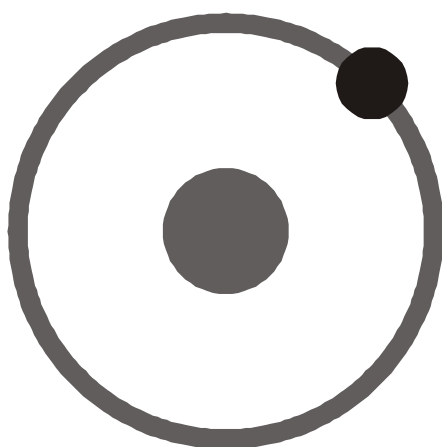


IIT CHEMISTRY

SURFACE CHEMISTRY



Physical & Inorganic

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NUCLEON IIT-JEE

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SURFACE CHEMISTRY

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SURFACE CHEMISTRY

INTRODUCTION :

Surface chemistry is that branch of chemistry which deals with study of the phenomena occurring at the surface or interface, i.e. at the boundary separating two bulk phases. In this chapter our main emphasis will be on three important topics related to surface chemistry, viz., adsorption, colloids and catalysis.

ADSORPTION :

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

Adsorbent and adsorbate :

The substance on the surface of which adsorption occurs is known as adsorbent. The substances that get adsorbed on the solid surface due to intermolecular attractions are called adsorbate.

Charcoal, silica, gel, alumina gel are good adsorbents because they have highly porous structures and have large surface area. Colloids on account of their extremely small dimensions possess enormous surface area per unit mass and are, therefore, also good adsorbents.

Examples of adsorption :

- **Adsorption of a gas by charcoal :**

Finely divided activated charcoal has a tendency to adsorb a number of gases like ammonia, sulphur dioxide, chlorine, phosgene, etc. In this case, charcoal acts as an adsorbent while gas molecules act as adsorbate.

- **Adsorption of a dye by charcoal :**

Animal charcoal is used for decolourising a number of organic substances in the form of their solutions. The discharge of the colour is due to the fact that the coloured component (generally an organic dye) gets adsorbed on the surface of the adsorbent (animal charcoal).

- **Sorption :** When both adsorption and absorption take place simultaneously.

Eg : Dyes get adsorbed as well as absorbed in the cotton fibre i.e. sorption takes place.

DISTINCTION BETWEEN ADSORPTION AND ABSORPTION

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

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

Thermodynamics of adsorption : Adsorption is an exothermic process. Therefore ΔH of adsorption is always negative. When a gas is adsorbed the entropy of the gas decreases i.e. ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as entropy of the system, for a process to be spontaneous requirement is that ΔG must be negative. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $-T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, ΔS is negative, and ΔH is also sufficiently negative and as a combination of these two factors, ΔG is negative. ΔH becomes less and less negative as adsorption proceeds further and further. Ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. This is the state at which equilibrium is attained.

Enthalpy of adsorption $\Delta H_{\text{adsorption}}$: It is the amount of the heat released when 1 mole of an adsorbate gets adsorbed on a particular adsorbent at adsorption equilibrium. It depends upon the nature of both the adsorbate as well as adsorbent.

TYPES OF ADSORPTION

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

If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' force, the adsorption is termed as physical adsorption or physisorption. When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed chemical adsorption or chemisorption. The chemical bonds may be covalent or ionic in nature. Chemisorption has a rather high energy of activation and is, therefore, often referred to as activated adsorption. Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, hydrogen is first adsorbed on nickel by van der Waals' force. Molecules of hydrogen then dissociate and hydrogen atoms are held on the surface by chemisorption.

COMPARISON OF PHYSI-SORPTION AND CHEMISORPTION

	Physical adsorption	Chemical adsorption
1.	It is caused by intermolecular van der Waals' forces.	It is caused by chemical bond formation.
2.	It is not specific.	It is highly specific.
3.	It is reversible.	It is irreversible.
4.	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It depends on the nature of gas. Gases which form compounds with the adsorbent exhibit chemisorption.
5.	Heat of adsorption is low.	Heat of adsorption is high.
6.	Low temperature is favourable. It decreases with increase of temperature.	High temperature is favourable. It increases with increase of temperature.
7.	No appreciable activation energy is involved.	High activation energy is involved.
8.	High pressure is favourable. Decrease of pressure causes desorption.	High pressure is favourable. Decrease of pressure does not cause desorption.
9.	It depends on the surface area. It increases with increase of surface area.	It also depends on the surface area. It increases with increase of surface area.
10.	It forms multilayers on adsorbent surface under high pressure.	It forms unimolecular layer.

Adsorption of gases on solids :

The extent of adsorption of a gas on a solid surface is affected by the following factors:

The nature of the gas (i.e. nature of the adsorbate). The easily liquefiable gases such as HCl, NH₃, Cl₂ etc. are adsorbed more than the permanent gases such as H₂, N₂ and O₂. The ease with which a gas can be liquefied is primarily determined by its critical temperature. Higher the critical temperature (T_c) of a gas, the more easily it will be liquefied and, therefore, more readily it will be adsorbed on the solid.

Gas	SO ₂	CH ₄	H ₂
T _c	330K	190 K	33 K

Nature of adsorbent. The extent of adsorption of a gas depends upon the nature of adsorbent. Activated charcoal (i.e. activated carbon), metal oxides (silica gel and aluminium oxide) and clay can adsorb gases which are easily liquified. Gases such as H₂, N₂ and O₂ are generally adsorbed on finely divided transition metals Ni and Co.

- **Activation of adsorbent.**

- (a) Metallic adsorbents are activated by mechanical rubbing or by subjecting it to some chemical reactions.
- (b) To increase the adsorbing power of adsorbents, they are sub-divided into smaller pieces. As a result, the surface area is increased and therefore, the adsorbing power increases.

- **Effect of temperature.**

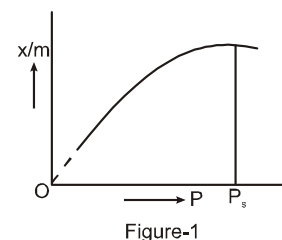
Mostly the process of adsorption is exothermic and the reverse process or desorption is endothermic. If the above equilibrium is subjected to increase in temperature, then according to Le-Chatelier's principle, with increase in temperature, the desorption will be favoured. Physical adsorption decreases continuously with increase in temperature whereas chemisorption increases initially, shows a maximum in the curve and then it decreases continuously.



The initial increase in chemisorption with increase in temperature is because of activation energy required. This is why the chemical adsorption is also known as “**Activated adsorption**”.

A graph between degree of adsorption (x/m) and temperature 't' at a constant pressure of adsorbate gas is known as **adsorption isobar**.

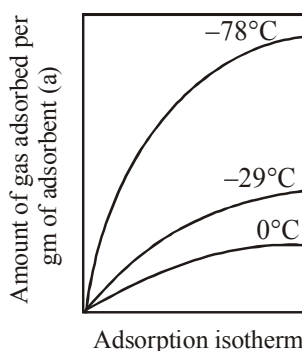
- **Effect of pressure.** The extent of adsorption of a gas per unit mass of adsorbent depends upon the pressure of the gas. The variation of extent of adsorption expressed as x/m (where x is the mole of adsorbate and m is the mass of the adsorbent) and the pressure is given as below. A graph between the amount of adsorption and gas pressure keeping the temperature constant is called an adsorption isotherm.



It is clear from the figure-1 that extent of adsorption (x/m) increases with pressure and becomes maximum corresponding to pressure P_s called equilibrium pressure. Since adsorption is a reversible process, the desorption also takes place simultaneously.

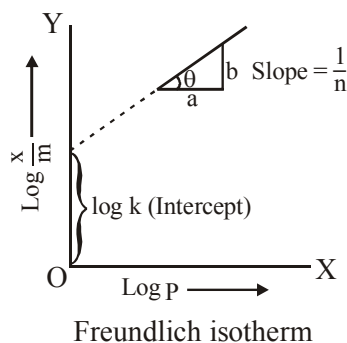
FREUNDLICH ADSORPTION ISOTHERM

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



$$\frac{x}{m} = k \cdot p^{1/n} \quad \dots(i)$$

where 'x' is the mass of the gas adsorbed on a mass 'm' of the adsorbent at a pressure P. k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.



Langmuir Adsorption Isotherm :

Langmuir derived it on theoretical considerations based on kinetic theory of gases.

It is based on the assumption (a) that every adsorption site is equivalent and (b) that the ability of a particle to bind there is independent of whether or not nearby sites are occupied.

He considered adsorption to consist of the following two opposing processes :

- (i) Adsorption of the gas molecules on the surface of the solid
- (ii) Desorption of the adsorbed molecules from the surface of the solid

He believed eventually a dynamic equilibrium is established between the above two opposing processes.

He also assumed that the layer of the adsorbed gas was unimolecular. This isotherm works particularly well for chemisorption.

It is represented by the relation : $\frac{x}{m} = \frac{ap}{1+bp}$ (a)

where 'a' and 'b' are Langmuir parameter.

At very high pressure $x/m = a/b$ (b)

At very low pressure : $x/m = ap$ (c)

For determination of the parameters 'a' and 'b', Eq. (a) may be written in its inverse form.

$$\frac{m}{x} = \frac{1+bp}{ap} = \frac{b}{a} + \frac{1}{ap} \quad \text{..... (d)}$$

A plot of m/x against $1/p$ gives a straight line with slope and intercept equal to $1/a$ and b/a respectively.

At low pressure according to Eq. (c) x/m increases linearly with p . At high pressure according to Eq. (b) x/m becomes constant i.e. the surface is fully covered and change in pressure has no effect and no further adsorption takes place which is clear from the Figure.

Applications of adsorption :

In gas masks : Activated charcoal is generally used in gas masks to adsorb poisonous and toxic gases from air. These masks are commonly used by the miners because there are poisonous gases like CO, CH₄ etc. in the atmosphere in coal mines.

In dyeing of cloths : Mordants such as alums are used in dyeing of cloths. They adsorb the dye particles which, otherwise, do not stick to the cloths.

In dehumidizers : Silica gel is commonly used to adsorb humidity or moisture from air.

Removal of colouring matter : Many substances such as sugar, juice and vegetable oils are coloured due to the presence of impurities. They can be decolourised by placing them in contact with adsorbents like activated charcoal or fuller's earth.

Heterogeneous catalysis : The phenomenon of adsorption is useful in the heterogeneous catalysis. The metals such as Fe, Ni, Pt, Pd, etc, are used in the manufacturing processes such as Contact process, Haber process and the hydrogenation of oils. Their use is based upon the phenomenon of adsorption.

Refining Petroleum : Silica gel is used as adsorbent in petroleum refining.

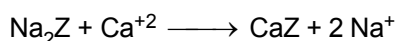
Chromatography : It is a method for separation of component and is based on preferential adsorption column is very common device used.

Creating vacuum : High vacuum can be created by removing gas by adsorption.

Adsorption Indicators : In volumetric analysis, adsorption indicator is used. Surface of certain precipitates such as silver halide have the property of adsorbing some dye like eosin, fluorescein, etc. In the case of precipitation titration (AgNO_3 vs NaCl) of the indicator is adsorbed at the end point producing a characteristic colour on the precipitate.

In froth floatation process : Refer metallurgy.

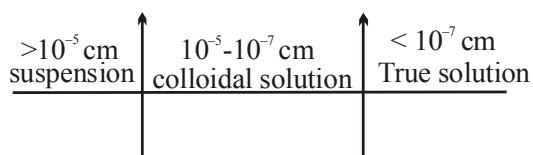
Softening of hard water : Ion exchange resins used for softening of hard water is based upon selective and competitive adsorption of ions on resins.



The organic polymers containing groups like $-\text{COOH}$, $-\text{SO}_3\text{H}$ and $-\text{NH}_2$ etc. possess the property of selective adsorption of ions from solution. These are quite useful in the softening of water.

COLLOIDAL SOLUTION

PARTICLE SIZE :



PHASE OF COLLOIDS :

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

- (a) **Dispersed Phase** : It is the component present in small proportion and is just like a solute in a true solution. For example, in the colloidal state of sulphur in water, the former acts as a dispersed phase.
- (b) **Dispersion Medium** : It is normally the component present in excess and is just like a solvent in a solution. The particles of the dispersed phase are scattered in the dispersion medium in a colloidal system.

CLASSIFICATION OF COLLOIDS :

Colloids can be classified in a number of ways based upon some of their important characteristics.

Physical state of Dispersed Phase & Dispersion Medium:

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gaseous, eight types of colloidal system are possible. A gas mixed with another gas forms a homogeneous mixture and not a colloidal system. Typical examples of various type along with their characteristic names are given in table.

Common Colloidal System

Dispersed Phase	Dispersion medium	Colloidal system	Examples
Gas	Liquid	Foam or froth	Soap sols, lemonade froth, whipped cream.
Gas	Solid	Solid foam	Pumice stone, styrene, foam, foam rubber.
Liquid	Gas	Aerosols of Liquids	Fog, clouds, fine insecticide sprays.
Liquid	Liquid	Emulsions	Milk
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies, curd.
Solid	Gas	Aerosols of Solid	Smoke, dust
Solid	Liquid	Sols	Must paint, starch dispersed in water, gold sol, muddy water, inks.
Solid	Solid	Solid sols	Ruby glass, some gem stones.

- * A colloidal system in which the dispersion medium is a liquid or gas are called sols. They are called hydrosols or aqua sols, if the dispersion medium is water. When the dispersion medium is alcohol or benzene, they are accordingly called alcosols or benzosol.
- * Colloidal systems in which the dispersion medium is a gas are called aerosols.
- * Colloids in which the dispersion medium is a solid are called gels, e.g. cheese etc. They have a more rigid structure. Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosol. But at low temperature and high gelatin concentration, the hydrosol can change into a gel.

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

- (i) **Lyophilic Colloids :** The colloidal system in which the particle of dispersed phase have great affinity for the dispersion medium, are called lyophilic (solvent-loving) colloids. In such colloids, the dispersed phase does not get easily precipitated and the sols are more stable. Such colloidal systems, even if precipitated, may be reconverted to the colloidal state by simply agitating them with the dispersion medium. Hence lyophilic colloids are reversible. When the dispersion medium is water, these are called hydrophilic colloids. Some common examples of lyophilic colloids are gum, gelatin, starch, rubber, proteins, etc.
- (ii) **Lyophobic colloids :** The colloidal system in which the dispersed phase have no affinity for the dispersion medium are called lyophobic (solvent hating) colloids. They are easily precipitated (or coagulated) on the addition of small amounts of the electrolyte, by heating or by shaking. They are less stable and irreversible. When the dispersion medium is water, these are known as hydrophobic colloids. Examples of lyophobic colloids include sols of metals and their insoluble compounds like sulphides and oxides. The essential differences between the lyophilic and lyophobic colloids are summarised in table.

Difference between Lyophilic and Lyophobic sols

Property	Lyophilic sols	Lyophobic sols
1. Nature	Reversible	Irreversible
2. Preparation	They are prepared very easily by shaking or warming the substance with dispersion medium. not required any electrolyte for stabilization.	They are difficult to prepare, Special methods are used. Addition of stabiliser They do is essential for their stability.
3. Stability	They are very stable and are not easily coagulated by electrolytes.	They are generally unstable and get easily coagulated on addition of electrolytes.
4. Charge	Particles carry no or very little charge depending upon the pH of the medium.	Colloidal particles have characteristic charge (positive or negative)
5. Viscosity	Viscosity is much higher than that of the medium.	Viscosity is nearly the same as that of the medium
6. Surface Tension	Surface tension is usually less than that of the medium.	Surface tension is nearly the same as that of the medium.
7. Migration in electric field	The particles may or may not migrate in an electric field.	The colloidal particles migrate either towards cathode or anode in an electric field.
8. Solvation	Particles are heavily solvated.	Particles are not solvated.
9. Visibility	The particles cannot be seen under ultra microscope.	The particles though invisible, can be seen under ultra microscope.
10. Tyndall effect	Less distinct.	More distinct.
11. Action of electrolyte	Large amount of electrolyte is required to cause coagulation.	Small amount of electrolyte is sufficient to cause cogulation.
12. Examples	Mostly organic substances e.g. starch, gums, proteins, gelatin etc.	Generally inorganic substance e.g., metal sols, sulphides and oxides sols.

On the basis of charge of on particles

(i) positive Sol

(a) Metal Oxide & Hydroxide - SnO_2 , TiO_2 , Fe_2O_3 , $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$.

(b) Basic Dyes Methylene blue, vismark brown.

(ii) negative Sol -

(a) Metal sol - Ag, Au, Pt, Cu

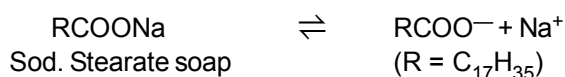
(b) Acidic dye - congo red, eosin

(c) Sulphide Sol- CdS , HgS , As_2S_3 , Sb_2S_3 .

(d) Natural sol - Blood, clay, charcoal, latex rubber, dust particle in water, starch carbon particle in smoke, gum.

Based on type of particles of the dispersed phase : Depending upon the molecular size, the colloidal system has been classified into three classes :

- (i) **Multimolecular colloids :** The multimolecular colloidal particles consists of aggregate of atoms of small molecules with diameters less than 10^{-9} m or 1 nm.
For example, a sol. of gold contains particles of various sizes having several atoms. A sol. of sulphur consists of particles containing a thousand or so S_2 molecules. These particles are held together by vander Waal's forces. These are usually lyophobic sols.
- (ii) **Macromolecular colloids :** The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varying from thousands to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polystyrene, dacron, synthetic rubber, plastics, etc. The size of these molecules are comparable to those of colloidal particles and therefore, their dispersion known as macromolecular colloids. Their dispersion also resemble true solutions in some respects.
- (iii) **The associated colloids or miscelles :** These colloids behave as normal electrolytes at low concentrations but colloids at higher concentrations. This is because at higher concentrations, they form aggregated (associated) particles called miscelles. Soap and synthetic detergents are examples of associated colloids. They furnish ions which may have colloidal dimensions.



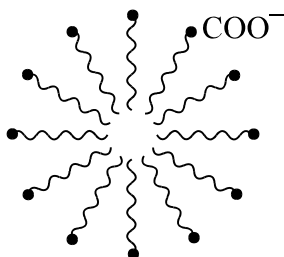
The long-chain RCOO^- ions associates or aggregate at higher concentrations and form miscelles and behave as colloids. They may contain 100 or more molecules.

Sodium stearate $\text{C}_{17}\text{H}_{35}\text{COONa}$ is an example of an associated colloid. In water it gives Na^+ and stearate, $\text{C}_{17}\text{H}_{35}\text{COO}^-$ ions. These ions associate to form miscelles of colloidal size.

Colloids which behave as normal electrolytes at low concentration, but exhibit colloidal properties at higher concentration due to the formation of aggregated particles called micelles are referred to as associated colloids. The micelles are formed by the association of dispersed particles above a certain concentration and certain minimum concentration is required for the process of aggregation to take place. The minimum concentration required for micelle formation is called micellisation concentration (CMC) and its value depends upon the nature of the dispersed phase. For soaps CMC is 10^{-3} mole L^{-1} .

Mechanism of Micelle Formation :

Micelles are formed by surface active molecules called surfactants such as soaps and detergents. These molecules have lyophilic group at one end and a lyophobic group at the other end. Let us take the example of a soap (say sodium oleate, $\text{C}_{17}\text{H}_{33}\text{COO}^- \text{Na}^+$). The long hydrocarbon part of oleate radical ($\text{C}_{17}\text{H}_{33}-$) is lyophobic end while COO^- part is lyophilic end. When the concentration of the solution is below its CMC, sodium oleate behaves as a normal electrolyte and ionises to give $\text{C}_{17}\text{H}_{33}\text{COO}^-$ and Na^+ ions. When the concentration exceeds CMC, the lyophobic part starts receding away from the solvent and tends to approach each other. However, the polar COO^- ends tends to interact with the solvent (water). This finally leads to the formation of bigger molecules having the dimensions of colloidal particles. Thus 100 or more oleate ions are grouped together in a spherical way keeping their hydrocarbon parts inside and the COO^- part remains projected in water.

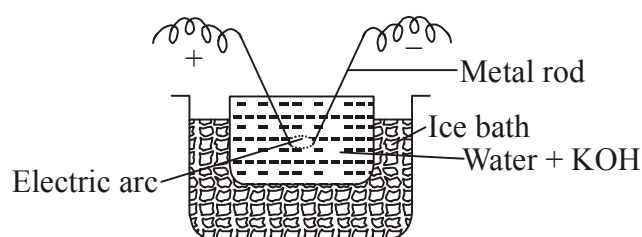


PREPARATION OF COLLOIDAL SOLUTIONS

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

Dispersion Methods

Electro-dispersion (Bredig's arc method) : This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum, etc. An arc is struck between the metal electrodes under the surface of water containing some stabilizing agents such as a trace of KOH. The water is cooled by immersing the

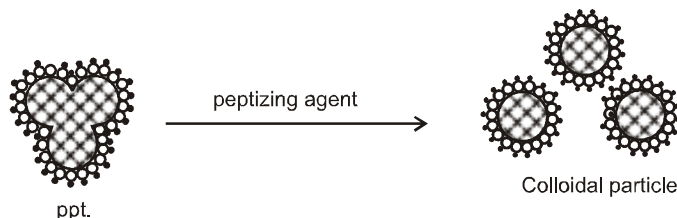


container in an ice bath. The intense heat of the arc vaporises some of the metal which condenses under cold water.

- Note :** (1) This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.
- (2) This method comprises both dispersion and condensation.

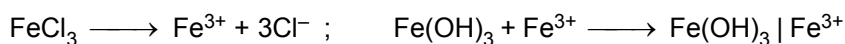
Peptization : The term has originated from the digestion of proteins by the enzyme pepsin. Peptization may be defined as (the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte). The electrolyte used for this purpose is called peptizing agent. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol. During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. The ion adsorbed on the surface is common either with the anion or cation of the electrolyte. This causes the development of positive or negative charge on precipitates which ultimately break up into smaller particles having the dimensions of colloids.

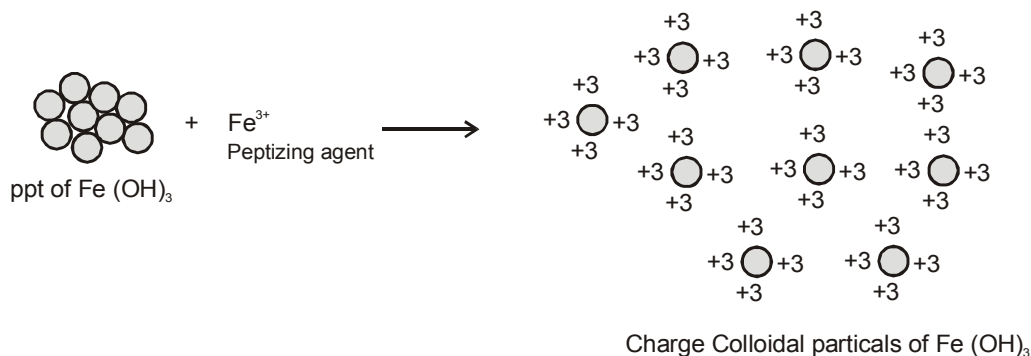
The process of peptization thus involves the adsorption of suitable ions (supplied by the electrolyte added—particularly a common ion) and electrically charged particles then split from the precipitate as colloidal particles.



For example :

(i) When freshly precipitated $\text{Fe}(\text{OH})_3$ is shaken with aqueous solution of FeCl_3 (peptizing agent) it adsorbs Fe^{3+} ions and thereby breaks up into small-sized particles.



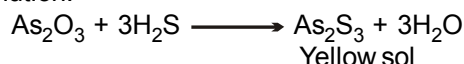


- (ii) Freshly prepared stannic oxide on treatment with a small amount of dilute hydrochloric acid forms a stable colloidal sol of stannic oxide, SnO_2 ; Sn^{4+} .
 $\text{SnO}_2 + 4\text{HCl} \rightarrow \text{Sn}^{4+} + 2\text{H}_2\text{O} + 4\text{Cl}^-$; $\text{SnO}_2 + \text{Sn}^{4+} \rightarrow \text{SnO}_2 / \text{Sn}^{4+}$.
- (iii) Freshly precipitated silver chloride can be converted into a colloidal sol by adding a small amount of hydrochloric acid, AgCl ; Cl^- .
- (iv) Cadmium sulphide can be peptised with the help of hydrogen sulphide, CdS ; S^{2-} .

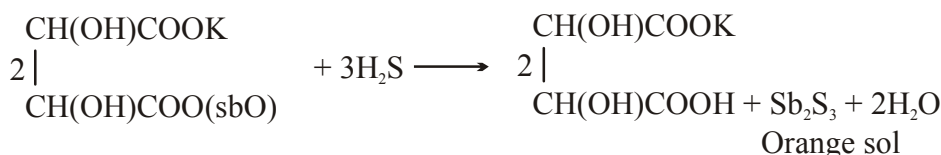
Condensation Methods

Chemical methods : The chemical methods involve chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of supersaturation is produced but the actual precipitation is avoided. Some familiar reactions used are :

(a) Double decomposition : (i) Arsenious sulphide sol : A 1% solution of arsenious oxide is prepared in hot water. The solution is cooled, filtered and is then gradually in hot water saturated with hydrogen sulphide. This is continued till an intense yellow-coloured solution is obtained. Excess of H_2S is removed by bubbling hydrogen through the solution.



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



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

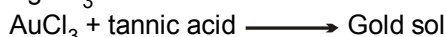
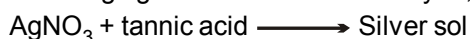


Sulphur sol can also be obtained when H_2S is bubbled through an oxidising agent (bromine water or nitric acid).

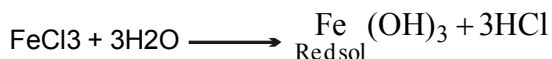
(c) Reduction : Colloidal solutions of metals like gold, silver, platinum, lead, etc., can be obtained when their salts solutions are acted upon by reducing agents.



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



(d) Hydrolysis : Colloidal solutions of some salts can be prepared by hydrolysis. A colloidal solution of ferric hydroxide is obtained by boiling a dilute solution of ferric chloride.]

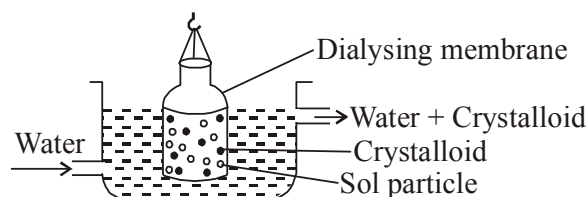


The colloidal solution of silicic acid is also obtained by hydrolysis of dilute solution of sodium silicate with 4N hydrochloric acid which is added drop by drop with constant stirring.

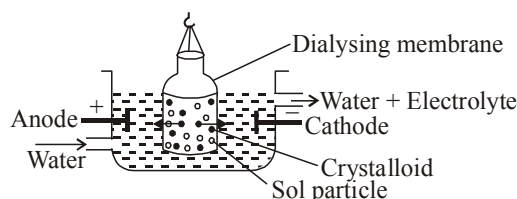
PURIFICATION OF COLLOIDAL SOLUTIONS

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. The process used for reducing of these impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods.

(i) Dialysis* : It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Since, particles in true solution (ions or smaller molecules) can pass through animal membranes (bladder) or parchment paper or cellophane sheet but colloidal particles do not, the above can be used for dialysis. The apparatus used for this purpose is called dialyser. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flown figure. The molecules and ions diffuse through the membrane into the outer water and pure colloidal solution is left behind.



(ii) Electro-dialysis : Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only electrolyte. The process is then named electro-dialysis. The colloidal solution is placed between two electrodes while pure water is taken in a compartment on each side. Electrodes are fitted in the compartment as shown in figure the ions present in the colloidal solution migrate out to the oppositely charged electrodes.



(iii) Ultrafiltration : Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by especially prepared filters, which are permeable to all substances except the colloidal particles.

Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with collodion solution and subsequently hardened by soaking in formaldehyde. The usual collodion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultrafilter paper may be prepared by soaking the filter paper in a collodion solution and hardened by formaldehyde and finally drying it. Thus, by using ultrafilter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is used.

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

PROPERTIES OF COLLOIDAL SOLUTIONS :

(1) Physical properties :

- (i) **Heterogeneity** : Colloidal solutions are heterogeneous in nature consisting of two phases viz, the dispersed phase and the dispersion medium. Experiments like dialysis and ultra filtration clearly indicate the heterogeneous character of colloidal system. Recent investigations however, shown that colloidal solutions are neither obviously homogeneous nor obviously heterogeneous.
- (ii) **Filterability** : Colloidal particles readily pass through ordinary filter papers. It is because the size of the pores of the filter paper is larger than that of the colloidal particles.
- (iii) **Non-settling nature** : Colloidal solutions are quite stable as the colloidal particles remain suspended in the dispersion medium indefinitely. Thus there is no effect of gravity on the colloidal particles.

- (iv) **Colour** : The colour of the colloidal solution is not always the same as the colour of the substances in the bulk. The colour of the colloidal solution depends upon the following factors :
- Size and shape of colloidal particles.
 - Wavelength of the source of light.
 - Method of preparation of the colloidal solution.
 - Nature of the colloidal solution.
 - The way an observer receives the light, i.e., whether by reflection or by transmission.
 - Stability** : Colloidal solutions are quite stable. Only a few solutions of larger particles may settle but very slowly.

Examples :

- Finest gold is red in colour. As the size of particles increases, it becomes purple.
- Dilute milk gives a bluish tinge in reflected light whereas reddish tinge in transmitted light.

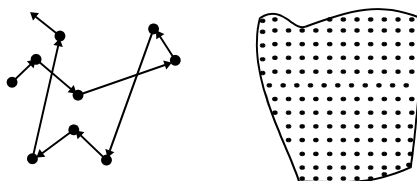
(2) Mechanical Properties :

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

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

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

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



Importance :

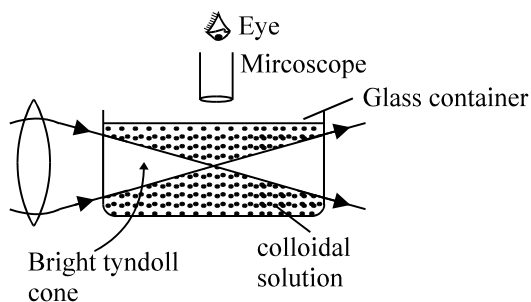
- Brownian movement is a direct demonstration of the assumption that the molecules in a gas or solution are in a state of constant ceaseless motion. Thus it confirms kinetic theory.
- Brownian movement does not allow the colloidal particles to settle down due to gravity and thus is responsible for their stability.
- Brownian movement helps to calculate the Avogadro's number (Detail beyond the scope of the book).

- (b) **Sedimentation** : Heavier sol. particle tend to settle down very slowly under the influence of gravity. This phenomenon is called sedimentation.

(3) Optical Properties (Tyndal Effect) :

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

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



The Tyndall effect is observed under the following conditions :

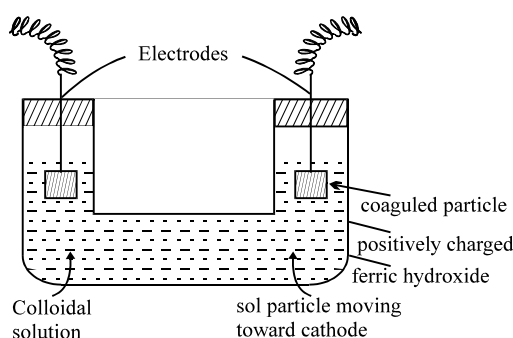
- (i) The diameter of the dispersed particles must not be much smaller than the wavelength of light employed.
- (ii) The refractive indices of the dispersed phase and the dispersion medium must differ widely. This condition is fulfilled by lyophobic colloids.

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

(4) **Electrical Properties :**

The two electrical properties of colloidal solutions are :

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

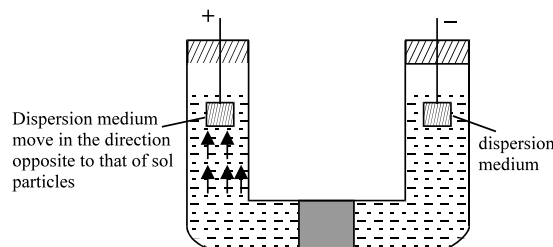


The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode, is called electrophoresis or cataphoresis.

This phenomenon is used to determine the charge on the colloidal particles. For example, when a sol. of ferric hydroxide is taken in a U-tube and subjected to electric field, the ferric hydroxide (sol.) particles get accumulated near the cathode (figure). This shows that ferric hydroxide sol. particles are positively charged. The sol. particles of metals and their sulphides are found to be negatively charged while those of metal hydroxides are positively charged. Basic dyes such as methylene blue haemoglobin are positively charged while acid dyes like are negatively charged.

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

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



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

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

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

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

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

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

The reciprocal of coagulation value is regarded as the coagulating power.

For example, the coagulation values of NaCl, BaCl₂ and AlCl₃ for arsenic sulphide sol. are 51, 0.69 and 0.093

millimoles/litre respectively. Thus their coagulating powers are $\frac{1}{51}$, $\frac{1}{0.69}$ and $\frac{1}{0.093}$ i.e., 0.0196, 1.449 and 10.75 respectively.

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

Coagulation values of different electrolytes

Arsenic sulphide sol.			Ferric hydroxide sol.		
Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)	Electrolyte	Valency of coagulating cation	coagulation value (millimoles/litre)
K ₂ SO ₄	1	63	KBr	1	138
NaCl	1	51	KNO ₃	1	132
KNO ₃	1	50	KCl	1	103
MgSO ₄	2	0.81	K ₂ CrO ₄	2	0.320
BaCl ₂	2	0.69	K ₂ SO ₄	2	0.215
AlCl ₃	3	0.093	K ₃ Fe(Cn) ₆	3	0.096

From the above table, it is clear that the coagulating power of Al³⁺ ions in precipitating the arsenic sulphide sol. is approximately 550 times more than that of sodium (Na⁺) or potassium (K⁺) ions. Again, it is observed that the negatively charged arsenic sulphide sol. is coagulated by cations while positively charged ferric hydroxide sol. is coagulated by anions.

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

Only the ions carrying charge opposite to the one present on the sol. particles are effective to cause coagulation, e.g., the negative charged sol. is best coagulated by cations and a positive sol. is coagulated by anions.

The charge on coagulating ion influences the coagulation of sol.

In general, the coagulating power of the active ion increases with the valency of the active ion.

After observing the regularities concerning the sing and valency of the active ion, a law was proposed by Hardy and Schulz which is termed as Hardy-Schulze law which is stated as follows:

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

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

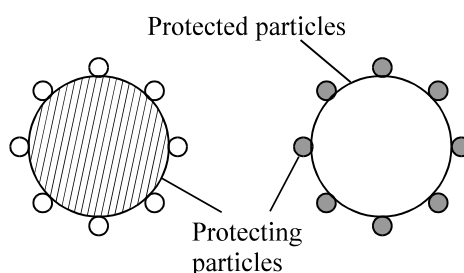
Similarly, to coagulating the positively charged sol. the coagulating power of anion is in the order of $[\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

Colligative properties : Colloidal solutions too exhibit colligative properties such as osmotic pressure, lowering of vapour pressure, depression in freezing point and elevation in boiling point. But the effect of colloidal particles on colligative properties except osmotic pressure is very small. This is due to the large size of colloidal particles. The number of colloidal particles produced by a given mass of colloid is much less than the number produced in a molecular solution, containing the same mass of solute. Hence the colligative effect in colloidal solutions is too less.

PROTECTIVE COLLOIDS :

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

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



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

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

Gold Number : Zsigmondy (1901) introduce a term called gold number it is defined as "the minimum amount of the protective colloid in milligrams which when added to 10 ml of a standard gold sol is just sufficient to prevent a colour change from red to blue on the addition of 1 ml of 10% sodium chloride solution. It may be noted that smaller of the gold number, greater will be protecting power of the protective colloid.

$$\text{Protecting power} \propto \frac{1}{\text{gold number}}$$

$$\text{Gold Number} = \frac{\text{weight of lyophilic sol in mg} \times 10}{\text{volume of gold sol in mL}}$$

The gold numbers of a few protective colloids are as follows :

Gelatin	Haemoglobin	Egg albumin	Gum arabic	Dextrin	Starch
0.005 - 0.01	0.03 - 0.07	0.1 - 0.2	0.15 - 0.25	6 - 6.2	20 - 25

Uses of protective action :

(i) Gelatin is added in the preparation of ice cream to protect the particle of ice.

(ii) Protargol and Argyrol, is a silver sol protected by organic material used as eye drop.

Isoelectric Point of Colloid :

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

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

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

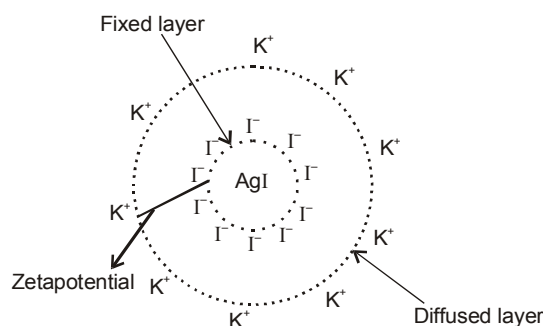
$$Z = \frac{4\pi\eta u}{D} \quad \text{where } \eta = \text{viscosity coefficient,} \quad D = \text{dielectric constant of medium.}$$

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

Example :

When silver nitrate solution is added to KI solution, the precipitation of AgI adsorbs iodide ions from the D.M. with the formation of fixed layer and negatively charged colloidal solution forms. However, when KI solution is added to AgNO₃ solution, positive charge sol results due to the adsorption of Ag⁺ ions from D.M.

AgI/I^- AgI/Ag^+
Negative charged Positively charged.
This fixed layer attracts counter ions from the medium forming a second layer.



EMULSIONS

An emulsion is a colloidal solution of a liquid. It may be defined as a heterogeneous system consisting of more than one immiscible liquids dispersed in one another in the form of droplets whose diameter, in general, exceeds 0.1 μ .

For example, milk is an emulsion in which small drops of liquid fat are dispersed in aqueous medium. Cod liver oil is an emulsion in which the water drops are dispersed in the oil. This means in most of the emulsions one of the liquids is water and the other liquid is oil. Here the term 'oil' is used to represent all organic substances which are soluble in water.

The emulsions are classified as :

- (1) **Oil in water type emulsion (O/W):** In this emulsion, oil is the dispersed phase and water is the dispersion medium. It is denoted by O/W or O in W. For example, milk (liquid fat dispersed in water), vanishing cream, etc.
- (2) **Water in oil type :** In this emulsion, water is the dispersed phase and oil is the dispersion medium. It is denoted by W/O or W in O. For example, butter, cod liver oil, cold cream, etc.

The type of emulsion obtained by agitating two immiscible liquids depends upon the relative amounts of two components liquids. The liquid that is in excess forms the dispersion medium. Thus, the two types of emulsions can be interconverted into each other by changing the concentration of one of the liquids.

Distinction between two types of emulsions : the two types of emulsions may be distinguished from each other in a number of ways.

- (1) **Dye test** : It involves the addition of oil soluble dye to the emulsion under experiment. If the emulsion acquires the colour of the dye readily, it is water-in-oil type emulsion and if the emulsion remains colourless, it is oil-in-water type emulsion.
- (2) **Conductivity test** : It involves the addition of electrolyte to the emulsion under experiment. If the conductivity of the emulsion increases appreciably with the addition of electrolyte, it is oil-in-water type emulsion and if conductivity is very small, it is water-in-oil type emulsion.
- (3) **Dilution test** : As a general rule, an emulsion can be diluted with the dispersion medium while the addition of the dispersed phase forms a separate layer. Thus, if an emulsion can be diluted with oil, it is water-in-oil type.

Properties of emulsion :

Demulsification : The process which involves the breaking of an emulsion into two separate liquid layers is called demulsification. The following methods may be used to bring demulsification:

Use of emulsion :

All paints are emulsions.

Soaps and detergents remove dust and dirt from the dirty piece of cloth by making an oil in water emulsion. Milk is an emulsion of liquid fats in water.

In the process of metallurgy, one of the important steps is the concentration of ore which is usually done by froth floatation process in which an oil is added to the finely-divided ore taken in water. The particles of ore go on the surface due to formation of foams while the other impurities are left at the bottom of the vessel.

GELS

Colloidal system in which liquids are the dispersed phase and solid act as the dispersion medium are called gels. The common examples are : boot polishes, jelly, gum arabic, agar agar, processed cheese and silicic acid.

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

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

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.
2. They absorb water when placed in it with simultaneous swelling. This phenomenon is called imbibation.

Non-elastic gels

1. They change to solid mass on dehydration which cannot be changed back to original form with water.
2. They do not exhibit imbibation.

USES OF COLLOIDS :

Smoke screens : Smoke screens which consist of titanium dioxide dispersed in air are used in warfare for the purpose of concealment and camouflage.

Formation of delta : The river waver carries with it charged clay particles and many other substances in the form of colloidal solution. When the sea water comes in contact with these particles, the colloidal particles in river water are coagulated by the electrolytes present in sea water to form deltas.

Exercise # 1

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Adsorption

- A-1. Why adsorption is always exothermic ?
- A-2. What is the difference between physical adsorption and chemisorption ?
- A-3. What are the factors which influence the adsorption of a gas on a solid ?
- A-4. What is an adsorption isotherm ?
- A-5. What do you understand by activation of adsorbent ? How is it achieved ?
- A-6. Which will be adsorbed more readily on the surface of charcoal and why— NH_3 or CO_2 ?
- A-7. In an Adsorption experiment a graph between $\log x/m$ versus $\log P$ was found to be linear with a slope of 45° the intercept of the $\log x/m$ was found to be 0.3010. Calculate the amount of gas adsorbed per gm of charcoal under a pressure of 0.6 bar.
- A-8. 1 g of charcoal adsorbs 100 mL of 0.5 M CH_3COOH to form mono layer and there by the molarity of CH_3COOH reduces to 0.49 M. Calculate the surface area of the charcoal adsorbed by each molecule of CH_3COOH . Surface area of charcoal = $3.01 \times 10^2 \text{ m}^2/\text{gm}$.
- A-9. What role does adsorption play in heterogeneous catalysis ?
- A-10. How many grams of gas would be adsorbed per gram of a substance at 8 atm by assuming Freundlich adsorption isotherm.

$$\frac{x}{m} = kp^{1/n}$$

and $k = 10^{-2} \text{ atm}^{-1/3}$ & $n = 3$.

- A-11. A $1 \text{ cm} \times 1 \text{ cm}$ square paper coated with a suitable adsorbant on both sides. The paper is dipped in a aqueous solution of glucose of volume 20 mL and concentration 20 ppm. Final concentration glucose was dropped to 19 ppm due to adsorption. Find the number of glucose particles per unit area of the paper.
- A-12. 10 mg of an adsorbate gets adsorbed on a surface. This causes the release of 3J of heat at constant pressure and at 27°C . [Molar mass of adsorbate = 100 g/mol].
- (i) Find ΔH_{AD} .
- (ii) Argue whether the adsorption is physical or chemical ?
- (iii) If 20 mg of adsorbate is adsorbed a temperature T_0 . Then compare T_0 and 27°C :

Section (B) : Catalysis

- B-1. Give two examples of heterogeneous catalysis.
- B-2. Identify the correct order of steps in heterogeneous catalysis.
- (i) Adsorption of reactant molecules on the surface of the catalyst.
- (ii) Diffusion of reactant to the surface of the catalyst.
- (iii) Formation of reactions product on the catalyst surface.
- (iv) Diffusion of reactions product from the catalyst surface or desorption.
- (v) Formation of activated intermediate.

Section (C) : Classification and Preparation of Colloid

- C-1. How are the colloidal solutions classified, on the basis of physical states of the dispersed phase and dispersion medium ?
- C-2. Explain the following terms with suitable examples.
- (a) Gel (b) Liquid Aerosol (c) Hydrosol

- C-3. How are associated colloids different from multimolecular and macromolecular colloids ?
- C-4. Give one example of multimolecular and macromolecular colloids.

Section (D) : Purification and Preparation of Colloid

- D-1. Describe a method each for the preparation of sols of sulphur and platinum in water
- D-2. Explain the following terms :
(a) Peptization (b) Electrophoresis (c) Dialysis (d) Brownian movement
- D-3. Why the sun looks red at the time of setting.
- D-4. Why is osmotic pressure of a colloidal solution less than that of true solution ?

Section (E) : Coagulation, Protection And application of colloid

- E-1. Which one of the following electrolytes is most effective for the coagulation of $\text{Fe}(\text{OH})_3$ sol and why ? NaCl , Na_2SO_4 , Na_3PO_4 .
- E-2. What do you understand by "isoelectric point" of a colloid ?
- E-3. Rivers form delta on meeting with ocean, why ?
- E-4. Artificial rain is made by spraying salt over clouds ?
- E-5. Which colloidal sol is administered to a patient suffering from arsenic poisoning ?

Section (F) : Emulsion, Micelle and Gel

- F-1. Name two demulsifier.
- F-2. What is the difference between sols and emulsions.
- F-3. What is demulsification ?

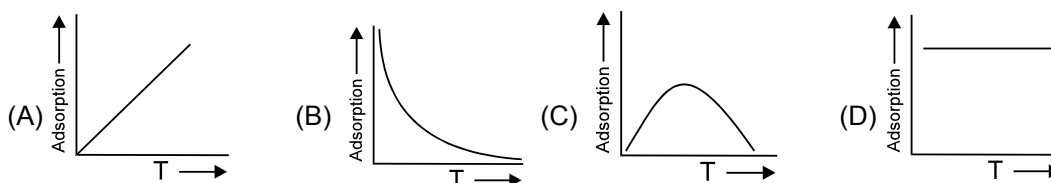
PART - II : OBJECTIVE QUESTIONS

* Marked Questions may have more than one correct option.

Section (A) : Adsorption

- A-1.* Which of the following statements about physical adsorption is correct ?
(A) It is usually monolayer
(B) It is reversible in nature
(C) It involves van der Waals interactions between adsorbent and adsorbate
(D) It involves small enthalpy of adsorption as compared to chemisorption.
- A-2. Which of the following statements about chemisorption is not applicable?
(A) It involves chemical forces between adsorbent and adsorbate
(B) It is irreversible in nature
(C) It involves high heat of adsorption
(D) It does not require activation energy
- A-3.* Which of the following statements regarding adsorption is correct ?
(A) Extent of adsorption of gases on charcoal increases with increase in pressure of the gas
(B) Extent of adsorption is independent of temperature
(C) Extent of chemisorption by a given mass of adsorbent is limited
(D) Extent of adsorption is dependent on the nature of adsorbent

A-4. Following is the variation of physical adsorption with temperature:



A-5. Adsorption is the phenomenon in which a substance:

- (A) accumulates on the surface of the other substance
- (B) goes into the body of the other substances
- (C) remains close to the other substance
- (D) none of these

A-6. Finely divided catalyst has greater surface area and has greater catalytic activity than the compact solid. If a total surface area of 6291456 cm^2 is required for adsorption in a catalysed gaseous reaction, then how many splits should be made to a cube of exactly 1 cm in length to achieve required surface area. (Given : One split of a cube gives eight cubes of same size)

- (A) 60
- (B) 80
- (C) 20
- (D) 22

A-7. Volume of N_2 at NTP required to form a mono layer on the surface of iron catalyst is 8.15 ml/gram of the adsorbent. What will be the surface area of the adsorbent per gm if each nitrogen molecule occupies $16 \times 10^{-22} \text{ m}^2$.

- (A) $16 \times 10^{-16} \text{ cm}^2$
- (B) $0.35 \text{ m}^2/\text{g}$
- (C) $39 \text{ m}^2/\text{g}$
- (D) 22400 cm^2

A-8. There is desorption of physical adsorption when:

- (A) temperature is increased
- (B) temperature is decreased
- (C) pressure is increased
- (D) concentration is increased

A-9. The rate of chemisorption :

- (A) decreases with increase of pressure
- (B) increases with increase of pressure
- (C) is independent of pressure
- (D) is independent of temperature

A-10.* Which of the following is characteristic of chemisorption?

- (A) it is irreversible
- (B) it is specific
- (C) it is multilayer phenomenon
- (D) heat of adsorption of about -400 kJ

A-11. Softening of hard water is done using sodium aluminium silicate (zeolite). The causes :

- (A) adsorption of Ca^{2+} and Mg^{2+} ions of hard water replacing Na^+ ions.
- (B) adsorption of Ca^{2+} and Mg^{2+} ions of hard water replacing Al^{3+} ions
- (C) both (A) and (B)
- (D) none of these

Section (B) : Catalysis

B-1. Which one is false in the following statement ?

- (A) A catalyst is specific in its action
- (B) A very small amount of the catalyst alters the rate of a reaction
- (C) The number of free vacancies on the surface of the catalyst increases on sub-division
- (D) Ni is used as a catalyst in the manufacture of ammonia

B-2. A catalyst increases rate of reaction by :

- (A) Decreasing enthalpy
- (B) Decreasing internal energy
- (C) Decreasing activation energy
- (D) Increasing activation energy

Section (C) : Classification and Preparation of Colloid

C-1. Colloidal solution of gold prepared by different methods of different colours because of :

- (A) different diameters of colloidal gold particles
- (B) variable valency of gold
- (C) different concentration of gold particles
- (D) impurities produced by different methods

- C-2.*** An example of extrinsic colloid (lyophobic colloids) is :
 (A) As_2S_3 sol (B) $\text{Fe}(\text{OH})_3$ sol (C) Egg albumin (D) Au sol
- C-3.*** Which of the following sols is positively charged?
 (A) Arsenious sulphide (B) Aluminium hydroxide
 (C) Ferric hydroxide (D) Silver iodide in silver nitrate solution

Section (D) : Purification and Preparation of Colloid

- D-1.** A colloidal solution can be purified by the following method :
 (A) dialysis (B) peptization (C) filtration (D) oxidation
- D-2.** Peptisation is :
 (A) conversion of a colloidal into precipitate form
 (B) conversion of precipitate into colloidal sol
 (C) conversion of metal into colloidal sol by passage of electric current
 (D) conversion of colloidal sol into macromolecules
- D-3.** Bleeding is stopped by the application of ferric chloride. This is because:
 (A) the blood starts flowing in opposite direction
 (B) the blood reacts and forms a solid, which seals the blood vessel
 (C) the blood is coagulated and thus the blood vessel is sealed
 (D) the ferric chloride seals the blood vessel.

Section (E) : Coagulation, Protection And application of colloid

- E-1.** Gold number of a lyophilic sol is such property that:
 (A) the larger its value, the greater is the peptising power
 (B) the lower its value, the greater is the peptising power
 (C) the lower its value, the greater is the protecting power
 (D) the larger its value, the greater is the protecting power
- E-2.** Protective sols are:
 (A) lyophilic (B) lyophobic (C) both (A) and (B) (D) none of (A) and (B)
- E-3.** For the coagulation of 200 mL of As_2S_3 solution, 10 mL of 1 M NaCl is required. What is the coagulating value (number of milli moles of solute needed for coagulation of 1 liter of solution) of NaCl.
 (A) 200 (B) 100 (C) 50 (D) 25
- E-4.** Which of the following ions is most effective in the coagulation of an arsenious sulphide solution ?
 (A) K^+ (B) Mg^{2+} (C) Al^{3+} (D) C
- E-5.** Which of the following ions is most effective in the coagulation of ferric hydroxide solution ?
 (A) Cl^- (B) Br^- (C) NO_2^- (D) SO_4^{2-}

Section (F) : Emulsion, Micelle and Gel

- F-1.** Small liquid droplets dispersed in another liquid is called :
 (A) Suspension (B) Emulsion (C) Gel (D) True solution
- F-2.** At CMC, the surfactant molecules :
 (A) Decomposes (B) Become completely soluble
 (C) Associate (D) Dissociate
- F-3.** Some type of gels like gelatin loose water slowly. The process is known as :
 (A) Syneresis (B) Thixotropy (C) Peptisation (D) Imbibition

PART - III : ASSERTION / REASONING

Each question has 5 choices (A), (B), (C), (D) and (E) out of which ONLY ONE is correct.

- (A) STATEMENT-1 is true, STATEMENT-2 is true and STATEMENT-2 is correct explanation for STATEMENT-1
(B) STATEMENT-1 is true, STATEMENT-2 is true and STATEMENT-2 is not correct explanation for STATEMENT-1
(C) STATEMENT-1 is true, STATEMENT-2 is false
(D) STATEMENT-1 is false, STATEMENT-2 is true
(E) Both STATEMENTS are false

- Statement-1** : All colloidal dispersions give very low osmotic pressure and show very small freezing point depression or boiling point elevation.
Statement-2 : Tyndall effect is due to scattering of light from the surface of colloidal particles.
- Statement-1** : The Brownian movement is due to the bombardment on colloidal particles by the molecules of dispersion medium which are in the constant motion like molecules in a gas.
Statement-2 : Brownian movement provides a visible proof of the random kinetic motion of molecules in a liquid.
- Statement-1** : In the coagulation of negatively charged arsenic sulphide sol, the coagulating power decreases in the order, $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$.
Statement-2 : Generally greater the valency of coagulating ion, the greater is its power of coagulation.
- Statement-1** : Gold number is the measure of protective powers of different colloids.
Statement-2 : The smaller the gold number of lyophilic colloid, the smaller is its protective power.
- Statement-1** : The property of adsorption is shown by solids to a much larger extent than liquids.
Statement-2 : Solids, particularly when finely divided, have a large surface area.
- Statement-1** : Aqueous gold colloidal solution is red in colour.
Statement-2 : The colour arises due to scattering of light of colloidal gold particles.
- Statement-1** : Isoelectric point is pH at which colloidal can move towards either of electrode
Statement-2 : At isoelectric point, colloidal particles become electrically neutral
- Statement-1** : A gas with higher critical temperature gets adsorbed to more extent than a gas with lower critical temperature.
Statement-2 : The easily liquefiable gases get adsorbed to more extent which have higher critical temperature.
- Statement-1** : When AgNO_3 is treated with excess of KI, colloidal particles gets attracted towards anode.
Statement-2 : Colloidal particles adsorb common ions and thus become charged.
- Statement-1** : Colloidal solution exhibit Tyndall effect while true solution do not.
Statement-2 : Because the size of the colloidal particles is large enough to scatter light as compared to size of the true solution particles.
- Statement-1** : Physisorption of molecules occurs on surface only.
Statement-2 : In this process; the bonds of the adsorbed molecules are broken.
- Statement-1** : Medicines in the colloidal state are more effective.
Statement-2 : In the colloidal state, the medicines are easily assimilated by the body.
- Statement-1** : Tetraethyl lead minimises the knocking effect when mixed with petrol.
Statement-2 : Because tetraethyl lead acts as a -ve catalyst.
- Statement-1** : In physisorption, adsorption increases with increases in temperature.
Statement-2 : Physisorption is of exothermic nature.

Exercise # 2

PART - I : SUBJECTIVE QUESTIONS

1. What happens when gelatin is added to gold sol ?
2. Which out of 'He' and 'Ne' would adsorb on the surface of charcoal more readily and why ?
3. Name two industrial processes in which heterogeneous catalysts are employed ?
4. Why is gelatin generally added to ice creams ?
5. How can metallic adsorbent be activated ?
6. Account for the following
(i) Curdling of milk (ii) Tail of comets
(iii) Use of potash alum in the purification of water (iv) Cleansing action of soap.
7. What is fire foam ?
8. Explain what is observed
(a) When an electrolyte NaCl is added to ferric hydroxide sol.
(b) When an emulsion is subjected to centrifugation.
(c) When direct current is passed through a colloidal sol.
(d) When a beam of light is passed through a colloidal solution.

PART - II : OBJECTIVE QUESTIONS

Single choice type

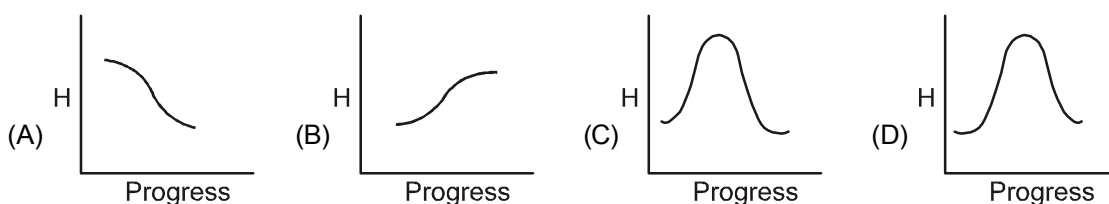
1. The pressure of the gas was found to decrease from 720 to 480 mm. When 5g of sample of activated charcoal was kept in a flask of one litre capacity maintained at 27°C. If the density of charcoal at 1.25 gm/mL. The volume of gas adsorbed per gm of charcoal at 480 mm of Hg is
(A) 80.03 mL (B) 32.20 mL (C) 100.08 mL (D) None of these
2. Coagulation value of the electrolytes AlCl_3 and NaCl for As_2S_3 sol are 0.093 and 52 respectively. How many times AlCl_3 has greater coagulating power than NaCl.
(A) 930 (B) 520 (C) 560 (D) None of these
3. Graph between $\log x/m$ and $\log p$ is a straight line inclined at an angle of 45°. When pressure is 0.5 atm and $\ln k = 0.693$, the amount of solute adsorbed per gm of adsorbent will be :
(A) 1 (B) 1.5 (C) 0.25 (D) 2.5
4. Which of the following statements is not correct for a lyophobic solution ?
(A) It can be easily solvated
(B) It carries charges
(C) The coagulation of this sol is irreversible in nature
(D) It is less stable in a solvent
5. Which of the following statements is correct for a lyophilic solution ?
(A) It is not easily solvated
(B) It is unstable
(C) The coagulation of this sol is irreversible in nature
(D) It is quite stable in a solvent
6. Liquid-liquid sol is known as
(A) aerosol (B) foam (C) emulsion (D) gel
7. The colloidal system consisting of a liquid adsorbate in a solid adsorbent is termed as :
(A) aerosol (B) foam (C) emulsion (D) gel

8. Which of the following statements is not correct ?
 (A) A colloidal solution is a heterogeneous two-phase system
 (B) Silver sol in water is an example of lyophilic solution.
 (C) Metal hydroxides in water are examples of lyophobic solution
 (D) Liquid-liquid colloidal solution is not a stable system
9. Size of colloidal particles may range from :
 (A) 1 to 1000 nm (B) 10 to 100 pm (C) 1 to 100 μm (D) 1 to 10 mm
10. Which of the following represents a multimolecular colloidal particles?
 (A) Starch (B) A sol of gold (C) Proteins (D) Soaps
11. Which of the following anions will have minimum flocculation value for the ferric oxide solution ?
 (A) Cl^- (B) Br^- (C) SO_4^{2-} (D) $[\text{Fe}(\text{CN})_6]^{3-}$
12. Which of the following represents a macromolecular colloidal particles ?
 (A) Solution of gold (B) Cellulose (C) Soaps (D) Synthetic detergents
13. Which of the following statements is not correct?
 (A) Peptization is the process by which certain substances are converted into the colloidal state.
 (B) Metal sols of gold, silver and platinum can be prepared by Bredig's arc method.
 (C) Impurities present in a solution makes it more stable.
 (D) Dialysis is a process to remove impurities of ions and molecules from a solution.
14. Select correct statement (s) :
 (A) hydrophilic colloid is a colloid in which there is a strong attraction between the dispersed phase and water
 (B) hydrophobic colloid is a colloid in which there is a lack of attraction between the dispersed phase and water
 (C) hydrophobic sols are often formed when a solid crystallises rapidly from a chemical reaction or a supersaturated solution
 (D) all of the above
15. A reddish brown sol (containing Fe^{3+}) is obtained by:
 (A) the addition of small amount of FeCl_3 solution to freshly prepared $\text{Fe}(\text{OH})_3$ precipitate
 (B) the addition of $\text{Fe}(\text{OH})_3$ to freshly prepared FeCl_3 solution
 (C) the addition of NH_4OH to FeCl_3 solution dropwise
 (D) the addition of NaOH to FeCl_3 solution dropwise
16. Which is an example of coagulation?
 (A) curdling of milk (B) purification of water by addition of alum
 (C) formation of deltas at the river beds (D) All the three are example of coagulation
17. Gold number of some lyophilic sols are :

I	:	Casein	:	0.01
II	:	Haemoglobin	:	0.03
III	:	Gum arabic	:	0.15
IV	:	Sodium oleate	:	0.40

 Which has maximum protective power :
 (A) I (B) II (C) III (D) IV
18. Gold number Of haemoglobin is 0.03. Hence, 100 mL of gold sol will require haemoglobin so that gold is not coagulated by 1 mL of 10% NaCl solution :
 (A) 0.03 mg (B) 30 mg (C) 0.30 mg (D) 3 mg
19. Which is not a purely surface phenomena :
 (A) surface tension. (B) adsorption. (C) absorption. (D) none of these.
20. Arsenic (III) sulphide forms a sol with a negative charge. Which of the following ionic substances should be most effective in coagulating the sol ?
 (A) KCl (B) MgCl_2 (C) $\text{Al}_2(\text{SO}_4)_3$ (D) Na_3PO_4

21. The stabilisation of a lyophobic colloid is due to :
 (A) preferential adsorption of similar charged particle on colloids surface.
 (B) the large electro-kinetic potential developed in the colloid.
 (C) the formation of a covalent bond between two phases.
 (D) the viscosity of the medium.
22. Smoke is a dispersion of :
 (A) gas in gas (B) gas in solid (C) solid in gas (D) liquid in gas
23. Smoke has generally blue tinge. It is due to :
 (A) scattering (B) coagulation (C) Brownian motion (D) electro-osmosis
24. Compared to common colloidal sols, micelles have :
 (A) higher colligative properties (B) lower colligative properties
 (C) same colligative properties (D) none of these
25. Which one of the following statements is false for hydrophilic sols ?
 (A) they do not require electrolytes for stability
 (B) their viscosity is of the order of that of water
 (C) their surface tension is usually lower than that of dispersion medium.
 (D) none of these
26. Which one of the following statements is correct:
 (A) Brownian movement is more pronounced for smaller particles than for bigger ones
 (B) Sols of metal sulphides are lyophilic
 (C) Schulze-Hardy law states, the bigger the size of the ion, the greater is its coagulating power
 (D) One would expect charcoal to adsorb hydrogen gas more strongly than chlorine.
27. Soaking of sponge by water is an example of :
 (A) Simple adsorption (B) Physical adsorption (C) Chemisorption (D) Absorption
28. The potential difference between the fixed charged layer and the diffused layer having opposite charge is called :
 (A) Water potential (B) Zeta potential (C) Electrode potential (D) None of these
29. Which one is not the characteristic of chemisorption :
 (A) Multilayer adsorption (B) Exothermic nature
 (C) Strong adsorption by adsorption sites (D) Irreversible
30. Identify the appropriate graph between enthalpy and progress of physical adsorption.



31. Hydrolysis of ester is catalysed by acid. Rates of hydrolysis of ester were obtained initially and after 50% ester has been hydrolysed as R_0 and R_{50} then (same temp.)
 (A) $R_0 = R_{50}$ (B) $R_0 < R_{50}$ (C) $R_0 > R_{50}$ (D) Cannot be determined

More than one choice type

32. The diameter of colloidal particle is of the order :
 (A) 10^{-3}m (B) 10^{-6}m (C) 10^{-15}m (D) 10^{-7}m
33. Which of the following colloidal solutions contain negatively charged colloidal particles?
 (A) $\text{Fe}(\text{OH})_3$ sol (B) As_2S_3 sol (C) Blood (D) Gold sol
34. Which of the following are examples of aerosols?
 (A) Whipped cream (B) Cloud (C) Fog (D) Soap lather

35. Which of the following statements are true for physisorption?
 (A) Extent of adsorption increases with increase in pressure.
 (B) It needs activation energy
 (C) It can be reversed easily
 (D) It occurs at high temperature.
36. Which of the following are hydrophobic sols?
 (A) Protein sol (B) Gold sol (C) Gum sol (D) $\text{Fe}(\text{OH})_3$ sol.
37. If Cl_2 gas is enclosed in presence of powdered charcoal in a closed vessel, the pressure of the gas decreases. It is because
 (A) the gas molecules are absorbed at the surface
 (B) the gas molecules concentrate at the surface of the charcoal
 (C) the gas molecules are adsorbed at the surface
 (D) the gas molecules are desorbed by the surface
38. When negatively charged colloids like As_2S_3 sol is added to positively charged $\text{Fe}(\text{OH})_3$ sol in suitable amounts
 (A) Both the sols are precipitated simultaneously .
 (B) This process is called mutual coagulation.
 (C) They become positively charged colloids.
 (D) They become negatively charged colloids.
39. Which of the following are incorrect statements ?
 (A) Hardy schulz rule is related to coagulation
 (B) Brownian movement and Tyndall effect are the characteristic of colloids.
 (C) In gel, the liquid is dispersed in liquid
 (D) Higher the gold number, more is the protective power of lyophilic sols.
40. Which of the following are multimolecular colloids ?
 (A) Sulphur (B) Egg albumin in water (C) Gold sol (D) Soap solution
41. The origin of charge on colloidal solution is
 (A) Self dissociation (in soaps and detergents) (B) Electron capture during Bredig's arc method
 (C) Selective adsorption of ion on their surface (D) It is due to addition of protective colloids
42. Which of the following are based on Tyndall effect.
 (A) Tail of comets (B) Deltas
 (C) Blue colour of sky (D) Coagulation

PART - III : MATCH THE COLUMN

1. Match list I with list II and select the correct answer :

List I	List II
(A) Coagulation	(p) Scattering of light
(B) Dialysis	(q) Formation of colloidal solution from precipitates.
(C) Peptization	(r) Purification of colloids
(D) Tyndall effect	(s) Accumulation of colloidal sols

2. Match list I with list II and select the correct answer :

List I	List II
(A) Mechanical property of colloid	(p) Dialysis
(B) Purification	(q) Peptization
(C) Gold number	(r) Brownian movement
(D) Formation of a sol	(s) Protection

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

Many lyophilic sols and few lyophobic sols when coagulated under some special conditions changes into semi rigid mass, enclosing whole amount of liquid within itself, it is called gel and the process is called gelation. Gelatin Agar-agar, gum-Arabic can be converted into gels by cooling them under moderate concentration conditions. Hydrophobic sols like silicic acid. $\text{Al}(\text{OH})_3$ are prepared by double decomposition and exchange of solvent method.

Types of Gel :

(i) **Elastic gel** : Those gel which have elastic properties.

Ex. Gelatin, Strach, Agar-Agar etc.

(ii) **Non- elastic gel** : Those gel which are rigid.

Eg : Silica gel.

Properties of Gel :

1.Syneresis/weeping of gel : The spontaneous liberation of liquid from a gel is called syneresis or weeping of gels. It is reverse of swelling.

Eg : Gelatin, Agar-Agar show syneresis at low concentration while silicic acid shows it at high concentration.

2. Imbibition or swelling of gel : When gel is kept in a suitable liquid (water) it absorb large volume of liquid. The phenomenon is called imbibition or swelling of gel.

3.Thixotropic : Some gels when shaken to form a sol, on keeping changes into gel are termed as thixotropic gel and phenomenon is called thixotropy.

Eg : Gelatin and silica liquify on shaking changing into corresponding sol and the sol on keeping changes back into gel.

- Which of the following is used to adsorb water ?
(A) Silica gel (B) Calcium acetate (C) Hair gel (D) Cheese
- The process of imbibing water when elastic gel are placed in water is called :
(A) imbibation (B) syneresis (C) coagulation (D) thixotropy
- Some types of gels like gelatin and silica liquify on shaking thereby changing into sols. The sols on standing change back into gels. This process is know as
(A) syneresis (B) thixotropy
(C) double decomposition (D) peptization

Comprehension # 2

The clouds consist of charged particles of water dispersed in air. Some of them are +vely charged, others are -vely charged. When +vely charged clouds come closer they cause lightening and thundering whereas when +ve and -ve charged colloids come closer they cause heavy rain by aggregation of minute particles. It is possible to cause artificial rain by throwing electrified sand or silver iodide from an aeroplane and thus coagulating the mist hanging in air.

Smoke screen is a cloud of smoke used to hide military, naval police etc. it consists of fine particles of TiO_2 .

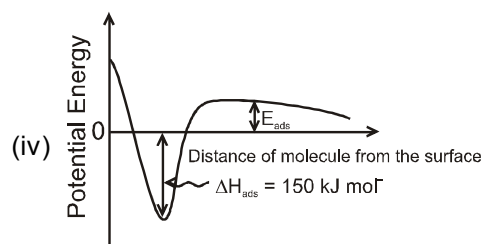
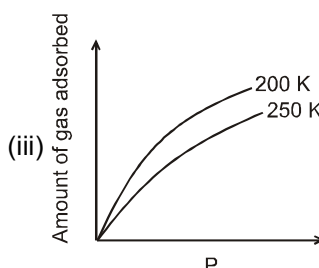
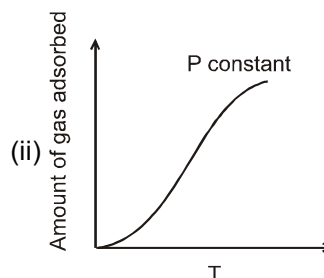
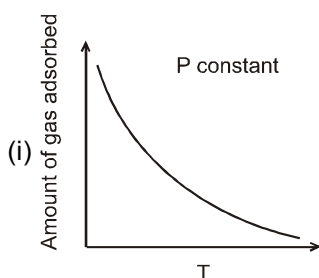
- When excess of AgNO_3 is treated with KI solution, AgI forms
(A) +ve charged sol (B) -vely charged sol (C) neutral sol (D) true solution
- AgI helps in artificial rain because :
(A) it helps in ionisation of water (B) it helps in dispersion process
(C) it helps in coagulation (D) all of them
- Smoke screens consist of
(A) fine particles of TiO_2 dispersed in air by aeroplanes
(B) fine particles of AgI dispersed in air by aeroplanes
(C) fine particles of Al_2O_3 dispersed in air by aeroplanes
(D) None of these

Exercise # 3

PART - I : IIT-JEE PROBLEMS (LAST 10 YEARS)

* Marked Questions are having more than one correct option.

- Rate of physisorption increases with [JEE 2003, 3/60]
(A) decrease in temperature (B) increase in temperature
(C) decrease in pressure (D) decrease in surface area
- Adsorption of gases on solid surface is generally exothermic because [JEE 2004, 3/84]
(A) enthalpy is positive (B) entropy decreases (C) entropy increases (D) free energy increases
- Lyophilic sols are [JEE 2005, 3/84]
(A) Irreversible sols (B) They are prepared from inorganic compound
(C) Coagulated by adding electrolytes (D) Self-stabilizing
- Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient condition is : [JEE 2008, 3/163]
(A) $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$ (B) $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$
(C) $\text{CH}_3(\text{CH}_2)_6\text{COO}^-\text{Na}^+$ (D) $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
- Among the electrolytes Na_2SO_4 , CaCl_2 , $\text{Al}_2(\text{SO}_4)_3$ and NH_4Cl , the most effective coagulating agent for Sb_2S_3 sol is : [JEE 2009, 3/160]
(A) Na_2SO_4 (B) CaCl_2 (C) $\text{Al}_2(\text{SO}_4)_3$ (D) NH_4Cl
- Silver (atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3} . The number of silver atoms on a surface of area 10^{-12} m^2 can be expressed in scientific notation as $y \times 10^x$. The value of x is : [JEE 2010, 3/163]
- The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are) [JEE 2011, 4/180]
(A) Adsorption is always exothermic
(B) Physisorption may transform into chemisorption at high temperature
(C) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature.
(D) Chemisorption is more exothermic than physisorption, however it is very slow due to higher energy of activation.
- Choose the correct reason(s) for the stability of the **lyophobic** colloidal particles. [JEE 2012, 4/168]
(A) Preferential adsorption of ions on their surface from the solution.
(B) Preferential adsorption of solvent on their surface from the solution.
(C) Attraction between different particles having opposite charges on their surface.
(D) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.
- The given graph / data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice (s) about I, II, III and IV is (are) correct [JEE 2012, 4/168]



- (A) I is physisorption and II is chemisorption (B) I is physisorption and III is chemisorption
(C) IV is chemisorption and II is chemisorption (D) IV is chemisorption and III is chemisorption

10. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25° C. For this process, the correct statement is : **[JEE (Advanced) 2013, 2/120]**
 (A) The adsorption requires activation at 25°C.
 (B) The adsorption is accompanied by a decreases in enthalpy.
 (C) The adsorption increases with increase of temperature.
 (D) The adsorption is irreversible.
11. When O₂ is adsorbed on a metallic surface, electron transfer occurs from the metal to O₂. The TRUE statement(s) regarding this adsorption is(are) **[JEE Advanced 2015-P2]**
 (A) O₂ is physisorbed (B) heat is released
 (C) occupancy of π_{2p} of O₂ is increased (D) bond length of O₂ is increased
12. The correct statement(s) about surface properties is (are) **[JEE Advance 2017_P2]**
 (A) Cloud is an emulsion type of colloid in which liquid is dispersed phase and gas is dispersion medium
 (B) Adsorption is accompanied by decrease in enthalpy and decrease in entropy of the system.
 (C) Brownian motion of colloidal particles does not depend on the size of the particles but depends on viscosity of the solution.
 (D) The critical temperature of ethane and nitrogen are 563K and 126K, respectively. The adsorption of ethane will be more than that of nitrogen on same amount of activated charcoal at a given temperature.

PART - II : AIEEE PROBLEMS (LAST 10 YEARS)

1. Which one of the following characteristics is not correct for physical adsorption? **[AIEEE 2003]**
 (1) Adsorption on solids is reversible (2) Adsorption increases with increase in temperature
 (3) Adsorption is spontaneous (4) Both enthalpy and entropy of adsorption are negative.
2. The disperse phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged, respectively. Which of the following statements is NOT correct? **[AIEEE 2005]**
 (1) Coagulation in both sols can be brought about by electrophoresis
 (2) Mixing the sols has no effect
 (3) Sodium sulphate solution causes coagulation in both sols
 (4) Magnesium chloride solution coagulates, the gold sol more readily than the iron (III) hydroxide sol.
3. The volume of colloidal particle V_c as compared to the volume of a solute particle in a true solution V_s could be: **[AIEEE 2005]**
 (1) ~ 1 (2) ~ 10²³ (3) ~ 10⁻³ (4) ~ 10³
4. In langmuir's model of adsorption of a gas on a solid surface : **[AIEEE 2006]**
 (1) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered
 (2) the adsorption at a single site on the surface may involve multiple molecules at the same time
 (3) the mass of gas striking a given area of surface is proportional to the pressure of the gas
 (4) the mass of gas striking a given area of surface is independent of the pressure of the gas
5. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is **[AIEEE 2008, 3/105]**
 (1) C < B < D < A (2) A < C < B < D (3) B < D < A < C (4) D < A < C < B
6. In context with the industrial preparation of hydrogen from water gas (CO + H₂), which of the following is the correct statement? **[AIEEE 2008, 3/105]**
 (1) CO is removed by absorption in aqueous Cu₂Cl₂ Solution
 (2) H₂ is removed through occlusion with Pd
 (3) CO is oxidized to CO₂ with steam in the presence of a catalyst followed by absorption of CO₂ in alkali
 (4) CO and H₂ are fractionally separated using differences in their densities
7. Which of the following statements is incorrect regarding physisorptions ? **[AIEEE 2009, 4/144]**
 (1) More easily liquefiable gases are adsorbed readily.
 (2) Under high pressure it results into multi molecular layer on adsorbent surface.
 (3) Enthalpy of adsorption ($\Delta H_{\text{adsorption}}$) is low and positive.
 (4) It occurs because of van der Waal's forces.

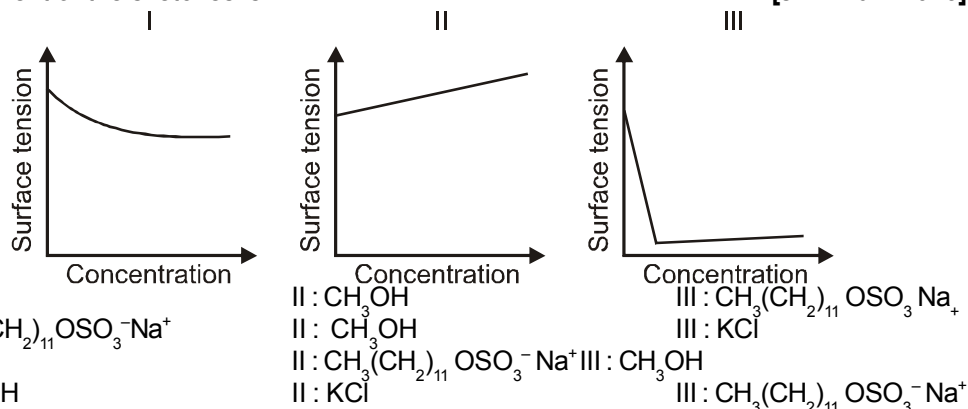
8. According to Freundlich adsorption isotherm which of the following is correct? [AIEEE 2012, 4/120]

- (1) $\frac{x}{m} \propto p^0$ (2) $\frac{x}{m} \propto p^1$ (3) $\frac{x}{m} \propto p^{1/n}$
 (4) All the above are correct for different ranges of pressure.

9. The coagulating power of electrolytes having ions Na^+ , Al^{3+} and Ba^{2+} for arsenic sulphide sol increases in the order : [JEE(Mains) 2013, 4/120]

- (1) $\text{Al}^{3+} < \text{Ba}^{2+} < \text{Na}^+$ (2) $\text{Na}^+ < \text{Ba}^{2+} < \text{Al}^{3+}$
 (3) $\text{Ba}^{2+} < \text{Na}^+ < \text{Al}^{3+}$ (4) $\text{Al}^{3+} < \text{Na}^+ < \text{Ba}^{2+}$

10. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of KCl, CH_3OH and $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$ at room temperature. The correct assignment of the sketches is [JEE Main 2016]



11. For a linear plot of $\log(x/m)$ versus $\log p$ in a Freundlich adsorption isotherm, which of the following statements is correct ? (k and n are constants) [JEE Main 2016]

- (A) Both k and $1/n$ appear in the slope term.
 (B) $1/n$ appears as the intercept.
 (C) Only $1/n$ appears as the slope.
 (D) $\log(1/n)$ appears as the intercept.

Answers

EXERCISE - 1

PART - I

A-1. Adsorption is accompanied by decrease of randomness, i.e. this factor opposes the process, i.e. ΔS is – ve. For the process to be spontaneous, ΔG must be – ve. Hence, according to eqn, $\Delta G = \Delta H - T\Delta S$, ΔG can be –ve only if ΔH is –ve.

A-2. Difference between physical adsorption and chemical adsorption

Physical Adsorption

- The forces between the adsorbate molecules and the adsorbent are weak van der Waal's forces.
- Low heat of adsorption of the order of 20–40 kJ mol^{–1}
- Usually occurs at low temperature and decreases with increasing temperature.
- It is reversible.
- The extent of adsorption depends upon the ease of liquefaction of the gas.
- It is less specific in nature, all gases are adsorbed on the surface of a solid to some extent.
- It forms multimolecular layers.
- extent of adsorption (x/m) increases with pressure.

Chemical Adsorption

- The forces between the adsorbate molecules and the adsorbent are strong chemical forces.
- High heat of adsorption of the order 200–400 kJ mol^{–1}
- It occurs at high temperature
- It is irreversible.
- There is no correlation between extent of adsorption and the ease of liquefaction of gas.
- It is highly specific in nature and occurs only when there is bond formation between adsorbent and adsorbate molecules.
- It forms mono-molecular layer.
- extent of adsorption (x/m) increases with pressure

A-3. (i) The nature of the gas (i.e. nature of the adsorbate). The easily liquefiable gases such as HCl, NH₃, Cl₂ etc. are adsorbed more than the permanent gases such as H₂, N₂ and O₂. The ease with which a gas can be liquefied is primarily determined by its critical temperature. Higher the critical temperature (T_c) of a gas, the more easily it will be liquefied and, therefore, more readily it will be adsorbed on the solid.

Gas	SO ₂	CH ₄	H ₂
T_c	330K	190 K	33 K

(ii) Nature of adsorbent. The extent of adsorption of a gas depends upon the nature of adsorbent. Activated charcoal (i.e. activated carbon), metal oxides (silica gel and aluminium oxide) and clay can adsorb gases which are easily liquified. Gases such as H₂, N₂ and O₂ are generally adsorbed on finely divided transition metals Ni and Co.

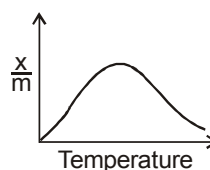
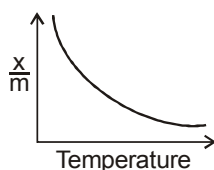
(iii) Activation of adsorbent.

(a) Metallic adsorbents are activated by mechanical rubbing or by subjecting it to some chemical reactions.

(b) To increase the adsorbing power of adsorbents, they are sub-divided into smaller pieces. As a results, the surface area is increased and therefore, the adsorbing power increases.

(iv) Effect of temperature.

Mostly the process of adsorption is exothermic and the reverse process or desorption is endothermic. If the above equilibrium is subjected to increase in temperature, then according to Le-Chatelier's principle, with increase in temperature, the desorption will be favoured. Physical adsorption decreases continuously with increase in temperature whereas chemisorption increases initially, shows a maximum in the curve and then it decreases continuously.



The initial increase in chemisorption with increase in temperature is because of activation energy required. This is why the chemical adsorption is also known as “**Activated adsorption**”.

A graph between degree of adsorption (x/m) and temperature ‘ t ’ at a constant pressure of adsorbate gas is known as **adsorption isobar**.

(v) Effect of pressure. The extent of adsorption of a gas per unit mass of adsorbent depends upon the pressure of the gas. The variation of extent of adsorption expressed as x/m (where x is the mole of adsorbate and m is the mass of the adsorbent) and the pressure is given as below. A graph between the amount of adsorption and gas pressure keeping the temperature constant is called an adsorption isotherm. It is clear from the figure that extent of adsorption (x/m) increases with pressure and becomes maximum corresponding to pressure P_s called equilibrium pressure. Since adsorption is a reversible process, the desorption also takes place simultaneously. At this pressure (P_s) the amount of gas adsorbed becomes equal to the amount of gas desorbed.

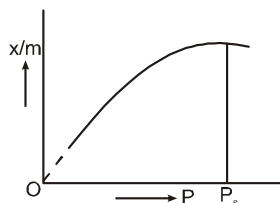


Figure-1

A-4. It represents the variation of the mass of the gas adsorbed per gram of the adsorbent with pressure at constant temperature.

A-5. It means increasing the adsorption power of an adsorbent and is done by increasing the surface area of the adsorbent by a suitable method (Refer text).

A-6. NH_3 has higher critical temperature than that of CO_2 , i.e. NH_3 is more easily liquefiable than CO_2 because, NH_3 has greater intermolecular forces of attraction and hence will be adsorbed more readily.

A-7. 1.2

A-8. $5 \times 10^{-19} \text{ m}^2$

A-9. In heterogeneous catalysis, generally the reactants are gaseous where as catalyst is a solid. The reactant molecules are adsorbed on the surface of the catalyst. As a result, the concentration of the reactant molecules on the surface increases and hence the rate of reaction increases.

A-10. $\frac{x}{m} = 10^{-2} \times 8^{1/3} = 0.02 \text{ g}$

A-11. Mass of glucose adsorbed = $(20 - 19) \times \frac{20}{10^6} = 2 \times 10^{-5} \text{ g}$.

$$\text{Moles of glucose adsorbed} = \frac{2 \times 10^{-5}}{180} = \frac{10^{-6}}{9}$$

$$\text{Number of glucose molecules} = \frac{10^{-6}}{9} \times 6 \times 10^{23} = \frac{20}{3} \times 10^{16}$$

$$\text{Number of glucose molecules per unit area} = \frac{1}{2} \times \frac{20}{3} \times 10^{16} = 3.33 \times 10^{16} \text{ cm}^{-2}$$

A-12. $T_0 < 27^\circ\text{C}$

B-1. (i) Mfg. of NH_3 (Haber's process) – using iron as catalyst
(ii) Mfg. of H_2SO_4 – using platinised asbestos or V_2O_5 as catalyst.

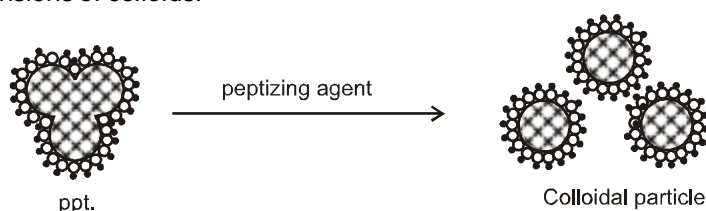
B-2. (ii) $\rightarrow$ (i) $\rightarrow$ (v) $\rightarrow$ (iii) $\rightarrow$ (iv)

C-1. On the bases of physical state of D.P. and D.M. colloidal solution may be divided into eight system.

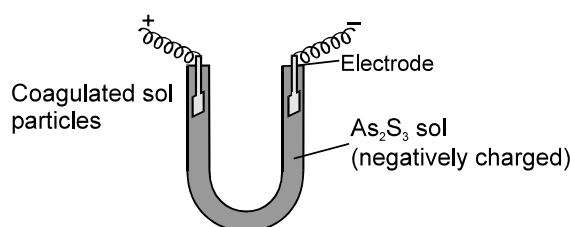
Table : Type of Colloidal Systems

D P	D M	Type of colloid	Examples
Solid	Solid	Solid Sol	Some coloured glasses, and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Liquid Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid Sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froath, whipped cream, soap lather.

- C-2.** (a) Gel – a colloidal dispersion of a liquid in a solid, e.g., butter
 (b) Liquid aerosol – a colloidal dispersion of a liquid in a gas, e.g., fog
 (c) Hydrosol – a colloidal sol of a solid in water as the dispersion medium, e.g, starch sol or gold sol.
- C-3.** Associated colloids are formed by electrolytes so that they are dissociated into ions and these ions associate together to form ionic micelles whose size lies in the colloidal range, e.g. soaps.
 Multimolecular colloids–formed by the aggregation of a large number of simple molecules. Macromolecular colloids – due to large size of the molecules themselves.
- C-4.** Multimolecular – S_8
 Macromolecular – starch
- D-1.** Sol of sulphur – Refer oxidation method or by exchange of solvent.
 Sol of platinum – Refer Bredig's electro-disintegration method.
- D-2.** **(a) Peptization:** The term has originated from the digestion of proteins by the enzyme pepsin. Peptization may be defined as (the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte). The electrolyte used for this purpose is called peptizing agent. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol. During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. The ion adsorbed on the surface is common either with the anion or cation of the electrolyte. This causes the development of positive or negative charge on precipitates which ultimately break up into smaller particles having the dimensions of colloids.



(b) Electrical Properties (Electrophoresis) : The particles of the colloids are electrically charged and carry positive or negative charge. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form bigger particles. That is why, a sol is stable and particles do not settle down. Arsenious sulphide, gold, silver and platinum particles in their respective colloidal sols are negatively charged while particles of ferric hydroxide, aluminium hydroxide are positively charged. The existence of the electric charge is shown by the phenomenon of electrophoresis. It involves the 'movement of colloidal particles either towards the cathode or anode, under the influence of the electric field'. The apparatus used for electrophoresis as shown in fig.



(Fig. : A set up for electrophoresis.)

The colloidal solution is placed in a U-tube fitted with platinum electrodes. On passing an electric current, the charged colloidal particles move towards the oppositely charged electrode. Thus, if arsenic sulphide sol is taken in the U-tube, in which negatively charged particles of arsenic sulphide move towards the anode.

* Earlier this process was called cataphoresis because most of the colloidal sols studied at that time were positively charged and moved towards cathode.

(C) Dialysis : It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. Since particles in true solution (ions or smaller molecules) can pass through an animal membrane or parchment paper or cellophane sheet but colloidal particles do not, the apparatus used for this purpose is called a Dialyser.

A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water continuously flows. The molecules and ions (crystalloids) diffuse through the membrane into the outer water & pure colloidal solution is left behind.

(d) Mechanical Properties

Brownian movement: Robert Brown, a botanist, discovered in 1827 that pollen grains placed in water do not remain at rest but move about continuously and randomly. Later on, this phenomenon was observed in the case of colloidal particles when they were seen under an ultramicroscope. The particles were seen to be in constant zig-zag motion as shown in fig. This zig-zag motion is called Brownian movement.

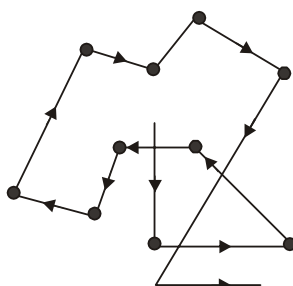


Figure : Brownian movement

- D-3.** At the time of settings, the sun is at the horizon. The light emitted by the sun has to travel a longer distance through the atmosphere. As a result, blue part of the light is scattered away by the dust particles in the atmosphere. Hence, the red part is visible.
- D-4.** Because colloidal solutions being bigger aggregate of a large number of molecules, the effective number of particles in colloidal solution is relatively much smaller.
- E-1.** According to Hardy – Schulze rule, greater the charge on the oppositely charged ion of the electrolyte added, more effective it is in bringing about coagulation. Hence Na_3PO_4 (PO_4^{3-}) is most effective.
- E-2. Isoelectric point** : The H^+ concentration at which the colloidal particles have no charge is known as the isoelectric point. At this point the stability of colloidal particles becomes very less & do not move under influence of electric field.
- E-3. Formation of deltas** : The river water contains colloidal particles of sand and clay which carry negative charge. The sea water contains +ve ions such as Na^+ , Mg^{2+} , Ca^{2+} , etc. As the river water meets sea water, these ions discharge the sand or clay particles which are precipitated in the form of delta.

- E-4. Artificial rain :** Cloud consists of charge particle of water disperse in air. Rain is caused by aggregation of these minute particles, artificial rain can be done by throwing electrified sand or AgI from aeroplanes, colloidal H₂O particle present in cloud will get coagulated by these sand or AgI particles to form bigger water drops causing rain.
- E-5.** Fe(OH)₃, since it adsorbs arsenic on itself and can be vomited out.
- F-1.** Alcohol, phenol.
- F-2.** (i) Sols are dispersions of solids in liquids while emulsions are dispersions of liquids in liquids.
(ii) Sols are quite stable wheres as emulsions are less stable.
- F-3.** The proess of separation of the constituent liquids of an emulsion is called demulsification.

PART - II

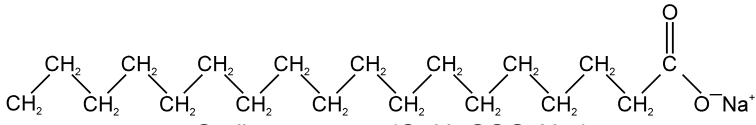
- | | | | | |
|----------------------|-----------------|----------------------|-----------------|-----------------------|
| A-1.* (B,C,D) | A-2. (D) | A-3.* (A,C,D) | A-4. (B) | A-5. (A) |
| A-6. (C) | A-7. (B) | A-8. (A) | A-9. (B) | A-10.* (A,B,D) |
| A-11. (A) | B-1. (D) | B-2. (C) | C-1. (A) | C-2.* (A,B,D) |
| C-3.* (B,C,D) | D-1. (A) | D-2. (B) | D-3. (C) | E-1. (C) |
| E-2. (A) | E-3. (C) | E-4. (C) | E-5. (D) | F-1. (B) |
| F-2. (C) | F-3. (A) | | | |

PART - III

- | | | | | |
|----------------|----------------|----------------|----------------|----------------|
| 1. (B) | 2. (B) | 3. (A) | 4. (C) | 5. (B) |
| 6. (A) | 7. (D) | 8. (B) | 9. (A) | 10. (A) |
| 11. (C) | 12. (A) | 13. (A) | 14. (D) | |

EXERCISE - 2

PART - I

- Gold sol which is lyophobic starts behaving like a lyophilic colloid.
 - Ne, because of greater vander Waal's forces of attraction in Ne than that of He.
 - Haber's process :
$$\text{N}_2 + 3\text{H}_2 \xrightarrow{\text{Fe(Mo)}\Delta} 2\text{NH}_3$$
 - Contact's process :
$$2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{V}_2\text{O}_3} 2\text{SO}_3$$
 - Gelatin is added in the preparation of ice cream to protect the particle of ice.
 - By making their surface rough
 - (i) & (iii) are based upon concept of coagulation of colloidal sol.
 - (ii) Tail of comet is visible because of Tyndall effect.
 - (iv) The Cleansing Action of Soaps :
It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon like central core. The cleansing action of soap is due to these micelles, because oil and grease can be solubilised in their hydrocarbon, like centres which are not otherwise soluble in water. This is shown diagrammatically in Fig. The dirt goes out along with the soap micelles.
- 

Sodium stearate (C₁₇H₃₅COO-Na⁺)
- CO₂ froth made by mixing solutions of NaHCO₃ and alum is called fire foam. It is used in fire extinguishers. A protective colloid such as glue or dextrin is added to stabilise the foam.
 - Positively charged colloidal particles of Fe(OH)₃ get coagulated by the oppositely charged Cl⁻ ions provided by NaCl.

- (b) Constituent liquids of the emulsion separate out i.e., demulsification occurs.
 (c) Colloidal particles move towards the oppositely charged electrodes, where they lose their charge and get coagulated.
 (d) Scattering of light by the colloidal particles takes place and the path of light becomes visible (Tyndall effect).

PART-II

- | | | | | |
|-------------|-----------|-------------|-----------|------------|
| 1. (C) | 2. (C) | 3. (A) | 4. (A) | 5. (D) |
| 6. (C) | 7. (D) | 8. (B) | 9. (A) | 10. (B) |
| 11. (D) | 12. (B) | 13. (C) | 14. (D) | 15. (A) |
| 16. (D) | 17. (A) | 18. (C) | 19. (C) | 20. (C) |
| 21. (A) | 22. (C) | 23. (A) | 24. (B) | 25. (B) |
| 26. (A) | 27. (D) | 28. (B) | 29. (A) | 30. (A) |
| 31. (B) | 32. (B,D) | 33. (B,C,D) | 34. (B,C) | 35. (A,C) |
| 36. (B,D) | 37. (B,C) | 38. (A,B) | 39. (C,D) | 40. (A, C) |
| 41. (A,B,C) | 42. (A,C) | | | |

PART-III

1. (A) → (s) ; (B) → (r) ; (C) → (q) ; (D) → (p) 2. (A) → (r) ; (B) → (p) ; (C) → (s) ; (D) → (q)

PART-IV

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (A) | 2. (A) | 3. (B) | 4. (A) | 5. (C) |
| 6. (A) | | | | |

EXERCISE - 3

PART-I

- | | | | | |
|-----------|------------|----------|----------|---------|
| 1. (A) | 2. (B) | 3. (D) | 4. (A) | 5. (C) |
| 6. 7 | 7. (A,B,D) | 8. (A,D) | 9. (A,C) | 10. (B) |
| 11. (BCD) | 12. BD | | | |

PART-II

- | | | | | |
|---------|--------|--------|--------|---------|
| 1. (2) | 2. (2) | 3. (4) | 4. (3) | 5. (2) |
| 6. (3) | 7. (3) | 8. (4) | 9. (2) | 10. (D) |
| 11. (C) | | | | |