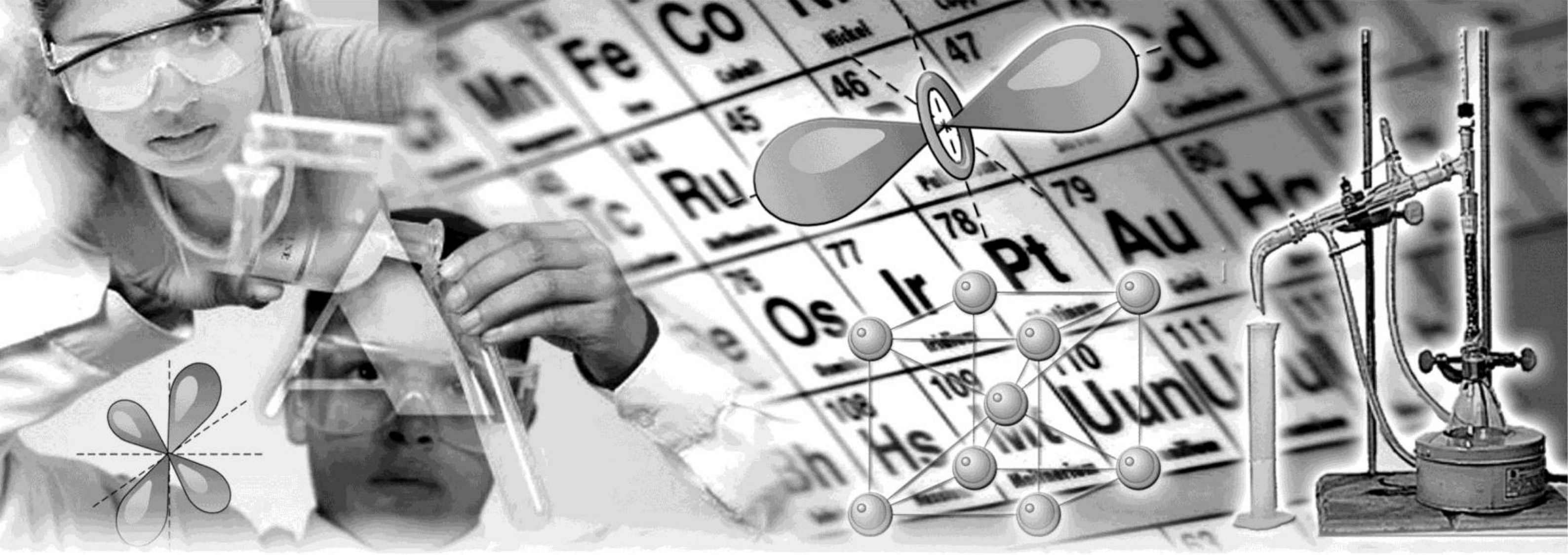


Chapter
14
Surface Chemistry

"The branch of physical chemistry, which deals the nature of surfaces and also with the chemical and physical processes which takes place on the surfaces, is called surface chemistry".

In surface chemistry, we study the phenomenon of adsorption, catalysis and colloidal properties.

Adsorption

(1) **Definition :** The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting in to higher concentration of the molecules on the surface is called ***adsorption***.

(2) **Causes of adsorption :** Unbalanced forces of attraction or free valencies which is present at the solid or liquid surface, have the property to attract and retain the molecules of a gas or a dissolved substance on to their surfaces with which they come in contact.

Example : Ammonia gas placed in contact with charcoal gets adsorbed on the charcoal whereas ammonia gas placed in contact with water gets absorbed into water,

Table : 14.1 Some basic terms used in adsorption

Interface : Any surface is a plane which separates any two phases in contact with each other. The plane which separates any two phase is generally called an **interface** between the two phases.	**Adsorbate and Adsorbent :** The substance which gets adsorbed on any surface is called **adsorbate** for example, if a gas gets adsorbed on to the surface of a solid, then the gas is termed as the adsorbate. The substance on the surface of which adsorption takes place is called **adsorbent.**
Desorption : The removal of the adsorbed substance from a surface is called **desorption.**	**Absorption :** When the molecules of a substance are uniformly distributed throughout the body of a solid or liquid. This phenomenon is called **absorption.**
Sorption : The phenomenon in which adsorption and absorption occur simultaneously is called **sorption.** **Mc. Bain** introduced a general term sorption describeing both the processes, however adsorption is instantaneous *i.e.* a fast process while absorption is a slow process.	**Occlusion :** When adsorption of gases occur on the surface of metals this is called **occlusion.**

(3) **Difference between adsorption and absorption**

Adsorption	Absorption
It is a surface phenomenon.	It concerns with the whole mass of the absorbent.
In it, the substance is only retained on the surface and does not go into the bulk or interior of the solid or liquid.	It implies that a substance is uniformly distributed, through the body of the solid or liquid.
In it the concentration of the adsorbed molecules is always greater at the free phase.	In it the concentration is low.
It is rapid in the beginning and slows down near the equilibrium.	It occurs at the uniform rate.
Examples : (i) Water vapours adsorbed by silica gel. (ii) NH_3 is adsorbed by charcoal.	*Examples :* (i) Water vapours absorbed by anhydrous $CaCl_2$ (ii) NH_3 is absorbed in water forming NH_4OH

(4) **Surface forces :** Only the surface atoms of an adsorbent play an active role in adsorption. These atoms posses unbalanced forces of various types such as, Vander Waal's forces and chemical bond forces.

Thus, ***the residual force-field on a free surface which is responsible for adsorption is produced***. For example, when a solid substance is broken into two pieces, two new surfaces are formed and therefore, the number of unbalanced forces becomes more. As a result the tendency for adsorption become large.

(5) **Reversible and Irreversible adsorption :** The adsorption is reversible, if the adsorbate can be easily removed from the surface of the adsorbent by physical methods.If the adsorbate can not be easily removed from the surface of the adsorbent is called irreversible adsorption.

Example for reversible adsorption: A gas adsorbed on a solid surface can be completely removed in vacuum.

Example for irreversible adsorption: Adsorption of O_2 on tungusten adsorbent.

(6) **Characteristics of adsorption**

(i) Adsorption refers to the existence of a higher concentration of any particular component at the surface of a liquid or a solid phase.

(ii) Adsorption is accompanied by decrease in the ΔG (free energy change) of the system when $\Delta G = 0$, ***adsorption equilibrium is said to be established.***

(iii) Adsorption is invariably accompanied by evolution of heat, *i.e.* it is an exothermic process. In other words, ***ΔH of adsorption is always negative.***

(iv) When a gas is adsorbed, the freedom of movement of its molecules becomes restricted. On account of it decrease in the entropy of the gas after adsorption, *i.e.* ***ΔS is negative.***

(v) For a process to be spontaneous, the thermodynamic requirement is that ΔG ***must be negative***, *i.e.* there is decrease in free energy. On the basis of ***Gibb's Helmholtz equation***, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value and $T\Delta S$ ***has positive value.***

Classification of adsorption

Adsorption can be classified into two categories as described below,

(1) **Depending upon the concentration :** In adsorption the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk or interior phase.

(i) ***Positive adsorption*** **:** If the concentration of adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called ***positive adsorption***.

Example : When a *concentrated* solution of *KCl* is shaken with blood charcoal, it shows positive adsorption.

(ii) ***Negative adsorption*** **:** If the concentration of the adsorbate is less than its concentration in the bulk then it is called ***negative adsorption.***

Example : When a *dilute* solution of *KCl* is shaken with blood charcoal, it shows negative adsorption.

(2) **Depending upon the nature of force existing between adsorbate molecule and adsorbent**

(i) ***Physical adsorption*** **:** If the forces of attraction existing between adsorbate and adsorbent are Vander Waal's forces, the adsorption is called physical adsorption. This type of adsorption is also known as ***physisorption or Vander Waal's adsorption.*** It can be easily reversed by heating or decreasing the pressure.

(ii) ***Chemical adsorption*** **:** If the forces of attraction existing between adsorbate particles and adsorbent are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is also called as ***chemisorption or Langmuir adsorption.*** This type of adsorption cannot be easily reversed.

Comparison between physisorption and chemisorption

Physisorption (Vander Waal's adsorption)	**Chemisorption** (Langmuir adsorption)
Low heat of adsorption usually in range of 20-40 *kJ/mol*	High heat of adsorption in the range of 50-400 *kJ/mol*
Force of attraction are ***Vander Waal's forces.***	Forces of attraction are ***chemical bond forces.***
It is reversible	It is irreversible
It is usually takes place at ***low temperature*** and decreases with increasing temperature.	It takes place at ***high temperature.***
It is related to the case of liquefication of the gas.	It is not related.
It forms *multimolecular layers.*	It forms *monomolecular layers.*
It does not require any activation energy.	It requires high *activation energy.*
High pressure is favourable. Decrease of pressure causes *desorption*	High pressure is favourable. Decrease of pressure does not cause desorption.
It is not very specific.	It is highly specific.

Factors which affect the extent of adsorption **:** The following are the factors which affect the adsorption,

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

(i) In general, easily liquefiable gases e.g., CO_2, NH_3, Cl_2 and SO_2 etc. are adsorbed to a greater extent than the elemental gases e.g. H_2, O_2, N_2, *He* etc. (while chemisorption is specific in nature.)

(ii) Porous and finely powdered solid e.g. charcoal, fullers earth, adsorb more as compared to the hard non-porous materials. Due to this property powdered charcoal is used in gas masks.

(2) **Surface area of the solid adsorbent**

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

(ii) Surface area of a powdered solid adsorbent depends upon its particle size. Smaller the particle size, greater is its surface area.

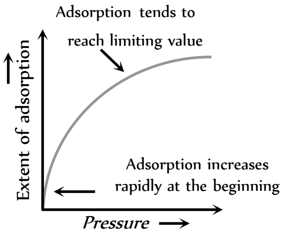
(3) **Effect of pressure on the adsorbate gas**

(i) An increase in the pressure of the adsorbate gas increases the extent of adsorption.

(ii) *At low temperature,* the extent of adsorption increases rapidly with pressure.

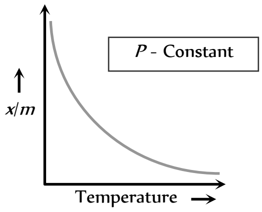
(iii) *Small range of pressure,* the extent of adsorption is found to be directly proportional to the pressure.

(iv) *At high pressure* (closer to the saturation vapour pressure of the gas), the adsorption tends to achieve a limiting value.

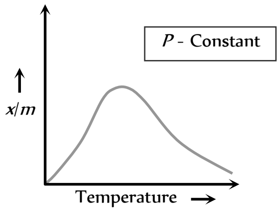


(4) **Effect of temperature**

(i) As adsorption is accompanied by evolution of heat, so according to the ***Le-Chatelier's principle***, the magnitude of adsorption should decrease with rise in temperature.



Physical adsorption



Chemical adsorption

(ii) The relationship between the extent of adsorption and temperature at any constant pressure is called ***adsorption isobar.***

(iii) A physical adsorption isobar shows a decrease in *x/m* (where '*m*' is the mass of the adsorbent and '*x*' that of adsorbate) as the temperature rises.

(iv) The isobar of chemisorption show an increase in the beginning and then decrease as the temperature rises.

Adsorption isotherms

A mathematical equation, which describes the relationship between pressure (p) of the gaseous adsorbate and the extent of adsorption at any fixed temperature, is called ***adsorption isotherms.***

The extent of adsorption is expressed as mass of the adsorbate adsorbed on one unit mass of the adsorbent.

Thus, if x *g* of an adsorbate is adsorbed on m *g* of the adsorbent, then

$$\text{Extent of adsorption} = \frac{x}{m}$$

Various adsorption isotherms are commonly employed in describing the adsorption data.

(1) **Freundlich adsorption isotherm**

(i) Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorbate forms a ***monomolecular*** *layer* on the surface of the adsorbent.

$\frac{x}{m} = kp^{\frac{1}{n}}$ (Freundlich adsorption isotherm) or

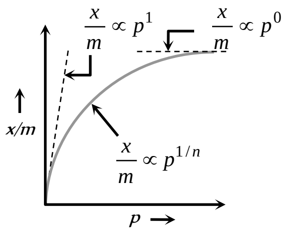
$$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

where x is the weight of the gas adsorbed by m *gm* of the adsorbent at a pressure *p,* thus *x/m* represents the amount of gas adsorbed by the adsorbents per *gm* (unit mass), k and n are constant at a particular temperature and for a particular adsorbent and adsorbate (gas), n is always greater than one, indicating ***that the amount of the gas adsorbed does not increase as rapidly as the pressure.***

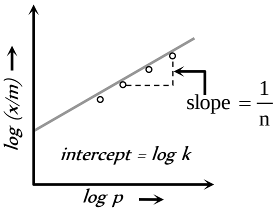
(ii) At *low pressure*, the extent of adsorption varies linearly with pressure. $\frac{x}{m} \propto p'$

(iii) At *high pressure*, it becomes independent of pressure. $\frac{x}{m} \propto p^0$

(iv) At *moderate pressure* $\frac{x}{m}$ depends upon pressure raised to powers $\frac{x}{m} \propto p^{\frac{1}{n}}$



Freundlich adsorption isotherm: plot of x/m against p



Plot of log x/m against log p for the adsorption of a gas on a solid

(2) **The Langmuir - adsorption isotherms**

(i) One of the drawbacks of Freundlich adsorption isotherm is that it fails at high pressure of the gas. ***Irving Langmuir in*** **1916** derived a simple adsorption isotherm, on theoretical considerations based on ***kinetic theory of gases.*** This is named as ***Langmuir adsorption isotherm.***

(a) Adsorption takes place on the surface of the solid only till the whole of the surface is completely covered with a unimolecular layer of the adsorbed gas.

(b) Adsorption consists of two opposing processes, namely ***Condensation*** of the gas molecules on the solid surface and ***Evaporation*** (desorption) of the gas molecules from the surface back into the gaseous phase.

(c) The rate of condensation depends upon the uncovered (bare) surface of the adsorbent available for condensation. Naturally, at start when whole of the surface is uncovered the rate of condensation is very high and as the surface is covered more and more, the rate of condensation progressively decreases. On the contrary, the rate of evaporation depends upon the covered surface and hence increases as more and more of the surface is covered ultimately an equilibrium will be set up at a stage when the rate of condensation becomes equal to the rate of evaporation (adsorption equilibrium).

(d) The rate of condensation also depends upon the pressure of the gas since according the kinetic theory of gases, ***the number of molecules striking per unit area is proportional to the pressure.***

Mathematically, $\frac{x}{m} = \frac{ap}{1+bp}$, where a and b are constants and their value depends upon the nature of gas (adsorbate), nature of the solid adsorbent and the temperature. Their values can be determined from the experimental data.

Limitation of Langmuir theory

(a) Langmuir's theory of unimolecular adsorption is valid only at ***low pressures and high temperatures.***

(b) When the pressure is increased or temperature is lowered, additional layers are formed. This has led to the modern concept of ***multilayer adsorption.***

Adsorption from solutions

(1) The process of adsorption can take place from solutions also.

(2) In any solution, there are two (or more) components ; ***solute*** and ***solvent.*** The solute may be present in the molecular or ionic form.

(3) The extent of adsorption from solution depends upon the concentration of the solute in the solution, and can be expressed by the ***Freundlich isotherm.***

(4) The Freundlich adsorption isotherm for the adsorption from solution is, $\frac{x}{m} = kc^{\frac{1}{n}}$ where, x is the mass of the solute adsorbed, m is the mass of the solid adsorbent, c is the equilibrium concentration of the solute in the solution, n is a constant having value greater than one,

k is the proportionality constant, (The value of k depends upon the nature of solid, its particle size, temperature, and the nature of solute and solvent etc.)

(5) The plot of *x/m* against c is similar to that Freundlich adsorption isotherm. The above equations may be written in the following form, $\log\frac{x}{m} = \log k + \frac{1}{n}\log c$ where *c,* is the equilibrium concentration of the solute in the solution.

Application of adsorption

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

(1) **Production of high vacuum**

(2) **In Gas masks** : This apparatus is used to adsorb poisonous gases (e.g. Cl_2, CO, oxide of sulphur etc.) and thus purify the air for breathing.

(3) **For desiccation or dehumidification :** These substances can be used to reduce/remove water vapours or moisture present in the air. Silica gel and alumina are used for dehumidification in electronic equipment.

(4) **Removel of colouring matter from solution :** (i) Animal charcoal removes colours of solutions by adsorbing coloured impurities. (ii) Animal charcoal is used as decolouriser in the manufacture of cane sugar.

(5) **Heterogeneous catalysis :** Mostly heterogeneous catalytic reactions proceed through the adsorption of gaseous reactants on solid catalyst. For example,

(i) Finely powdered nickel is used for the hydrogenation of oils.

(ii) Finely divided vanadium pentaoxide (V_2O_5) is used in the contact process for the manufacture of sulphuric acid.

(6) **Separation of inert gases :** Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

(7) **Softening of hard water**

(i) The hard water is made to pass through a column packed with zeolite (sodium aluminium silicate)

(ii) *Ca, Mg* ions which are responsible for hardness, get adsorbed on zeolite, exchanging sodium ions.

$$Na_2Al_2Si_2O_8 + CaCl_2 \longrightarrow CaAl_2Si_2O_8 + 2NaCl$$

(iii) The exhausted zeolite is regenerated with 10% of sodium chloride solution.

$$CaAl_2Si_2O_8 + 2NaCl \longrightarrow Na_2Al_2Si_2O_8 + CaCl_2$$

(8) **De-ionisation of water**

(i) Water can be de-ionised by removing all dissolved salts with the help of cation and anion-exchanger resin.

(ii) Cation-exchanger is an organic synthetic resin such as polystyrene-containing a macroanion $(R-SO_3^-$ etc.) which has adsorbed H ions.

(iii) A resin containing a basic group $(R_3N^+$ etc.) which has adsorbed OH^- ions acts as anion exchanger.

(9) **In curing diseases :** A number of drugs are adsorbed on the germs and kill them or these are adsorbed on the tissues and heat them.

(10) **Cleaning agents :** Soap and detergents get adsorbed on the interface and thus reduce the surface tension between dirt and cloth, subsequently the dirt is removed from the cloth.

(11) **Froth floatation process**

A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method.

(12) **In adsorption indicators**

Surface of certain precipitates such as silver halide, have the property of adsorbing some dyes like eosin, fluorescein etc.

(13) **Chromatographic analysis**

The phenomenon of adsorption has given an excellent technique of analysis known as chromatographic analysis.

(14) **In dyeing :** Many dyes get adsorbed on the cloth either directly or by the use of mordants.

Catalysis

"Catalyst is a substance which speeds up and speeds down a chemical reaction without itself being used up."

Berzelius (1836) introduced the term ***catalysis*** and ***catalyst***.

Ostwald (1895) redefined a catalyst as, "*A substance which changes the reaction rate without affecting the overall energetics of the reaction is termed as a catalyst and the phenomenon is known as catalysis.*"

Types of catalysis

Catalytic reactions can be broadly divided into the following types,

(1) **Homogeneous catalysis** : When the reactants and the catalyst are in the same phase (*i.e.* solid, liquid or gas). The catalysis is said to be ***homogeneous***. The following are some of the examples of homogeneous catalysis.

(i) In the lead chamber process

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

(ii) In the hydrolysis of ester

$$CH_3COOCH_3(l)+H_2O(l)\xrightarrow{HCl(l)}$$

$$CH_3COOH(l)+CH_3OH(l)$$

(iii) In the hydrolysis of sugar

$$\underset{\text{(Sucrose solution)}}{C_{12}H_{22}O_{11}(l)}+H_2O(l)\xrightarrow{H_2SO_4(l)}$$

$$\underset{\text{(Glucose solution)}}{C_6H_{12}O_6(l)}+\underset{\text{(Fructose solution)}}{C_6H_{12}O_6(l)}$$

(2) **Heterogeneous catalysis** : The catalytic process in which the reactants and the catalyst are in different phases is known as ***heterogeneous catalysis***. Some of the examples of heterogeneous catalysis are given below.

(i) In contact process for H_2SO_4

$$2SO_2(g)+O_2(g)\xrightarrow[BrV_2O_5]{Pt(s)}2SO_3(g)$$

(ii) In Haber's process for NH_3

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

(iii) In Ostwald's process for HNO_3

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

(3) **Positive catalysis** : When the rate of the reaction is accelerated by the foreign substance, it is said to be a ***positive catalyst*** and phenomenon as ***positive catalysis***. Some examples of positive catalysis are given below.

(i) Decomposition of $KClO_3$

$$2KClO_3(s)\xrightarrow[270^oC]{MnO_2(s)}2KCl(s)+3O_2(g)$$

(ii) Oxidation of SO_2

$$2SO_2(g)+O_2(g)\xrightarrow[or\ Pt(s)]{V_2O_5(s)}2SO_3(g)$$

(iii) Decon's process

$$4HCl(g)+O_2(g)\xrightarrow[450^oC]{CuCl_2(s)}2Cl_2(g)+2H_2O(g)$$

(4) **Negative catalysis** : There are certain, substance which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called ***negative catalyst*** or ***inhibitors*** and the phenomenon is known as ***negative catalysis***. Some examples are as follows.

(i) Oxidation of sodium sulphite

$$2Na_2SO_3(s)+O_2(g)\xrightarrow{Alcohol(l)}2Na_2SO_4(s)$$

(ii) Oxidation of benzaldehyde

$$2C_6H_5CHO(l)+O_2(g)\xrightarrow[amine\ (l)]{Diphenyl}2C_6H_5COOH(l)$$

(iii) Tetra ethyl lead (TEL) is added to petrol to retard the ignition of petrol vapours on compression in an internal combustion engine and thus minimise the ***knocking effect***.

(5) **Auto-catalysis :** In certain reactions, one of the product acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existences the reaction rate increases. This type of phenomenon is known as ***auto-catalysis***. Some examples are as follows,

(i) The rate of oxidation of oxalic acid by acidified potassium permanganate increases as the reaction progresses. This acceleration is due to the presence of Mn^{2+} ions which are formed during reaction. Thus Mn^{2+} ions act as auto-catalyst.

$$5H_2C_2O_4+2KMnO_4+3H_2SO_4\to 2MnSO_4+K_2SO_4$$

$$+10CO_2+8H_2O$$

(ii) When nitric acid is poured on copper, the reaction is very slow in the beginning, gradually the reaction becomes faster due to the formation of nitrous acid during the reaction which acts as an auto-catalyst.

(6) **Induced catalysis :** When one reaction influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as ***induced catalysis***. Some examples are as follows,

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

(ii) The reduction of mercuric chloride $(HgCl_2)$ with oxalic acid is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of potassium permanganate and $HgCl_2$ both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of mercuric chloride.

(7) **Acid-base catalysis** : According to the ***Arrhenius*** and ***Ostwald*** H or H ion act as a catalyst.

(i) For example, Hydrolysis of an ester,

$$CH_3COOC_2H_5(l)+H_2O(l)\xrightarrow[OH^-]{H^+\ or}CH_3COOH(l)+C_2H_5OH(l)$$

(ii) Inversion of cane sugar,

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}(l)}+H_2O\xrightarrow{H^+}\underset{\text{Fructose}}{C_6H_{12}O_6(l)}+\underset{\text{Glucose}}{C_6H_{12}O_6(l)}$$

(iii) Conversion of acetone into diacetone alcohol,

$$CH_3COCH_3(l)+CH_3COCH_3(l)\xrightarrow{OH^-}$$

$$CH_3COCH_2.C(CH_3)_2OH(l)$$

Characteristics of catalysis

The following are the characteristics which are common to must of catalytic reactions.

(1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

(2) **A small quantity of the catalyst is generally sufficient to catalyses almost unlimited reactions**

(i) For example, in the decomposition of hydrogen peroxide, one gram of colloidal platinum can catalyses 10^8 litres of hydrogen peroxide.

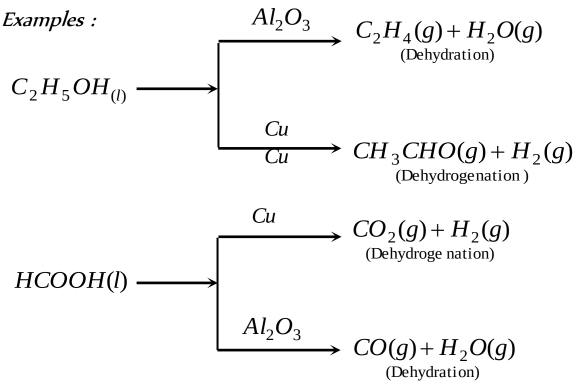
(ii) In Friedel craft's reaction, anhydrous aluminium chloride is required in relatively large amount to the extent of 30% of the mass of benzene,

$$C_6H_6+C_2H_5Cl\xrightarrow{AlCl_3}C_6H_5C_2H_5+HCl$$

(3) **The catalyst can not initiate the reaction:** The function of the catalyst is to alter the speed of the reaction rather than to start it.

(4) **The catalyst is generally specific in nature:** A substance, which acts as a catalyst for a particular reaction , fails to catalyse the other reaction , different catalysts for the same reactant may for different products.

Examples :



(5) **The catalyst can not change the position of equilibrium :** The catalyst catalyse both forward and backward reactions to the same extent in a reversible reaction and thus have no effect on the equilibrium constant.

(6) **Catalytic promoters :** Substances which themselves are not catalysts, but when mixed in small quantities with the catalysts increase their efficiency are called as ***promoters*** or ***activators.***

(i) For example, in Haber's process for the synthesis of ammonia, traces of molybdenum increases the activity of finely divided iron which acts as a catalyst.

(ii) In the manufacture of methyl alcohol from water gas $(CO+H_2)$, chromic oxide (Cr_2O_3) is used as a promoter with the catalyst zinc oxide (ZnO).

(7) **Catalytic poisons :** Substances which destroy the activity of the catalyst by their presence are known as ***catalytic poisons.***

(i) For example, the presence of traces of arsenious oxide (As_2O_3) in the reacting gases reduces the activity of platinized asbestos which is used as catalyst in contact process for the manufacture of sulphuric acid.

(ii) The activity of iron catalyst is destroyed by the presence of H_2S or CO in the synthesis of ammonia by Haber's process.

(iii) The platinum catalyst used in the oxidation of hydrogen is poisoned by CO .

(8) **Change of temperature alters the rate of catalytic reaction as it does for the same reaction in absence of catalyst :** By increasing the temperature, there is an increase in the catalytic power of a catalyst but after a certain temperature its power begins to decrease. A catalyst has thus, a particular temperature at which its catalytic activity is maximum. This temperature is termed as ***optimum temperature.***

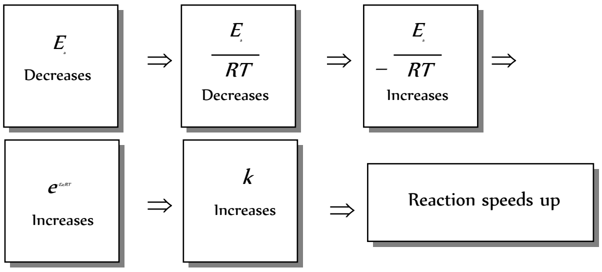
(9) **A positive catalyst lowers the activation energy**

(i) According to the collision theory, a reaction occurs on account of effective collisions between the reacting molecules.

(ii) For effective collision, it is necessary that the molecules must possess a minimum amount of energy known as activation energy (E).

(iii) After the collision molecules form an activated complex which dissociate to yield the product molecules.

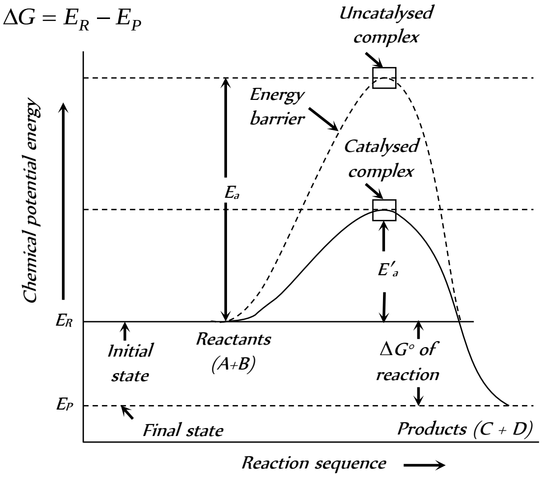
(iv) The catalyst provides a new pathway involving lower amount of activation energy. Thus,



larger number of effective collisions occur in the presence of a catalyst in comparison to effective collisions at the same temperature in absence of a catalyst. Hence the presence of a catalyst makes the reaction to go faster.

(v) Figure shows that activation energy E_a , in absence of a catalyst is higher than the activation energy E'_a in presence of a catalyst.

(vi) E_R and E_p represent the average energies of reactants and products. The difference gives the value of ΔG , *i.e.,* $\Delta G=E_R-E_P$



Theories of catalysis

There are two theories of catalysis which is described as follows.

(1) **Intermediate compound theory**

(i) This theory was proposed by ***Clement and Desormes in*** 1806. According to this theory, the desired reaction is brought about by a path involving the formation of an unstable intermediate compound, followed by its decomposition into the desired end products with the regeneration of the catalyst.

(ii) The intermediate compund may be formed in either of two ways

(a) When the intermediate compound is reactive and reacts with the other reactants.

$$AB + X \rightarrow \underset{\text{intermediate}}{BX} + A$$

$$BX + C \rightarrow CB + X \qquad .....(i)$$

(b) When the intermediate is unstable and decomposes to give the final product.

$$A + B + X \rightarrow \underset{\text{intermediate}}{ABX} \rightarrow AB + X \qquad .....(ii)$$

Where, *A, B* and *C* are the reactant molecules and *X* is the molecule of the catalyst. The first type of reaction sums up to, $AB + C \rightarrow CB + A$

While the second to, $A + B \rightarrow AB$ in many cases, the intermediate compounds postulated to be formed are known compounds and often their presence is detected.

(2) **Adsorption theory**

(i) This theory is applicable to reactions between gases in the presence of a solid catalyst. Some typical examples are as follows.

(ii) The contact process for the oxidation of SO_2 to SO_3 with atmospheric oxygen in the presence of platinum as the catalyst.

(iii) The Haber's process for the synthesis of ammonia with iron as the catalyst.

(iv) Adsorption results in the loosening of the chemical bonds in the reactant molecules, so that their rupture becomes easier. This is confirmed by the observed lower activation energies for heterogeneous catalytic reactions in the presence of the catalysts as compared to that for the same reaction in the absence of the catalyst.

Enzyme catalysis

(1) Enzymes are complex nitrogenous substances these are actually protein molecules of higher molecular mass.

(2) Enzymes catalyse numerous reactions, especially those connected with natural processes.

(3) Numerous reactions occur in the bodies of animals and plants to maintain the life process. These reactions are catalysed by enzymes. The enzymes are thus, termed as ***bio-chemical catalysts*** and the phenomenon is known as ***bio-chemical catalysis.***

(4) ***Nitrogenase*** an enzyme present in bacteria on the root nodules of leguminous plants such as peas and beans, catalyses the conversion of atmospheric N_2 to NH_3.

(5) In the human body, the enzyme carbonic anhydrase catalyses the reaction of CO_2 with H_2O,

$$CO_2(aq) + H_2O(l) \square H^+(aq.) + HCO_3^-(aq.)$$

The forward reaction occurs when the blood takes up CO_2 in the tissues, and the reverse reaction occurs when the blood releases CO_2 in lungs.

(6) **In manufacturing of ethyl alcohol**

(i) $C_{12}H_{22}O_{11}(l) + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6(l)} + \underset{\text{Fructose}}{C_6H_{12}O_6(l)}$

$$C_6H_{12}O_6(l) \xrightarrow{\text{Zymase}} 2C_2H_5OH(l) + 2CO_2(l)$$

(ii) Starch $(l) \xrightarrow{\text{Diastase}}$ Maltose(l)

Maltose $\xrightarrow{\text{Maltase}}$ Glucose $\xrightarrow{\text{Zyamase}}$ Alcohol

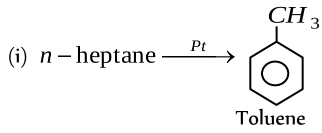
Activity and Selectivity

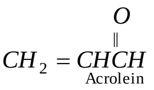
(1) **Activity :** Activity is the ability of catalysts to accelerate chemical reaction, the degree of acceleration can be as high as 10^{10} times in certain reactions. For example reaction between H_2 and O_2 to form H_2O in presence of platinum as catalyst takes place with explosive violence.

In absence of catalyst, H_2 and O_2 can be stored indefinitely without any reaction.

(2) **Selectivity :** Is the ability of catalysts to direct reaction to yield particular products (excluding other).

Example :





$$\text{(ii)}\ CH_3CH = CH_2 \xrightarrow{BiMoO_4} CH_2 = \underset{\text{Acrolein}}{CH\overset{\overset{O}{\|}}{C}H}$$

Zeolite (Shape selective catalysis)

(1) Zeolite are alumino–silicates of the general formula, $M_{x/n}[AlO_2]_x.(SiO_2)_y.mH_2O$, where, *M* may be simple cation like Na^+, K^+ or Ca^{2+}, *n* is the charge on the simple cation, *m* is the number of molecules of water of crystallization.

(2) Some well known zeolites are as follows,

Erionite $\rightarrow Na_2K_2CaMg(AlO_2)_2(SiO_2)_2.6H_2O$

Gemelinite $\rightarrow Na_2Ca(AlO_2)_2(SiO_2)_4.6H_2O$

Faujasite (natural) $\rightarrow Na_{56}(AlO_2)_{56}(SiO_2)_{136}.250H_2O$

ZSM-5 $\rightarrow H_x[(AlO_2)_x(SiO_2)_{96-x}].16H_2O$

Linde-A (synthetic) $\rightarrow [Na_{12}(AlO_2)_{12}(SiO_2)_{12}.27H_2O]_8$

(3) The characteristic feature of zeolites is the openness of the structure, which permits cavities of different sizes.

(4) The open structure is provided by silica in which aluminium occupies *x/(x+y)* fraction of the telrahedral sites.

(5) The negative charge of the aluminosilicate framework is neutralized by the replaceable cations.

(6) The void space forms more than 50% of the total volume, which is occupied by water molecules.

(7) The reaction- selectivity of zeolites depends upon the size of cavities (cages), pores (apertures) and the distribution of pores in the structure. The pore size in zeolites generally varies from 260 *pm* to 740 *pm.*

(8) Zeolite have high porosity due to the presence of one, two, or three dimensional networks of interconnected channels and cavities of molecular dimensions.

(9) There is a new class of highly siliceous zeolites with an optimal pore diameter of 550*pm.* ZSM-5 is one such zeolite having the formula. $[H_x(AlO_2)_x.(SiO_2)_{96-x}].16H_2O$

(10) The zeolite catalyst ZSM-5 converts alcohols to gasoline (petrol) by dehydrating the alcohol and producing a mixture of wide variety of hydrocarbons.

Colloidal state

(1) The foundation of colloidal chemistry was laid down by an English scientist, ***Thomas Graham***, in 1861. The credit for the various advances in this field goes to eminent scientists like ***Tyndall, Hardy, Zsigmondy, N.R. Dhar, S.S. Bhatnagar and others.***

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

(i) ***Crystalloids*** **:** They have higher rate of diffusion and diffused from parchment paper.

Examples : All organic acids, bases and salts and organic compounds such as sugar, urea etc.

(ii) ***Colloids*** (*Greek word, kolla, meaning glue-like*) **:** They have slower rate of diffusion and can not diffused from parchment paper.

Examples : Starch, gelatin, gums, silicic acid and hdemoglobin etc.

(3) The above classification was discarded *i.e.,* the terms colloid does not apply to a particular class of substances but is a state of matter like solid, liquid and gas. Any substance can be brought into colloidal state.

(4) The colloidal state depends on the particle size. If is regarded as intermediate state between true solution and suspension.

Table : 14.2 Features of the three types of solutions

Property	**Suspension**	**Colloid solution**	**True solution**
Nature	Heterogeneous	Heterogeneous	Homogeneous
Particle size	$> 100\ nm$	$1\ nm - 100\ nm$	$< 1\ nm$
Separation by (i) Ordinary filtration (ii) Ultra- filtration	 Possible Possible	 Not possible Possible	 Not possible Not possible
Settling of particles	Settle under gravity	Settle only on centrifugation	Do not settle
Appearance	Opaque	Generally transparent	Transparent
Tyndall effect	Shows	Shows	Does not show
Diffusion of particles	Does not diffuse	Diffuses slowly	Diffuses rapidly
Brownian movement	May show	Shows	Negligible

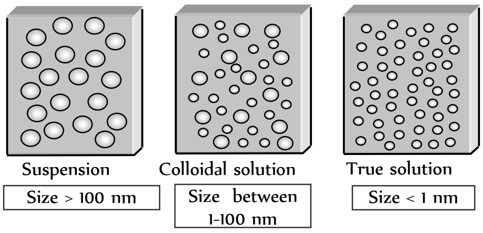


Fig. 14.1 Three types solutions

Phases of colloids and Their classification

(1) **Phases of colloids :** We know that a colloidal solution is of heterogeneous nature. It consists of two phases which are as follows

(i) ***Internal phase or Dispersed phase*** (Discontinuous phase) **:** It is the component present in small proportion and is just like a solute in a solution. For example in the colloidal solution of silver in water (silver acts as a dispersed phase)

(ii) ***External phase or Dispersion medium*** (continuous phase) **:** It is generally component present in excess and is just like a solvent in a solution. For example, in the colloidal solution of silver in water. Water act as a dispersion medium.

(2) **Classification of colloids :** The colloids are classified on the basis of the following criteria

(i) ***Classification based on the physical state of the dispersed phase and dispersion medium*** **:** Depending upon the physical state of dispersed phase and dispersion medium whether these are solids, liquids or gases, eight types of colloidal systems are possible.

Table : 14.3 Different types of colloidal systems

Dispersed phase	**Dispersion Medium**	**Colloidal System**	**Examples**
Liquid	Gas	Aerosol of liquids	Fogs, clouds, mists, fine insecticide sprays
Solid	Gas	Aerosol of solids	Smoke, volcanic dust, haze
Gas	Liquid	Foam or froth	Soap lather. Lemonade froth, foam, whipped cream, soda water
Liquid	Liquid	Emulsions	Milk, emulsified oils, medicines
Solid	Liquid	Sols	Most paints, starch in water, proteins, gold sol, arsenic sulphide sol, ink
Gas	Solid	Solid foam	Pumice stone, styrene rubber, foam rubber
Liquid	Solid	Gels	Cheese, butter, boot polish, jelly, curd
Solid	Solid	Solid sols (coloured glass)	Ruby glass, some gem stones and alloys

(ii) ***Classification based on Nature of interaction between dispersed phase and dispersion medium***: Depending upon the nature of interactions between dispersed phase and the dispersion medium, the colloidal solutions can be classified into two types as (a) Lyophilic and (b) Lyophobic sols.

(a) *Lyophilic colloids* (water loving) : "The colloidal solutions in which the particles of the dispersed phase have a great affinity for the dispersion medium, are called ***lyophilic collodis."***

(b) *Lyophobic colloids* (water hateing) : *"The colloidal solutions in which* there *is no affinity between particles of the dispersed phase and the dispersion medium are called* ***lyophobic colloids.***"

Distinction between lyophilic and lyophobic sols

Property	**Lyophilic sols (suspensoid)**	**Lyophobic sols (Emulsoid)**
Surface tension	Lower than that of the medium	Same as that of the medium
Viscosity	Much higher than that of the medium	Same as that of the medium
Reversibility	Reversible	Irreversible
Stability	More stable	Less stable
Visibility	Particles can't be detected even under ultramicroscope	Particles can be detected under ultramicroscope.
Migration	Particles may migrate in either direction or do not migrate in an electric field because do not carry any charge.	Particles migrate either towards cathode or anode in an electric field because they carry charge.
Action of electrolyte	Addition of smaller quantity of electrolyte has little effect	Coagulation takes place
Hydration	Extensive hydration takes place	No hydration
Examples	Gum, gelatin, starch, proteins, rubber etc.	Metals like Ag and Au, hydroxides like $Al(OH)_3$, $Fe(OH)_3$ metal sulphides like AS_2S_3 etc.

(iii) ***Classification based on types of particle of dispersed phase*** **:** Depending upon the type of the particles of the dispersed phase, the colloids are classified as follows.

(a) *Multimolecular colloids*

- When on dissolution, atoms or smaller molecules of substances (having diameter less than 1*nm*) aggregate together to form particles of colloidal dimensions, the particles thus formed are called ***multimolecular colloids.***

- In these sols the dispersed phase consists of aggregates of atoms or molecules with molecular size less than 1 *nm.*

- For example, sols of gold atoms and sulphur (S_8) molecules. In these colloids, the particles are held together by ***Vander Waal's forces.*** They have usually ***lyophilic character.***

(b) *Macromolecular colloids*

- These are the substances having big size molecules (called macromolecules) which on dissolution form size in the colloidal range. Such substances are called ***macromolecular colloids.***

- These macromolecules forming the dispersed phase are generally ***polymers*** having very high molecular masses.

- Naturally occurring macromolecules are starch, cellulose, proteins, enzymes, gelatin etc. Artificial macromolecules are synthetic polymers such as nylon, polythene, plastics, polystyrene etc.

- They have usually ***lyophobic character.***

(c) *Associated colloids*

- These are the substances which on dissolved in a medium behave as normal electrolytes at low concentration but behave, as colloidal particles at higher concentration due to the formation of aggregated particles. The aggregates particles thus formed are called ***micelles.***

- Their molecules contain both ***lyophilic*** and ***lyophobic*** groups.

Micelles

- Micelles are the cluster or aggregated particles formed by association of colloid in solution.

- The common examples of micelles are ***soaps*** and ***detergents.***

- The formation of micelles takes place above a particular temperature called ***Kraft temperature*** (T_k) and above a particular concentration called ***critical micellization concentration*** (CMC).

- They are capable of forming ions.

- Micelles may contain as many as 100 molecules or more.

- For example sodium stearate $(C_{17}H_{35}COONa)$ is a typical example of such type of molecules.

- When sodium stearate is dissolved in water, it gives Na^+ and $C_{17}H_{35}COO^-$ ions.

$$\underset{\text{Sodium stearate}}{C_{17}H_{35}COONa} \rightleftharpoons \underset{\text{Stearate ion}}{C_{17}H_{35}COO^-} + Na^+$$

The stearate ions associate to form ***ionic micelles*** of colloidal size.

- It has long hydrocarbon part of $C_{17}H_{35}$ radical. Which is ***lyophobic*** and COO^- part which is ***lyophilic.***

- In the figure, the chain corresponds to stearate ion, $(C_{17}H_{35}COO^-)$. When the concentration of the solution is below from its CMC $(10^{-3}\ mol\ L^{-1})$, it behaves as normal electrolyte. But above this concentration it is aggregated to behave as micelles.

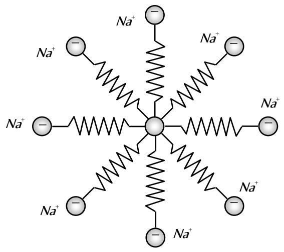


Fig. 14.2 Aggregation of several ions to form ionic micelle

- The main function of a soap is to reduce oily and greasy dirt to colloidal particles (an emulsion). Soap therefore, are known as ***emulsifying agents.***

- Some other examples of micelles are sodium palmitate $(C_{15}H_{31}COONa)$, Sodium lauryl sulphate $[CH_3(CH_2)_{11}SO_3O^-Na^+]$, Cetyl trimethyl ammonium bromide $CH_3(CH_2)_{15}(CH_2)_3N^+Br^-$ etc.

General methods of preparation of colloids

Lyophilic and lyophobic colloidal solutions (or sols) are generally prepared by different types of methods. Some of the common methods are as follows.

(1) **Preparation of Lyophilic colloids**

(i) The lyophilic colloids have strong affinity between particles of dispersed phase and dispersion medium.

(ii) Simply mixing the dispersed phase and dispersion medium under ordinary conditions readily forms these colloidal solutions.

(iii) For example, the substance like gelatin, gum, starch, egg, albumin etc. pass readily into water to give colloidal solution.

(iv) They are reversible in nature become these can be precipitated and directly converted into colloidal state.

(2) **Preparation of Lyophobic colloids** : Lyophobic colloids can be prepared by mainly two types of methods.

(i) ***Condensation method*** **:** In these method, smaller particles of dispersed phase are condensed suitably to be of colloidal size. This is done by the following methods.

(a) *By oxidation* **:** A colloidal solution of sulphur can be obtained by bubbling oxygen (or any other oxidising agent like HNO_3, Br_2 etc.) through a solution of hydrogen sulphide in water.

$$2H_2S + O_2\ (\text{or any other oxidisingagent}) \longrightarrow 2H_2O + 2S$$

(b) *By reduction* **:** A number of metals such as silver, gold and platinum, have been obtained in colloidal state by treating the aqueous solution of their salts, with a suitable reducing agent such as formaldehyde, phenyl hydrazine, hydrogen peroxide, stannous chloride etc.

$$2AuCl_3 + 3SnCl_2 \longrightarrow 3SnCl_4 + \underset{\text{Gold sol}}{2Au}$$

$$2AuCl_3 + 3HCHO + 3H_2O \longrightarrow \underset{\text{Gold sol}}{2Au} + 3HCOOH + 6HCl$$

The gold sol, thus prepared, has a purple colour and is called purple of cassius.

(c) *By hydrolysis* **:** Many salt solutions are rapidly hydrolysed by boiling dilute solutions of their salts. For example, ferric hydroxide and aluminium hydroxide sols are obtained by boiling solutions of the corresponding chlorides.

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

Similarly silicic acid sol is obtained by the hydrolysis of sodium silicate.

(d) *By double decomposition* **:** A sol of arsenic sulphide is obtained by passing hydrogen sulphide through a cold solution of arsenious oxide in water.

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

(e) *By excessive cooling* **:** A colloidal solution of ice in an organic solvent like ether or chloroform can be prepared by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution, separately combine to form particles of colloidal size.

(f) *By exchange of solvent* **:** Colloidal solution of certain substances such as sulphur, phosphorus, which are soluble in alcohol but insoluble in water can be prepared by pouring their alcoholic solution in excess of water. For example, alcoholic solution of sulphur on pouring into water gives milky colloidal solution of sulphur.

(g) *By change of physical state* **:** Sols of substances like mercury and sulphur are prepared by passing their vapour's through a cold water containing a suitable stabilizer such as ammonium salt or citrate.

(ii) ***Dispersion methods*** **:** In these methods, larger particles of a substance (suspensions) are broken into smaller particles. The following methods are employed.

(a) *Mechanical dispersion*

- In this method, the substance is first ground to coarse particles.
- It is then mixed with the dispersion medium to get a suspension.
- The suspension is then grinded in colloidal mill.

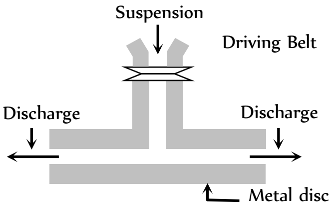


Fig. 14.3 Colloidal mill

- It consists of two metallic discs nearly touching each other and rotating in opposite directions at a very high speed about 7000 revolution per minute.
- The space between the discs of the mill is so adjusted that coarse suspension is subjected to great shearing force giving rise to particles of colloidal size.
- Colloidal solutions of black ink, paints, varnishes, dyes etc. are obtained by this method.

(b) *By electrical dispersion or Bredig's arc method*

- This method is used to prepare sols of platinum, silver, copper or gold.
- The metal whose sol is to be prepared is made as two electrodes which immerged in dispersion medium such as water etc.
- The dispersion medium is kept cooled by ice.

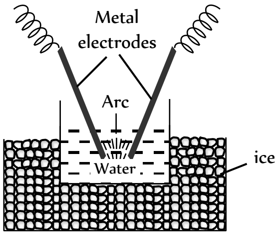


Fig. 14.4 Bredig's arc method

- An electric arc is struck between the electrodes.
- The tremendous heat generate by this method and give colloidal solution.
- The colloidal solution prepared is stabilised by adding a small amount of KOH to it.

(c) *By peptisation*

- The process of converting a freshly prepared precipitate into colloidal form by the addition of suitable electrolyte is called ***peptisation.***
- The electrolyte is used for this purpose is called ***peptizing agent*** or ***stabilizing agent.***
- Cause of peptisation is the adsorption of the ions of the electrolyte by the particles of the precipitate.
- Important peptizing agents are sugar, gum, gelatin and electrolytes.
- Freshly prepared ferric hydroxide can be converted into colloidal state by shaking it with water containing Fe^{3+} or OH^- ions, viz. $FeCl_3$ or NH_4OH respectively.

$$\underset{\text{Precipitate}}{Fe(OH)_3} + \underset{\text{electrolyte}}{FeCl_3} \longrightarrow \underset{\text{Colloidal sol}}{[Fe(OH)_3 Fe]^{3+}} + 3Cl^-$$

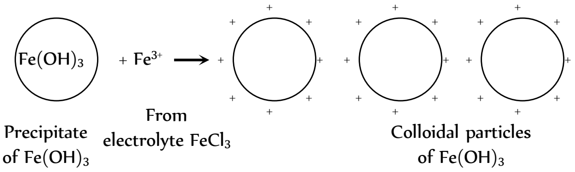


Fig. 14.5 Preparation of colloidal sol by peptisation

- A stable sol of stannic oxide is obtained by adding a small amount of dilute HCl to stannic oxide precipitates.
- Similarly, a colloidal solution of $Al(OH)_3$ and $AgCl$ are obtained by treating the corresponding freshly prepared precipitate with very dilute solution of HCl and $AgNO_3$ or KCl respectively.

Purification of colloidal solution

The following methods are commonly used for the purification of colloidal solutions.

(1) **Dialysis**

(i) The process of separating the particles of colloid from those of crystalloid, by means of diffusion through a suitable membrane is called dialysis.

(ii) It's principle is based upon the fact that colloidal particles can not pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it.

(iii) The impurities slowly diffused out of the bag leaving behind pure colloidal solution

(iv) The distilled water is changed frequently to avoid accumulation of the crystalloids otherwise they may start diffusing back into the bag.

(v) Dialysis can be used for removing HCl from the ferric hydroxide sol.

(2) **Electrodialysis**

(i) The ordinary process of dialysis is slow.

(ii) To increase the process of purification, the dialysis is carried out by applying electric field. This process is called ***electrodialysis.***

(iii) The important application of electrodialysis process in the artificial kidney machine used for the purification of blood of the patients whose kidneys have failed to work. The artificial kidney machine works on the principle of ***dialysis.***

(3) **Ultra – filtration**

(i) Sol particles directly pass through ordinary filter paper because their pores are larger (more than 1μ or $1000m\mu$) than the size of sol particles (less than $200m\mu$).

(ii) If the pores of the ordinary filter paper are made smaller by soaking the filter paper in a solution of gelatin of colloidion and subsequently hardened by soaking in formaldehyde, the treated filter paper may retain colloidal particles and allow the true solution particles to escape. Such filter paper is known as ***ultra - filter*** and the process of separating colloids by using ultra – filters is known as ***ultra – filtration.***

(4) **Ultra – centrifugation**

(i) The sol particles are prevented from setting out under the action of gravity by kinetic impacts of the molecules of the medium.

(ii) The setting force can be enhanced by using high speed centrifugal machines having 15,000 or more revolutions per minute. Such machines are known as ***ultra–centrifuges***.

Properties of colloidal solutions

The main characteristic properties of colloidal solutions are as follows.

(1) **Physical properties**

(i) ***Heterogeneous nature*** : Colloidal sols are heterogeneous in nature. They consists of two phases; the dispersed phase and the dispersion medium.

(ii) ***Stable nature*** : The colloidal solutions are quite stable. Their particles are in a state of motion and do not settle down at the bottom of the container.

(iii) ***Filterability*** : Colloidal particles are readily passed through the ordinary filter papers. However they can be retained by special filters known as ultrafilters (parchment paper).

(2) **Colligative properties**

(i) Due to formation of associated molecules, observed values of colligative properties like relative decrease in vapour pressure, elevation in boiling point, depression in freezing point, osmotic pressure are smaller than expected.

(ii) For a given colloidal sol the number of particles will be very small as compared to the true solution.

(3) **Mechanical properties**

(i) ***Brownian movement***

(a) ***Robert Brown***, a botanist discovered in 1827 that the ***pollen grains*** suspended in water do not remain at rest but move about continuously and randomly in all directions.

(b) Later on, it was observed that the colloidal particles are moving at random in a ***zig – zag*** motion. This type of motion is called ***Brownian movement.***

(c) The molecules of the dispersion medium are constantly colloiding with the particles of the dispersed phase. It was stated by ***Wiener*** in 1863 that *the impacts of the dispersion medium particles are unequal, thus causing a zig-zag motion of the dispersed phase particles.*

(d) The Brownian movement explains the force of gravity acting on colloidal particles. This helps in providing stability to colloidal sols by not allowing them to settle down.

(ii) ***Diffusion*** : The sol particles diffuse from higher concentration to lower concentration region. However, due to bigger size, they diffuse at a lesser speed.

(iii) ***Sedimentation*** : The colloidal particles settle down under the influence of gravity at a very slow rate. This phenomenon is used for determining the molecular mass of the macromolecules.

(4) **Optical properties** : ***Tyandall effect***

(i) When light passes through a sol, its path becomes visible because of scattering of light by particles. It is called ***Tyndall effect.*** This phenomenon was studied for the first time by ***Tyndall.*** The illuminated path of the beam is called ***Tyndall cone.***

(ii) The intensity of the scattered light depends on the difference between the refractive indices of the dispersed phase and the dispersion medium.

(iii) In lyophobic colloids, the difference is appreciable and, therefore, the Tyndall effect is well - defined. But in lyophilic sols, the difference is very small and the Tyndall effect is very weak.

(iv) The Tyndall effect confirms the ***heterogeneous nature of the colloidal solution.***

(v) The Tyndall effect has also been observed by an instrument called ***ultra – microscope.***

Some example of Tyndall effect are as follows

(a) *Tail of comets is seen as a **Tyndall cone due** to the scattering of light by the tiny solid particles left by the comet in its path.*

(b) *Due to scattering the sky looks blue.*

(c) *The blue colour of water in the sea is due to scattering of blue light by water molecules.*

(d) *Visibility of projector path and circus light.*

(e) *Visibility of sharp ray of sunlight passing through a slit in dark room.*

(5) **Electrical properties**

(i) ***Electrophoresis***

(a) The phenomenon of movement of colloidal particles under an applied electric field is called ***electrophoresis.***

(b) If the particles accumulate near the negative electrode, the charge on the particles is ***positive.***

(c) On the other hand, if the sol particles accumulate near the positive electrode, the charge on the particles is ***negative.***

(d) The apparatus consists of a U-tube with two *Pt*-electrodes in each limb.

(e) When electrophoresis of a sol is carried out with out stirring, the bottom layer gradually becomes more concentrated while the top layer which contain pure and concentrated colloidal solution may be decanted. This is called ***electro decanation*** and is used for the purification as well as for concentrating the sol.

(f) The reverse of electrophoresis is called ***Sedimentation potential or Dorn effect.*** The sedimentation potential is setup when a particle is forced to move in a resting liquid. This phenomenon was discovered by ***Dorn*** and is also called ***Dorn effect.***

(ii) ***Electrical double layer theory***

(a) The electrical properties of colloids can also be explained by electrical double layer theory. According to this theory ***a double layer of ions appear at the surface of solid.***

(b) The ion preferentially adsorbed is held in fixed part and imparts charge to colloidal particles.

(c) The second part consists of a diffuse mobile layer of ions. This second layer consists of both the type of charges. The net charge on the second layer is exactly equal to that on the fixed part.

(d) The existence of opposite sign on fixed and diffuse parts of double layer leads to appearance of a difference of potential, known as ***zeta potential or electrokinetic potential.*** Now when electric field is employed the particles move (electrophoresis)

(iii) ***Electro-osmosis***

(a) In it the movement of the dispersed particles are prevented from moving by ***semipermeable membrane.***

(b) Electro-osmosis is a phenomenon in which dispersion medium is allowed to move under the influence of an electrical field, whereas colloidal particles are not allowed to move.

(c) The existence of electro-osmosis has suggested that when liquid forced through a porous material or a capillary tube, a potential difference is setup between the two sides called as streaming potential. So the reverse of electro-osmosis is called ***streaming potential.***

Origin of the charge on colloidal particles

The origin of the charge on the sol particles in most cases is due to the preferential adsorption of either positive or negative ions on their surface. The sol particles acquire electrical charge in any one or more of the following ways.

(1) **Due to the dissociation of the surface molecules :** Some colloidal particles develope electrical charge due to the dissociation / ionisation of the surface molecules. The charge on the colloidal particles is balanced by the oppositely charged ions in the sol. For example, an aqueous solution of soap (sodium palmitate) which dissociates into ions as,

$$\underset{\text{Sodium palmitate}}{C_{15}H_{31}COONa} \square C_{15}H_{31}COO^- + Na^+$$

The cations (Na) pass into the solution while the anions $(C_{15}H_{31}COO^-)$ have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains.

(2) **Due to frictional electrification**

(i) It is believed that the frictional electrification due to the rubbing of the dispersed phase particles with that of dispersion medium results in some charge on the colloidal particles.

(ii) The dispersion medium must also get some charge, because of the friction. Since it does not carry any charge, the theory does not seem to be correct.

(3) **Due to selective adsorption of ions**

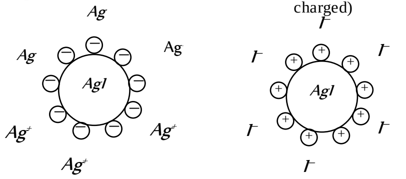
(i) The particles constituting the dispersed phase adsorb only those ions preferentially which are common with their own lattice ions.

(ii) For example, when a small quantity of silver nitrate $(AgNO_3)$ solution is added to a large quantity of potassium iodide (KI) solution, the colloidal particles of silver iodide adsorb I^- from the solution to become ***negatively charged,*** *(at this stage* KI *is in excess, and* I^- *being common to* AgI*)*

$$\underset{\text{(Colloidal particle)}}{AgI} + \underset{\text{(in excess in the medium)}}{I^-} \longrightarrow \underset{\text{(Colloidal particle becomes positively charged)}}{(AgI)I^-}$$

But, when a small quantity of potassium iodide (KI) solution is added to a large quantity of silver nitrate solution $(AgNO_3)$; the colloidal silver iodide particles adsorb Ag^+ from the solution to become ***positively charged,*** *(at this stage* $AgNO_3$ *is in excess and* Ag^+ *is common to* AgI*),*

$$\underset{\text{(Colloidal particle)}}{AgI} + \underset{\text{(in excess in the medium)}}{Ag^+} \longrightarrow \underset{\text{(Colloidal particle becomes positively charged)}}{(AgI)Ag^+}$$



Ag ions remain in dispersed medium (AgI, I Sol)

I ions remain in dispersion medium (AgI, Ag Sol)

Fig. 14.6

(iii) Depending upon the nature of charge on the particles of the dispersed phase, the colloidal solutions are classified into positively charged and negatively charged colloids. Some typical examples are as follows

(a) Negatively charged colloids	(b) Positively charged colloids
• Metal sulphides : As_2S_3, CdS	• Metal hydroxides : $Al(OH)_3$, $Fe(OH)_3$
• Metal dispersions : Ag, Au, Pt	• Metal oxide : TiO_2
• Acid dyes : Eosin, congo red	• Basic dyes : Methylene blue
• Sols of starch, gums, gold, gelatin etc.	• Haemoglobin
	• Sulphur sol

Stability of sols

Sols are thermodynamically unstable and the dispersed phase (colloidal particles) tend to separate out on long standing due to the ***Vander Waal's attractive forces.*** However sols tend to exhibit some stability due to

(1) **Stronger repulsive forces between the similarly charged particles**

(2) **Particle-solvent interactions :** Due to strong particle-solvent (dispersion medium) interactions, the colloidal particles get strongly solvated.

Coagulation or Flocculation or Precipitation

"The phenomenon of the precipitation of a colloidal solution by the addition of the excess of an electrolyte is called ***coagulation or flocculation.****"*

The coagulation of the ***lyophobic sols*** can be carried out by following methods.

(1) **By electrophoresis :** In electrophoresis the colloidal particles move towards oppositely charged electrode. When these come in contact with the electrode for long these are discharged and precipitated.

(2) **By mixing two oppositely charged sols :** When oppositely charged sols are mixed in almost equal proportions, their charges are neutralised. Both sols may be partially or completely precipitated as the mixing of ferric hydroxide (+*ve* sol) and arsenious sulphide (–*ve* sol) bring them in precipitated form. This type of coagulation is called ***mutual coagulation*** *or* ***meteral coagulation.***

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

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

(5) **By addition of electrolytes :** The particles of the dispersed phase *i.e.,* colloids bear some charge. When an electrolyte is added to sol, the colloidal particles take up ions carrying opposite charge from the electrolyte. As a result, their charge gets neutralised and this causes the uncharged, particles to come closer and to get coagulated or precipitated. For example, if $BaCl_2$ solution is added to As_2S_3 sol the Ba^{2+} ions are attracted by the negatively charged sol particles and their charge gets neutralised. This lead to coagulation.

(6) **Hardy schulze rule :** The coagulation capacity of different electrolytes is different. It depends upon the valency of the active ion are called flocculating ion, which is the ion carrying charge opposite to the charge on the colloidal particles. "*According to Hardy Schulze rule, greater the valency of the active ion or flocculating ion, greater will be its coagulating power*" thus, Hardy Schulze law state:

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

(ii) *Coagulating power of an electrolyte is directly proportional to the valency of the active ions (ions causing coagulation).*

For example to coagulate ***negative sol*** of As_2S_3, the ***coagulation power*** of different cations has been found to ***decrease*** in the order as, $Al^{3+} > Mg^{2+} > Na^+$

Similarly, to coagulate a ***positive sol*** such as $Fe(OH)_3$, the ***coagulating power*** of different anions has been found to ***decrease*** in the order : $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

(7) **Coagulation or flocculation value**

"The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol is known as ***flocculation value.****"*

or

"The number of millimoles of an electrolyte required to bring about the coagulation of one litre of a colloidal solution is called its ***flocculation value.****"*

$$\text{Coagulation value or flocculating value} \propto \frac{1}{\text{Coagulating power}}$$

(8) **Coagulation of lyophilic sols**

(i) There are two factors which are responsible for the stability of lyophilic sols.

(ii) These factors are the charge and solvation of the colloidal particles.

(iii) When these two factors are removed, a lyophilic sol can be coagulated.

(iv) This is done (i) by adding electrolyte (ii) and by adding suitable solvent.

(v) When solvent such as alcohol and acetone are added to hydrophilic sols the dehydration of dispersed phase occurs. Under this condition a small quantity of electrolyte can bring about coagulation.

Protection of colloids and Gold number

- Lyophilic sols are more stable than lyophobic sols.
- Lyophobic sols can be easily coagulated by the addition of small quantity of an electrolyte.
- When a lyophilic sol is added to any lyophobic sol, it becomes less sensitive towards electrolytes. Thus, lyophilic colloids can prevent the coagulation of any lyophobic sol.

"The phenomenon of preventing the coagulation of a lyophobic sol due to the addition of some lyophilic colloid is called sol protection or protection of colloids."

- The protecting power of different protective (lyophilic) colloids is different. The efficiency of any protective colloid is expressed in terms of ***gold number.***

Gold number **:** ***Zsigmondy*** introduced a term called ***gold number*** to describe the protective power of different colloids. This is defined as, *"weight of the dried protective agent in milligrams, which when added to 10 ml of a standard gold sol* (0.0053 to 0.0058%) *is just sufficient to prevent a colour change from red to blue on the addition of 1 ml of 10 % sodium chloride solution, is equal to the gold number of that protective colloid."*

Thus, smaller is the gold number, higher is the protective action of the protective agent.

$$\text{Protective power} \propto \frac{1}{\text{Gold number}}$$

Table : 14.4 Gold numbers of some hydrophilic substances

Hydrophilic substance	Gold number	Hydrophilic substance	Gold number
Gelatin	0.005 - 0.01	Sodium oleate	0.4 – 1.0
Sodium caseinate	0.01	Gum tragacanth	2
Hamoglobin	0.03 – 0.07	Potato starch	25
Gum arabic	0.15 – 0.25		

Congo rubin number : ***Ostwald*** introduced congo rubin number to account for protective nature of colloids. It is defined as "*the amount of protective colloid in milligrams which prevents colour change in 100 ml of 0.01 % congo rubin dye to which 0.16 g equivalent of KCl is added."*

Mechanism of sol protection

(i) The actual mechanism of sol protection is very complex. However it may be due to the adsorption of the protective colloid on the lyophobic sol particles, followed by its solvation. Thus it stabilises the sol *via* ***solvation effects.***

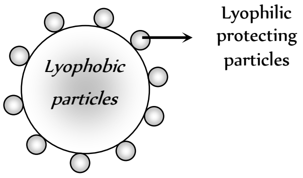


Fig. 14.7 Protection of colloids

(ii) Solvation effects contribute much towards the stability of lyophilic systems. For example, gelatin has a sufficiently strong affinity for water. It is only because of the solvation effects that even the addition of electrolytes in small amounts does not cause any flocculation of hydrophilic sols. However at higher concentration, precipitation occurs. This phenomenon is called ***salting out.***

(iii) The salting out efficiency of an electrolyte depends upon the tendency of its constituents ions to get hydrated *i.e,* the tendency to squeeze out water initially fied up with the colloidal particle.

(iv) The cations and the anions can be arranged in the decreasing order of the salting out power, such an arrangement is called ***lyotropic series.***

Cations $: Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^{+} > Na^{+} > K^{+} > NH_4^{+} > Rb^{+} > Cs^{+}$

Anions : $\text{Citrate}^{3-} > SO_4^{2-} > Cl^{-} > NH_3^{-} > I^{-} > CNS^{-}$

Ammonium sulphate, due to its very high solubility in water, is oftenly used for precipitating proteins from aqueous solutions.

(v) The precipitation of lyophilic colloids can also be affected by the addition of organic solvents of non-electrolytes. For example, the addition of acetone or alcohol to aqueous gelatin solution causes precipitation of gelatin. Addition of petroleum ether to a solution of rubber in benzene causes the precipitation of rubber.

Emulsion

"The colloidal systems in which fine droplets of one liquid are dispersed in another liquid are called emulsions the two liquids otherwise being mutually immiscible." **or**

"Emulsion are the colloidal solutions in which both the dispersed phase and the dispersion medium are liquids."

A good example of an emulsion is milk in which fat globules are dispersed in water. The size of the emulsified globules is generally of the order of 10^{-6} *m.* Emulsion resemble lyophobic sols in some properties.

(1) **Types of Emulsion :** Depending upon the nature of the dispersed phase, the emulsions are classified as;

(i) ***Oil-in-water emulsions*** *(O/W)* **:** The emulsion in which oil is present as the dispersed phase and water as the dispersion medium ***(continuous phase)*** is called an oil-in-water emulsion. Milk is an example of the oil-in-water type of emulsion. In milk liquid fat globules are dispersed in water. Other examples are, vanishing cream etc.

(ii) ***Water-in-oil emulsion*** *(W/O)* **:** The emulsion in which water forms the dispersed phase, and the oil acts as the dispersion medium is called a water-in-oil emulsion. These emulsion are also termed ***oil emulsions. Butter*** and ***cold cream*** are typical examples of this types of emulsions. Other examples are cod liver oil etc.

(2) **Properties of emulsion**

(i) Emulsions show all the characteristic properties of colloidal solution such as Brownian movement, Tyndall effect, electrophoresis etc.

(ii) These are coagulated by the addition of electrolytes containing polyvalent metal ions indicating the negative charge on the globules.

(iii) The size of the dispersed particles in emulsions in larger than those in the sols. It ranges from 1000 Å to 10,000 Å. However, the size is smaller than the particles in suspensioins.

(iv) Emulsions can be converted into two separate liquids by heating, centrifuging, freezing etc. This process is also known as ***demulsification.***

(3) **Applications of emulsions**

(i) Concentration of ores in metallurgy

(ii) In medicine (Emulsion water-in-oil type)

(iii) Cleansing action of soaps.

(iv) Milk, which is an important constituent of our diet an emulsion of fat in water.

(v) Digestion of fats in intestine is through ***emulsification***.

Gels

(1) "A gel is a colloidal system in which a liquid is dispersed in a solid."

(2) The lyophilic sols may be coagulated to give a semisolid jelly like mass, which encloses all the liquid present in the sol. The process of gel formation is called ***gelation*** and the colloidal system formed called ***gel***.

(3) Some gels are known to liquify on shaking and reset on being allowed to stand. This reversible ***sol-gel transformation*** is called ***thixotropy***.

(4) The common examples of gel are gum arabic, gelatin, processed cheese, silicic acid, ferric hydroxide etc.

(5) Gels may shrink by loosing some liquid help them. This is known as ***synereises or weeping***.

(6) Gels may be classified into two types

(i) ***Elastic gels*** **:** These are the gels which possess the property of elasticity. They readily change their shape on applying force and return to original shape when the applied force is removed. Common examples are gelatin, agar-agar, starch etc.

(ii) ***Non-elastic gels*** **:** These are the gels which are rigid and do not have the property of elasticity. For example, silica gel.

Application of colloids

(1) **Purification of water by alum** (coagulation) **:** Alum which yield Al^{3+} ions, is added to water to coagulate the negatively charged clay particles.

(2) **In rubber and tanning industry** (coagulation and mutual coagulation) **:** Several industrial processes such as rubber plating, chrome tanning, dyeing, lubrication etc are of colloidal nature

(i) In rubber platting, the negatively charged particles of rubber (latex) are made to deposit on the wires or handle of various tools by means of electrophoresis. The article on which rubber is to be deposited is made anode.

(ii) In tanning the positively charged colloidal particles of hides and leather are coagulated by impregnating, them in negatively charged tanning materials (present in the barks of trees). Among the tanning agent chromium salts are most commonly used for the coagulation of the hide material and the process is called ***chrome tanning***.

(3) **Artificial rains :** It is possible to cause artificial rain by throwing the electrified sand or silver iodide from an aeroplane and thus coagulating the mist hanging in air.

(4) **Smoke precipitation** (Coagulation) **:** Smoke is a *negative* sol consisting of carbon particles dispersed in air. Thus, these particles are removed by passing through a chamber provided with highly positively charged metallic knob.

(5) **Formation of deltas** (coagulation) **:** River water consists of negatively charged clay particles of colloidal dimension. When the river falls into the sea, the clay particles are coagulated by the positive Na^+, K^+, Mg^{2+} ions etc. present in sea water and new lands called deltas are formed.

(6) **Clot formation :** Blood consists of negatively charged colloidal particles (albuminoid substance). The colloidal nature of blood explains why bleeding stops by applying a ferric chloride solution to the wound. Actually ferric chloride solution causes coagulation of blood to form a clot which stops further bleeding.

(7) **Colloidal medicine :** Argyrol and protargyrol are colloidal solution of silver and are used as eye lotions colloidal sulphur is used as disinfectant colloidal gold, calcium and iron are used as tonics.

(8) **Coating of Photographic plates :** These are thin glass plates coated with gelatin containing a fine suspension of silver bromide. The particles of silver bromide are colloidal in nature.

Tips & Tricks

- Chemisorption and physisorption both are exothermic.
- Charcoal adsorbs many gases. It even adsorbs polluting gases present in air in small concentration.
- The langmuir adsorption isotherm is restricted to the formation of unimolecular layer of gas molecules on the surface of solids. However, it was suggested that there is possibility of multimolecular layer of gas molecules on the surface of the solids rather than single layer on this basis Brunauer, Emmett and Teller proposed a new theory known as B.E.T. theory.
- All Bronsted acids and bases act as acid base catalysts.
- The principle of electrophoresis is employed for the separation of proteins from nucleic acids removing sludge from sewage waste etc.
- Hydrophilic sols show greater stability than hydrophobic sols.
- Colloidal solution of graphite is called aquadug.
- The phase in which the emulsifier is more soluble becomes outer phase of the emulsion that is called Ben croft rule.