5

Surface Chemistry

Introduction :

There are many properties of substances particularly of solids and liquids which depend upon the nature of the surface. The branch of chemistry which deals with the nature of surfaces and changes occurring on the surface is called surface chemistry. Adsorption on solid or on solution surfaces and colloidal properties are important surface effects which are useful to understand many physical and chemical properties of the substances.

5.1 ADSORPTION

The phenomenon of higher concentration of molecular species (gases or liquids) on the surface of a solid than in the bulk is called adsorption.

Adsorbate : The substances that get adsorbed on the solid surface due to inter molecular attractions are called adsorbate.

Adsorbent : The solid substance on the surface of which adsorption occurs is known as adsorbent.

Interface : Surface of the adsorbent at which adsorbate get concentrated is known as interface.

Positive adsorption : When the concentration of adsorbate is more on the surface of adsorbent relative to its concentration in the bulk it is called positive adsorption.

Negative adsorption : When the concentration of the adsorbate is less on the surface relative to its concentration in the bulk it is called negative adsorption.

Adsorption in different actions :

(i) Finely divided activated charcoal has a tendency to adsorb a number of gases like O_2, Cl_2, NH_3, SO_2 etc. In this case, charcoal acts as an adsorbent while gas molecules act as adsorbate.

(ii) Animal charcoal is used for decolouring organic dye like methylene blue.

(iii) Palladium and Nickel metal easily adsorbed H_2 gas at their surface.

(iv) Silica get adsorbed water vapour from air.

Desorption : The process of removal of an adsorbed substance from the surface on which it is adsorbed is called desorption.

Absorption : In absorption the molecules of a substance are uniformly distributed in the bulk of the other.

Table 5.1 : Differences between Adsorption and Absorption.

	Adsorption	Absorption
1.	It is the phenomenon of higher concentration of particles of gas or liquid on the surface then in the bulk of the solid.	It is the phenomenon in which the particles of gas or liquid get uniformly distributed through out the body of the solid
2.	It is a surface phenomenon.	It is a bulk phenomenon.
3.	Adsorption is rapid in the begining and its rate slowly decreases.	Absorption occurs at uniform rate.
4.	Adsorption of water vapour by silica.	Absorption of water vapour by calcium chloride.

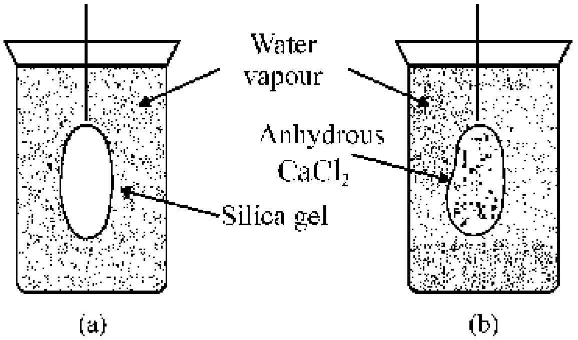


Fig. 5.1 : (a) Higher concentration of water vapour on silica gel (Phenomenon of adsorption) (b) Uniform distribution of water vapour in bulk of calcium chloride (Phenomenon of absorption)

Sorption: In some cases both adsorption and absorption occur together and are not distinguishable.

Example:

(i) H_2 gas adsorbed by charcoal but after some time it gets uniformly distributed in the bulk of solid.

(ii) Dye get adsorbed on the surface of fibre and finally gets uniformly distributed in the bulk of solid i.e. fibre.

5.2 Thermodynamic Feasibility of Adsorption

(i) During adsorption, new forces of attraction come into existence. As a result all adsorptions are accompanied by release of energy and are found to be exothermic. The enthapy change taking place for adsorption of one mole of adsorbate on an adsrbent surface is called **molar heat of adsorption.**

(ii) Since adsorption is an exothermic process therefore **ΔH = -ve**

(iii) It is also observed that during adsorption there is a decrease in entropy i.e. **ΔS= -ve**

(iv) Gibbs Helmholtz equation **$\Delta G = \Delta H - T\Delta S$**

At normal temperature $\Delta H > T\Delta S$ thus for the process of adsorption to occurs, ΔG must be negative and adsorption is a spontaneous process.

5.3 Types of Adsorption

Depending upon the nature of forces which hold the molecules of adsorbate on the surface of the absorbent the adsorbption is classified into two types:-

(1) Physical or vanderwaals adsorption : Adsorbate are held to the surface of the adsorbent by the physical forces such as Vander Waals forces. The adsorption is called physical adsorption. The attractive forces are weak and therefore, these can by easily overcome either by increasing the temperature or by decreasing the pressure. It is not specific in nature.

(2) Chemical adsorption or Langmuir adsorption: When the molecules of the adsorbate are held to the surface of the adsorbent by the chemical forces the adsorption is called chemical adsorption. This type of adsorption is irreversible.

Table 5.2 : Differences between physical and chemical adsorption

Physical adsorption	Chemical Adsorption
1. Low heat of adsorption of the order of 20-40 kJ mol^{-1}	1. High heat of adsorption of the order of 200-400 kJ mol^{-1}
2. Usually occurs at low temperature and decreases with increasing temperature	2. It occurs at high temperature
3. It is reversible	3. It is irreversible
4. The extent of adsorption depends upon the ease of liquefication of the gas.	4. There is no correlation between extent of adsorption and the ease of liquification of gas.
5. It is not specific in nature, i.e., all gases are adsorbed on the surface of a solid to some extent.	5. It is highly specific in nature and occurs only when there is bond formation between adsorbent and adsorbate molecules.

Physical adsorption	Chemical Adsorption
6. The state of adsorbate is same as in the bulk	6. State of adsorbate molecules may be different from that on the bulk
7. It forms multi molecular layers	7. It forms mono-molecular layer
8. Rate of adsorption increases with increase in pressure of adsorbate	8. Rate of adsorption usually decreases as the pressure increases.

5.4 Adsorption of Gases on Solids

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

1. Nature of gas or adsorbate :

The adsorption depends upon the nature of the gases adsorbed. The easily liquifiable gases such as HCl, NH_3, Cl_2 etc. are adsorbed more than the permanent gases such as H_2, N_2 and O_2.

The ease of liquefication of a gas depends upon its critical temperature. The critical temperature of a gas is the minimum temperature above which a gas cannot be liquefied however high the pressure may be applied. The higher the critical temperature, the more easily a gas is liquefied and hence more readily it will be adsorbed. For example, 1g of activated charcoal can adsorb the following amounts of gases.

Gas	$SO_2 >$	$NH_3 >$	$HCl >$	$CO_2 >$	$CH_4 >$	$CO >$	$N_2 >$	H_2
Critical temp. K	430	406	324	304	190	134	126	33
Amt. adsorbed (in ml.)	380	180	72	48	16.2	9.3	8.0	4.5

(Ease of liquefication decreases →)

However, in the case of chemical adsorption, a gas gets adsorbed on the solid only if it forms chemical bonds.

2. Nature of adsorbent :

Since physical adsorption is non specific in nature, every gas will get adsorbed on the surface of any solid to a lesser or greater extent. Specific area of an adsorbing solid is the surface area available for adsorption per gram of the adsorbent. Greater the specific area of the solid greater would be its adsorbent power.

The adsorbent power of various metals is as follows :

Colloid Pd > Pt > Au > Ni

3. Effect of pressure :

The extent of adsorption of a gas per unit mass of adsorbent depends upon the pressure of the gas. The relation between the amount of substance adsorbed by the adsorbent and the equilibrium gas pressure (or concentration for solutions) at constant temperature is called an **adsorption isotherm.** This may be expressed in the form of an equation or graphical curve (or plot).

The extent of adsorption is usually expressed as $\frac{x}{m}$ where x is the mass of adsorbate and m is the mass of the adsorbent. The simplest type of adsorption is shown in Fig. 5.2.

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 take place simultaneously. At this pressure (p_s) the amount of gas adsorbed becomes equal to the amount of gas desorbed so that the extent of adsorption becomes constant even though the pressure is increased. This state is also called saturation state and p_s is called **saturation pressure.**

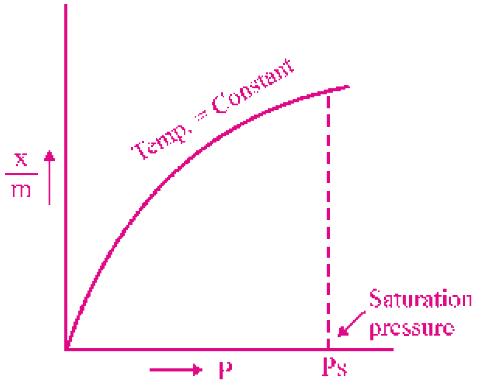
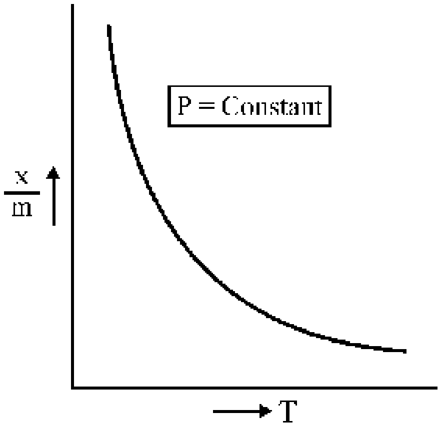


Fig. 5.2

4. Effect of Temperature :

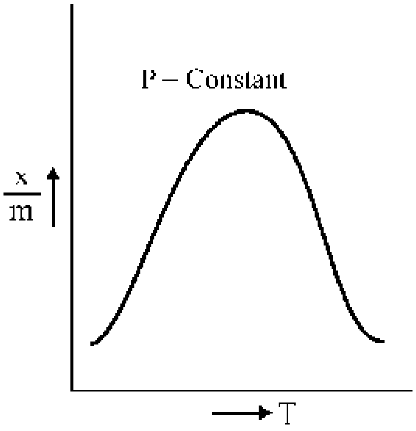
The process of adsorption is **exothermic.** Therefore, the reverse process i.e. desorption is endothermic. If the above equilibrium is subjected to increase in temperature, then according to Le-Chatelier's principle, with increase in temperature, the desorption will be favoured. Thus, the rate of adsorption will not be favoured by the increase in temperature. With the increase in temperature at constant pressure, the extent of adsorption (x/m) will decrease. The graph between extent of adsorption and temperature at constant pressure is called adsorption isobar. However, this is true for physical adsorption as shown in Fig. 5.3.



(Physical adsorption)

Fig. 5.3

In case of chemisorption, the adsorption initially increases with rise in temperature and then decreases as shown in Fig. 5.4. This behaviour is expected because like all chemical reactions, some activation energy is required for chemisorption. At low temperature, x/m is small. As temperature is increased, the molecules of the adsorbate gain energy and become equal to activation energy so that proper bonds are formed with the adsorbent molecules. Therefore, initially amount of gas absorbed increases with rise in temperature. Further increase of temprature will increase the energy of molecules which have already been adsorbed. This would increase the rate of desorption and therefore, decrease the extent of adsorption.



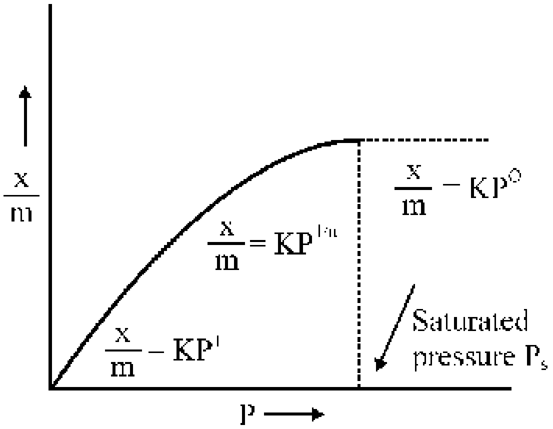
(Chemical adsorption)

Fig. 5.4

Adsorption Isotherm : The scientists have tried to explain the adsorption in terms of some empirical mathematical relations called adsorption isotherms. The most common type is discussed below:

Freundlich Adsorption Isotherms : The variation of extent of adsorption (x/m) with pressure (p) was given mathematically by Freundlich. Form the adsorption isotherm (fig. 5.5), The following observation can be easily made :

(i) At low pressure- The graph is straight line which indicates that $\left(\frac{x}{m}\right)$ is directly proportional to the pressure.



Adsorption isotherm

Fig. 5.5

$$\frac{x}{m} \propto P^1 , \frac{x}{m} = kP \qquad ...(1)$$

Where K = Constant

(ii) At high pressure: The graph becomes almost constant which means that $\frac{x}{m}$ becomes independent of pressure. This may be expressed as :

$$\frac{x}{m} \propto P^o \text{ or } \frac{x}{m} \propto KP^o \qquad ...(2)$$

$P^o = 1$

$$p^o = 1 \quad \frac{x}{m} = K$$

(iii) Intermediate pressure: $\frac{x}{m}$ will depend upon the power of pressure which lies between 0 to 1 i.e. fractional power of pressure. This may be expressed as

$$\frac{x}{m} \propto P^{1/n}$$

$$\frac{x}{m} = KP^{1/n} \qquad ...(3)$$

Where n and k are constant which depends upon the nature of adsorbate on adsorbent. The above relationship is also called **Freundlich adsorption isotherms.**

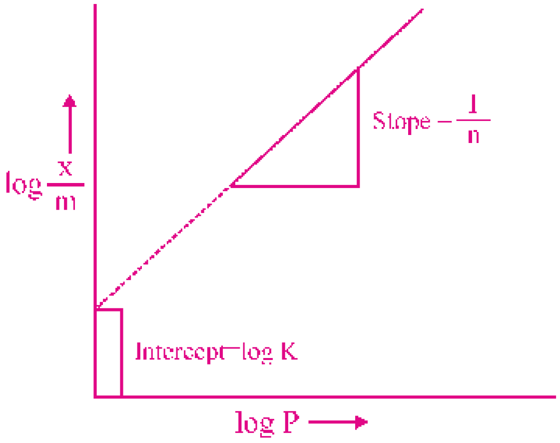


Fig. 5.6 : Graph between log x/m and log p

Taking logarithms on both side of eq. (3) we get

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log P \qquad ...(4)$$

Thus if we plot a graph between $\log \frac{x}{m}$ and log P, a straight line will be obtained. The slop of the line (fig. 5.6) is equal to $\frac{1}{n}$ and the intercept is equal to logK.

5.6 Adsorption from Solution Phase

The process of adsorption can take place from solutions also. It is observed that solid adsorbents adsorb certain solutes from solution in preference to other solutes and solvents. For example, animal charcoal decolourises impure sugar solution by adsorbing colouring dye in preference to sugar molecules. The Freundlich's adsorption isotherms obtained for the adsorption of gases on the surface of solid adsorbents have also been found to be applicable to the adsorption of solutes from the solutions. Here, the equilibrium pressure in the adsorption of gases has been replaced by the equilibrium concentrations (c) of the adsorbates in solution. The adsorption isotherm may be represented as:

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

Taking logarithms, Eq. (i) becomes

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

where x = quantity of adsorbate
m = mass of solid adsorbent
c = concentration of solute in solution at equilibrium
n = constant
k = constant.

Constant k value depends on nature of solid, particle size, temperature, and nature of solute and solvent

5.7 Application of Adsorption

1. **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, CH_4 etc. in the atmosphere in the coal mines. Therefore, these masks help to purify the air for breathing.
2. **In dyeing of cloth :** Mordants such as alums are used in dyeing of cloth. They adsorb the dye particles which, otherwise, do not stick to the cloth.
3. **In dehumidizers :** Silica gel is commonly used to adsorb humidity or moisture from air. This is necessary for storage of delicate instruments which might otherwise be damaged by moisture.
4. **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 in contact with adsorbents like activated charcoal or fuller's earth. This method is commonly used in the manufacture of can sugar. The coloured sugar solution is treated with animal charcoal or activated charcoal.
5. **Heterogeneous catalysis :** The phenomenon of adsorption is useful in the heterogeneous catalysis. The metal such as Fe, Ni, Pt, Pd, etc. are used in the manufacturing processes such as Contact process, Haber process and the hydrogenation of oils. Its use is based upon the phenomenon of adsorption.
6. **In ion-exchange resins :** The organic polymers containing groups like -COOH, $-SO_3H$ and $-NH_2$ etc. possess the property of selective adsorption of ions from solutions. These are quite useful in the softening of water.
7. **In adsorption indicators :** Many adsorption indicators are being used in volumetric analysis, e.g. dyes such as eosin and fluorescein are used as adsorption indicators.
8. **In qualitative analysis :** Certain qualitative tests such as the lake test for the confirmation of Al^{3+} ions are based upon adsorption i.e. $Al(OH)_3$ has the capacity to adsorb the colour of blue litmus from the solution.
9. **Production of high vacuum :** The adsorption of air in liquid air helps to create a high vaccum in a vessel. This process is used in high vacuum instruments as Dewar flask for storage of liquid air or liquid hydrogen.

5.8 CATALYSIS

Berzelius in 1835 observed that there are many substances which change the speed of reactions.

Example: Potassium chlorate is easily dissociated at low temperature in presence of magnese dioxide.

$$2KClO_3 \xrightarrow[600^\circ C]{\text{In absence of catalyst}} 2KCl + 3O_2$$

$$2KClO_3 \xrightarrow[338^\circ C]{\text{Catalyst } MnO_2} 2KCl + 3O_2$$

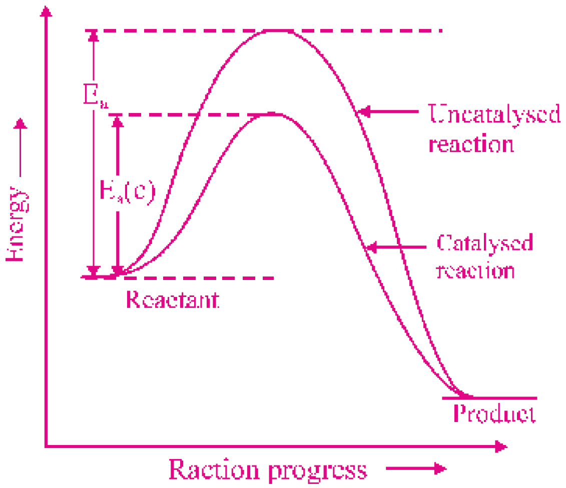
Thus a substance which changes the speed of a reaction without being used up itself is called a catalyst. The phenomenon of increasing the rate of reaction by the use of catalyst is called catalysis.

Types of Catalyst

1. Positive catalyst:

Substance which increases the rate of chemical reaction is called positive catalyst.

Example: In the absence of catalyst the activation energy required for the decomposition of H_2O_2 is 76KJ/mole. but only 57KJ i.e. activation energy is required in presence of colloid pt. Thus catalyst changes the mechanism of chemical reactions and decreases the activation energy value.



2. Negative catalyst :

Substance which decreases the rate of chemical reaction is called negative catalyst.

Example :

(i) The decomposition of H_2O_2 in the presence of glycerol gets retarted.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

(ii) Sodium sulphite oxidised slowly in presence of ethyl alcohol

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

(iii) Tetra ethyl lead is added in petrol for reducing knocking.

3. Auto catalyst :

When a product formed in the chemical reaction itself act as a catalyst for the same reaction then it is known as auto catalyst.

Example:

(i) Hydrolysis of an ester is catalysed by the presence and formation of an acid.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

(ii) Mn^{+2} ion obtained from oxalic acid by acedified $KMnO_4$ work as auto catalyst and initiate the reaction which proceed slowly initially.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \rightarrow$$
$$K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

(iii) Induced catalyst :

When one reaction influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as induced catalysis. Example- Sodium arsenite solution is not oxidised by air. If, however air is passed through a mixture of the solution of sodium arsenite and sodium sulphite both of them undergoes simultaneous oxidation.

$$2Na_2SO_3 + O_2 \xrightarrow{\text{Fast}} 2Na_2SO_4$$

$$Na_3AsO_3 + O_2 \longrightarrow \text{No reaction}$$

$$Na_2SO_3 + Na_3AsO_3 + O_2 \rightarrow Na_2SO_4 + Na_3AsO_4$$

5.8.1 Classification of Catalysis :

1. Homogeneous catalysts :

When the catalyst is in the same phase as the reactants and products, it is called homogeneous catalyst. In these reactions, the catalysts, reactants and products are in the same phase and are called homogeneous catalytic reactions.

For example :

(i) In lead chamber process, SO_2 is oxidised to SO_3 in the presence of nitric oxide:

$$SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{NO(g)} SO_3(g)$$

(ii) Hydrolysis of an ester is catalysed by the presence of an acid:

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+(aq)}$$
$$CH_3COOH + C_2H_5OH$$

(iii) Hydrolysis of sucrose is catalysed by the presence of HCl:

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

(iv) Preparation of diethyl ether from ethyl alcohol using conc. H_2SO_4 at 413K.

$$2CH_3CH_2OH \xrightarrow[413K]{Conc.H_2SO_4}$$

$$\underset{\text{Diethyl ether}}{CH_3CH_2OCH_2CH_3} + H_2O$$

Mechanism of Homogeneous catalytic reactions

These reaction can be explained on the basis of intermediate compound formation. According to this theory, the catalyst combines with one of the reactants to form an intermediate. Intermediate compound being unstable combines with the other reactant to form the product.

For example: $A + B \longrightarrow AB$ is slow process. However in the presence of X(catalyst), the reaction becomes fast.

$$A + X \longrightarrow AX \quad \text{(Intermediate)}$$

$$AX + B \longrightarrow AB + X$$

Example:

(i) In reaction $SO_2 + \frac{1}{2}O_2 \xrightarrow{NO} SO_3$

$$\underset{\text{Catalyst}}{NO_2} + \frac{1}{2}O_2 \longrightarrow \underset{\text{Intermediate}}{NO_2} \quad \text{Fast}$$

$$NO_2 + SO_2 \longrightarrow SO_3 + \underset{\substack{\text{Regenerated}\\ \text{Catalyst}}}{NO}$$

(ii) $2C_2H_5OH \xrightarrow{H_2SO_4} C_2H_5OC_2H_5 + H_2O$

(William continuous etherification)

$$C_2H_5OH + H_2SO_4 \longrightarrow \underset{\text{Intermidate}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 + HOC_2H_5 \longrightarrow$$

$$C_2H_5OC_2H_5 + \underset{\substack{\text{Regenerated}\\ \text{Catalyst}}}{H_2SO_4}$$

Intermidate compound theory unable to explain the following factors :

(i) Mechanism of Heterogenous catalysis.

(ii) Mechanism of Cocatalyst and inhibitors.

(iii) Importance of active centres.

2. Heterogeneous catalysts :

When the catalyst is in different phase than the reactants, it is called hetergeneous catalyst. Such reactions are called heterogeneous catalyst reactions. These are very important reactions in industries. For example,

(i) Manufacture of HNO_3 by Ostwald's Method

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

(ii) Hydrogenation of oils

$$\text{Vegetable oil } (\ell) + H_2(g) \xrightarrow{Ni(s)} \text{Vegetable fats}$$

Mechanism of heterogeneous catalytic reaction:

The heterogeneous catalysis is a surface phenomenon. It involves the following steps:

(i) Diffusion of the reactants at the surface of the catalyst.

(ii) Adsorption of the molecules of the reactant at the active sites.

(iii) Occurrence of the chemical reactions on the surface of the catalyst.

(iv) Desorption of product molecules from the surface.

(v) Diffusion of products away from the surface of catalyst.

The role of heterogeneous catalysts can be explained in terms of adsorption of reactants on the surface of the catalyst. The adsorption helps the reaction in the following ways:

1. Adsorption increases the concentration of reactants on the surface of the catalyst. Due to increased concentration of the reactants, the reactions proceed rapidly.
2. Adsorbed molecules get dissociated to form active species like free radicals which react faster than molecules.
3. The adsorbed molecules are not free to move about and therefore, they collide with other molecules on the surfaces.
4. The heat of adsorption evolved acts as energy of activation for the reaction (chemisorption).

5.8.2 Enzyme Catalysis

Large number of organic reactions are taking place in the body of animals and plants to maintain the life processes. These reactions are generally very slow and are remarkably catalysed by organic compounds known as enzymes. These are also called biological catalysts and are produced by the living cells in our bodies.

Thus, enzymes are biological catalysts produced by living cells which catalyze the biochemical reactions in living organisms.

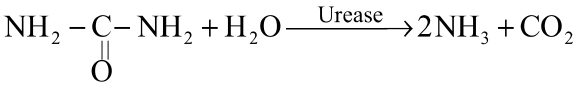
Chemically all enzymes are proteins. Without enzymes, the living processes would be very slow to sustain life. For example, without the presence of enzymes in our digestive tract, it would take about 50 years to digest a single meal. About 3000 enzymes have been indentified. The enzymes differ from other types of catalysts in being highly selective and specific.

Some common examples of enzymes catalysis reaction are:

(i) Normal conversion of glucose into ethanol by zymase (enzyme) present in yeast

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2 \uparrow$$

(ii) Hydrolysis of urea (NH_2CONH_2) by urease (enzyme) present in soya bean.



$$NH_2-\underset{\underset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$$

(iii) Hydrolysis of starch into maltose by diastase (enzyme)

$$2(C_6H_{10}O_5)_n + H_2O \xrightarrow{\text{Diastase}} C_{12}H_{22}O_{11}\text{Maltose}$$

(iv) $C_2H_5OH + O_2 \xrightarrow[\text{Actie}]{\text{Micodema}} CH_3COOH + H_2O$

(v) Dissociation of sucrose into glucose and fructose by invertase enzyme.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Gulcose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(vi) $\text{Protein} \xrightarrow{\text{Pepsin}} \text{Amino acid}$

(vii) $\text{Starch} \xrightarrow{\text{Amylase}} \text{Glucose}$

(viii) $\text{Starch} \xrightarrow{\text{Tyline}} \text{Sugar}$

(ix) $\text{Milk} \xrightarrow[\text{Basily}]{\text{Lactic}} \text{Curd}$

Characteristics of Enzyme :

The important characteristics of enzymes catalyst are:

1. **High efficiency:** Enzyme catalysts increase the speed of reactions up to 10 million times as compared to the uncatalysed reactions.
2. **Extremely small quantities:** Extremely small quantities of enzyme catalysts-as small as millionth of a mole-can increase the rate of reaction by factors of 10^3 to 10^6.
3. **Specificity:** The enzyme catalysts are highly specific in nature. Almost every biochemical reaction is controlled by its own specific enzymes. For example, Maltose catalyses the hydrolysis of maltose. No other enzyme can catalyse its hydrolysis.
4. **Optimum temperature and pH:** The enzyme catalysts are active at moderate temperature (about 37ºC) and pH (around 7).
5. **Control of activity of enzymes:** The action of enzyme catalytic reactions are controlled by various mechanisms and are inhibited by various organic and inorganic molecules.
6. The activity of most enzyme catalysts is closely regulated.
7. Catalytic activity of enzymes is greatly enhanced by the presence of activators or coenzymes. Activators are metal ions (Na^+, Mn^{2+}, Co^{2+}, Cu^{2+} etc.) which get weakly bonded to enzyme molecules and therefore, promote their catalytic action. In some cases, most active enzymes are associated with some non-protein components required for their activity. These are generally metal

ions or small organic molecules and are collectively called coenzymes. The common metal ions are Zn, Mg, Mn, Fe, Cu, Co, Mo, K and Na. In some cases, the enzyme activity can be reduced or inhibited by the presence of certain compounds known as enzyme inhibitors.

5.8.3 Mechanism of enzyme catalysed reaction

It proceeds into folowing steps :-

(i) Formation of complex by the addition enzyme and substrate-

E+S → ES where ES known Enzyme-substrate complex.

(ii) Formation of product in complex structure. ES → EP where EP known as Enzyme-product complex.

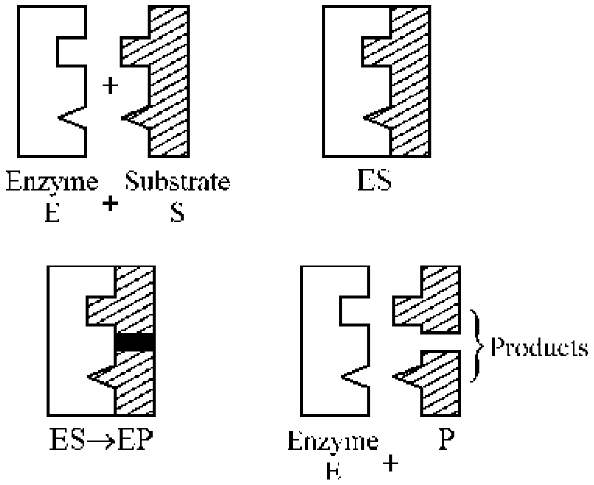


Fig. 5.8

(iii) Formation of product EP → E+P the shape of active site on a given enzyme is such that only a specific substrate can bind with it. This specific binding of the active site with the substrate results in the formation of product.

5.8.3 Shape selective catalysis by zeolites

Zeolites are microporous aluminosilicates of the general formula $M_{x/h}$ $[(AlO_2)_x (SiO_2)y]. mH_2O$ where n is the valency of the metal cation, M^{n+}. They are three dimensional network silicates in which some silicon atoms are replaced by aluminium atoms. They are found in nature as such and are also synthesised in the laboratories. Zeolites to be used as catalysts are heated in vaccum so as to push out molecules of hydration. The loss of molecules of hydration causes cavities of molecular dimensions in the network structure and makes it porous. The pore size in zeolites is generally in range 260-740 pm. The catalytic activity of zeolites depend upon the size of cavities (cages) or pores (apertures) present in them. Pores can trap only those molecules whose size is small enough to enter or leave the cavities. Bigger or larger molecules cannot enter the cavities. Thus, zeolites can act as molecular sieves or selective absorbents. Depending upon the sizes of reactant and product molecular relative to the sizes of cavities and apertures of the zeolite, reactions proceed in a specific manner. For example, alcohols are converted into gasoline using a zeolite catalyst ZSM-5 (Zeolite Sieve of Molecular porosity-5). ZSM-5 has the formula.

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

Other examples are : Permutit $Na_2Al_2Si_2O_8$ xH_2O, Irrinoite $Na_2K_2Ca\,Mg(AlO_2)_2(SiO_2)_2 6H_2O$

5.9 COLLOIDAL STATE

Thomas Graham in 1861 observed that certain solutes such as starch, gelatin etc. could not pass through the pherchment membrane while the ordinary solutes such sodium chloride, urea, sugar etc. easily do so. Graham called the former solutes as colloids (Greek, kolla meaning glue) while the latter were called crystalloids. However, the above classification of solutes into crystalloids and colloids proved unsatisfactory because a particular substance would be crystalloid in one solvent and a colloidal in the other. For example in aqueous solution, NaCl is a crystalloid, while in benzene, it behaves as colloid. Similarly, soap is a typical colloid in water but it acts as a crystalloid in alcohol. Further studies of the behaviour of these solutes have shown that the nature of the substance whether colloid or crystalloid depends upon the particle size. When the size of the particles is between 10^{-9}m (1nm) to 10^{-7}m (100nm), it behaves like a colloid and in case, it is less than this range, it gives the characteristics of crystalloid. Thus, colloid is not a substances but it is a state of a substance which depends upon the molecular size.

Three Types of Solutions

On the basis of particles size of the substance, the solution may be divided into three types. These are:

1. True solutions,
2. Suspensions,
3. Colloidal solutions

1. **True solutions** is a homogeneous solution which contains small solute particles (molecules or ions) dispersed throughout a solvent. For example, the Solution of sodium chloride in water. The particle size is less than 1 nm. The particles of a solute in a true solution are invisible even under microscope and its particles can pass through ordinary filter paper as well as through animal membrane.
2. **Suspensions** is a heterogeneous mixture which contains small insoluble particles. The particle size is more than 100 nm. For example, dirt particles in water. The particles of a suspension may not be visible to the naked eye but are visible under a microscope. The particles of a suspension can neither pass through an ordinary filter paper nor through animal membrane.
3. **Colloidal solutions** is a heterogeneous solution which contains particles of intermediate size. For example, milk. The particles of a colloidal solution have diameters between 1 to 100 nm. Such particles cannot be normally seen with a naked eye. However, light reflected by them can be seen under an ultra-microscope. The particles of a colloidal solution can pass through ordinary filter paper but not through animal membrane.

Thus, colloidal solutions are intermediate between true solutions and suspensions. In other words, the size of dispersed particles in colloidal solutions is more than that of solute particles in the true solution and smaller than that of a suspension.

Table 5.3 : Distinction among true solution, colloid solution and susension

S.No.	Property	True Solution	Colloid Solution	Suspens ion
1.	Nature	Homogenous	Heterogenous	Hetrogenous
2.	Phase number	1	2	2
3.	Phase size	$<10^{-7}$cm	10^{-5}–10^{-7}cm	$> 10^{-5}$cm
4.	Appearance	Transparent	Generally transparent	Opaqve
5.	Gravititational effect	Negligible	Negligible	May Show
6.	Adsorbtion	Negligible	highly adsorbed	Negligible
7.	Separation by			
	(i) Ordinary filteration	Not possible	Not possible	Possible
	(ii) Ultra filteration	Not possible	Possible	Possible
8.	Brownian movement	does not show	may show	Negligible
9.	Tyndall effect	does not show	may show	Does not show
10.	Diffusion	Rapidly	Slowly	Not Possible
11.	Elective field	Cation and anion moves towards opposite charged plates	All particles cogulated on the same plate	Does not Show
12.	Visibility	Transparent	Generally Transparent	Unvisible

5.9.1 Phases of Colloids

We have learnt that a colloidal solution is of heterogeneous nature. It consists of two phases i.e. a dispersed phase and a dispersion medium.

1. **Dispersed Phase :** It is the component present in small proportion and is just like a solute in a solution. For example, in the colloidal solution of silver in water, the farmer acts as a dispersed phase.

2. **Dispersion Medium :** It is generally component present in excess and is just like a solvent in a solution. In the above example, water acts as a dispersion medium.

Depending upon the nature of the dispersion medium, colloidal solutions are sometimes given specific names. For example,

Dispersion medium	Name of colloidal solution
Water	Hydrosols
Alcohol	Alcosols
Benzene	Benzosols
Air	Aerosols

On the basis of physical state of dispersed phase and dispersion medium there are 8 types of colloidal solutions

Table 5.4

Sr. N.	Disper-sion phase	Disper-sion medium	Colloid system	Example
1.	Gas	Liquid	Foam	Soap leather, whipped cream, soda water
2.	Gas	Solid	Solid foam rubber	Pumice stone, foam
3.	Liquid	Gas	Aerosol of liquid	Mist, Fog, cloud insecticide spray
4.	Liquid	Liquid	Imulsion	Milk, emulsified oils
5.	Liquid	Solid	Gel	Jelly, butter, cheese, curd
6.	Solid	Gas	Aero sol of solid	Smoke, dust, storm, haze
7.	Solid	Liquid	Sol	Gold sol, Starch dispersed in water, paints
8.	Solid	Solid	Solid sol	Alloys, gemstones, ruby glass

5.9.2 Classification of Colloids

1. On the basis of interaction between phases :

Depending upon the nature of interactions betweens dispersed phase and the dispersion medium, the colloidal solutions can be classified into two types as: lyophilic and lyophobic sols.

(i) Lyophilic collloids:

The colloidal solutions in which the particles of the dispersed phase have a great affinity (or love) for the dispersion medium, are called lyophilic colloids. These solutions are easily formed and the lyophilic colloids are reversible in nature. In case water acts as the dispersion medium, the lyophilic colloid is called hydrophilic colloid.

The common examples of lyophilic colloids are glue, gelatin, starch, proteins, rubber, etc.

(ii) Lyophobic colloids:

The colloidal solutions in which there is no affinity (or love rather they have hatred) between particles of the dispersed phase and the dispersion medium are called lyophobic colloids.

Such solutions are formed with difficulty. These are irreversible in nature. In case, the dispersion medium is water, the lyophobic sol is called hydrophobic colloid. For example, the solution of metals like Ag and Au, hydroxides like $Al(OH)_3$, $Fe(OH)_3$, metal sulphides like As_2S_3 etc.

Table 5.4 : Distinction between lyophilic and lyophobic colloids.

S.No.	Property	Lyophilic colloids	Lyophobic colloids
1.	Ease of preparation	These are easily formed by direct mixing.	These are formed only by special methods
2.	Reversible or irreversible nature	These are reversible in nature.	These are irreversible in nature.
3.	Particles nature	The particles of colloids are true molecules and are bid in size.	The particles are aggregates of many molecules.
4.	Visibility	The particles are not easily visible even under ultramicroscope.	The particles are easily detected under ultramicroscope.

S.No.	Property	Lyophilic colloids	Lyophobic colloids
5.	Stability	These are very stable.	These are unstable and require traces of stabilizers
6.	Action of electrolytes	The addition of small amount of electrolytes causes precipitation (called coagulation) of colloidal solution.	The addition of small amount of electrolytes has less effect. Larger quantities of electrolytes are required to cause coagulation.
7.	Charge on particles	The particles do not carry any charge the particles may migrate in any direction or even not under the influence of an electric field.	The particles move in a specific direction i.e., either towards anode or cathode depending upon their charge.
8.	Hydration	The particles of colloids are heavily hydrated due to the attraction for the solvent.	The particles of colloids are not appreciably hydrated due to the hatred for the solvent.
9.	Viscosity	The viscosity and surface tension of the sols are much higher than that of dispersion medium.	The viscosity and surface tension are nearly the same as that of the dispersion medium.
10.	Tyndall effect	They do not show Tyndall effect.	They show Tyndall effect.

2. On the basis of particles of dispersed phase

Depending upon the molecular size, the colloids can be classified as:

(i) **Multimolucular Colloid :** When on dissolution, atoms or smaller molecules of substance s (having diameter less than 1nm) aggregate together to form particles of colloidal dimensions, the particles thus formed are called multimolecular colloids. Therefore, in these sols the dispersed phase consists of aggregates of atoms or molecules with molecular size less than 1nm. For example, sols of gold atoms and sulphur (S_8) molecules. In these colloids, the particles are held together by Van der Waals forces.

(ii) **Macromolecular Colloid :** These are the substances having big size molecules (called macro molecules) which on dissolution form solution in which the dispersed phase particles have size in the colloidal range. Such substances are called macromolecular colloids. These macromolecules forming the dispersed phase are generally polymers having very high molecular masses. Naturally occurring macromolecules are starch, cellulose, proteins, enzymes, gelatin, etc. Artificial macromolecules are synthetic polymers such as nylon, polythene, plastics, polystyrene, etc. Since these macromolecules have large sizes comparable to those of colloidal particles, the solutions of such molecules are called macromolecular colloidal solutions. Their solutions are quite stable and resemble true solution in many respects. Thus, the common examples of macromolecular colloids are starch, cellulose, proteins, plastics, etc.

(iii) **Associated colloids:** These are the substances which when dissolved in a medium behave as normal electrolytes at low concentration but behave as colloidal particles at higher concentration. For example, in aqueous solution, soap (sodium stearate) ionises as:

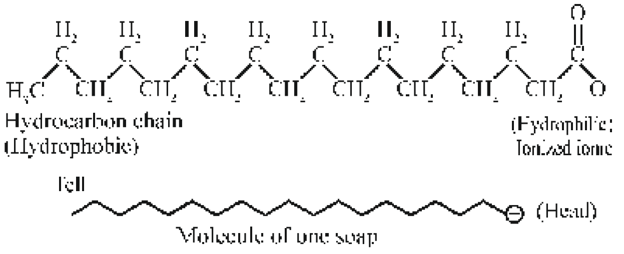
$$C_{17}H_{35}COONa \rightleftharpoons \underset{\text{Stearate ion}}{C_{17}H_{35}COO^-} + Na^-$$

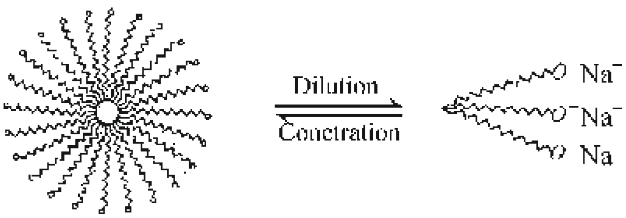
In concentrated solution, these ions get associated to form an aggregate of colloidal size.

The colloidal behaviour of such substances is due to the formation of aggregates or clusters in solutions. Such aggregated particles are called micelles. Thus micelles are the cluster or aggregated particles formed by association of colloids in solution. The formation of micelles take place above certain concentration called critical micellization concentration (CMC). For example, CMC for soaps is 10^{-3} mol L^{-1}. Different micelles have different values CMC.

Mechanism of Micelle Formation :

Micelle are generally formed by the aggregation of several ions or molecules with lyophobic as well as lyophilic parts. These molecules or ions are called surface active molecules. For example in soap sodium stereate the stearate ions associate to form ionic micelles of colloidal size. It has long hydrocarbon part of $C_{17}H_{35}$ radical which is lyophobic end and COO^- part which is lyophilic. The dirt is held on the surface of clothes by the oil or grease which is present there. Since oil or grease are not soluble in water, therefore the diot particles cannot be removed by simply washing the clothes with water. When soap is applied, the non polar alkyl group dissolves in oil droplets while the polar groups remain dissolved in water. In this way each oil droplet is surrounded by negative charge. This negatively charged oil droplets cannot coalesce and a stable emulsion is formed. These oil droplets (containing dirt particles) can be washed away with water along with dirt particles.





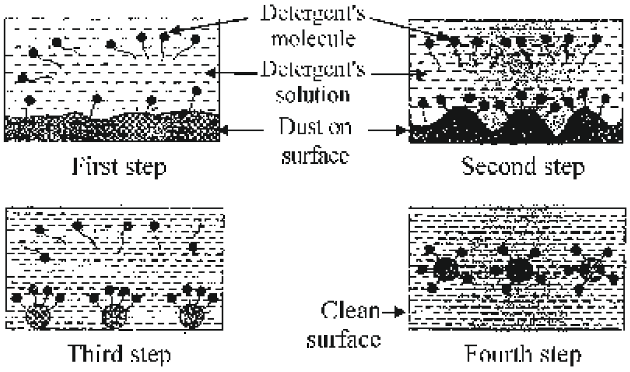


Fig. 5.9

Methods of Preparation of colloidal solutions

General Methods of Preparation of sols

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

Preparation of Lyophilic Colloids

The lyophilic colloids have strong affinity between particles of dispersed phase and dispersion medium. Therefore, these colloidal solutions are readily formed by simply mixing the dispersed phase and dispersion medium under ordinary conditions. For example, the substances like gelatin, gum, etc. pass readily into water to give colloidal solution. They are reversible in nature because these can be precipitated and directly converted into colloidal state.

Preparation of Lyophobic Colloids

Lyophobic sols can be prepared by mainly two types of methods:

1. Dispersion methods
2. Condensation methods

1. Dispersion methods:

(i) Mechanical dispersion:

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

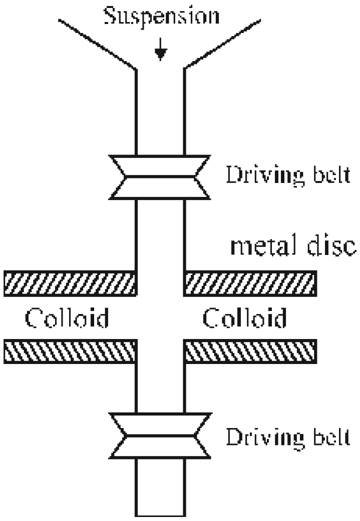


Fig. 5.10 : Colloidal Mill

2. Electrical dispersion

Bredig's arc method is a method of preparation of colloidal solution, of metals such as gold, silver or platinum. This method consists of both dispersion and condensation. An arc is struck between electrodes, under the surface of water containing some stabilizing agent such as traces of KOH (potassium hydroxide). The intense heat of the arc vaporizes some of the metal which then condenses under cold water. The water is kept cold as an ice bath.The Colloidal particles prepared is stabilised by adding a small amount of KOH to it.

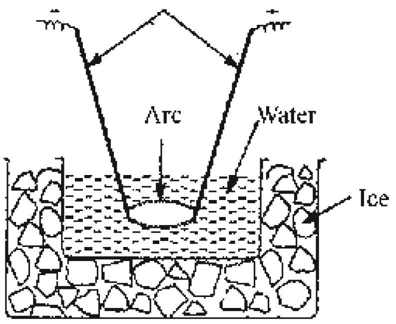


Fig. 5.11 : Bredg's arc method

Condensation methods

(1) Reduction: The colloidal solutions of metals Au, Ag, Pt are obtained by reduction of their compounds. Formaldehyde and tannic acid are used as reducing agents.

$$2AuCl_3 + 3HCHO + 3HOH \longrightarrow \underset{\text{Colloid}}{2Au} + 3HCOOH + 6HCl$$

$$\underset{\text{Chlor auoric acid}}{2HAuCl_4} + 3H_2O_2 \longrightarrow \underset{\text{Colloid}}{2Au} + 8HCl + 3O_2$$

$$PtCl_2 + HCHO + HOH \longrightarrow \underset{\text{Colloid}}{Pt} + HCOOH + 2HCl$$

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

$$AgCl + \text{Tannic acid} \longrightarrow \text{Ag Colloid}$$

The gold Sol, thus prepared, has a purple colour and is called purple of cassius. In gold sol and silver sol gelatine and egg yolk added for stabilization.

(2) **Oxidation:** The colloidal solution for sulphur, selenium, iodine are obtained by this method.

$$2H_2S + SO_2 \longrightarrow \underset{\text{Colloid}}{3S} + 2H_2O$$

$$H_2S + 2HNO_3 \longrightarrow \underset{\text{Colloid}}{S} + 2NO_2 + 2H_2O$$

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + \underset{\text{Colloid}}{S} + H_2O$$

$$5HI + HIO_3 \longrightarrow \underset{\text{Colloid}}{3I_2} + 3H_2O$$

$$2H_2Se + O_2 \longrightarrow 2H_2O + \underset{\text{Colloid}}{Se}$$

(3) **Double decomposition:** These types of reactions is sued for the preparation of colloidal solution of insoluble salts.

Example:

$$Hg(CN)_2 + H_2S \longrightarrow \underset{\text{colloid}}{HgS} + 2HCN$$

$$As_2O_3 + 3H_2S \longrightarrow \underset{\text{colloid}}{As_2S_3} + 3H_2O$$

$$AgNO_3 + \underset{(x=Br,I)}{K-X} \longrightarrow \underset{\text{colloid}}{AgX} + KNO_3$$

$$CdO + H_2S \longrightarrow \underset{\text{colloid}}{CdS} + H_2O$$

(4) Hydrolysis: Colloidal solution of Ferric, Aluminium and chromium hydroxide are prepared when a concentrated solution of salts are added drop wise to hot water.

$$FeCl_3 + 3HOH \longrightarrow \underset{\text{red sol}}{Fe(OH)_3} + 3HCl$$

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

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

5.9.3 Purification of colloidal solutions

The colloidal solutions prepared by the above methods usually contain impurities especially electrolytes which can destabilize the sols. These impurities must be eliminated to make the colloidal solutions stable. The following methods are commonly used for the purification of colloidal solutions.

1. **Dialysis:** The process of separating the particles of colloids from those of crystalloids by means of diffusion through a suitable membrane is called dialysis. Its principle is based upon the fact that colloidal particles cannot pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it. The colloidal solution is taken in a bag made of cellophane or parchment. The bag is suspended in fresh water. The impurities slowly diffuse out of the bag leaving behind pure colloidal solution. The distilled water is changed frequently to avoid accumulation of the crystalloids otherwise they may start diffusing back into the bag, Dialysis can be used for removing HCl from the ferric hydroxide sol. The method is shown in Fig. 5.12.

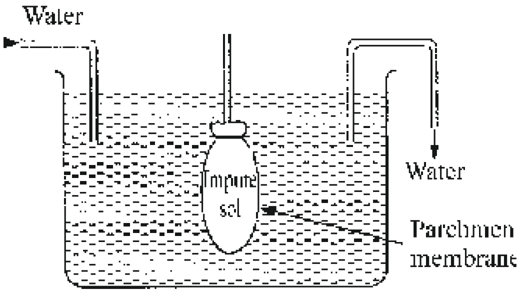


Fig. 5.12 : Dialysis process for removal of soluble impurities from sol

2. **Electro Dialysis–** The ordinary process of dialysis is slow. To increase the process of purification, the dialysis is carried out by applying electric field. This process is called electrodialysis and is shown in Fig. 5.13

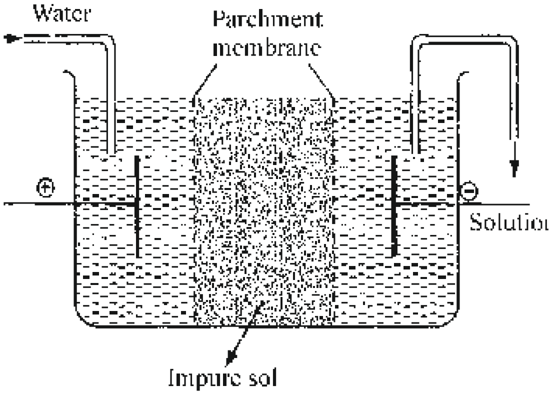


Fig. 5.13 : Electro Dialysis process

3. **Ultramicrofilteration–** It is the process of removing the impurities form the colloidal solution by passing it through graded filter papers called ultra-filter papers, These filter paper are made from ordinary filter papers by impregnating them with colloidal solutions. As a result, the size of the pores gets reduced. These filter papers allow the ions and molecules of the impurities to pass but retain colloidal particles. Ordinary filter papers cannot be used for the purpose since the colloidal particles can easily pass through the pores of these papers.

5.9.4 Properties of colloidal solutions

(A) Physical properties

1. **Heterogeneous nature:** Colloidal system is of two phases: (a) dispersed phase and (b) dispersion medium. In a colloidal solution, each particle is contained within its own boundary surfaces which separate it from the dispersion medium.
2. **Stable nature:** The colloidal solutions are quite stable. Their particles are in a state of motion and do not settle down at the bottom of the container. However, particles of certain colloidal sols, which have comparatively large size may settle down but very slowly.
3. **Surface Area:** The surface area of dispersed phase particles in colloidal solution is high enough so these acts as a best adsorbents and used as effective catalysts.
4. **Colour:** The size of colloidal particles present in the solution determines the colour of the colloidal dispersion. Larger the size of the particles longer will be the wavelengths of light being absorbed and hence these particles conduct small wavelengths. **Example:** Silver sol colour is yellow-orange when particle size is 6×10^{-5} mm and orange-red when particle size is 9×10^{-5}mm.
5. **Sedimentation:** The colloidal particles settle down under the influence if gravity at a very slow rate. This phenomenon is called sedimentation and is used to determine the molecular mass of macromolecules.

(b) Mechanical Properties

Brownain movement: Robert Brown, a botanist discovered in 1828 that pollan grains placed in water do not remain at rest but move about continuously and randomly. later or, this phenomenon was observed in case of colloidal particles when they were seen under the ultramicroscope. The particles were see to be in constant motion in Zig-Zag path in all possible direction (fig. 5.14). This Zig-Zag motion of colloidal particles called Brownian movement.

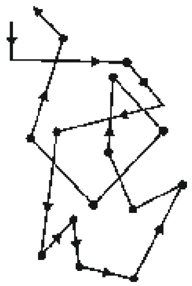


Fig. 5.14 : Brownian movement of colloidal particles

3. Optical properties–

Tyndall effect– Tyndall effect when a strong beam of light is passed through a true solution placed in a beaker, in a dark room, the path of the light does not become visible. However, if the light is passed through a sol, placed in the same room, the path of the light becomes visible when viewed form a direction at right angle to that of the incident beam.

This phenomenon was studied for the first time by Tyndall and therefore, it is called Tyndall effect. The cause of Tyndall effect is the scattering of light by the colloidal particles i.e. these particles first absorb the incident light and then a part of it gets scattered by them. Since the intensity of the scattered light is at right angles to the plane of the incident light, the path becomes visible only when see in that direction.

The particles in true solution are too small in size to cause any scattering i.e. the Tyndall effect is not observed in true solutions. Thus, the phenomenon of scattering of light by colloidal particles as a result of which the path of the beam becomes visible is called Tyndall effect. The illuminated path of the beam is called Tyndall cone.

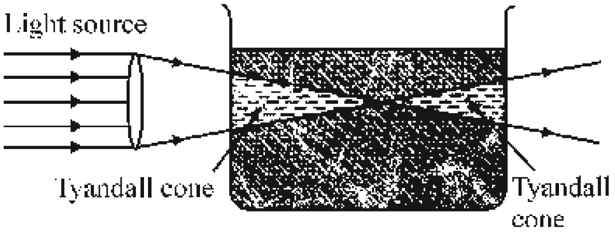


Fig. 5.15 : Tyndall effect

Example: Blue colour of the sky is due to the scattering of light by colloidal dust particles present in the air (Tyndall effect)

4. Electrical properties–

The particles of the colloidal solution are electrically charged and carry same type of charge; either positive or negative. 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. Some common positively charged and negatively charged colloids are given below in Table 5.6.

Table 5.6 : Colloidal Sol of positive and Negative charged colloid particles.

Negative Charged Colloid Sol	Positive Charged Colloid Sol
• Metals like Au, Ag, Cu, Pt, etc.	• Hydrolyzed mettalic compound e.g. $Al_2O_3.xH_2O$, $Fe_2O_3.xH_2O$ or $Al(OH)_3$ & $Fe(OH)_3$
• Metal sulphide e.g. CdS, As_2S_3,Sb_2S_3, etc.	• Oxide like TiO_2
• Starch, gelatin	• Basic Dye like methylene blue
• Silisilic acid, send.	• Himoglobien (Blood)
• Acid dyes e.g. iosin, congo red	

Origin of charge on colloids:

The reasons for the origin of electrical charge on colloidal particles are given below:

(i) Frictional electrification: The rubbing of colloidal particles with molecules of dispersion medium leads to appearance of electrical charges on colloidal particles.

(ii) Dissociation of surface molecules: Soaps expel alkali ions to acquire a negative charge. Dye particles can dissociate to furnish positive or negative ions in the solution according to their composition.

(iii) Preferential adsorption of ions from solutions: An ionic colloid adsorbs ions common to its own lattice structure:

Example:

(a) $Fe(OH)_3$ sol is prepared by hydrolysis of $FeCl_3$ by hot water, there is adsorption of Fe^{3+} ions and particles acquire positive charge

$$FeCl_3 \rightleftharpoons Fe^{3+} + 3Cl^-$$

$$Fe(OH)_3 + Fe^{3+} \rightarrow \underset{\text{(+) Colloid}}{Fe(OH)_3 \mid Fe^{3+}}$$

$$AgI + Ag^+ \rightarrow \underset{\text{(+) colloid}}{AgI \mid Ag^+}$$

(b) by using excess of $AgNO_3$ solution the sol adsorbs Ag^+ ions and become positively charged.

But AgI particles can adsorbs I^- ions if excess of KI is used its preparation

$$AgNO_3(aq.) + \underset{\text{excess}}{KI(aq.)} \rightarrow \underset{\text{(−) colloid}}{AgI \mid I^-}$$

(c) As_2S_3 sol prepared by the double decomposition of As_2O_3 and H_2S gas has negative charge because it adsorbs S^{-2} ions on its surface from the solution

$$As_2O_3 + 3H_2S \rightarrow \underset{\text{(−) colloid}}{As_2S_3 \mid S^{2-}} + 3H_2O$$

(d) $Al(OH)_3$ sol prepared by the hydrolysis of $AlCl_3$ has positive charge because it adsorbs Al^{3+} ions on its surface from the solution

$$Al(OH)_3 + AlCl_3 \rightarrow \underset{\text{(+) colloid}}{[Al(OH)_3] \mid Al^{3+}} + 3Cl^-$$

Adsorbed ions on the surface of sol particles are stable and in form of electrical level. This stable level is known as primary electrical level.

Other ions present in solution formed mobile second electrical level. The total charges present in primary and secondary level and equal but opposite.

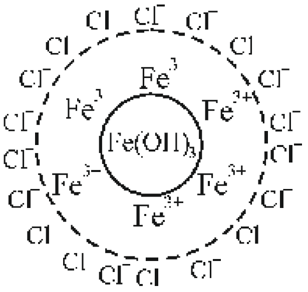


Fig. 5.16

(4) Electrophoresis:

The existence of the electrical charge can be shown by the process of 'Electrophoresis'. It involves the movement of colloidal particles towards one or the other electrode when placed under the influence of an electric field. The movement of colloidal particles under the influence of an electric field is called Electrophoresis.

As soon as the colloidal particles reach the oppositely charged electrode, they gat neutralized and coagulated. Electrophoresis can be used to find out the nature of the charge that the colloidal particles carry.

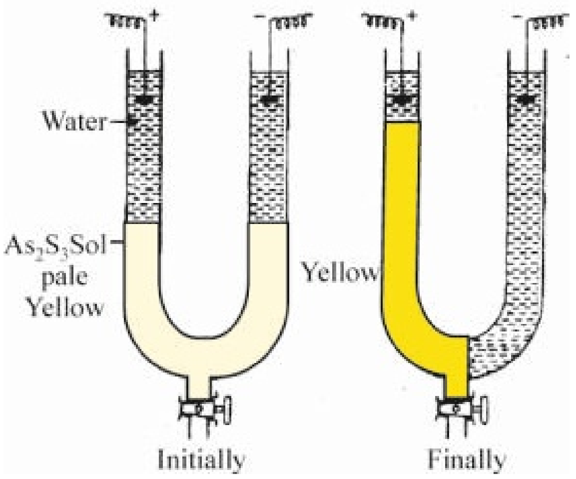


Fig. 5.17 : Electrophoresis

5. Coagulation of Colloidal Solutions

The precipitation of colloid through induced aggregation by the addition of some suitable electroly is called coagulation of colloidal solutions can be achieved by the following methods.

(i) **By repeated dialysis:** The stability of colloidal sol is due to the presence of a small amount of electrolyte. If the electrolyte is completely removed by repeated dialysis, the sol will get coagulated.

(ii) **By adding electrolyte:** The particles of the dispersed phase i.e. colloids bear some charge. When an electrolyte is added to the sol, the colloidal particles take up ions carrying opposite charge from the electrolyte. As a result, their charge gets neutralized and this causes the uncharged particles to come closer and to get coagulated or precipitated. For example, if $BaCl_2$ solution is added to AS_2S_3 sol, the Ba^{2+} ions are attracted by the negatively charged sol particles and their charge gets neutralized. This leads to coagulation.

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$$

$$\underset{\text{negative sol particles}}{[As_2S_3]S^{2-}} + Ba^{2+} \longrightarrow \underset{\text{nautral particles}}{[As_2S_3]S^{2-} \mid Ba^{2+}}$$

Hardy Schulze rule: The coagulation capacity of different electrolytes is different. It depends upon the valency of the active ion or called flocculating ion, which is the ion carrying charge opposite to the charge on the colloidal particles. According to Hardy Schulze rule, greater the valency of the active ion or flocculating ion, greater will be its coagulating power.

Thus, according to Hardy Schulze rule:

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

(ii) Coagulating power of an electrolyte is directly proportional to the valency of the active ions (ions causing coagulation). For example, to coagulate negative sol of As_2,S_3, the coagulating power of different cations has been found to decrease in the order as:

$$Sn^{4+} > Al^{3+} > Ba^{2+} > Na^+$$

Similarly, to coagulate a positive sol such as $Fe(OH)_3$, the coagulating power of different anions has been found to decrease in the order:

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$$

The minimum concentration of an electrolyte which is required to cause the coagulation or flocculation of a sol is known as flocculation value. It is usually expressed as millimoles per litre. For

$$\text{Flocculation value} = \frac{\text{quantity of electrolyte} \times \text{Molarity}}{\text{Total volume}} \times 100$$

The flocculation values for the coagulation of negatively charged AS_2S_3 are given below:

Electrolyte	LiCl,	NaCl,	KCl,	$PbCl_2$,	$MgCl_2$,	$CaCl_2$,	$BaCl_2$	$AlCl_3$
Flocculation Value millmoles/litre	57.9,	52.9,	98.6,	38.5,	0.90,	0.83,	0.77,	0.085

5.9.5 Protection of colloids

Lyophobic sols such as those of metals like gold, silver etc., can be easily precipitated by the addition of a small amount of electrolytes. They can be prevented from coagulation by the previous addition of some stable lyophilic colloids like gelatin, albumin, etc. For example, if a small amount of gelatin is added to gold sol, it is not readily precipitated by the addition of sodium chloride. This process of protecting the lyophobic colloidal solutions from precipitation by the electrolytes due to the previous addition of some lyophilic colloid is called protection. The colloid which is added to prevent coagulation of the colloidal sol is called protecting colloid.

The protecting power of different protective (lyophilic) colloids is expressed in terms of gold number.

Gold number: The different protecting colloids differ in their protecting powers. Zsigmondy introduced a term called gold number to describe the protective power of different colloids. This is defined as the minimum amount of the protective colloid in milligrams required to just prevent the coagulation of a 10ml of a given gold sol when 1ml of a 10% solution of sodium chloride is added to it.

Gelating = 0.005 – 0.31, Egg. Albumin 0.15 – 0.25

Casine = 0.01 – 0.02, Arabic Gum = 0.15 – 0.25

Dextrin = 6.0 – 20.0, Starch = 20.0 – 25.0

The coagulation of gold sol is indicated by change in colour from red to blue. The gold numbers of a few protective colloids are as follows:

5.9.6 Emulsions:

Emulsions are colloidal solutions in which dispersed phase as well as dispersion medium are liquids. Emulsions can be bradly classified into two types.

(i) **Water in oil emulsions:** In this type of emulsions water acts as dispersed phase and oil acts as dispersion medium. For example, cold cream, butter, cod liver oil etc. It is indicated by W/O

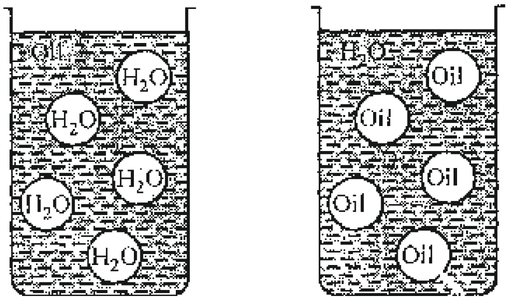


Fig. 5.18 : Emulsion

(ii) **Oil in water emulsions:** In this type of emulsions oil acts as dispersed phase and water acts as dispersion medium. For example, milk, vanishing cream etc. It is indicated by O/W

Identification of emulsion

The following tests may be employed to distinguish between the two types of emulsions:

(i) **Dye test:** To the emulsion some oil soluble dye is added. If the background becomes coloured the emulsion is water in oil type and if the droplets become coloured the emulsion in oil in water type.

(ii) **Dilution test:** If the emulsion can be diluted with water, this indicates that water is the dispersion medium and the emulsion is of oil-in-water type. In case the added water forms a separate layer, the emulsion is water-in-oil type.

(iii) **Conductive method:** Thus method is based upon adding a small amount of an electrolyte to the emulsion. If the conductance increases the emulsion is oil water type and if there is no significant change, it is water-in-oil type.

Properties of emulsions

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

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

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

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

(v) Emulsions can be destroyed by : Addition of electrolyte in excess or by removal of emulsifior.

Application of Emulsion

(i) Concentration of ores in metallurgy: The concentration of the sulphide ore of a metal by froth floatation process involves the use of some oil such as pine oil. The oil forms emulsion with ore particles. When air is bubbled through the emulsion, it rises to the surface as foam and is skimmed off.

(ii) In medicine: The various pharmaceuticals and cosmetics available in liquid form such as codliver oil, B-complex, ointments, etc. are emulsions of water-in-oil type. These are readily adsorbed in the intestines.

(iii) Cleansing action of soaps: The cleansing action of soap is based upon the formation of oil-in-water type emulsion.

5.9.7 Application of Colloid

Important applications of colloide are as follows:-

(1) Colloidal Medicines–

(i) Argyrol and protigyrol :- Protactive sol of siver is known as argyrol. It is used as an eye lotion.

(ii) Colloid Gold, Calcium, iron, copper are used healthy tonic.

(iii) Colloidal sulphur is used to treat eczema and dermatitis.

(iv) Colloid antimony is used in the treatment of tuberculosis

(2) Cottrell Precipitator– In bin cities, the factories work round the clock and the smoke coming out of the chimneys contain a lot of unburnt carbon particles. These are quite injurious to health and have to be precipitated from the smoke. In fact, smoke is a colloidal system in which the carbon particles are suspended in air. The carbon particles are charged in nature and they do not get coagulated or precipitated. The charge on the carbon particles is neutralized by bringing them in contact with the oppositely charged metal plate. They, thus, get precipitated and the smoke coming out of the chimney is free from dust. This precipitation of smoke particles is carried out by Cottrell smoke precipitator shown in Fig. 7.29. In this method, the smoke is allowed to pass through a chamber having a series of plates charged to very high potential (20,000 to 70,000V). Charged particles of smoke get attracted by charged plates, get precipitated and the gases coming out of chimney become free of charged particles.

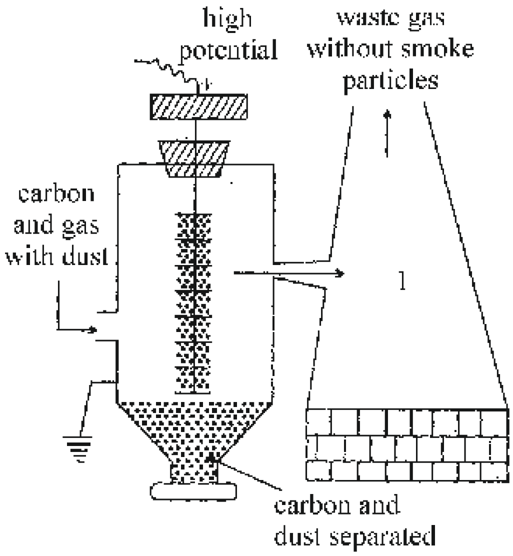


Fig. 5.19 : Cottrell Precipitator

3. Sewage disposal: The sewage disposal contains dust particles suspended in water. They are, therefore, colloidal in nature and are also charged.

They can be separated from the dirty water by placing it in a big tank fitted with electrodes. The colloidal particles migrate towards the oppositely charge electrodes where their charge is neutralised and they get coagulated. The coagulated mass can be used as a manure.

4. **Rubber industry:** Latex is a colloidal solution of negatively charged colloidal rubber particles. Rubber can be obtained from latex by coagulation. These rubber particles can be deposited over articles to be rubber plated by electrophoresis. The article to be rubber plated is made the anode in the rubber plating bath.

5. **Purification of drinking water:** The drinking water can be purified by precipitation of suspended colloidal particles. For this purpose, a small amount of alum $[K_2SO_4Al_2(SO_2)_3.24H_2O]$ is added. The Al^{3+} ions neutralise the charge on the particles and they get coagulated.

6. **Formation of delta:** River water is muddy and contains charged colloidal particles of clay, sand and many other materials. Sea water contains in it a number of dissolved electrolytes. When the river water comes in contact with the sea water, the electrolytes present in sea water coagulate the suspended colloidal particles which ultimately settle down at the point of contact. As a result, the level of the river bed rises. Thus, there is the formation of the delta at the point where the river enters the sea.

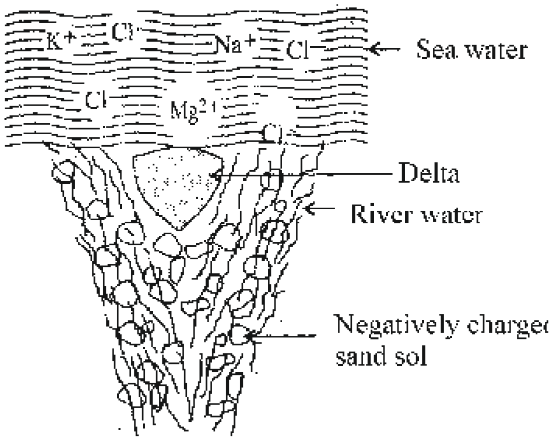


Fig. 5.20 : Formation of delta

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

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

9. **Artificial rain:** Artificial rain can be caused by spraying oppositely charged colloidal dust or sand particles over a cloud from an aeroplane. The colloidal water particles present in the cloud will get neutralized and will coagulate to form bigger water drops causing artificial rain.

10. **Cogulation of Blood :** Bleeding stops when ferric chloride solution is applied to a bleeding part. This is due to coagulation of blood by an electrolyte forming a blood clot.

11. **Blue colour of sky :** Blue colour of the sky is due to the scattering of light by colloidal dust particles present in the air (Tyndall effect). Similarly, sea water looks green due to scattering of light by the colloidal impurities present in sea water.

EXERCISE QUESTIONS

Multiple Choice Questions

(1) Equation for adsorption isotherm is -

(a) $\frac{x}{m} = KP^{1/n}$ (b) $\frac{x}{m} = KP^{n}$

(c) $\frac{x}{m} = KP^{-n}$ (d) all of above

(2) Shape selective catalysis is catalysed through :

(a) enzyme

(b) zeolite

(c) platinum

(d) Ziegler natta catalysts

(3) Which statement is not correct for physical adsorption -

(a) adsorption is reversible on solid surface

(b) extent of adsorption is increases by increasing temprature

(c) adsorption is an instaneous process

(d) enthalpy and entropy both remains negative for adsoption

(4) Which compound has lowest Gold number

(a) gelatin (b) albumin

(c) gum arebic (d) starch

(5) Arsenic sulphide sol carries a negative charge. The maximum precipitating power of this sol is possessed by

(a) $AlCl_3$ (b) Na_3PO_4

(c) $CaCl_2$ (d) K_2SO_4

(6) Enzymes are most active at :

(a) 300 K (b) 310 K

(c) 320 K (d) 330 K

(7) Lyophilic sols are stable than lyophobic sols due to:

(a) colloid particles are positively charged

(b) no charge on colloid particles

(c) colloid particles

(d) stable elecrical charge exists among negatively charged colloid particles

(8) The extent of adsorption of adsorbent increases by-

(a) increased surface area

(b) sub divided into smaller pieces

(c) by making porous

(d) all of above

(9) Which one is not a surface phenomenon.

(a) Homogenous catalysis

(b) Mixing of solids

(c) Corrosion

(d) electrolytic process

(10) Ferric chloride sulphide sol carries a positive charge. The maximum precipitating power of this sol is possessed by

(a) H_2SO_4 (b) Na_3PO_4

(c) $CaCl_2$ (d) $AlCl_3$

(11) Method of purify blood in human body is

(a) Electrophoresis (b) Electrodialysis

(c) dialysis (d) coagulation

(12) Red sol is obtained when dil. HCl is mixed with fresh Ferric oxide solution. The process is known as :

(a) Precipitation (b) dialysis

(c) protention (d) separable

(13) The random motion of colloid particles studied by

(a) Zigmondy (b) Ostwald

(c) Robert Brown (d) Tyndall

(14) Basis of chromatography is :

(a) physical adsorption

(b) chemical adsorption

(c) hydrogen bond

(d) sedimentation

(15) Gold number related with

(a) Electrophoresis

(b) purple of cassius

(c) protection of colloid

(d) amount of pure gold

Very Short Answer Questions

1. Explain why colloidal particles in sols are good adsorbent.
2. Cheese is which type of colloid ?
3. Give one example each of Homogenous and Heterogenous catalysis.
4. Colloid solution shows Tyndall effect. Give two reasons.
5. Explain why Alum is used for bleeding part on the human body.

6. Define Multimolecular colloids.
7. Write two differences between adsorption and absorption.
8. Which adsorbent is used for removal of hardness of water.
9. Define sorption.
10. Write a chemical equation for auto catalysis.
11. Which catalys and booster is used in Haber's process
12. The catalytic property of enzyme works on which process. It is given by which scientist.
13. Define gold number.
14. Explain why finally divided compound are good adsorbent?
15. Give one example of each type of Emulsion.
16. What is purple of cassius.
17. Write the name of catalyst which convert methanol into gasoline.
18. Why soap do not cleansing in acidic medium.
19. Write an equation for induce catalysis
20. Classify following compounds into Lyophilic and Lyophobic colloids.
    (a) As_2S_3 (b) gum
    (c) Starch (d) Au Sol

Short Answer Type Questions

1. Explain the mechanism of micellization.
2. Write short notes on-
    (a) dialysis
    (b) Cottrell precipitator
3. Describle the formation of platnum hydrosol by dispersion method. Draw the related diagram
4. What is electrophoresis. Explain with diagram.
5. Gives the mathematical equation for Freundlich's adsorption isotherm.
6. Give four differences between physical and chemical adsorptions.
7. What is the difference between multimolecular and macromolecular colloids? Give one example of each type.
8. Explain what happens when :
    (a) beam of light is passed through colloidal solution.
    (b) an electrical current is passed through a colloidal soution.
9. Give properties of Enzyme Catalysis.

Long Answer Questions

1. Describe following with digrams :
    (i) Tyndall effect
    (ii) Brownian movement
2. Explain the following :
    (i) Bredig's arc method
    (ii) Colloidal mill
3. Write note on shape selective catalysis by zeolites.
4. Give reasons.
    (i) Alum purifies drinking water.
    (ii) Same compound can acts as both crytalloid and colloid.
    (iii) Sky seems blule in colour.
5. Decribe factors affecting adsorption of Gases on solids.

Answers (Multiple Choice Questions)

1. (a), 2. (b), 3. (b), 4. (a),
5. (a), 6. (b), 7. (d), 8. (d),
9. (d), 10. (d), 11. (b), 12. (a),
13. (c), 14. (b), 15. (c).

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