal electrolytes. In this case there are two parts, one is tail, i.e. hydrocarbon part $C_{17}H_{33}$, and the other is head COONa. The COONa is an ionisable lyophillic group which tries to go in to water resulting into ions. The $C_{17}H_{33}$ part tends to go away from solution. But if the concentration is increased the hydrocarbon part forms the aggregate micelle is therefore that of anions and may contain hundred or more oleate ions clamped together.

- **Critical micelle concentration (CMC) :** In very dilute solutions, sodium and potassium oleate and other similar substances, remain as individual molecules ionising into positive and negative ions. According to Davies and Bury the concentration at which micelle becomes appreciable, is termed as critical micelle concentration. At this concentration there is an abrupt change in the properties, it decreases with the increase of temperature. Every colloidal electrolyte has a definite value of CMC.
- **Type of ionic micelles :** McBain suggested the presence of more than one type of ionic micelles in a given solution of a colloidal electrolyte. Some of them are described below :



(i) Lamellar micelle :

In consists of double leaflet of soap molecules placed end to end and side by side. X-ray study has revealed the existence of other kind of micelle in which molecules are laid end to end, side by side, as in lameller micelle. The difference from each other and are separated by layer of water, depending upon concentration. Hoffman's investigation has shown that the molecules in the micelle are rotated at an angle of 55 . According to Stuff the molecules are closely packed side by side in an irregular manner as in a liquid crystal. (Fig.1)

(ii) Spherical micelle :

According to Hartley ionic micelles can be spherical. Although this consent is employed but is open to criticism.

(iii) Elleipsoidal or cylindrical micelle :

Klevens has suggested that the micelle may also be an elongated ellipsoidal or of cylindrical model.

❑ 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 pollishes, jelly, gum arabic, agar agar, processed cheese and silicic acid. When the gels are allowed to stand for a long time, they give out small quantities of trapped liquids with accumulate on its surface. This action of gels is known as Synresis of Weeping. Some gels such as silica, geltin and ferric hydroxide liquify on shaking and reset on alloweing to stand. This phenomenon of Sol-gel transformation is called thixotropy.

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

	Elastic gels	Non-elastic gels
1	They change to solid mass on dehydration which can be changed back to original form by addition of water followed by warming.	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 sewlling. This phenomenon is called imbibation.	They do not exhibit imbibation.

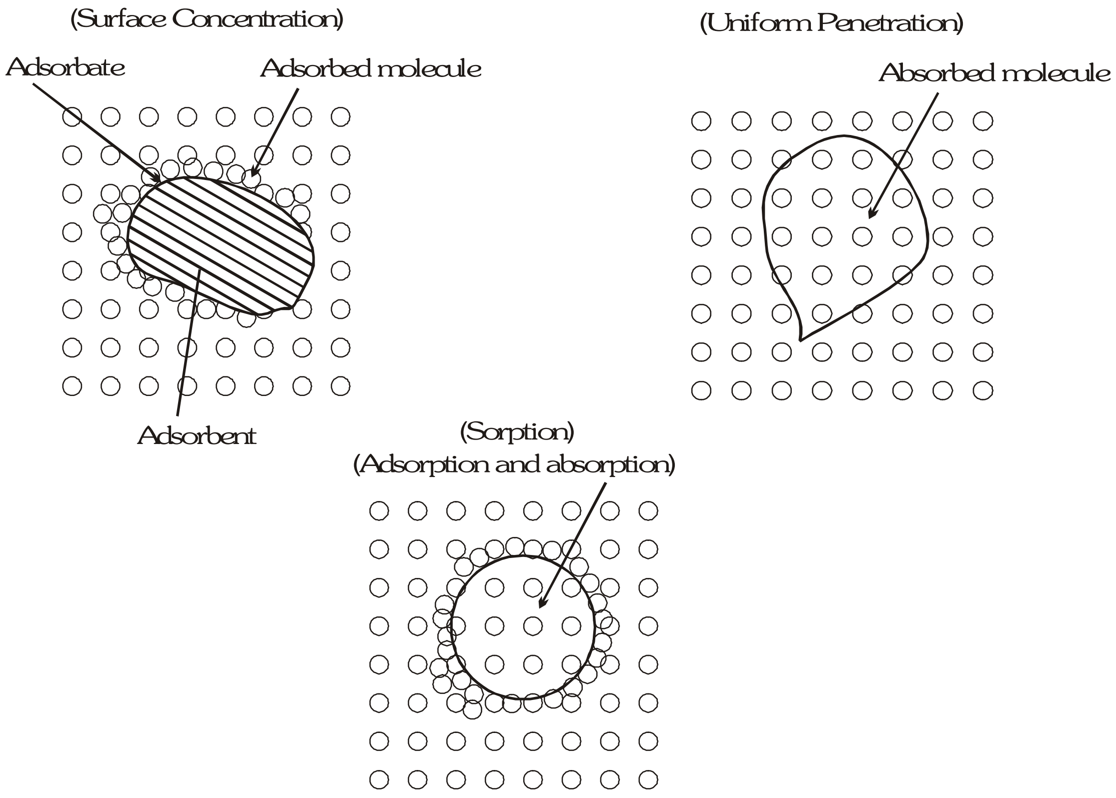
❑ INTRODUCTION : SURFACE CHEMISTRY

It has been known that the surface of a liquid is in a state of strain or unsaturation due to the unbalanced or residual forces which act along the surface of a liquid. Similar to it, the surface of a solid may also have residual forces or valances. Thus, the surface of a solid has a tendency to attract and to retain molecules of other species (gas or liquids) with which such surfaces come in contact. This phenomenon of surfaces is termed as adsorption.

As the molecules remain only at the surface, and do not go deeper into the bulk of the solid, the concentration of adsorbed gas or liquid is more at the surface than in the bulk. Hence this discussion may follow up by the definition of adsorption.

"Adsorption is a technical term coined to denote the taking up (Latin, surbere, to such up) of gas, vapour, liquid by a surface or interface.

Differences between Adsorption, Absorption and Sorption. Adsorption is a surface phenomenon whereas absorption is a bulk phenomenon in which the substance assimilated is uniformly distributed throughout the body of a solid or liquid to form a solution or a compound. The phenomenon of adsorption and absorption are illustrated in figure.



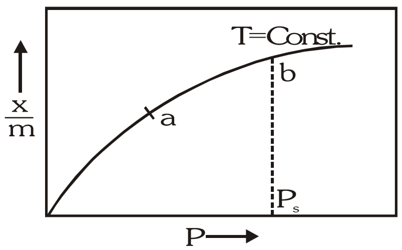
Adsorption should be distinguished carefully from absorption.

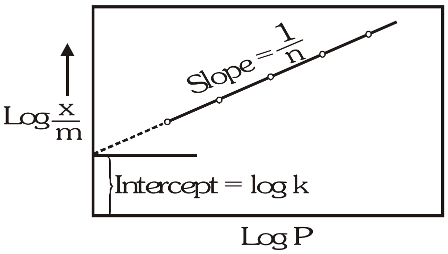
(i) In absorption, the substance is distributed throughout the body of a solid or a liquid to form a solution or a compound. On the other hand, adsorption only takes place on the surface and not in the body of adsorbent. Thus, adsorption is a surface phenomenon, and absorption is a bulk phenomenon.

(ii) In absorption, the concentration of the adsorbed molecules is always found to be greater in the immediate vicinity of the surface (Adsorbent) than in the free phase (Adsorbate). On the contrary, absorption involves bulk penetration of the molecules into the structure of the solid or liquid by some process of diffusion.

(iii) In case of adsorption, the equilibrium is easily attained in a very short time whereas in absorption the equilibrium takes place slowly.

(iv) According to freundlich absorption isotherm $\frac{x}{m} = k \times p^{1/n}$





- **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 aluminimum hydroxide.

(v) When a hot crucible is allowed to cool in air, a film of moisture is formed at the surface. This is the 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.

- **Nomenclature used in Adsorption** : The material on the surface of which adsorption takes place is called the adsorbent and the substance adsorbed is called the adsorbate. The common surface separating two phases, where the adsorbed molecule concentrates is referred to as the interface. The large the surface area of the adsorbent, the more the adsorption. Due to this reason colloids are good adsorbents due to their high surface area per unit mass although they have very small dimensions.

Adsorption stands for different concentrations of a substance at an interface. If the concentration is more at an interface, the adsorption is said to be positive; if the concentration is less at an interface, the adsorption is said to be negative. The reverse process of removal of an adsorbed substance from the surface of a solid is known as desorption.

- **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.

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-gas. The gas-solid interface has probably received the most attention in the literature and is the 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

$\Delta G = \Delta H - T\Delta S$ ... (i)

or $\Delta H = \Delta G + T\Delta S$ ... (ii)

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 ΔH decreases. This decrease in heat content (ΔH) appears as heat. Hence the adsorption process must always be exothermic.

❑ SORPTION AND OCCLUSION :

In many examples, the initial rapid adsorption is followed by a slow process of absorption of the substance into the interior of the solid. In these cases, the effect of absorption cannot be distinguished from those of adsorption. Therefore, the two new terms were introduced:

(i) **Sorption** : The process in which both adsorption and absorption take place simultaneously is generally termed as sorption. This term was suggested by Mcbain (1990). Examples are-

(a) The uptake of gases by zeolites is a striking example of sorption

(b) When hydrogen is taken up by charcoal, it first condenses on its surface. This is adsorption. After sometime, the hydrogen diffuses slowly into the interior of the charcoal forming a true solid solution and hence, this is absorption. So the charcoal has adsorbed as well as absorbed hydrogen gas. Therefore, it is an example of sorption.

(c) The direct dye-stuff taken up by cotton fibres are also in the adsorbed as well as in the absorbed state.

(ii) **Occulusion** : In 1886 T Graham proposed the term occlusion which possesses a similar significance to sorption. But this term occlusion is restricted to the sorption of gases by metals only.

❑ ADSORPTION OF GASES ON SOLIDS :

(1) Introductory :

The study of the gas-solid adsorption process has excited the interest of both academic and industrial scientists for many years, and the reactions are not hard to find. Industrially, it is known that this phenomenon plays an essential role in the catalytic process. The ability of surface to selectively accelerate the rates of many chemical reactions is the basis of much of the heavy-chemical production in the world.

It is generally believed that all gases or vapours are adsorbed on the surfaces of all solids with which they are in contact. The phenomenon was first described in 1773 by Scheele, who discovered the uptake of gases by charcoal.

(2) Factors on which Adsorption depends :

The phenomenon of adsorption of gases by solids depends upon the following factors:

(i) Nature of adsorbent and adsorbate :

The amount of the gas adsorbed depends upon the nature of the adsorbent and the gas (adsorbate) which is to be adsorbed.

Gases like SO_2, NH_3 , HCl and CO_2 which liquefy more easily are adsorbed more readily than the permanent gases like H_2, N_2 and O_2 which do not liquefy easily. This is because the easily liquefiable gases have greater van der waal's or the molecular forces of attraction or cohesive forces.

As the critical temperatures of the easily liquefiable gases are more than the permanent gases, it follows that higher the critical temperature of the gas (adsorbate), the greater the extent of adsorption.

(ii) Surface area of the adsorbent :

The extent of adsorption of gases by solids depends upon the exposed surface area of the adsorbent. It is well known that larger the surface area of the adsorbent, the large will be the extent of adsorption under given conditions of temperature and pressure. It is for this reason that silica gel and charcoal obtained from different animal and vegetable sources become activated because they posses a porous structure and thereby render a larger surface.

(iii) The partial pressure of the gas in the phase :

For a given gas and a given adsorbent, the extent of adsorption depends on the pressure of the gas. Adsorption of a gas is followed by a decrease of pressure. Therefore, in accordance with Le chatelier's principle, the magnitude of adsorption decreases with the decrease in pressure and vice-versa. The variation of adsorption with pressure at constant temperature is expressed graphically by a curve known as adsorption isotherm.

(iv) Effect of temperature :

For a given adsorbate and a adsorbent, the extent of adsorption depends upon the temperature of the experiment. As discussed earlier, adsorption usually takes place with the evolution of heat. Therefore, according to the Le chatelier's principle, the decrease in temperature will increase the adsorption and vice-versa. An example is that if the temperature of the coconut charcoal is lowered from –29 to –78 C, the amount of nitrogen gas adsorbed increases from 20 to 45 mL. under the same pressure.

(3) Types of Adsorption of the gases on solids :

Based on the nature of forces between the gas and the solid surface, there are two types of adsorption.

(1) Physisorption or Physical Adsorption :

If the physical forces of attraction hold the gas molecules to the solid, the adsorption is known as physical adsorption or physisorption. The forces of attraction bringing about physical adsorption are :

(i) Permanent dipole moment in the adsorbed molecule.

(ii) Polarisation

(iii) Dispersion effect

(iv) Short range repulsive effect

In case of physisorption, the forces of attraction which hold the gas molecules to the solid are very weak. Therefore it is characterised by a low heat of adsorption, usually of the order of 40 kJ per mole. This value is of the same order of magnitude as the heat of vaporisation of the adsorbate and lends credence to the concept of a weak "physical" bonding. Physical adsorption is usually observed at low temperature or on relatively "inert" surfaces.

Examples of physisorption are as follows:

(i) Adsorption of various gases on charcoal (ii) Adsorption of nitrogen on mica

(2) Chemisorption or chemical Adsorption :

If the chemical forces hold the gas molecules to the surface of the adsorbent, the adsorption is known as chemisorption. In this case the adsorbate undergoes a strong chemical interaction with the unsaturated surface and gives rise to a high heat of adsorption, usually of the order of 400 kJ per mole. Chemisorption is often characterised by taking place at elevated temperatures and is often an activated process. It may be dissociative, non- dissociative or reactive in nature. Some examples of chemisorption are :

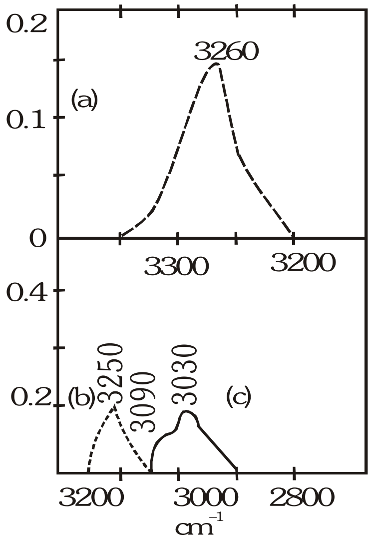
(a) Ethyl alcohol vapours condensed on the divided nickel.

(b) Adsorption of oxygen on tungsten

(c) Adsorption of hydrogen on nickel.

(3) Distinction between Physisorption and Chemisorption :

Exact differentiation between chemical and physical adsorption is often difficult and usually unprofitable. To the practising chemist a physically adsorbed species is usually considered to be an adsorbed material that can be completely removed from the surface, without decomposition, by prolonged evacuation at room temperature or by heating to 120 C. This experimental choice of conditions is completely arbitrary, and the final decision is always left with the experimenter. However, the advent of infrared spectroscopy had led to a better means of distinguishing between the two processes.



(Infrared spectra of (a) acetylene in liquid solution, (b) acetylene on porous silica glass (c) acetylene on porous silica glass coated with palladium)

We know that the infrared spectrum of a molecule arises as a result of the vibrations of the atoms within the molecules. If the molecule is physically adsorbed, the infrared spectrum is altered only slightly and small frequency shifts, usually less than 1 percent, are observed. During the chemisorption process, the symmetry of the adsorbed molecule is completely different from that of the gaseous molecule. In this case a completely new infrared spectrum is observed and band shifts and intensities are removed from those of the gaseous absorbate.

Let us illustrate this method by considering the IR spectra of acetylene in solution and adsorbed on silica and on palladium coated silica. These spectra are shown in figure (a) which represents the infrared spectrum of acetylene in liquid solution, (b) represents of acetylene on porous silica glass, and (c) of acetylene on porous silica glass coated with palladium. The IR spectrum on silica (fig b) is like that in solution (fig-a) except for a small shift to lower frequencies, but the IR spectrum on palladium (fig-c) is completely different and contains extra new bands. These spectra can be explained by saying that the latter case is a chemisorption with formation of new bonds (fig c) whereas the former case (fig b) is a typical physical adsorption.

(4) Differences between physisorption and chemisorption :

The various differences are as follows:

(a) Specificity :

Physisorptions are non-specific. Thus, every gas is adsorbed to a lesser or a greater extent on all solid surfaces. On the other hand, chemisorptions are more specific in nature. A gas will be chemisorbed on such solids only with which it can combine chemically.

(b) Speed :

Physisorptions are instantaneous. Chemisorptions may sometimes be quite slow depending upon the nature of chemical reaction involved. A rough estimate is that adsorbable impurities of air are adsorbed by gas masks in a contact of less than 0.01 second.

(c) Reversibility :

Physisorption equilibrium is reversible and is rapidly established. Chemisorption is irreversible. Physically adsorbed layer can be removed very easily by changing pressure or concentration. On the other hand the removal of a chemisorbed layer, however, requires much more rugged conditions such as high temperature, etc.

(d) Heat of adsorption :

Physical adsorption is generally characterised by low heats of adsorption which is about 40 kJ/mole or less.

Chemisorption is characterised by high heats of adsorption viz. 40 to 400 kJ per mole which indicates that forces are similar to those involved in chemical reactions. Therefore, it is highly probable that gas molecules from a chemical compound with the surface of the adsorbent.

(e) Nature of adsorbate and adsorbent :

Physical adsorption like condensation can occur with any gas-solid system provided only that the conditions of temperature and pressure are suitable. The chemisorption will take place only if the gas is capable of forming a chemical bond with the surface atoms.

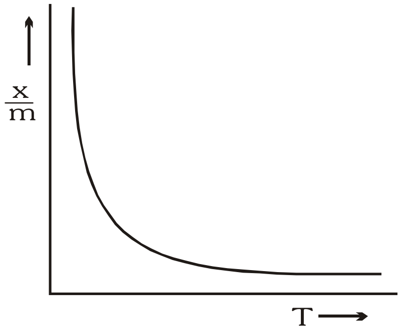
(f) Effect of Pressure :

As the pressure of the adsorbate increases, the rate of physical adsorption increases. The rate of chemisorption decreases with the increase of pressure of adsorbate.

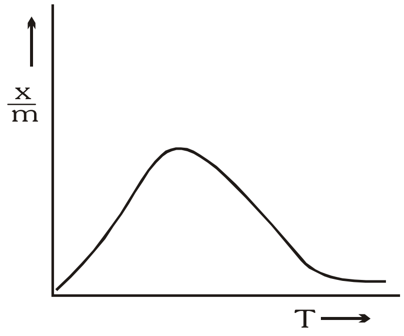
(g) Effect of temperature :

Physical adsorption occurs to an appreciable extent at temperatures close to those required for liquefaction of adsorbed gases. Generally, chemisorption occurs at high temperatures. But certain examples are known in which it occurs at low temperature. Chemisorption increases at first and then falls off with rising temperature.

A graph drawn between amount adsorbed (x/m) and temperature (T) at a constant equilibrium pressure of adsorbate gas is called an adsorption isobar. Adsorption isobars of physisorption and chemisorption show on important difference (fig) and this difference is used for experimentally distinguishing chemisorption from physisorption. While the physical adsorption isobar shows a decrease in x/m along the rise in temperature, the chemisorption isobar shows an initial increase with temperature and then the expected decreases. The initial increase shows that, like the chemical reactions, chemisorption also needs activation energy. However, the latter decrease indicates that at higher temperatures desorption does occur in chemisorption process. Frequently during the high temperature desorptions the evolved gas carries with it some atoms of the adsorbent as well in a chemically bound form.



Physical adsorption



Chemisorption

The various differences between physorption and chemisorption are summarised in table.

	Physical adsorption	Chemisorption
(i)	It involves physical forces.	It involves transfer of electrons between gas and solid.
(ii)	Heat of adsorption is generally less than 40 kJ/mole	Heat of adsorption is 40-400 kJ/mol
(iii)	It is reversible	It is not reversible.
(iv)	It is general phenomenon which will occur with any gas-solid system provided only that the conditions of temperature and pressure are suitable.	It will only take place if the gas is capable of forming chemical bond with the surface atoms
(v)	Multilayers are possible in physical adsorption	Only monolayer is formed.
(vi)	It is appreciable at low temperatures high pressures	It can occur at high temperatures. The rate of chemisorption decreases with the increase of pressure
(vii)	No appreciable activation energy is involved.	Chemisorption is an activated phenome non and involves appreciable activation energy.
(viii)	It is an instantaneous process	It may be rapid or slow.
(ix)	Physical adsorption is a function of coverage of surface	It is adsorbed at fixed sites on the sirface. These sites are known as active centres.
(x)	Not very specific	Often very specific

❑ PHYSICAL ADSORPTION

Types of adsorption curves : As discussed earlier, the magnitude of adsorption depends on the pressure of the gas and the temperatures of the experiment for a given gas and a given adsorbent. Hence, the amount of the gas adsorbed is a function of temperature and pressure only. Mathematically, it can be expressed as

$a = f\ (P.T.)$ ... (i)

where a is the amount of gas adsorbed, P is the pressure, and T is the temperature.

When equation (i) is represented graphically, three different curves are obtained.

(i) **Adsorption Isotherm** - If the temperature is kept constant and pressure is changed, the curve between a and P is known as adsorption isotherm.

$a = f(P)$ if T is constant.

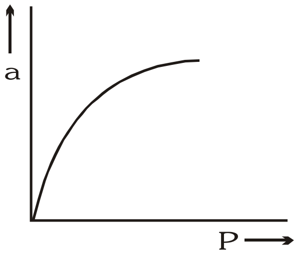
(ii) **Adsorption Isobar** : If pressure is kept constant and temperature is varied, the curve between a and T is called the adsorption isobar.

$a = f(T)$ if P is constant

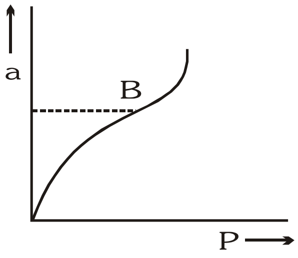
(iii) **Adsorption Isostere** : If the amount adsorbed is kept constant, the curve between P and T is known as adsorption isostere.

$P = f(T)$ if a is constant.

◆ **Types of Adsorption Isotherms (Physical)** : Seven types of physical adsorption isotherms have been reported. These are give below in the figure.



(I)



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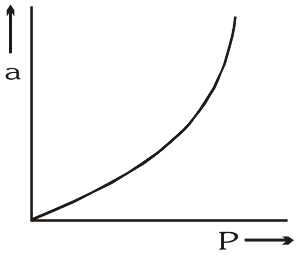
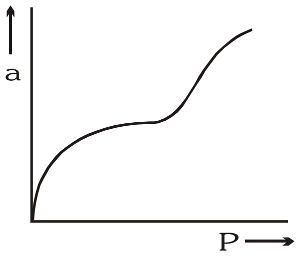
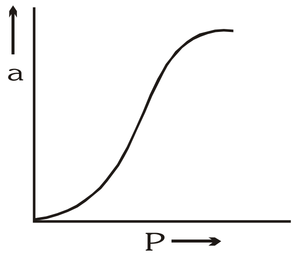


(III)



(IV)



(V)

Type I : This type of curve is obtained in such cases where mono-molecular layer is formed on the surface of the adsorbent. This curve shows that a saturation state is reached. It means that there is no change in the value of 'a' (the amount adsorbed) with the increase in pressure onwards. This type of the curve is rare. Example is the adsorption of nitrogen on charcoal at –195 C.

Type II : This type of isotherm has a transition point 'B' which represents the pressure at which the formation of monomolecular layer is complete and that of the multi-molecular layer is being started. For many years it was the practice to take point B at the knee of the curve as the point of completion of a monolayer, and the surface areas obtained by the method are fairly consistent with those found using adsorbates that give type I isotherms. Example is the adsorption of nitrogen on silica gel at –195 C.

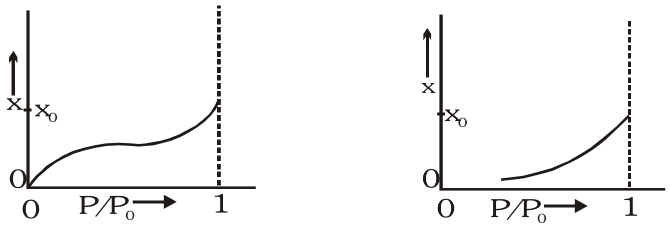
Type-III : In this type of isotherm there is no transition point. In this the multi-molecular layer formation starts even before the formation of monomolecular layer is complete.

Example is the adsorption of bromine or iodine vapours on silica gel at 79 C. Type III This type is relatively rare and a recent example of this is that of the adsorption of nitrogen on ice. This type seems to be characterised by a heat of adsorption equal to or less than the heat of liquefaction of the adsorbate.

Type IV : In this case there is a tendency for a saturation state to be reached in the multimolecular region as well. In fact that can be regarded as a duplication of the II type. Example is the adsorption of benzene vapour on ferric oxide get at 50 C.

Type V : This isotherm indicates multimolecular layer formation in the beginning. At higher pressure, there is a tendency for 'a' (amount absorbed) to remain constant. It means that the saturation state has been reached. Example is the adsorption of water vapour on charcoal at 100 C.

Type VI and Type VII : There is a need to recognise at least the two additional isotherms shown in fig. These are expected for non wetting adsorbate-adsorbent systems.



(VI)

(VII)

(Two additional types of adsorption isotherms expected for non-wetting adsorbate-adsorbent systems)

❑ VARIOUS ADSORPTION ISOTHERMS :

The various types of adsorption isotherms are :

(i) Classical Freundlich adsorption isotherm in 1909, Freundlich proposed an empirical equation and was known as Freundlich adsorption isotherm. This equation is as follows:

$$x/m = kp^{1/n} \qquad \text{... (i)}$$

where x is amount of adsorbate, m is the amount of adsorbent, p is the pressure, k and n are two constants depending upon the nature of the adsorbent and adsorbate, and n being less than unity.

Equation (i) is applicable to the adsorption of gases on solids.

In case of solution, equation (i) takes the form

$$x/m = kc^{1/n} \qquad \text{...(ii)}$$

where c is the concentration of the solute in gm moles per litre.

Equations (i) and (ii) predict the effect of pressure (or concentration) on the adsorption of gases (or solution) at constant temperature in a quantitative manner.

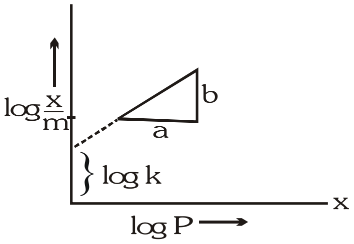
Test of Freundlich's Adsorption Isotherm.

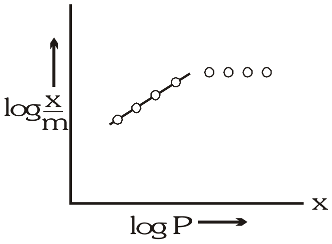
Taking logarithms of equations (i) and (ii), we get

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad \text{... (iii)}$$

$$\text{and } \log \frac{x}{m} = \log k + \frac{1}{n} \log c \qquad \text{... (iv)}$$

If $\log \frac{x}{m}$ is plotted against log p or log c, a straight line should be obtained as shown in fig. The slope of the line will give the value of $\frac{1}{n}$ and the intercept on the Y-axis gives the value of log k, i.e.





Intercept = log k

and slope $= \frac{b}{a} = \frac{1}{n}$

Thus by using equations (iii) and (iv), the values of k and n can be calculated from the graph (fig). Analysis of the graph shows that as p increases $\frac{x}{m}$, also increase and, thus, the Freundlich's equation indicates no limit to this increase. But experimental values, when plotted, show some deviations from linearity especially at low pressures. This is seen in fig. If we compare theoretical and experimental curves (fig), the two agree over a certain range of pressure only. Thus, Freundlich's equation has a limitation that it is valid over a certain range of pressure only.

Limitations of Freundlich's Equation :

(1) It is valid over a certain range of pressure only.

(2) The constant k and n vary with the temperature.

(3) Freundlich adsorption equation is a purely empirical formula without theoretical foundation.

(ii) Langmuir Adsorption Isotherm : It has already been stated that Frenudlich adsorption isotherm holds good for a certain range of pressure only. To solve this difficulty, Langmuir (1916) worked out an adsorption isotherm known as Langmuir's adsorption isotherm The various assumptions are :

(a) The adsorbed layer on the solid adsorbent is assumed to be unimolecular in thickness. This view is widely accepted for adsorption at low pressure or at moderately high temperature. However, the adsorbed molecules can hold other gas molecules by van der Waal's forces, so that multimolecular layers are possible. Such behaviour is apparent only at relatively low temperatures and at pressure approaching the saturation value. But Langmuir only considered the formation of unimolecular layer while deriving this relation.

(b) The adsorption is taking place on the fixed sites and there is no interaction between the adsorbed molecules on the surface. One site adsorbs one molecule. When the whole surface is completely covered by a unimolecular layer of the gas, further adsorption is not possible and indicates a maximum of saturation of adsorption.

(c) The process of adsorption is a dynamic process which consists of two opposing processes:

(i) Condensation Process : It involves the condensation of the molecules of the gas on the surface of their solid.

(ii) Evaporation Process : It involves evaporation of the molecules of adsorbate from the surface of the adsorbent.

When adsorption starts, the whole adsorbent surface remains bare and so the initial rate of condensation is maximum. As the surface becomes gradually covered, the rate of condensation becomes smaller and smaller. On the contrary, the initial rate of evaporation (desorption) of the condensed molecules is smallest at the beginning of adsorption, but increases as the surface becomes more and more covered.

Ultimately, when the equilibrium is reached, the rate of condensation becomes equal to the rate of evaporation. It means that the number of gas molecules condensing on the given surface is equal to the number of molecules evaporating away per unit time from the same surface, i.e. the arrangement of the adsorbed molecule on the surface in unidirectional.

(d) Gas behaves ideally. (e) Surface is uniform energetically.

◆ **Derivation :**

On the basis of above postulates, Langmuir deduced the equation describing the quantitative relationship between the pressure and the amount of gas adsorbed at constant temperature. Suppose n is the number of molecules of the gas striking one square cm of the surface per second. Let α be the fraction of the molecules condensing on the surface. Then αn is the total number of molecules which condense on the surface. This condensation is not taking place on the whole surface but it is taking place at only $n\,\alpha(1-\theta)$ sq. cm.,where θ sq. cm. is the fraction of the area already covered by the gas molecules and 1 sq. cm is the total surface area.

$\therefore$ Rate of condensation of gaseous molecules on the surface

$$= (1-\theta)\,\alpha\, n \qquad \ldots (v)$$

One know that :

Rate of evaporation $\propto$ area of surface covered.

$\propto \theta$

or Rate of evaporation = $k\theta$

where k is the proportionality constant. When equilibrium is set up, the rate of condensation is equal to the rate of evaporation, i.e.

$$k\theta = (1-\theta)\,\alpha\, n \qquad \ldots(vi)$$

or $k\theta + \theta\,\alpha\, n = \alpha\, n$

or $$\theta = \frac{\alpha n}{k + \alpha n} \qquad \text{... (vii)}$$

From kinetic theory of gases, it follows that Number of molecules $\propto$ pressure of the gas striking the surface

or $n \propto p$

$$n = \beta\ p \qquad \text{... (viii)}$$

where β is the proportionality constant.

Now $$\frac{k + \alpha n}{\alpha n} = \frac{k}{\alpha n} + 1 \qquad \text{... (ix)}$$

$$= \frac{k}{\beta p \alpha} + 1 \qquad \{\text{From equation (8) } \beta p = n\}$$

$$= \frac{1}{k_1 p} + 1 = \frac{1 + k_1 p}{k_1 p} \qquad \text{... (x)}$$

Where $k_1 = \left(\frac{\alpha\beta}{k}\right)$ is another constant equation (x) can be written as

$$\frac{k + \alpha n}{\alpha n} = \frac{1 + k_1 p}{k_1 p} \qquad \text{... (xi)}$$

or $$\frac{\alpha n}{k + \alpha n} = \frac{k_1 p}{1 + k_1 p}$$

comparing equations (vii) and (xi), we obtain

$$\theta = \frac{k_1 p}{1 + k_1 p} \qquad \text{... (xii)}$$

If it is supposed that one molecule thick layer of the gas is formed on the surface, then

$$\frac{x}{m} \propto \theta \qquad \text{... (xiii)}$$

or $$\frac{x}{m} = k_2 \theta \qquad \text{... (xiv)}$$

where k_2 is another proportionality constant.

Equation (xiii) implies that amount of gas adsorbed per unit mass of adsorbent is proportional to fraction of the surface covered. Substituting the value of θ from equation (xii) into the equation (xiv), we obtain

$$\frac{x}{m} = \frac{k_2 k_1 p}{1 + k_1 p} \qquad \text{... (xv)}$$

or $$\frac{1}{x/m} = \frac{1 + k_1 p}{k_2 k_1 p}$$

or $$\frac{p}{x/m} = \frac{1}{k_1 k_2} + \frac{p}{k_2} \qquad \text{... (xvi)}$$

Equation (xvi) is known as Langmuir's adsorption isotherm.

A plot of $\frac{p}{x/m}$ against p should be a straight line.

Another form of equation (xvi) can be obtained by introducing the term V_m which is equal to the volume of adsorbate required to complete a unimolecular layer, i.e, to saturate the surface. The fraction, θ, of the surface covered is then equal to V/V_m where V is the volume adsorbed at a given pressure p. Hence equation (xii) becomes as

$$\frac{V}{V_m} = \frac{k_1 p}{1 + k_1 p} \text{ or } \frac{p}{V} = \frac{1}{k_1 V_m} + \frac{p}{V_m} \qquad \text{... (xvi A)}$$

Equation (xvi A) is another form of the Langmuir equation.

Discussion : Three different cases may arise :

Case I : When pressure of the gas is very low, k_1p is negligible as compared to unity. It implies that θ, the fraction covered by adsorption, is quite small. In such a special case, equation (xv) becomes as

$$\frac{x}{m} = k_1k_2p \qquad \text{... (xvii)}$$

or $$\frac{x}{m} \propto p \qquad \text{... (xviii)}$$

Thus, under low pressure, the amount of the gas adsorbed per unit quantity of adsorbent is directly proportional to the pressure. This has been confirmed by experimental observation.

Case II : When pressure is very large, k_1p becomes larger than unity. In such a special case equation (xv) becomes as :

$$\frac{x}{m} = \frac{k_1k_2p}{k_1p} \qquad (\because\ k_1p >> 1)$$

or $$\frac{x}{m} = k_2 \qquad \text{... (xix)}$$

This equation shows that at high pressure, the amount of adsorbed gas is independent of pressure.

Case III : At low pressure, equation (xviii) is

$$\frac{x}{m} \propto p \quad \text{or} \quad \frac{x}{m} = \text{constant} \quad p$$

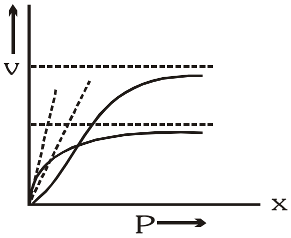
At high pressure, equation (xix) is $\frac{x}{m}$ = constant

Therefore, at moderate pressure, Langmuir adsorption equation becomes as

$$\frac{x}{m} = \text{constant} \quad p^{1/n}$$

or $$\frac{x}{m} = kp^{1/n} \qquad \text{... (xx)}$$

Equation (xx) is the Freundlich adsorption equation (i). In equation (xx), $1/n$ lies between zero and unity. Some typical shapes of Langmuir's curves are illustrated in figure.



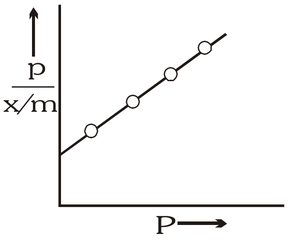
As pressure is increased or temperature is decreased, additional layers are formed. This has let to the modern concept of multi-molecular adsorption.

Test of the Langmuir adsoprtion isotherm

From equation (xvi), we have

$$\frac{p}{x/m} = \frac{1}{k_1k_2} + \frac{p}{k_2}$$

A plot of $\frac{p}{x/m}$ versus p should give a straight line. The slope of this is $\frac{1}{k_2}$ and the intercept on the y-axis gives $\frac{1}{k_2}$ (fig.)



In certain cases, the experimental curves are not straight. This may be due to the following reasons:

(i) non-uniformity of surfaces.

(ii) formation of multiple layers in some cases.

(iii) partial adsorption, and

(iv) some chemical reaction of the adsorbate with the adsorbent.

◆ **Successes of the theory** :

(i) The mechanism of adsorption presented by Langmuir explains chemical adsorption or chemisorption.

(ii) Langmuir's theory is more satisfactory than the Feundlich's equation while explaining physical adsorption of gases on different adsorbent whenever saturation is approached.

◆ **Limitations** : The main limitations are :

(i) Langmuir postulated that a saturated value of adsorption is independent of temperature. But experiment shows that it is actually falling off with rising temperatures.

(ii) Langmuir assumed that an adsorption film on a plane surface will never be over a molecule thick. In actual practice, much thicker films have been reported.

(iii) This theory cannot explain all the five types of adsorption isotherms.