

# Surface Chemistry

## ABSORPTION & ADSORPTION

## Section - 1

There are many properties of matter, which are related to their surface. Such properties become predominant if the substance is in finely divided form or its surface is rough. Under these conditions the surface area increases enormously and large amount of material is present in the surface. The surface related properties of matter are adsorption, colloidal state and emulsions.

There are residual forces acting along the surface of liquids and solids. Due to residual forces, the surface of a solid (or a liquid) has a tendency to attract and retain molecules of other species with which it is brought into contact. Concentration of these species is more at the surface than in the bulk of the solid or liquid.

The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid (or liquid) is known as **adsorption**. Solid, particularly when finely divided, have a large surface area, hence this behaviour is predominant on solid surfaces. The solid that takes up a gas or vapour or a solute from solution, is called the **adsorbent** while the gas or the solute, which is held to the surface of the solid is called the **adsorbate**.

If the concentration of a substance at the surface of another substance is more than in the bulk of the adjoining phases, it is called positive adsorption. If the concentration of a substance at the surface of another substance is less than in the bulk of the adjoining phases, it is called negative adsorption. This type of adsorption takes place only in case of solutions.

The removal of the **adsorbed** substance from a surface is called **desorption**. When equilibrium is reached,

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

### Difference between Adsorption and Absorption

Adsorption is different from absorption. Absorption of a substance A by a substance B means that A is uniformly distributed all over B. Adsorption on the other hand, means that A is present on the surface of B, but the concentration of A in parts of B away from the surface is negligible.

In some cases, adsorption and absorption take place simultaneously and it is difficult to determine the relative extent of adsorption and **adsorption**. The term **sorption** is widely used in such cases.

S.No.	Adsorption	Absorption
1.	It is surface phenomenon.	It is bulk phenomenon.
2.	Adsorbate is accumulated at the surface.	The substance getting absorbed is uniformly distributed throughout the bulk of the substance.
3.	The rate of adsorption is very rapid in the beginning. The rate however decreases gradually until equilibrium is reached.	Absorption proceeds at a steady rate.

## Types of Adsorption

Depending upon the nature of forces between the adsorbate (solute) and adsorbent (solvent) molecules, adsorption can be classified into two groups :

1. Physical adsorption
2. Chemical adsorption

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

**Note :** There are mainly two types of adsorption of gases of solids. If accumulation of gas on the surface of a solid occurs on account of weak van der Waal's forces, the adsorption is termed as **physical adsorption** or **physisorption**. **Chemisorption**, on the other hand is when the gas molecules or atoms are held to the solid surface by chemical bonds. Chemical bonds involved may be covalent or ionic in nature. Chemisorption involves a 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, dihydrogen is first adsorbed on nickel by van der Waal's forces. Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface by chemisorption.

### Factors affecting adsorption :

The extent of adsorption of a gas on the surface of a solid depends on the following factors :

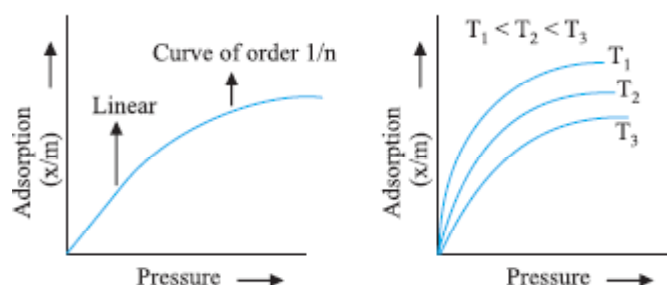
- (i) **Nature of gas :** Since physical adsorption is non specific in nature, any gas will be adsorbed on the surface of a solid to some extent or other. However, under any given conditions of temperature and pressure, easily liquefiable gases such as  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{HCl}$ ,  $\text{CO}$  etc. are adsorbed more than permanent gases like  $\text{O}_2$ ,  $\text{N}_2$  etc. Chemisorption is specific in nature. Therefore, only those gases will be adsorbed which form chemical bonds with it.
- (ii) **Nature of solid :** Activated charcoal is the most common adsorbent for easily liquefiable gases. Poisonous gases such as  $\text{CH}_4$  and  $\text{CO}$  fall in this group. Therefore, it is used in gas masks. Other gases such as  $\text{O}_2$ ,  $\text{H}_2$  and  $\text{N}_2$  adsorb more on metals such as  $\text{Ni}$ ,  $\text{Pt}$  and  $\text{Pd}$ .
- (iii) **Specific area of solid :** Specific area of an adsorbent is the surface area available for adsorption per gm of adsorbent. Greater the specific area of an adsorbent, greater will be the adsorption. The specific area of an adsorbent can be increased by making the surface rough. The pores must be large enough to allow penetrations of gas molecules.
- (iv) **Pressure of gas :** As physical adsorption is reversible, it is accompanied by decrease in pressure. Therefore, it is expected that at a given temperature the extent of adsorption will increase with the increase of pressure of the gas. The extent of adsorption is measured as  $x/m$  where  $m$  is the mass of adsorbent and  $x$  that of adsorbate (can be explained in terms of **Le-Chatelier Principle**).

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

At low pressure,  $x/m$  varies linearly with  $p$

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

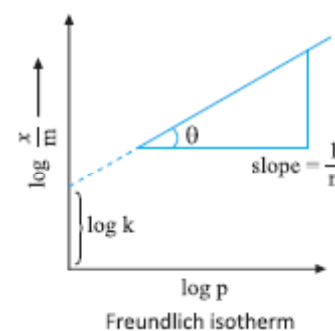
This is called **Freundlich adsorption isotherm**.



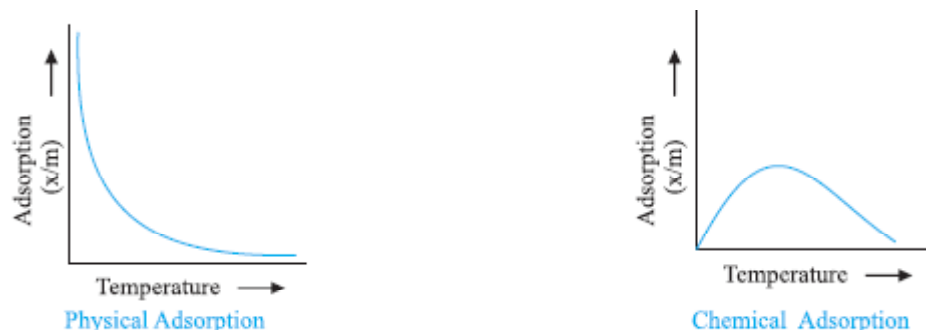
The factor  $\frac{1}{n}$  can have value between 0 and 1. (probable range 0.1 to 0.5)

When  $\frac{1}{n} = 0$ ,  $\frac{x}{m} = \text{constant}$ , the adsorption is independent of pressure.

When  $\frac{1}{n} = 1$ ,  $\frac{x}{m} = kp$ , i.e.  $\frac{x}{m} \propto P$ , the adsorption varies directly with pressure.



- (v) **Temperature :** As adsorption is accompanied by release of heat energy, so in accordance with Le-Chatelier's principle, the increase of temperature should decrease the extent of adsorption. This has indeed been found to be so. A plot of  $x/m$  vs temperature at constant pressure is called **adsorption isobar**. In the case, physical adsorption  $x/m$  decreases with increase of temperature whereas in the case of chemisorption,  $x/m$  initially increases with temperature and then decreases. The initial increase is due to the fact that chemisorption requires activation energy.



- (vi) **Activation of solid :** Activation of adsorbent means increasing its absorbing power. This is increased by increasing specific area either by making the surface rough or by breaking the solid into smaller particles. But care must be taken so that particles do not become very small then inter-particle spaces will be too small to allow penetration of gas molecules.

Adsorbing power of an adsorbent can be increased by :

- By making the surface of the adsorbent rough.
- By subdividing the adsorbent into smaller pieces or grains.
- By removing gases already **absorbed**.

### Adsorption from Solution :

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. The litmus solution when shaken with charcoal becomes colourless.

The following observations have been made in the case of adsorption from solution phase :

- The extent of adsorption decreases with the increase of temperature.
- The extent of adsorption increases with the increase of surface area of the adsorbent.
- The extent of adsorption depends on the concentration of the solute in solution.
- The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

The adsorption of a solute from solutions is very similar to the adsorption of a gas on the surface of a solid. Therefore, Freundlich adsorption isotherm is applicable even in the adsorption from solutions. If  $C$  is the concentration of a solution in  $\text{mol L}^{-1}$ , then extent of adsorptions ( $x/m$ ) is given by

$$\frac{x}{m} = k(C)^{\frac{1}{n}}$$

Taking log on both sides we get :  $\log \frac{x}{m} = \log k + \frac{1}{n} \log C$

Graph of  $\log x/m$  vs  $\log C$  is a straight line with a slope of  $(1/n)$ .

### Applications of Adsorption

The phenomenon of adsorption finds a numbers of applications. Some of them are:

- (i) Activated charcoal is used in gas masks to remove poisonous gases such as carbon monoxide, methane etc. Animal charcoal is used to remove colouring matter from cane-sugar juice in the manufacture of sugar.
- (ii) Ion exchange resin is used to remove hardness of water.
- (iii) Several organic compounds are purified by chromatographic adsorption.
- (iv) Silica gel is used for removing and controlling humidity.
- (v) The catalytic effect of a number of catalysts, like spongy iron in the manufacture of ammonia and nickel, platinum or palladium in the reduction of unsaturated hydrocarbons, is based on the principle of adsorption.
- (vi) Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

## COLLOIDAL STATE

## Section - 2

Thomas Graham classified the soluble substances into two categories depending upon the rate of their diffusion through animal and vegetable membranes or parchment paper. He observed that certain substances diffuse freely through the membrane, whereas others do not diffuse. The former type of substances on account of their crystalline nature like common salt, sugar, urea, etc., were named **crystalloids** while the second type of substances were termed as **colloids** (Greek word, kola, meaning glue-like). All inorganic acids, bases and salts and organic compounds such as sugar, urea, etc., were included in crystalloids while substance such as starch, gelatine, gums, silicic acid, etc., belonged to the colloidal group.

It was soon realised that the above classification was not perfect since many crystalline substances can be converted into colloidal form by suitable means. The colloidal form of sodium chloride, a crystalloid, can be obtained in benzene. Thus, the above classification was discarded, i.e., the term colloid does not apply to a particular class of substances but is a state of matter like solid, liquid and gas. Any substance can be brought into colloidal state by suitable means. Therefore, there is no separate class of substances called colloidal substance. It is just a state of matter into which every substance can be obtained by a suitable method.

## Types Colloidal Solutions

### (a) Classification on the basis on the size of the particle of the colloids :

The nature of a substance whether crystalloid or colloid depends upon the size of the solute particles. When the size of solute particles lies between **1 nm to 100 nm** it behaves like a **colloid**. If size of solute particles is greater than 100 nm, it exists as **suspension** and if particle size is less than 1 nm it exists as a true solution.

S.No.	Property	Suspension	Colloid	Solution
1.	Particle size	$>10^{-5}\text{cm}$ or $10^3\text{\AA}$ or $100\mu\text{m}$	$10^{-7}\text{cm}$ to $10^{-5}\text{cm}$ or $10\text{\AA}$ to $10^3\text{\AA}$ or $1\mu\text{m}$ to $100\mu\text{m}$	$<10^{-7}\text{cm}$ or $10\text{\AA}$ or $1\mu\text{m}$
2.	Visibility	Visible with naked eye.	Visible with ultra microscope.	Not visible with any of the optical means.
3.	Diffusion	Does not diffuse	Diffuse very slowly	Diffuse rapidly
4.	Settling	Settles under gravity	Does not settle but it may settle under centrifuge	Does not settle
5.	Nature	Heterogeneous	Heterogeneous	Homogeneous
6.	Appearance	Opaque	Generally clear	Clear

### (b) Classification on the basis on the physical state of dispersed phase and dispersion medium :

Colloidal solution is heterogeneous in nature and always consists of at least two phases-namely **disperse phase** and **dispersion medium**. The component present in small proportion and consisting of particles of colloidal dimensions is called disperse phase. The medium in which colloidal particles are dispersed is called dispersion medium. The two phases can be solid, liquid or gas. There are eight different types of colloidal solutions.

Disperse phase	Dispersion medium	Common name	Example
Solid	Solid	Solid sol	Alloys
Solid	Liquid	Sol	Au sol
Solid	Gas	Aerosol	Smoke
Liquid	Solid	Gels	Cheese
Liquid	Liquid	Emulsion	Milk
Liquid	Gas	Liquid aerosol	Mist, Cloud
Gas	Solid	Solid foam	Pumice stone
Gas	Liquid	Foam	Soap lather

If colloidal solution has fluid like appearance it is called **sol**. The dispersion medium in such cases is generally liquid. Depending upon the nature of medium, colloids are sometimes given special names. For example:

Dispersion medium	Name of the sol
Water	Hydrosol
Alcohol	Alcosol
Benzene	Benzosol
Gases	Aerosol

**Note :** Colloidal solutions of solids in liquids are abbreviated as sols.

**(c) Classification on the basis of interaction between different phases:**

Depending upon the nature of interaction between phase and dispersion medium, colloids are classified as :

- (i) Lyophilic colloids :** The disperse phase has great affinity for dispersion medium. In such cases the disperse phase does not easily get precipitated and the colloids are quite stable. The solids obtained after evaporation of the medium can be easily brought back to the colloidal state by shaking the solids with the dispersion medium. The colloids are thus reversible, e.g., gum, gelatin, starch, proteins and certain polymers in organic solvents. If water is used as the dispersion medium the colloid is called hydrophilic colloid.
- (ii) Lyophobic colloids :** The disperse phase has little affinity for the dispersion medium. These sols are relatively less stable. They can be easily precipitated by addition of small amount of electrolyte. Once the sol is precipitated, it cannot be easily brought back to the colloidal state. They are thus irreversible, e.g., gold sol and sulphur sol, etc. If water is used as the dispersion medium. The sol is called hydrolyophobic colloid.

S.No.	Property	Lyophilic Sols	Lyophobic Sols
1.	Surface tension	Lower than that of the medium.	Same as that of the medium.
2.	Viscosity	Much higher than that of the medium.	Same as that of the medium.
3.	Reversibility	Reversible	Irreversible
4.	Stability	More stable	Less stable
5.	Visibility	Particles can't be detected even under ultramicroscope.	Particles can be detected under ultramicroscope.
6.	Migration	Particles may migrate in either direction or do not migrate in an electric field.	Particles migrate either towards cathode or anode in an electric field.
7.	Action of electrolyte	Addition of smaller quantity of electrolyte has little effect.	Coagulation takes place.
8.	Hydration	Extensive hydration takes place.	No hydration takes place.

**(d) Classification on the basis of the particles of the dispersed phase**

S.No.	Multimolecular Colloids	Macromolecular Colloids	Associated Colloids
1.	They are formed by the aggregation of a large number of atoms or molecules generally have diameters less than 1 nm, e.g., sols of gold, sulphur.	They are molecules of large size, e.g., polymers like rubber, nylon, starch, proteins etc.	They are formed by the aggregation of large no. of ions in conc. solution e.g., soap sol.
2.	Their molecular masses are not very high.	They have high molecular masses.	Their molecular masses are generally high.
3.	Their atoms or molecules are held together by weak van der Waal's forces.	They usually have lyophobic character.	Their molecules contain both lyophilic and lyophobic groups.

**Preparation of Colloidal Solutions**

Different type of methods are used for the preparation of lyophobic and lyophilic sols:

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

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



## Dispersion Methods

1. **Mechanical dispersion** : Solid material is first finely ground by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the colloid mill. The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution. Colloidal graphite (a lubricant) and printing ink are made by this method. Tannin is used as a stabilizer in the preparation of colloidal graphite and gum arabic in lampblack colloidal solution (Indian ink).

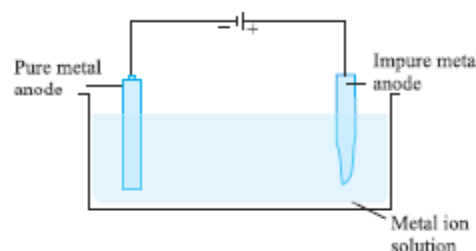
**Note :**

- (i) This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.
- (ii) This method comprises both dispersion and condensation.

2. **Electrical disintegration or Bredig's arc methods** :

This process involves dispersion as well as condensation.

Colloidal solutions of metals such as gold, silver, copper, platinum etc., can be prepared by this method. In this method electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vaporises some of the metal, which then condenses to form particles of colloidal size.



3. **Peptization** : This is a process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte. The electrolyte used for this purpose is called **peptizing agent**. This method is generally applied to convert fresh precipitate into colloidal solutions because such precipitates are simply aggregates of colloidal particles held by weak forces.

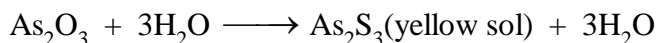
**Causes of peptization** : During peptization, the precipitate adsorbs one of the ion of the electrolyte on its surface. The adsorbed ion is generally common with those of precipitate. This causes the development of positive or negative charge on the precipitates, which ultimately breaks into particles of colloidal dimensions. For example, when freshly precipitated ferric hydroxide is shaken with aqueous solution of ferric chloride (peptizing agent) it adsorbs  $\text{Fe}^{3+}$ . Similarly, a precipitate of  $\text{AgCl}$  on shaking with dilute solution of  $\text{AgNO}_3$  adsorbs  $\text{Ag}^+$  ion and get peptised to colloidal particles of the type  $[\text{AgCl}]\text{Ag}^+$ . In some cases, peptization can also be achieved by organic solvents. For example, cellulose nitrate is peptised by ethanol. The colloidal solution of cellulose nitrate in ethanol is called 'collodion'.

## Condensation Methods

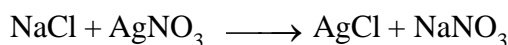
1. **By exchange of solvent** : If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility in water. Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.

2. **By change of physical state :** Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabilizer (an ammonium salt or a citrate).
3. **Chemical methods :** The chemical method involves chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of super-saturation is produced but the actual precipitation is avoided.

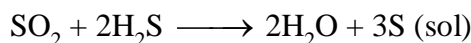
(a) **Double decomposition :** A colloidal solution of arsenic sulphide is obtained by passing hydrogen sulphide into solution of arsenic oxide in distilled water.



Sols of silver halide are obtained by mixing dilute solutions of silver salts and alkali metal halides in equivalent amounts.

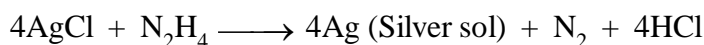
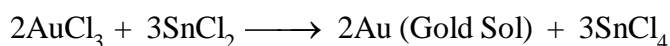


(b) **Oxidation :** A colloidal solution of sulphur can be prepared by passing hydrogen sulphide into a solution of sulphur dioxide in water or through a solution of an oxidising agent like bromine water or nitric acid.

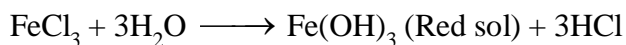


Sulphur sol can also be obtained when  $\text{H}_2\text{S}$  is bubbled through an oxidising agent (bromine water or nitric acid).

(c) **Reduction :** A colloidal solution of a metal like silver, gold or platinum can be prepared by the reduction of its salt solution with a suitable reducing agent such as stannous chloride, formaldehyde, hydrazine etc.



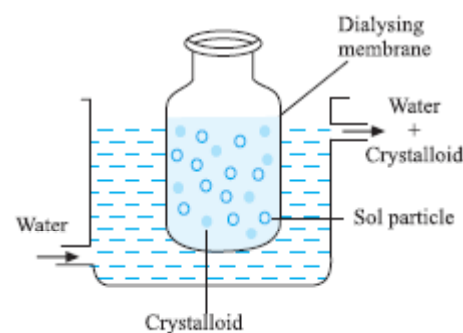
(d) **Hydrolysis :** By this method hydroxide sols of less electropositive metals like Fe, Al or Sn are prepared. A red sol of ferric hydroxide is obtained by the hydrolysis of ferric chloride with boiling water.



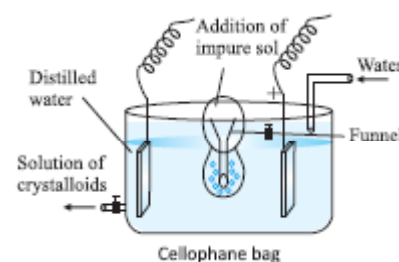
### Purification of Colloidal Solutions

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 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 suspended in a vessel through which fresh water is continuously flown. The molecules and ions diffuse through the membrane into the outer colloidal solution are 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. The ions present in the colloidal solution migrate out to the oppositely charged electrodes.



(iii) **Ultra Filtration** : In this method, colloidal solutions are purified by carrying out filtration through special type of graded filter papers called ultra-filters. These filter-papers are made from ordinary filter paper by impregnating them with colloidon solution and subsequently hardened by soaking in formaldehyde and finally drying it. These filter papers allow the electrolytes to pass through them but not the colloidal particles. The ultra-filtration is generally a slow process and can be hastened by the application of suction. The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

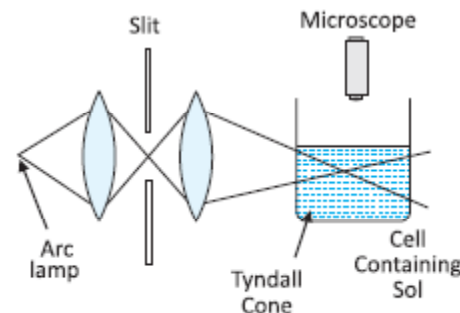
(iv) **Ultra Centrifugation** : In this method, the colloidal solution is placed in a high speed ultracentrifuge. On centrifuging the colloidal particles settle down. The impurities remain in the dispersion medium and are removed by decantation. The settled colloidal particles are shaken with water containing peptizing agent to form the colloidal solution again.

## Properties of Colloidal Solutions

The characteristic properties of colloidal solutions are as given below:

- (i) **Heterogeneous Nature** : A colloidal solution is heterogeneous in nature. It consists of two phases namely the dispersed phase and the dispersion medium.
- (ii) **Visibility** : Colloidal particles are too small to be seen with naked eye. But they become visible as bright **sports** against dark background when viewed through an ultra microscope due to scattering of light caused by them.
- (iii) **Filterability** : The size of solute particles is smaller than the pore size of filter paper and therefore, they can readily pass through a filter paper. Colloidal particles, however cannot pass through ultra filters, parchment paper or animal membrane.

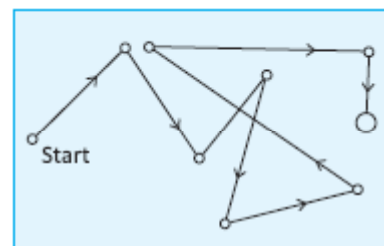
- (iv) **Surface tension and viscosity :** The surface tension and viscosity of lyophobic sols are not very different from those of the dispersion medium. On the other hand, lyophilic sols show higher viscosity and lower surface tension in comparison to the dispersion medium.
- (v) **Colligative Properties :** A colloidal solution has very small value of mole fraction of dispersed phase due to high average molecular mass of the colloidal particles. As a result all the colligative properties, colloidal solutions have quite low values when compared to true solutions, having same concentration. However, the low osmotic pressure of a colloidal solution is measurable and can be used to determine the molecular weight of colloidal particles.
- (vi) **Tyndall Effect :** Scattering of light by the colloidal particles present in a colloidal solution is known as **Tyndall effect** and is caused by the scattering of blue part of light by the colloidal particles. If a strong beam of light is passed through a colloidal solution placed in a dark place, the path of the beam gets illuminated. The illuminated path of beam is called **Tyndall Cone**.



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

Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied:

- The diameter of the dispersed particles is not much smaller than the wavelength of the light used.
  - The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude. This condition is satisfied by lyophobic sols. The lyophilic sols show little or no Tyndall effect as there is very small difference in the refractive indices of the dispersed phase and the dispersion medium.
- (vii) **Brownian movement :** The colloidal particles of a colloidal solution when viewed through an ultra microscope show a constant zig-zag motion. This type of motion was first observed by Robert Brown and hence known as Brownian movement. It is caused by the uneven impacts of the particles of the dispersion medium on the colloidal particles. As the size of the particles increases, the probability of uneven impacts decreases and the Brownian movement becomes slow. When the dispersed particles acquire the dimensions of suspension, no Brownian movement is observed.



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

### Importance of Brownian motion

- (a) Brownian movement provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.
- (b) It counters the force of gravity acting on colloidal particles and hence helps in providing stability to colloidal sols by not allowing them to settle down.
- (viii) **Diffusion** : Colloidal particles like solute particles of a true solution diffuse from a region of higher concentration to that of lower concentration. However, colloidal particles diffuse at a slower rate due to their large size and high molecular mass.
- (ix) **Sedimentation** : The colloidal particles tend to settle down very slowly under the influence of gravity. The sedimentation or the rate of settling down can be increased by ultracentrifuge.
- (x) **Electrophoresis** : When electric potential is applied across two platinum electrodes dipping in a colloidal solution the colloidal particles move towards one or the other electrode. This movement of colloidal particles under an applied electric field is called **electrophoresis**. Positively charged particles move towards the cathode while negatively charged particles move towards anode.

The particles of the colloidal solution carry same type of charge, either positive or negative. The dispersion medium carries an equal and opposite charge. The colloidal solutions as a whole are electrically neutral. Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form aggregates. This makes a colloidal solution stable and the colloidal particles do not settle down.

Some of the common positively and negatively charged colloids are given below:

**Positively charged** :  $\text{Fe}(\text{OH})_3$  sol,  $\text{Cr}(\text{OH})_3$  sol,  $\text{Al}(\text{OH})_3$  sol,  $\text{Ca}(\text{OH})_2$  sol, dyes like methylene blue and haemoglobin.

**Negatively charged** :  $\text{As}_2\text{S}_3$  sol,  $\text{Sb}_2\text{S}_3$  sol,  $\text{CdS}$  sol,  $\text{Au}$  sol,  $\text{Cu}$  sol,  $\text{Ag}$  sol and acid dyes like congo red.

When electrophoresis i.e., movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed electro-osmosis.

### Coagulation of Colloidal Solutions

The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If, the charge is removed, the particles will come nearer to each other and thus, aggregate or flocculate and settle down under the force of gravity. The flocculation and settling down of the colloidal particles is called coagulation or precipitation of the sol.

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

- (i) **By mutual precipitation :** When two oppositely charged sol such as  $\text{Cr}(\text{OH})_3$  and  $\text{Sb}_2\text{S}_3$  are mixed in equimolar proportion, they neutralise each other and get coagulated.
- (ii) **By electrophoresis :** During electrophoresis of a sol, the colloidal particles move towards oppositely charged electrode. The particles touch the electrode, lose charge and get coagulated.
- (iii) **By boiling :** When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately they settle down to form a precipitate.
- (iv) **By persistent dialysis :** On prolonged dialysis, the traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable.
- (v) **By addition of electrolytes :** When excess of an electrolyte is added. The colloidal particles are precipitated. The reason is that colloidal particles taken up ions carrying charged opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for neutralisation of charge on the particles is called the flocculating ion.

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

- (a) The ions carrying charge opposite to that of sol particles are effective in carrying the coagulation of the sol.
- (b) Coagulation power of an electrolyte is directly proportional to the fourth power of the valency of the ions causing coagulation.

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



Similarly, in the coagulation of a positive sol, the flocculation power of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  is in the order of



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

- (vi) **Protection of colloids :** Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, i.e., colloidal particles are covered by a sheath of the liquid in which they are dispersed.

Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and, thus, protect the latter from electrolytes. Lyophilic colloids used for this purpose are called **protective colloids**.

The lyophilic colloids differ in their protective power. The protective power is measured in terms of **Gold Number** and is defined as the number of milligrams of a lyophilic colloid that will just prevent the precipitation of 10 ml of a gold sol on the addition of 1 ml of 10% sodium chloride solution.

S.No.	Protective Colloid	Gold number
1.	Gelatin	0.005 – 0.01
2.	Heamolglobin	0.03
3.	Gum arabic	0.15
4.	Egg albumin	0.08 – 0.10
5.	Potato starch	25
6.	Sodium oleate	0.4
7.	Gum tragacanth	2
8.	Starch	25 – 50

Higher is the gold number, lower will be the protective power.

## GELS AND EMULSIONS

## Section - 3

Certain colloidal systems have the property of setting into a semi-solid, jelly-like form when they are present at high concentration. Such a process is called gelatine and the colloidal systems with jelly-like form are called gels. Gel, usually, consists of two components; one is solid, such as gelatine, silicic acid, sodium oleate, etc., and the other is a liquid such as water.

Gels possess rigid structure formed due to interlocking of particles of disperse phase and create a loose framework. The particles of dispersion medium are trapped into the loose framework. The degree of rigidity varies from substance to substance. When gels are allowed to stand for long time, they give out small quantity of trapped liquid, which accumulates on the surface. This is called syneresis or *weeping of the gel*.

### Emulsions

Emulsions are colloidal solutions in which both the dispersion phase and the dispersion medium are liquids. It can be defined as the dispersion of finely divided droplets in another liquid.

### Types of Emulsions

There are two types of emulsions.

1. **Oil in water type emulsions (O/W type)** : In this type of emulsion, oil is the dispersed phase and water is the dispersion medium. For example milk, vanishing cream etc.



- 2. Water in oil type emulsions (W/O type) :** In this type of emulsions water is the dispersed phase and oil is the dispersions medium. For example butter, cod liver oil, cold cream etc.

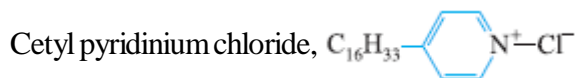
Emulsions of oil and water are unstable and sometimes they separate into two layers on standing. For the stabilization of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agents form an interfacial film between suspended particles and the medium. The principal agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. For W/O emulsions, the principal emulsifying agents are heavy metal salts of fatty acids, long chain alcohols, lamp black, etc.

## Surfactants

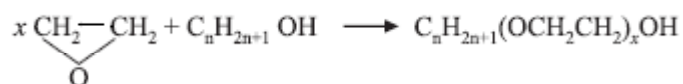
Surfactants are substances which get preferentially adsorbed at the air-water, oil-water and solid-water interfaces, forming an oriented monolayer where in the hydrophilic groups point towards the aqueous phase and hydrocarbon chains point towards the air or the oil phase. The surfactants can be cationic,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

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

Cationic surfactants are those which dissociate in water to yield positively charged ions. Examples are :



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



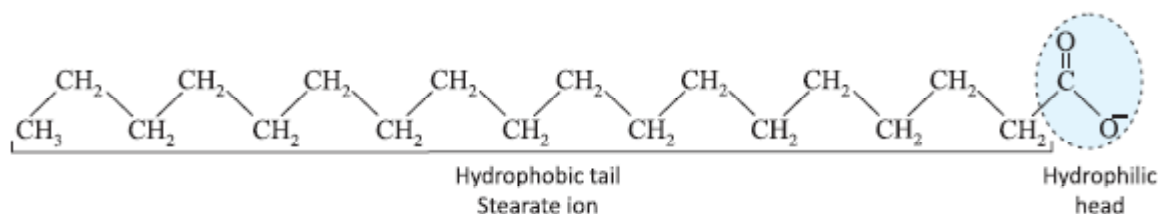
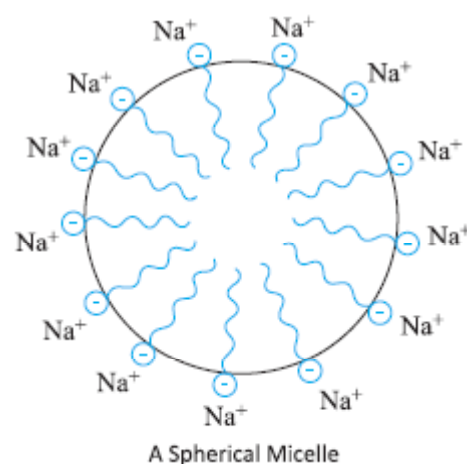
The hydrophilic nature of hydroxyethylated surfactants can be controlled during their synthesis by varying not only the number of carbon atoms in a hydrophobic chain but also the number of hydroxy ethylene groups. These surfactants are soluble even in hard water. Hydrophobic surfaces become hydrophilic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



## Micelles

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

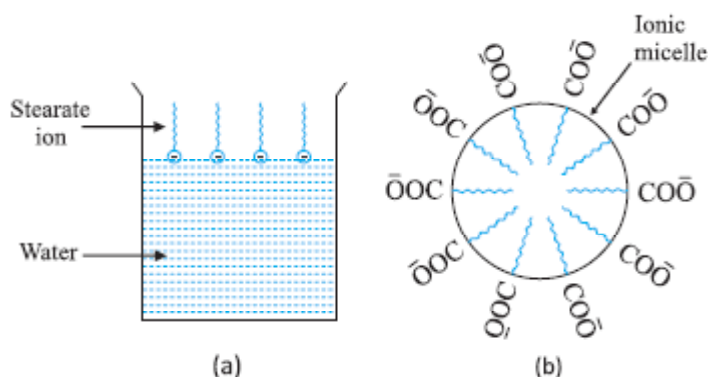
The formation of micelles takes place only above a particular temperature called Kraft temperature ( $T_k$ ) and above a particular concentration called critical micelle concentration (CMC). On dilution, these colloids revert back to individual ions. Surface active agents such as soaps and synthetic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



## Mechanism of micelle formation

Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as  $\text{RCOO}^-\text{Na}^+$ . (e.g.: sodium stearate  $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$ ). When dissolved in water, it dissociates into  $\text{RCOO}^-$  and  $\text{Na}^+$  ions. The  $\text{RCOO}^-$  ions, however, consist of two parts - a long hydrocarbon chain R which is hydrophobic and a polar group  $\text{COO}^-$  which is hydrophilic.

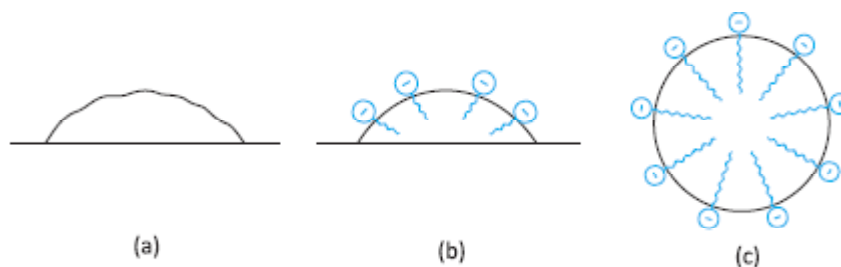
The  $\text{RCOO}^-$  ions are, therefore, present on the surface with their  $\text{COO}^-$  groups in water and the hydrocarbon chains R staying away from it and remain at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a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



- (a) Arrangement of stearate ions on the surface of water at low concentrations of soap.
- (b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap.

### Cleansing action of soaps

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



- (a) Grease on cloth
- (b) Stearate ions arranging around the grease droplet and
- (c) Grease droplet surrounded by stearate ions (micelle formed)

### IN-CHAPTER EXERCISE - A

1. Why does physisorption decrease with the increase of temperature ?
2. Give reason why a finely divided substance is more effective as an adsorbent.
3. Why is adsorption always exothermic ?
4. Discuss the effect of pressure and temperature on the adsorption of gases on solids.
5. Explain what is observed :
  - (i) When a beam of light is passed through a colloidal solution.
  - (ii) an electrolyte, NaCl is added to hydrated ferric oxide solution.
  - (iii) electric current is passed through a colloidal solution ?
6. Give four uses of emulsions.
7. Comment on the statement that “colloid is not a substance but a state of substance”.
8. What is an adsorption isotherm ? Describe Freundlich adsorption isotherm.
9. What is demulsification ? Name two demulsifiers.

## CATALYSIS

## Section - 4

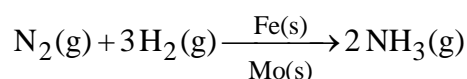
Catalysis is the phenomenon by which rate of a chemical reaction is changed due to the participation of a substance called a catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself. A catalyst may participate in multiple chemical transformations.

**Characteristics of Catalytic Reactions**

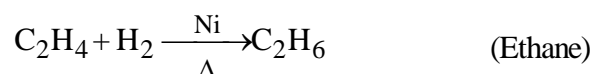
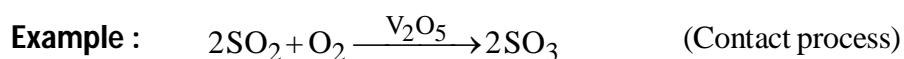
- (i) The catalyst remains unchanged in amount and chemical composition at the end of the reaction ; it may, however, undergo considerable change in physical form.
- (ii) The reaction of a catalyst is specific to a large extent. Thus, the decomposition of  $\text{KClO}_3$  is catalyzed by  $\text{MnO}_2$  but not by platinum.
- (iii) The catalyst does not initiate a reaction ; it merely accelerates the reaction that is already occurring.
- (iv) A catalyst does not alter the final state of equilibrium in a reversible reaction.

A certain minimum energy must be possessed by the reactants, so that they may react and produce the products. This is called the activation energy ( $E_a$ ) for the reaction. A catalyst is said to lower the activation energy and thus increase the rate of the reaction. Thus, a catalyst increase the rate of a reaction by providing a pathway whose activation energy is lower than the activation energy of the uncatalyzed reaction.

Promoters are substance that increase the catalytic activity, even though they are not catalysts by themselves. For example, in Haber's process for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as catalyst.

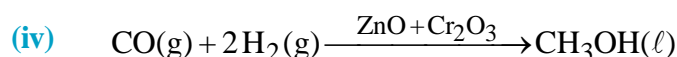
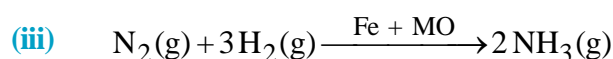
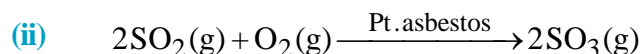
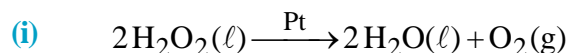
**Type of Catalysis**

- (i) **Positive Catalysis** : The catalyst increases the rate of reaction.



**(iv) Heterogeneous Catalysis :** A catalytic process in which the catalyst and the reactants are in different phases is called heterogeneous catalysis. This process is also called contact or surface catalysis.

**Example :**



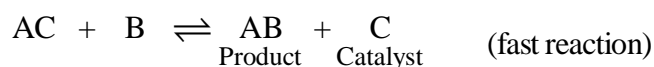
## General Principle of Catalysis

It is not possible to give a uniform explanation of the mechanism of the phenomenon of catalysis as catalytic reaction are of varied nature. However, two broad theories of catalytic action have been proposed. First theory, known as intermediate compound formation theory explains successfully the homogeneous catalysis. The second theory termed as adsorption theory explains the heterogeneous catalysis.

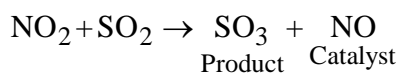
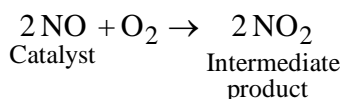
### (i) Intermediate Compound formation Theory :

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

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



Many catalytic reactions can be explained on the basis of this theory. Consider the catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the lead-chamber process. This occurs as follows,



## (ii) Adsorption Theory

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

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

The mechanism involves five steps :

- (a) Diffusion of reactants to the surface of the catalyst.
- (b) Some form of association between the catalyst surface and the reactants occurs. This is assumed to be adsorption.
- (c) Occurrence of chemical reaction on the catalyst surface.
- (d) Desorption of reaction products away from the catalyst surface.
- (e) Diffusion of reaction products away from the catalyst surface.

## SUBJECTIVE SOLVED EXAMPLES

**Example - 1** What would be the total surface area of a cube of edge length 1 cm. Also what would be the total surface area of the same material if it were subdivided into colloidal size cubes, each having an edge length of  $10^{-7}$  cm.

**SOLUTION :**

Surface area of cube of edge length 1 cm  $6 \times 1 \text{ cm}^2$

Surface area of cube of edge length  $1 \times 10^{-7}$  cm  $= 6 \times 10^{-14} \text{ cm}^2$

Let  $n$  cubes of  $6 \times 10^{-14} \text{ cm}^2$  are present on breaking the cube of 6  $\text{cm}^2$

$$\therefore n \times \text{volume of cube of edge length } 10^{-7} \text{ cm} \\ = \text{volume of cube of edge length 1 cm.}$$

$$n \times \frac{4}{3} \times \pi \times [10^{-7}]^3 = \frac{4}{3} \times \pi \times (1)^3$$

$$\therefore n = 10^{21}$$

$$\therefore \text{New total surface area} = 10^{21} \times 6 \times 10^{-14} = 6 \times 10^7$$

**Example - 2** Calculate the surface area of a catalyst that adsorbs  $10^3 \text{ cm}^3$  of nitrogen reduced to STP per gram in order to form the monolayer. The effective area occupied by  $\text{N}_2$  molecule on the surface is  $1.62 \times 10^{-15} \text{ cm}^2$ .

**SOLUTION :**

$$\text{No. of } \text{N}_2 \text{ molecules} = \frac{10^3 \times 6.023 \times 10^{23}}{22400} = 2.69 \times 10^{22}$$

$$\text{Total area covered by } \text{N}_2 = 2.69 \times 10^5 \text{ cm}^2 = 4358 \text{ m}^2$$

**Example - 3** 1 g of activated charcoal has a surface area  $10^3 \text{ m}^2$ . If complete monolayer coverage is assumed and effective surface area of  $\text{NH}_3$  molecule is  $0.129 \text{ nm}^2$ , how much  $\text{NH}_3$  in  $\text{cm}^3$  at STP could be adsorbed on 25g of charcoal.

**SOLUTION :**

$$\text{Total surface area available for adsorption} = 25 \times 10^3 \text{ m}^2$$

Effective surface area of one  $\text{NH}_3$  molecule  $= 0.129 \times 10^{-18} \text{ m}^2$

$$\therefore \text{Number of molecule of } \text{NH}_3 \text{ adsorbed} = \frac{25 \times 10^3}{0.129 \times 10^{-18}} = 1.94 \times 10^{23}$$

$$\therefore \text{Mole of } \text{NH}_3 = \frac{1.94 \times 10^{23}}{6 \times 10^{23}} = 0.323$$

$$\text{Volume of } \text{NH}_3 = 0.323 \times 22400 = 7235 \text{ cm}^3$$

**Example - 4**

One gram of activated charcoal has a surface area of  $10^3 \text{ m}^2$ . If complete coverage of monolayer is assumed, how much  $\text{NH}_3$  in  $\text{cm}^3$  at STP would be adsorbed on the surface of 25g of the charcoal. Given diameter of  $\text{NH}_3$  molecule  $= 0.3 \text{ nm}$ .

**SOLUTION :**

Total surface area to be covered  $= 25 \times 10^3 \text{ m}^2$

$$2r \text{ for } \text{NH}_3 = 0.3 \times 10^{-9} \text{ m}$$

$$= 0.3 \times 10^{-9} \times 10^2 \text{ cm} = 0.3 \times 10^{-7} \text{ cm}$$

$$\therefore r = 1.5 \times 10^{-8} \text{ cm}$$

$$\therefore \text{Surface area of 1 molecule} = \pi r^2$$

$$= 3.14 \times (1.5 \times 10^{-8})^2 = 7.065 \times 10^{-16} \text{ cm}^2$$

Number of  $\text{NH}_3$  molecules adsorbed

$$= \frac{25 \times 10^3}{7.065 \times 10^{-16}} = 3.539 \times 10^{23}$$

$$\therefore \text{Mole of } \text{NH}_3 \text{ adsorbed} = \frac{3.539 \times 10^{23}}{6.023 \times 10^{23}} = 0.5875$$

Now using  $PV = nRT$

$$V = \frac{0.5875 \times 0.0821 \times 273}{1}$$

$$\therefore V = 13.168 \text{ litre}$$

**Example - 5**

20% surface sites have adsorbed  $N_2$ . On heating  $N_2$  gas is evolved from sites and were collected at 0.001 atm 298 K in a container of volume  $2.46 \text{ cm}^3$ . Density of surface sites is  $6.023 \times 10^{14} \text{ cm}^{-2}$  and surface area is  $1000 \text{ cm}^2$ . Find out the number of surface sites occupied per molecule of  $N_2$ .

**SOLUTION :**

For adsorbed  $N_2$  on surface sites

$$P_{N_2} = 0.001 \text{ atm}, \quad V = 2.46 \text{ cm}^3 = 2.46 \times 10^{-3} \text{ litre},$$

$$T = 298 \text{ K}$$

$$\therefore n_{N_2} = \frac{PV}{RT} = \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 298} = 1.0 \times 10^{-7}$$

$\therefore$  Molecules of adsorbed

$$N_2 = 1.0 \times 10^{-7} \times 6.0 \times 10^{23} = 6.023 \times 10^{16}$$

Total surface sites available = No. of sites per  $\text{cm}^2 \times \text{area}$

$$= 6.023 \times 10^{14} \times 1000 = 6.023 \times 10^{17}$$

Surface sites on which  $N_2$  is adsorbed

$$= 20\% \times \text{Available sites}$$

$$= \frac{20}{100} \times 6.023 \times 10^{17} = 12.046 \times 10^{16}$$

$\therefore$  Number of sites adsorbed per molecule of

$$N_2 = \frac{12.046 \times 10^{16}}{6.023 \times 10^{16}} = 2$$

**Example - 6**

1g of charcoal adsorbs 100 mL of 0.5 M  $\text{CH}_3\text{COOH}$  to form a monolayer and there by the molarity of  $\text{CH}_3\text{COOH}$  reduces to 0.49. Calculate the surface area of charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal  $= 3.01 \times 10^2 \text{ m}^2 / \text{g}$ .

**SOLUTION :**

$$\text{Millimole of acetic acid taken} = 100 \times 0.5 = 50$$

$$\text{Millimole of acetic acid left} = 100 \times 0.49 = 49$$

$$\text{Millimole of acetic acid adsorbed} = 50 - 49 = 1$$

$$\text{Molecules of acetic acid adsorbed} = 1 \times 10^{-3} \times 6.023 \times 10^{23} = 6.023 \times 10^{20}$$



Total area of 1g charcoal covered by these molecules  $= 3.01 \times 10^2 \text{ m}^2$

$$\begin{aligned} \therefore \text{Area covered by 1 molecule} &= \frac{3.01 \times 10^2}{6.023 \times 10^{20}} & (\because \text{unilayer adsorption}) \\ &= 5 \times 10^{-19} \text{ m}^2 \end{aligned}$$

**Example - 7** *It is observed that five hours are needed to dissolve a 1cm cube of NaCl in large amount of water. Calculate the time required for dissolution, if the cube is ground to a powder containing  $10^{16}$  equal size spheres. Assume that the rate of dissolution is directly proportional to initial area of contact between NaCl and water.*

**SOLUTION :**

Volume of cm cube  $= 1 \text{ cm}^3$

Volume of powder in spherical shape

$$= 10^{16} \times \frac{4}{3} \pi r^3 \quad (\text{Volume of one sphere} = \frac{4}{3} \pi r^3)$$

$$\therefore \frac{4}{3} \pi r^3 \times 10^{16} = 1 \text{ cm}^3 \text{ and } r = 2.88 \times 10^{-6} \text{ cm}$$

$$\begin{aligned} \therefore \text{Total surface area} &= \pi r^2 \\ &= \frac{22}{7} \times (2.88 \times 10^{-6})^2 \times 10^{16} = 2.61 \times 10^5 \end{aligned}$$

Initial surface area of cube  $6 \times 1^2 = 6 \text{ cm}^2$

Rate of dissolution  $\propto$  surface area

$$\text{or } \frac{ds}{dt} \propto \text{surface area}$$

Thus, time required for dissolution of same amount is  $t \propto \frac{1}{\text{surface area}}$

$$\therefore 5 \propto \frac{1}{6}$$

$$t \propto \frac{1}{2.61 \times 10^5}$$

$$\therefore t = 1.15 \times 10^{-4} \text{ hr} = 1.15 \times 10^{-4} \times 3600 \text{ sec} = 0.41 \text{ sec}$$

**Example - 8**

$H_2$  gas was adsorbed on 1g powdered copper surface forming monolayer of molecules. On desorption total  $H_2$  collected measured  $1.36 \text{ cm}^3$  at STP. Assuming volume of 1 molecule of  $H_2$   $4.742 \times 10^{-23} \text{ cm}^3$ , calculate specific area of copper powder.

**SOLUTION :**

Number of molecules of  $H_2$  in  $1.36 \text{ cm}^3$

$$= \frac{6.023 \times 10^{23} \times 1.36}{22400} = 3.66 \times 10^{19}$$

$\therefore$  Volume of  $H_2$  molecule  $= 4.742 \times 10^{-23}$

$$\therefore \frac{4}{3} \pi r^3 = 4.742 \times 10^{-23}$$

$$\therefore r = 2.246 \times 10^{-8} \text{ cm}$$

$\therefore$  Area of cross-section of  $H_2$  molecule

$$= \pi r^2 = 3.14 \times (2.246 \times 10^{-8})^2 = 1.583 \times 10^{-15} \text{ cm}^2$$

Area of molecules of adsorbed

$$= (3.66 \times 10^{19}) \times 1.583 \times 10^{-15} \text{ cm}^2$$

Area of adsorption of Cu powder = specific area of Cu powder, i.e. area/g.

$\therefore$  Specific area of adsorption of Cu

$$= 1.583 \times 10^{-15} \times 3.66 \times 10^{19} = 5.79 \times 10^4 \text{ cm}^2$$

**Example - 9**

A solution of palmitic acid ( $M = 256 \text{ g mol}^{-1}$ ) in benzene contains 4.24 g of acid per litre. This solution on pouring on water surface forms a monomolecular layer of palmitic acid as benzene gets evaporated. If  $500 \text{ cm}^2$  area of water surface is to be covered by a monolayer, what volume of solution in benzene is needed. Area covered by one molecule of palmitic acid is  $0.21 \text{ nm}^2$ .

**SOLUTION :**

Let V litre of solution be needed to do so

$$\text{Mass of palmitic acid} = V \times d = V \times 4.24 \text{ g}$$

$$\text{Mole of palmitic acid} = \frac{V \times 4.24}{256}$$

$$\therefore \text{Number of molecules of palmitic acid} = \frac{4.24 \times V \times 6.023 \times 10^{23}}{256}$$

∴ Total area covered

$$= \frac{4.24 \times V \times 6.023 \times 10^{23}}{256} \times 0.21 \times 10^{-18} \times 10^4 \text{ cm}^2$$

or  $500 = \frac{4.24 \times V \times 6.023 \times 10^{23} \times 0.21 \times 10^{-18} \times 10^4}{256}$

∴  $V = 2.386 \times 10^{-5} \text{ litre}$

**Example - 10**

A graph plotted between  $\log_{10} \frac{x}{m}$  vs.  $\log_{10} P$  ( $P$  is pressure of gas in atm) shows a straight line with slope equal to 1 and intercept equal to 0.4771. The extent of adsorption ( $x/m$ ) of gas at the pressure 2 atm is :

**SOLUTION :**

$$\therefore \log \frac{x}{m} = \log K + \frac{1}{n} \log P$$

$$\therefore \log K = 0.4771 \quad \text{or} \quad K = 3$$

$$\therefore \log \frac{x}{m} = \log 3 + \frac{1}{n} \times 0 \quad (\because P = 1)$$

$$\text{Slope} = \frac{1}{n} = 1$$

$$\therefore n = 1$$

$$\text{Now } \frac{X}{m} = KP^{1/n} = 3 \times (2)^1 = 6$$

**NOW ATTEMPT OBJECTIVE WORKSHEET BEFORE PROCEEDING AHEAD IN THIS EBOOK**

## SOLUTIONS TO IN-CHAPTER EXERCISE-A

1. As we know that  $\Delta H < 0$  for adsorption. So by Le-chatelier principle physisorption should decrease with increase in temperature.
2. With each division, surface area available for adsorption increases. E.g. divide a cube into 8 small cubes and compare old and new surface area.
3. New attraction forces come into picture in case of adsorption. Which leads to lowering in potential energy, so energy is released.
4. High pressure, low temperature is favourable for adsorption.
5.
  - (i) Tyndall effect.
  - (ii) Colloidal solution of  $\text{FeCl}_3$  comes into picture.
  - (iii) When electric current is passed, coagulation occurs and colloidal particles settle down.
6.
  - (i) Pharmaceutical
  - (ii) Making of cosmetic products such as creams, oils.
  - (iii) Paints
  - (iv) Making waxes.
7. Refer theory
8. Refer page No. 33
9. Process which is used to separate emulsions is called demulsification  
Examples are Ethylene oxide, Glycerol

## My Chapter Notes





