SURFACE CHEMISTRY

1. GENERAL INTRODUCTION

Surface Chemistry is that branch of chemistry which deals with the study of the phenomena occurring at the surface or interface, i.e., at the boundary separating two bulk phases.

The two bulk phases can be pure compounds or solutions. The interface is represented by putting a hyphen or a slash between the two bulk phases involved, e.g., solid-liquid or solid/liquid. No interface exists between gases as they are completely miscible. Important phenomena occur at the interface, e.g., dissolution, crystallisation, corrosion, heterogeneous catalysis, electrode processes, etc.

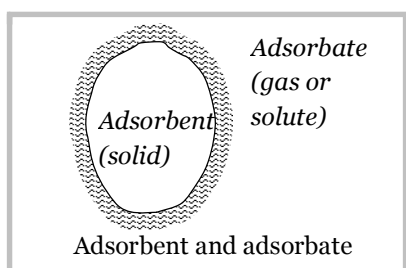## 2. ADSORPTION

2.1 Definition

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting in to higher concentration of the molecules on the surface is called *adsorption*. Adsorption of gases at metal surface is called occlusion

2.2 Adsorbate and Adsorbent

The substance which gets adsorbed on any surface is called **adsorbate** for example, if a gas gets adsorbed on to the surface of a solid, then the gas is termed as the adsorbate.

The substance on the surface of which adsorption takes place is called **adsorbent**.

Adsorbent may be a solid or a liquid. Metal powders, powdered charcoal, animal charcoal silica powder etc. are commonly used as adsorbents.
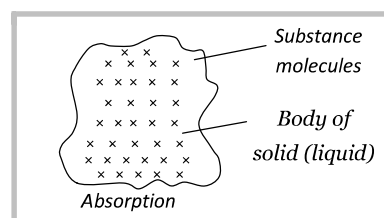

Adsorbent and adsorbate

2.3 Desorption

The removal of the adsorbed substance from a surface is called **desorption**. This can be done by heating or reducing the pressure of the system.
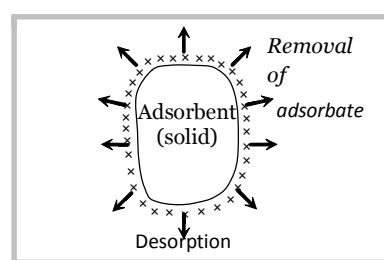
2.4 Absorption

When the molecules of a substance are uniformly distributed throughout the body of a solid or liquid, this phenomenon is called **absorption**.

2.5 Sorption

The phenomenon in which adsorption and absorption occur simultaneously is called **sorption**. Dyes are absorbed as well absorbed in cotton fibre.

Adsorption is instantaneous *i.e.* a fast process while absorption is a slow process.
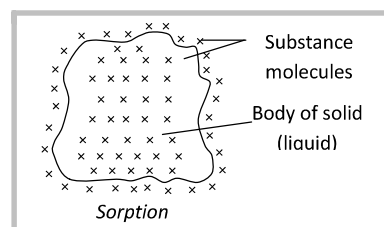
2.6 Difference between Adsorption and Absorption

Main points of difference between adsorption and absorption are given below.

DIFFERENCE BETWEEN ADSORPTION AND ABSORPTION
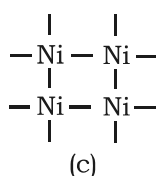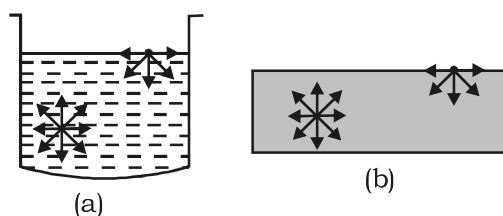
Adsorption	Absorption
1. It is a surface phenomenon.	1. It concerns with the whole mass of the absorbent.
2. In it, the substance is only retained on the surface and does not go into the bulk or interior of the solid or liquid.	2. It implies that a substance is uniformly distributed, through the body of the solid or liquid.
3. In it the concentration of the adsorbed molecules is always greater at the free phase.	3. In it the concentration is low.
4. It is rapid in the begining and slows down to attain equilibrium	4. It occurs at the uniform rate.
Examples	**Examples**
(i) Water vapours are adsorbed by $CaCl_2$.	(i) Water vapours are absorbed by anhydrous silica gel.
(ii) NH_3 is adsorbed by charcoal.	(ii) NH_3 is absorbed in water forming NH_4OH.
(v) Decolourisation of sugar solution by activated or animal charcoal.	
(vi) Ink is adsorbed by blotting paper.	

2.7 Mechanism of adsorption

(a)

(b)

$$-Ni-Ni-$$
$$-Ni-Ni-$$

(c)

Molecules at the surface experiencing a net inward force of attraction in case of

(a) liquid (b) solid (c) metal with free valencies

Only the surface atoms of an adsorbent play an active role in adsorption. These atoms possess unbalanced forces of various types such as, Vander Waal's forces and chemical bond forces (free valencies).

Thus, due to residual or unbalanced inward forces of attraction or free valancies at the surface, liquids and solids have the property to attract and retain the molecules of a gas or a dissolved substance on to their surface.

2.8 Characterstics of adsorption

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

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

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

Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system and hence ΔG *also decreases.*

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

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

2.9 Classification of adsorption

Adsorption can be classified into two categories as described below.

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

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

COMPARISON BETWEEN PHYSISORPTION AND CHEMISORPTION

Physisorption (Vander Waal's adsorption)	Chemisorption (Langmuir adsorption)
1. Low heat of adsorption usually in range of 20-40 kJ/mol	1. High heat of adsorption in the range of 50-400 kJ mol.
2. Force of attraction are Vander Waal's forces.	2. Forces of attraction are Chemical bond forces.
3. It is reversible.	3. It is irreversible.
4. It usually takes place at low temperature and decreases with increasing temperature.	4. It takes place at high temperature.
5. It is related to the case of liquefication of the gas.	5. It is not related.
6. It forms multimolecular layers.	6. It forms monomolecular layers.
7. It does not require any activation energy.	7. It requires high activation energy.
8. High pressure is favourable. Decrease of pressure causes desorption.	8. High pressure is favourable. Decrease of pressure does not cause desorption
9. It is not very specific.	9. It is highly specific.

Note :

☐ *Due to formation of multilayers physical adsorption decreases after some times.*

☐ *Chemisorption and physisorption both are **exothermic**.*

2.10 Factors which affect the extent of adsorption on solid surface

The following are the factors which affect the adsorption of gases on solid surface.

2.10.1 Nature of the adsorbate (gas) and adsorbent (solid)

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

◆ Gases with high critical temperature are adsorbed at higher extent as compared to gases with lower critical temperatures.

Volumes of gases at N.T.P., adsorbed by 1g of charcoal at 288 k

Gas	H_2	N_2	CO	CH_4	CO_2	HCl	NH_3	SO_2
Volume adsorbed (mL)	4.7	8.0	9.3	16.2	48	72	181	380
Critical temp (K)	33	126	134	190	304	324	406	430

Critical temperature increases →

Ease of liquefaction increases →

Adsorption increases →

2.10.2 Surface area of the solid adsorbent : The extent of adsorption depends directly upon the surface area of the adsorbent, *i.e. larger the surface area of the adsorbent, greater is the extent of adsorption.*

2.10.3 Effect of pressure on the adsorbate gas :

- An increase in the pressure of the adsorbate gas increases the extent of adsorption.

- *At low temperature,* the extent of adsorption increases rapidly with pressure.

- *At low pressure,* the extent of adsorption is found to be directly proportional to the pressure.

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

Variation of adsorption of N_2 on charcoal with pressure at different constant temperatures
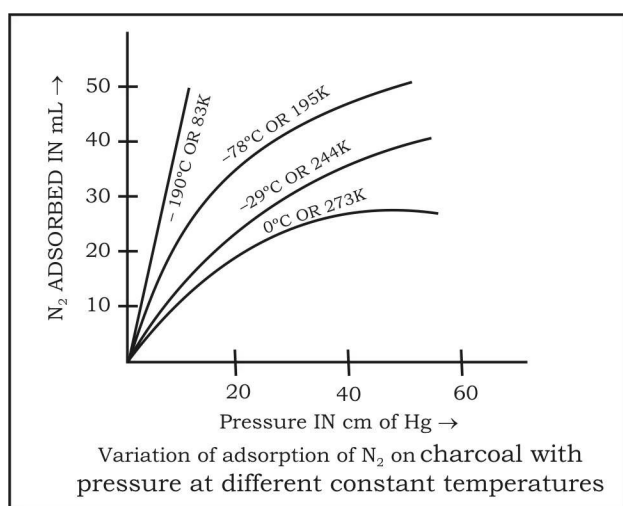
2.10.4 Effect of temperature : As adsorption is accompanied by evolution of heat, so according to the *Le-Chatelier's principle*, the magnitude of adsorption should decrease with rise in temperature.

The amount of heat when one mole of the gas is adsorbed on the adsorbent is called the **heat of adsorption.**

2.11 Adsorption Isotherms

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

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

Extent of adsorption $= \dfrac{x}{m}$

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

$$\frac{x}{m} = kP^{\frac{1}{n}}$$ or $$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

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

At *low pressure*, the extent of adsorption varies linearly with pressure $\dfrac{x}{m} \propto P^1$

- At *high pressure*, it becomes independent of pressure $\dfrac{x}{m} \propto P^0$

- At *moderate pressure* $\dfrac{x}{m}$ depends upon pressure raised to powers $\dfrac{x}{m} \propto P^{\frac{1}{n}}$

Freundlich adsorption isotherm : plot of x/m against p

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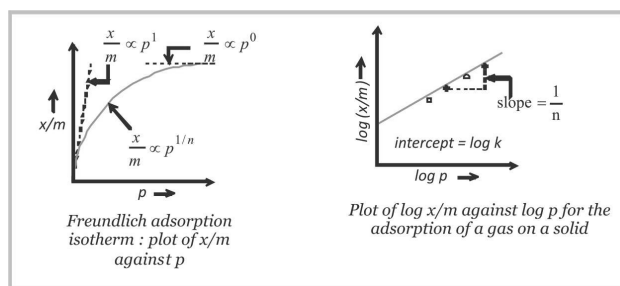
2.12 Adsorption Isobar

A graph drawn between the amount of the gas adsorbed per gram of the adsorbent (x/m) and temperature 't' at a constant equilibrium pressure of adsorbate gas is known as adsorption isobar.

Physical adsorption

Chemical adsorption
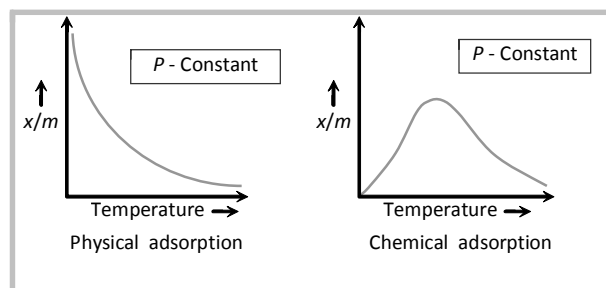
The physical adsorption isobar shows a decrease in x/m throughout with rise in temperature, the chemisorption isobar shows an initial increase with temperature and then the expected decrease. The initial increase is because of the fact that the heat supplied acts as activation energy required in chemisorption (like chemical reactions).

2.13 Adsorption from Solutions

Solid surfaces can also adsorb solutes from solutions. A few examples are :

◆ When litmus solution is shaken with charcoal, it becomes colour less because the dye of the litmus solution is adsorbed by charcol.

◆ When the colourless $Mg(OH)_2$ is precipitated in the presence of magneson reagent (a blue coloured dye). it acquires blue colour because the dye is adsorbed on the solid precipitate.

The extent of adsorption from solution depends upon the concentration of the solute in the solution, and can be expressed by the *Freundlich isotherm*. The Freundlich adsorption isotherm for the adsorption from solution is, $\frac{x}{m} = kc^{\frac{1}{n}}$ where, x is the mass of the solute adsorbed, m is the mass of the solid adsorbent, c is the equilibrium concentration of the solute in the solution, n is a constant having value greater than one. k is the proportionality constant, (The value of k depends upon the nature of solid, its particle size, temperature, and the nature of solute and solvent etc.) The plot of x/m against c is similar to that Freundlich adsorption isotherm. The above equations may be written in the following form, $\log \frac{x}{m} = \log k + \frac{1}{n} \log c$ where c, is the equilibrium concentration of the solute in the solution.

2.14 Factors affecting adsorption from solution

The adsorption from solutions by solid adsorbents is found to depend upon the following factors :

2.14.1 Nature of the adsorbate and the adsorbent.

2.14.2 The adsorption decreases with **temperature**.

2.14.3 Greater the **surface area of the adsorbent** greater is the adsorption.

2.14.4 Concentration of the solute in the solution.

2.15 Positive and Negative Adsorption

In case of adsorption by solids from the solutions, mostly the solute is adsorbed on the surface of the solid adsorbent so that concentration of solute on the surface of the adsrobent is greater than in the bulk. However in some cases. the solvent from the solution may be adsorbed by the adsorbent so that the concentration of the solution increases as compared to initial concentration.

When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is called positive adsorption. If the concentration of the adsorbate increases in the bulk after adsorption, it is called negative adsorption.

Blood solution + Conc. KCl solution $\rightarrow$ Positive adsorption

Blood solution + dilute KCl solution $\rightarrow$ Negative adsorption

2.16 Applications of Adsorption

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

2.16.1 Production of high vacuum : A bulk of charcoal cooled in liquid air is *connected* to a vessel which has already been exhausted as for as possible by a vacuum pump. The remaining traces of air are adsorbed by the charcoal to produce a very high vacuum.

2.16.2 In Gas masks : It is a device which consists of activated charcoal or a mixture of adsorbents. This apparatus is used to adsorb poisonous gases (e.g. Cl_2 , CO, oxide of sulphur etc.) and thus purify the air for breathing is coal mines.

2.16.3 For desiccation or dehumidification : Certain substances have a strong tendency to absorb water such as silica and alumina (Al_2O_3). These substances can be used to reduce/remove water vapours or moisture present in the air. Silica gel is also used for dehumidification in electronic equipment.

2.16.4 Removal of colouring matter from solution : Animal charcoal removes colours of solutions by adsorbing coloured impurities. It is also used as decolouriser in the manufacture of cane sugar.

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

- Finely powdered nickel is used for the hydrogenation of oils.

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

- *Pt, Pd* are used in many industrial processes as catalyst.

- Manufacture of ammonia using iron as a catalyst.

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

2.16.7 Softening of hard water :

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

2.16.8 De-ionisation of water :

- For softening water can be de-ionised by removing all dissolved salts with the help of cation and anion-exchanger resin.

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

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

2.16.11 Froth floatation process :

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

- The finely divided ore is added to water containing pine oil and foaming agent.

- The air is bubbled through the mixture.

- The foam formed rises to the surface on which mineral particles wetted with oil are adsorbed while earthy matter settle down at the bottom.

2.16.12 In adsorption indicators : Surface of certain precipitates such as silver halide, have the property of adsorbing some dyes like eosin, fluorescein etc. In this case of precipitation titrations (for example $AgNO_3$ Versus $NaCl$) the indicator is adsorbed at the end point producing a characteristic colour on the precipitate.

2.16.13 Chromatographic analysis : The phenomenon of adsorption has given an excellent technique of analysis known as chromatographic analysis. The technique finds a number of applications in analytical and industrial fields. Chromatographic technique is based on differential adsorption of different constituents of a mixture.

2.16.14 In dyeing : Many dyes get adsorbed on the cloth either directly or by the use of mordants.

"Catalyst is a substance which speeds up and speeds down a chemical reaction without itself being used up at the end of the reaction and the phenomenon is known as catalysis.

3.1 Types of catalysis

Catalytic reactions can be broadly divided into the following types,

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

- Oxidation of sulphur dioxide into sulphur trioxide with oxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.

$$2SO_2(g) + _2(g) \xrightarrow{NO(g)} 2SO_3(g)$$
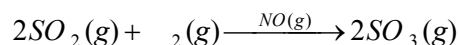
The reactants, products and catalyst all are in gaseous state *i.e.* same phase.

- Hydrolysis of methyl acetate is catalysed by H^+ ions furnished by hydrochloric acid .

$$CH_3COOCH_3(\ell) + H_2O(\ell) \xrightarrow{HCl(\ell)}$$
$$CH_3COOH(\ell) + CH_3OH(\ell)$$
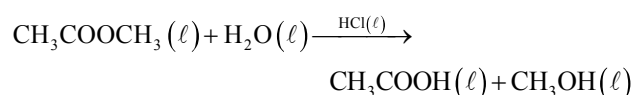
- Hydrolysis of sugar is catalysed by H^+ ions furnished by sulphuric acid.

$$\underset{\text{(Sucrose solution)}}{C_{12}H_{22}O_{11}(\ell)} + H_2O(\ell) \xrightarrow{H_2SO_4(\ell)}$$
$$\underset{\text{(Glucose solution)}}{C_6H_{12}O_6(\ell)} + C_2H_{12}O_6(\ell)$$
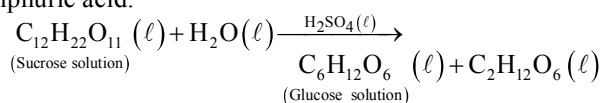
3.1.2 Heterogeneous catalysis : The catalytic process in which the reactants and the catalyst are in different phases is known as *heterogeneous catalysis.* Some of the examples of heterogeneous catalysis are given below.

- Oxidation of sulphur dioxide into sulphur trioxide in the presence of platinum metal or vanadium pentaoxide as catalyst in the contact process for the manufacture of sulphuric acid. The reactants are in gaseous state while the catalyst is in solid state. $2SO_2(g) + _2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

- Combination between nitrogen and hydrogen to form ammonia in the presence of finely divided iron in *Haber's process.*

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

- Oxidation of ammonia into nitric oxide in the presence of platinum gauze as a catalyst in *Ostwald's process.*

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

- Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.

Vegetable oils (l) + $H_2(g)$ $\xrightarrow{Ni(s)}$ Vegetable Ghee (g)

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

- Decomposition of H_2O_2 in presence of colloidal platinum.

$$2H_2O_2(l) \xrightarrow{Pt} 2H_2O(l) + O_2(g)$$

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

- The oxidation of chloroform by air is retarded if some alcohol is added to it.

$$2CHCl_3(l) + O_2(g) \xrightarrow{Alcohol(l)} 2COCl_2(g) + 2HCl(g)$$

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

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

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

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

- In hydrolysis of ethyl acetate, acetic acid and ethyl alcohol are formed. The reaction is initially very slow but gradually its rate increases. This is due to formation of acetic acid which acts as an auto-catalyst in this reaction.

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

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

3.1.7 Acid-base catalysis : According to the *Arrhenius* and *Ostwald* H^+ or OH^- ions act as catalysts.

- For example, Hydrolysis of an ester,

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

- Inversion of cane sugar,

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

- Conversion of acetone into diacetone alcohol,

$$CH_3COCH_3(l) + CH_3COCH_3(l) \xrightarrow{OH^-}$$
$$CH_3COCH_2 \cdot C(CH_3)_2OH(l)$$

- Decomposition of nitramide,

$$NH_2NO_2(l) \xrightarrow{OH^-} N_2O(g) + H_2O(l)$$

3.2 Characteristics of catalysis

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

3.2.1 A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

3.2.2 The catalyst can not initiate the reaction: The function of the catalyst is to alter the speed of the reaction rather than to start it.

3.2.3 The catalyst is generally specific in nature: A substance, which acts as a catalyst for a particular reaction,

fails to catalyse the other reaction , different catalysts for the same reactant may for different products.

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

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

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

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

A positive catalyst lowers the activation energy
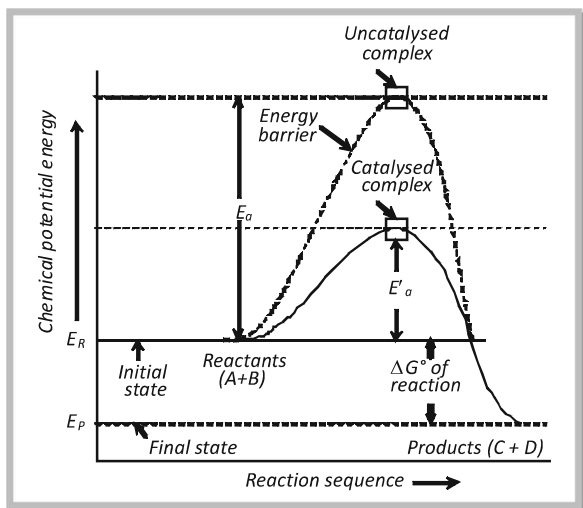
3.3 Theories of Catalysis

3.3.1 Collision Theory of Homogeneous Catalysis : According to the collision theory, a reaction occurs on account of effective collisions between the reacting molecules. For effective collision, it is necessary that the molecules must possess a minimum amount of energy known as activation energy (E_a). After the collision molecules form an activated complex which dissociate to yield the product molecules. The catalyst provides a new pathway involving lower amount of activation energy. Thus,
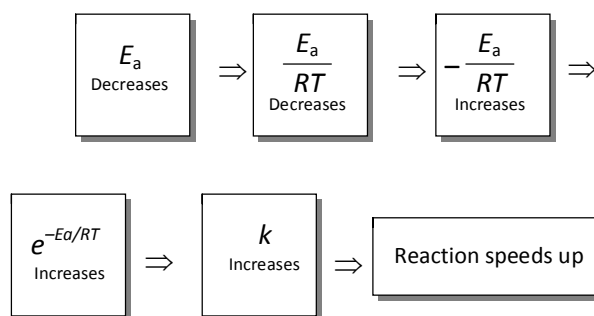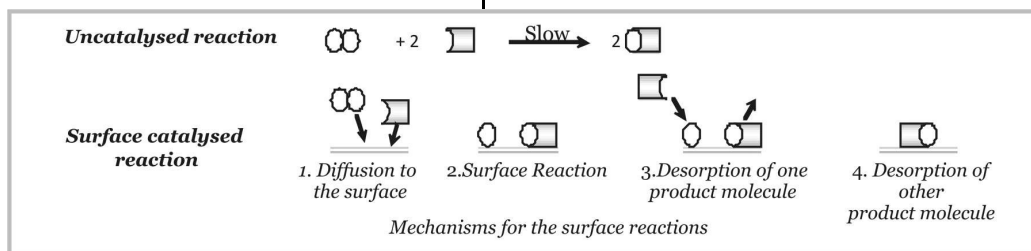

3.3.2 Adsorption theory of Heterogeneous Catalysis : Heterogeneous catalytic reactions generally proceed via adsorption of reactants on the surface of the catalyst.

Mechanism of such surface reactions may be explained in terms of ***diffusion theory of catalysis.*** This theory postulates the following sequence for gaseous reactions on a solid surface.
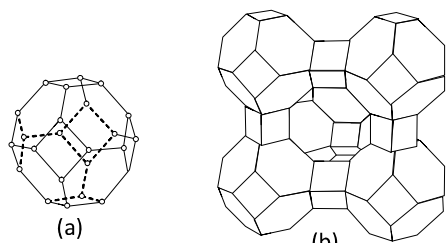
Step: (i) Diffusion of the reactants to the surface.

Step: (ii) Adsorption of the reactant molecules onto the surface.

Step: (iii) Actual chemical reaction on the surface.

Step: (iv) Desorption of the products from the surface.

Step: (v) Diffusion of the products away from the surface.

In generally, Step (iii) determines the rate of reaction. However step (ii) and (iv) may be rate determining.
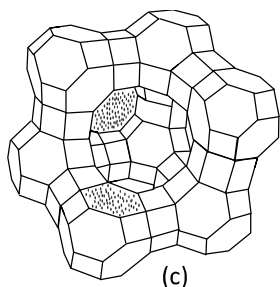

Mechanisms for the surface reactions

3.3.3 Advantages of modern adsorption theory : This theory can explain the following :

- Small quantity of the catalyst is sufficient because the catalyst is regenerated again and again.

- The catalyst takes part in the reaction but is produced back unchanged in mass and chemical composition at the end of the reaction.

- Catalytic poisons, if present, are preferentially adsorbed on the catalyst surface, thereby hindering the adsorption of the reactant molecules. Hence, they slow down the activity of the catalyst.

  This theory, however, cannot explain satisfactorily the action of catalytic promoters.

3.4 Enzyme catalysis

Enzymes are complex nitrogenous substances secreted by low forms of vegetables & organisms. Enzymes are actually protein molecules of higher molecular mass. (ranging from 15,000 – 1,000,000 g/mol) Enzymes form colloidal solutions in water and are very effective catalysts. They catalyse numerous reactions, especially those connected with natural processes. Numerous reactions occur in the bodies of animals and plants to maintain the life process. These reactions are catalysed by enzymes. The enzymes are thus, termed as ***bio-chemical catalysts*** and the phenomenon is known as ***bio-chemical catalysis***. eg.

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

- In the human body, the enzyme **carbonic anhydrase** catalyses the reaction of CO_2 with H_2O,

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

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

Enzyme (catalyst) + Substrate (reactants) → Enzyme-Substrate complex → Enzyme + Products

Thus, the enzyme catalysed reactions take place in two steps as follows :

Step 1. Formation of enzyme-substrate complex.

$$\underset{\text{Enzyme}}{E} + \underset{\text{Substrate}}{S} \rightleftharpoons \underset{\substack{\text{Enzyme} - \\ \text{Substrate complex}}}{ES} \qquad \text{(Fast and Reversible)}$$

Step 2. Dissociation of enzyme-substrate complex to form the products.

$$\underset{\substack{\text{Enzyme} \\ \text{Substrate complex}}}{ES} \xrightarrow{\;+\;} \underset{\substack{\text{Enzyme} - \text{Pr oduct} \\ \text{association}}}{[EP]} \longrightarrow$$

$$\underset{\substack{\text{Enzyme} \\ (\text{Re generated})}}{E} + \underset{\text{Product}}{P} \qquad (\text{Slow and Rate determining})$$

The rate of formation of product depends upon the concentration of ES.

3.5 Activity and selectivity

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

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

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

Example : (i) n-heptane $\xrightarrow{\text{Pt}}$ toluene (with CH_3 group)

(ii) $CH_3CH{=}CH_2 \xrightarrow{\text{BiMoO}_4} CH_2{=}CHCH{=}O$ (Acrolein)

3.6 Zeolites (shape selective catalysis)

Zeolites are alumino–silicates of the general formula, $M_n[AlO_2]_x.(SiO_2)_y.mH_2O$, where, M may be simple cation like Na^+, K^+ or Ca^{2+}, n is the charge on the simple cation, m is the number of molecules of water of crystallization. They have honey comb like structure called β cage. The reactions catalyzed by zeolites depend upon the shape and size of the reactant and product molecules. That is why these types of reactions are called shape selective-catalysis.

(a)

(b)

(a) The sodalite (or β-) cage, (b) zeolite-A

(c)

, (c) Faujasite.

Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerization. An important zeolite catalyst used in the petroleum industry is ZSM–5*** (Zeolite Sieve of Molecular Porosity 5). It converts alcohols directly into gasoline (petrol) by first dehydrating them so that a mixture of hydrocarbons is formed.

$$\text{Alcohols} \xrightarrow[\text{Dehydration}]{\text{ZSM–5}} \text{Hydrocarbons}$$
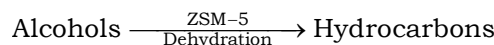
hydrated zeolites are used as 'ion-exchangers' in softening of hard water.

3.7 Catalysis used in Industries

SOME INDUSTRIAL CATALYTIC PROCESSES

Process	Reactions with catalyst and other conditions
Haber's process for the manufacture of ammonia	$N_2(g) + 3\ H_2(g) \xrightarrow[\substack{\text{Molydenum (Promoter)} \\ \text{200 bar pressure} \\ \text{723–773 K temp.}}]{\text{Finely divided iron (catalyst)}} 2\ NH_3(g)$
Ostwald's process for the manufacture of nitric acid	$4\ NH_3(g) + 5\ O_2(g) \xrightarrow[\text{asbestos (catalyst)}]{\text{Platinised}} 4\ NO(g) + 6\ H_2O(g)$ $2\ NO(g) + O_2(g) \xrightarrow{573K} 2\ NO_2(g)$ $4\ NO_2(g) + 2\ H_2O(l) + O_2(g) \rightarrow 4\ HNO_3(l)$
Contact process for the manufacture of sulphuric acid	$2\ SO_2(g) + O_2(g) \underset{\text{or V}_2\text{O}_5\text{ (catalyst)}}{\overset{\text{Platinised asbestos}}{\rightleftharpoons}} 2\ SO_3(g)$ $SO_3(g) + H_2SO_4(l) \xrightarrow{673–723K} H_2S_2O_7(l) \xrightarrow{+H_2O(l)} 2H_2SO_4(aq)$ Oleum
Bosch's process for the manufacture of hydrogen.	$\underbrace{CO + H_2}_{\text{Water gas}} + H_2O(g) \xrightarrow[\substack{+Cr_2O_3\text{ (promoter)} \\ 673–873K}]{Fe_2O_3\text{ (Catalyst)}} CO_2(g) + 2\ H_2(g)$
Deacon's process for the manufacture of chlorine	$4\ HCl(g) + O_2(g) \xrightarrow[773K]{CuCl_2} 2H_2O(l) + 2\ Cl_2(g)$
Synthesis of methanol	$CO(g) + 2\ H_2(g) \xrightarrow[\substack{\text{200 bar} \\ \text{432 K}}]{ZnO + Cr_2O_3} CH_3OH(l)$
Hydrogenation of vegetable oils	$Oil(l) + H_2(g) \xrightarrow[\substack{423–473\ K \\ \text{High pressure}}]{\text{Finely divided Ni}} \text{Vanaspati ghee (s)}$

4. COLLOIDAL STATE

The colloidal state depends on the particle size. It is regarded as intermediate state between true solution and suspension.

4.1 True solution

In true solutions the size of the particles of solute is very small and thus, these can not be detected by any optical means and freely diffuse through membranes. It is a homogenous system.

Three types solutions
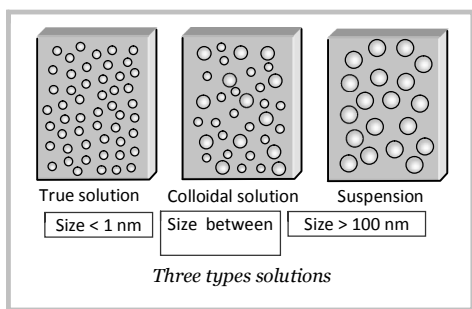
4.2 Suspension

The size of particles is large and, thus it can be seen by naked eye and do not pass through filter paper. It is a heterogeneous system.

The size of different solutions are sometimes expressed in other units also as given below :

True solutions	Colloids	Suspensions	Relation
$<10^{-9}$m	10^{-9}m to 10^{-7}m	$>10^{-7}$m	
<1nm	1 nm – 100 nm	>100 nm	1 nm $=10^{-9}$m
<10 Å	10 Å – 1000 Å	>1000 Å	1 Å $=10^{-10}$m
<1000 pm	1000 pm – 10^5 pm	$>10^5$ pm	1 pm $=10^{-12}$m

CHARACTERISTICS OF TRUE SOLUTIONS, COLLOIDAL SOLUTIONS AND SUSPENSIONS

S.No	Property	True Solutions	Colloidal Solutions	Suspensions
1.	Nature	Homogeneous	Heterogeneous	Heterogeneous
2.	Particle size (diameters)	Less than 10^{-9} m or 1 nm (i.e., <10 Å)	Between 10^{-9} to 10^{-6}m or 1 nm to 1000 nm	More than 10^{-6}m or 1000 nm (i.e., >10000Å
3.	Filtrability	Pass through ordinary filter paper as well as animal membrane.	Pass through ordinary filter paper but not through animal membrane.	Do not pass through filter paper and animal membrane.
4.	Settling	Do not settle.	Do not settle.	Settle on standing.
5.	Visibility	Particles are invisible.	Scattering of light by the particles is observed under ultra-microscope.	Particles are visible to naked eye or under a microscope.
6.	Diffusion	Diffuse quickly.	Diffuse slowly.	Do not diffuse.
7.	Appearance	Clear and transparent	Transluscent.	Opaque.

4.3 Dispersed phase and Dispersion Medium

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

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

4.4 Classification of Colloids

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

DIFFERENT TYPES OF COLLOIDAL SYSTEMS

Sr. No	Dispersed phase	Dispersion	Colloidal System	Examples
1.	Liquid	Gas	Aerosol of liquids	Fogs, clouds, mists, fine insecticide sprays
2.	Solid	Gas	Aerosol of solids	Smoke, volcanic dust, haze Foam or froth Soap lather.
3.	Gas	Liquid		Lemonade froth, foam, whipped cream, soda water
4.	Liquid	Liquid	Emulsions	Milk, emulsified oils, medicines
5.	Solid	Liquid	Sols	Most paints, starch in water, proteins, gold sol, arsenic sulphide sol, ink
6.	Gas	Solid	Solid foam	Pumice stone, styrene rubber, foam rubber
7.	Liquid	Solid	Gels	Cheese, butter, boot polish, jelly, curd
8.	Solid	Solid	Solid sols (coloured glass)	Ruby glass, some gem stones and alloys

4.4.2 Classification based on Nature of interaction between dispersed phase and dispersion medium :

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

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

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

DISTINCTION BETWEEN LYOPHILIC AND LYOPHOBIC SOLS

Sr. No	Property	Lyophilic (suspensiod)	Lyophobic Sols (Emulsoid)
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 because do not carry any charge.	Particles migrate either towards cathode or anode in an electric field because they carry charge.
7.	Action of electrolyte	Addition of smaller quantity of electrolyte has little effect	Coagulation takes place
8.	Hydration Examples	Extensive hydration takes place Gum, gelatin, starch, proteins, rubber etc. like As_2S_3 etc.	No hydration Metals like Ag and Au, hydroxides like $Al(OH)_3$, $Fe(OH)_3$, metal sulphides

4.4.3 Classification based on types of particles of dispersed phase : Depending upon the type of the particles of the dispersed phase, the colloids are classified as follows.

◆ **Multimolecular colloids :** When on dissolution, atoms or smaller molecules of substances (having diameter less than 1nm) aggregate together to form particles of colloidal dimensions, the particles thus formed are called *multimolecular colloids*. In these sols the dispersed phase consists of aggregates of atoms or molecules with molecular size less than 1 nm. For example, sols of gold atoms and sulphur (S_8) molecules. In these colloids, the particles are held together by *Vander Waal's forces.* They have usually *lyophilic character.*

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

These macromolecules forming the dispersed phase are generally *polymers* having very high molecular masses. Naturally occurring macromolecules are starch, cellulose, proteins, enzymes, gelatin etc. Artificial macromolecules are synthetic polymers such as nylon, polythene, plastics, polystyrene etc. Their solutions are quite stable and resemble with true solution in many respects. They have usually *lyophobic character.* The molecules are flexible and can take any shape.

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

Their molecules contain both *lyophilic* and *lyophobic* groups. The colloidal behaviour of such substances is due to the formation of aggregates or clusters in solutions. Such aggregated particles are called *micelles.*

DIFFERENCE BETWEEN DIFFERENT TYPES OF COLLOIDS

Multimolecular colloids	Macromolecular colloids	Associated colloids
1. They are formed by the aggregation of a large number of atoms or molecules which generally have diameters less than 1 nm, e.g., sols of gold, sulphur, etc.	They are molecules of large size, e.g., polymers like rubber, nylon, starch, proteins, etc.	They are formed by of aggergation of a large no. of ions in concentrated 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 Waals forces.	Due to long chain, the van der Waals forces holding them are comparatively stronger.	Higher is the concentration, greater are the van der Waals forces.

4.5 Micelles

Micelles are the clusters or aggregated particles formed by association of colloid in solution. The common examples of micelles are *soaps* and *detergents*. The formation of micelles takes place above a particular temperature called *Kraft temperature* (T_k) and above a particular concentration called *critical micellization concentration* (CMC). They are capable of forming ions. Micelles may contain as many as 100 molecules or more.

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

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

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

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

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

Hydrophobic tail and hydrophilic head of stearate ion
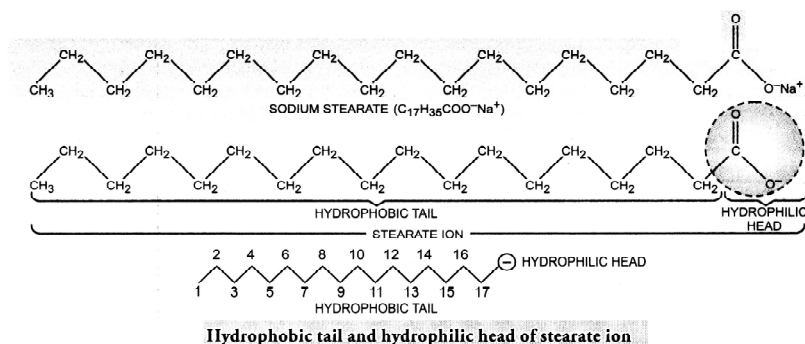
4.5.1 Cleansing action of Soaps : When oil droplet comes in contact with soap solution, the stearate ions arrange themselves around it in such a way that hydrophobic parts of the stearate ions are in the oil (or grease) and the hydrophilc.

As hydrophilic part is polar, these polar groups can interact with the water molecules present around the oil droplet. As a result, the oil droplet is pulled away from the surface of the cloth into water to form ionic micelle which is then washed away with the excess of water.
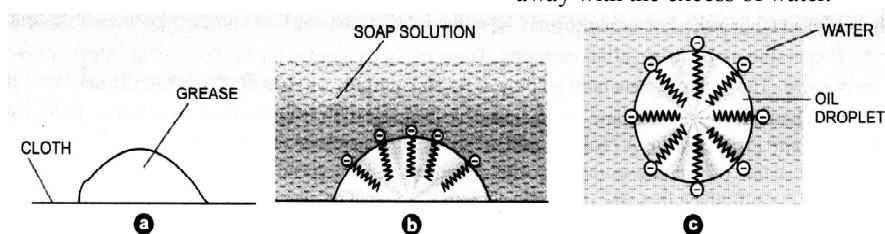
(a) Grease or oil on surface of cloth (b) Stearate ions arranged around the oil droplet

(c) Ionic micelle formed surrounded by sheath of negative charge.

In fact, the stearate ions of soap molecules help in making a stable emulsion of oil with water which is washed away with the excess of water. It may be noted that a sheath of negative charge is formed around the oil globule.

Similarly, in case of detergents, e.g., sodium lauryl sulphate, viz, $CH_3(CH_2)_{11} OSO_3^- Na^+$, the polar group is OSO_3^- alongwith the long hydrocarbon chain. It is an example of an **anionic** detergent as anions associate together to form an ionic micelle, similar to that of soap. A well known example of a cationic detergent forming an associated colloid is that of cetyl trimethyl ammonium bromide, $CH_3(CH_2)_{15}(CH_3)_3N^+Br^-$.

4.6 General Methods of preparation of Colloids

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

4.6.1 Preparation of Lyophilic colloids :

♦ The lyophilic colloids have strong affinity between particles of dispersed phase and dispersion medium.These colloidal solutions are readily formed by simply mixing the dispersed phase and dispersion medium under ordinary conditions.

♦ For example, the substance like gelatin, gum, starch, egg, albumin 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.

4.6.2 Preparation of Lyophobic colloids :

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

$$2H_2S + \text{ }_2 \text{ (or any other oxidising agent)} \longrightarrow 2H_2 + 2S$$
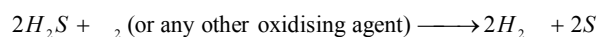
4.6.2.2 By reduction : A number of metals such as silver, gold and platinum, have been obtained in colloidal state by treating the aqueous solution of their salts, with a suitable reducing agent such as formaldehyde, phenyl hydrazine, hydrogen peroxide, stannous chloride etc.

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

$$2AuCl_3 + 3HCHO + 3H_2 \longrightarrow \underset{\text{Gold sol}}{2Au} + 3HCOOH + 6HCl$$
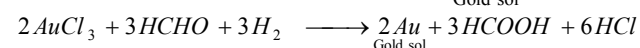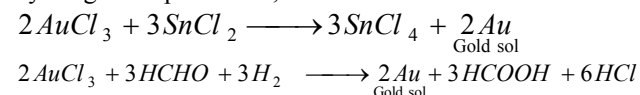
The gold sol, thus prepared, has a purple colour and is called purple of cassius.

4.6.2.3 By hydrolysis : Many salt solutions are rapidly hydrolysed by boiling dilute solutions of their salts. For example, ferric hydroxide and aluminium hydroxide sols are obtained by boiling solutions of the corresponding chlorides. $FeCl_3 + 3H_2O \longrightarrow \underset{\text{Colloidal sol}}{Fe(OH)_3} + 3HCl$

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

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

$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2$

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

Colloid Mill
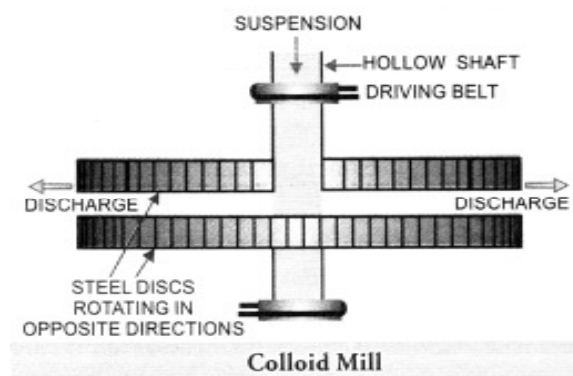
4.6.2.6 By electrical dispersion or Bredig's arc method : This method is used to prepare sols of platinum, silver, copper or gold.

The metal whose sol is to be prepared is made as two electrodes which are immersed in dispersion medium such as water etc. The dispersion medium is kept cooled by ice. An electric arc is struck between the electrodes. The tremendous heat generates by this method and give colloidal solution. The colloidal solution prepared is stabilised by adding a small amount of KOH to it.

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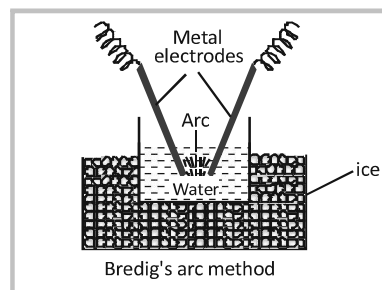
4.6.2.7 By Peptization : The process of converting a freshly prepared precipitate into colloidal form by the addition of suitable electrolyte is called *peptization.* The electrolyte is used for this purpose is called *peptizing agent* or *stabilizing agent.* Cause of peptisation is the adsorption of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

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

Preparation of colloidal sol by peptisation
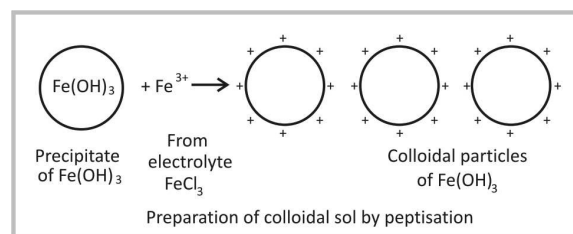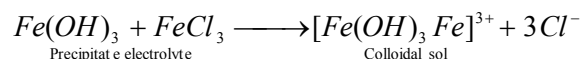
**4.7 Purification of colloidal solution**

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.

4.7.1 Dialysis : The process of separating the particles of colloid from those of crystalloid, by means of diffusion through a suitable membrane is called dialysis. It's principle is based upon the fact that colloidal particles can not pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it.

Dialysis
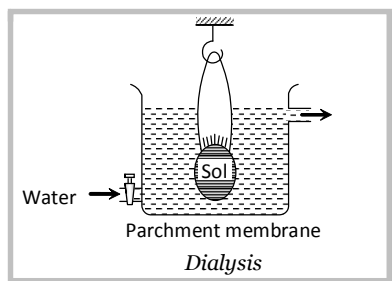
The colloidal solution is taken in a bag (parchment paper).The bag is suspended in fresh water. The impurities slowly diffused out of the bag leaving behind pure colloidal solution The distilled water is changed frequently to avoid accumulation of the crystalloids otherwise they may start diffusing back into the bag. Dialysis can be used for removing HCl from the ferric hydroxide sol.

4.7.2 Electrodialysis : *The ordinary process of dialysis is slow.* To increase the pace of purification, the dialysis is carried out by applying electric field. This process is called *electrodialysis.* Kidneys in the human body act as dialysers to purify blood which is colloidal in nature. The important application of dialysis process in the artificial kidney machine used for the purification of blood of the patients whose kidneys have failed to work. The artificial kidney machine works on the principle of *dialysis.*

Electro-dialyser
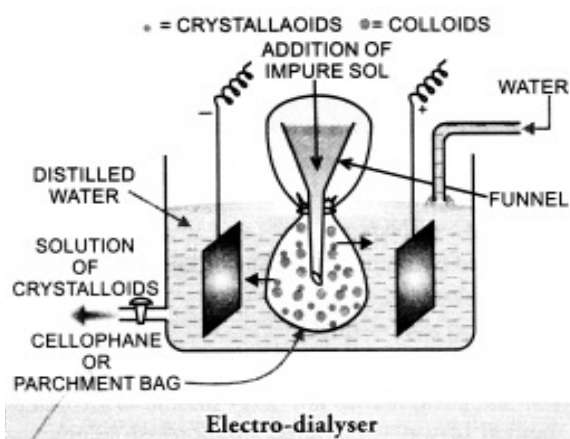
4.7.3 Ultra – filtration : Sol particles directly pass through ordinary filter paper because their pores are larger (more than 1μ or $1000\,m\mu$) than the size of sol particles (less than $200\,m\mu$). If the pores of the ordinary filter paper are made smaller by soaking the filter paper in a solution of gelatin or colloidion and subsequently hardened by soaking in

formaldehyde, the treated filter paper may retain colloidal particles and allow the true solution particles to escape. Such filter paper is known as *ultra - filter* and the process of separating colloids by using ultra – filters is known as *ultra – filtration.*

4.7.4 Ultra – centrifugation : The sol particles are prevented from setting out under the action of gravity by kinetic impacts of the molecules of the medium. The setting force can be enhanced by using high speed centrifugal machines having 15,000 or more revolutions per minute. Such machines are known as *ultra–centrifuges*.

4.8 Properties of colloidal solutions

The main characteristic properties of colloidal solutions are as follows.

4.8.1 Physical properties :

- **Heterogeneous nature :** Colloidal sols are heterogeneous in nature. They consists of two phases; the Dispersed Phase and the Dispersion Medium.

- **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.

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

4.8.2 Colligative properties :

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

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

4.8.3 Mechanical properties :

- **Brownian movement :**

The colloidal particles are moving at random in a *zig – zag* motion. This type of motion is called *Brownian movement.*


Brownian movement of colloidal particles
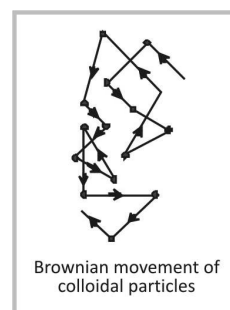
The reason of brownian motion is that the molecules of the dispersion medium are constantly colloiding with the particles of the dispersed phase.

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

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

4.8.4 Optical properties : Tyandall effect :

When light passes through a sol, its path becomes visible because of scattering of light by particles. It is called *Tyndall effect.* This phenomenon was studied for the first time by *Tyndall.* The illuminated path of the beam is called *Tyndall cone. In a true solution, there are no particles of sufficiently large diameter to scatter light and hence no Tyndall effect is observed. The Tyndall effect has also been observed by an instrument called* **ultra – microscope.**

Tyndall effect
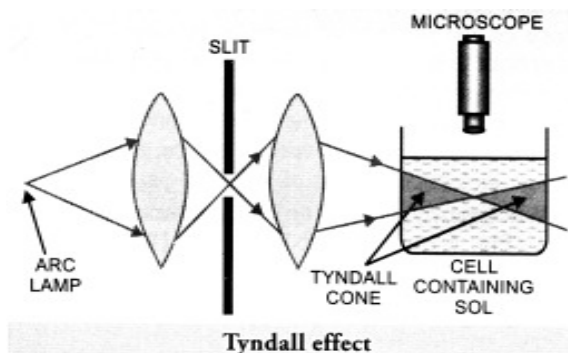
4.8.5 Electrical properties :

Colloidal particles carry an electric charge and the dispersion medium has an opposite and equal charge, the system as a whole being electrically neutral. The presence of equal and similar charges on colloidal particles is largely responsible in giving stability to the system because the mutual forces of repulsion between similarly charged particles prevent them from coalescing and coagulating when they come closer to one another.

4.9 Origin of the charge on colloidal particles

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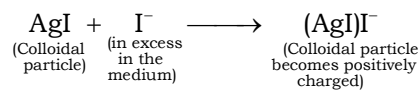
4.9.1 Due to the dissociation of the surface molecules:

Some colloidal particles develop electrical charge due to the dissociation / ionisation of the surface molecules. The charge on the colloidal particles is balanced by the oppositely charged ions in the sol. For example, an aqueous solution of soap (sodium palmitate) which dissociates into ions as, $C_{15}H_{31}COONa \rightleftharpoons C_{15}H_{31}COO^- + Na^+$.
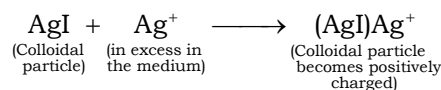Sodium palmitate

The cations (Na^+) pass into the solution while the anions ($C_{15}H_{31}COO^-$) have a tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains.
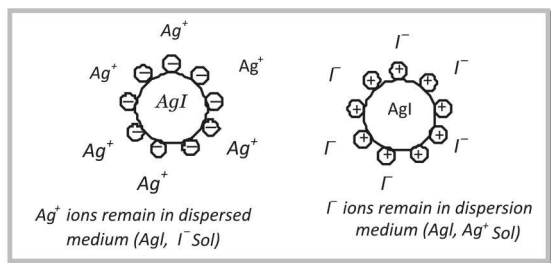
4.9.2 Due to frictional electrification :
It is believed that the frictional electrification due to the rubbing of the dispersed phase particles with that of dispersion medium results in some charge on the colloidal particles. The dispersion medium must also get some charge, because of the friction. Since it does not carry any charge, the theory does not seem to be correct.

4.9.3 Due to selective adsorption of ions :
The particles constituting the dispersed phase adsorb only those ions preferentially which are common with their own lattice ions. For example, when a small quantity of silver nitrate ($AgNO_3$) solution is added to a large quantity of potassium iodide (KI) solution, the colloidal particles of silver iodide adsorb I^- from the solution to become ***negatively charged,*** *(at this stage KI is in excess, and I^- being common to AgI)*

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

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

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

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

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

Similarly, the ferric hydroxide colloidal particles develop positive charge due to the adsorption of Fe^{3+} ions from the solution.

$$Fe(OH)_3 + Fe^{3+} \longrightarrow Fe(OH)_3.Fe^{3+}$$
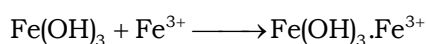
(Colloidal particle)   (in exess in the medium)   (Colloidal particle of ferric hydroxide get positively charged due to the adsorption of Fe^{3+} ions on it)

Ferric hydroxide colloidal particles develop negative charge due to adsorption of either OH^- or

$$Fe(OH)_3 + OH^- \longrightarrow Fe(OH)_3 \cdot OH^-$$
(Colloidal particle)   (in excess)   (Negatively charged ferric hydroxide colloidal particle)

$$Fe(OH)_3 + Cl^- \longrightarrow Fe(OH)_3 \cdot Cl^-$$
(Colloidal particle)   (in excess)   (Negatively charged ferric hydroxide colloidal particle)
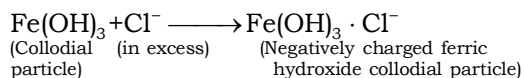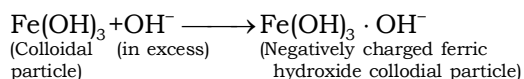
4.10 Electrophoresis

The phenomenon of movement of colloidal particles under an applied electric field is called *electrophoresis.* If the particles accumulate near the negative electrode, the charge on the particles is *positive.* On the other hand, if the sol particles accumulate near the positive electrode, the charge on the particles is *negative.*

(a) *Before electrophoresis*

(b) *After electrophoresis*

Process of electrophoresis
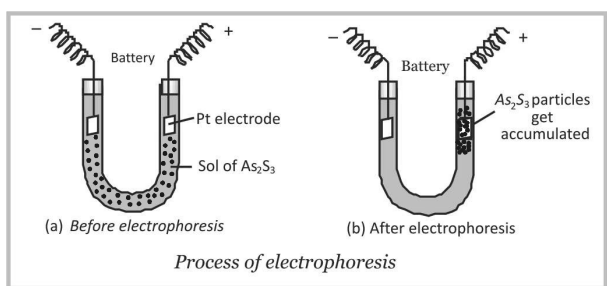
4.10.1 Electrical double layer theory : The electrical properties of colloids can also be explained by electrical double layer theory. According to this theory *a double layer of ions appear at the surface of solid.* The ion preferentially adsorbed is held in fixed part and imparts charge to colloidal particles. The second part consists of a diffused mobile layer of ions. This second layer consists of both the type of charges. The net charge on the second layer is exactly equal to that on the fixed part. The existence of opposite sign on fixed and diffuse parts of double layer leads to appearance of a difference of potential, known as *zeta potential or electrokinetic potential.* Now when electric field is employed the particles move (electrophoresis)

Formation of electrical double layer
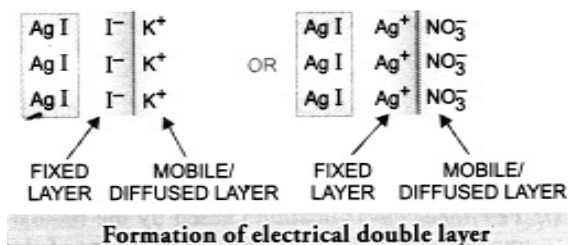
4.10.2 Electro-osmosis : In it the movement of the dispersed particles is prevented from moving by *semipermeable membrane.* Electro-osmosis is a phenomenon in which dispersion medium is allowed to move under the influence of an electrical field, whereas colloidal particles are not allowed to move. The existence of electro-osmosis has suggested that when liquid is forced through a porous material or a capillary tube, a potential difference is setup between the two sides called as **streaming potential.**

Electro-osmosis
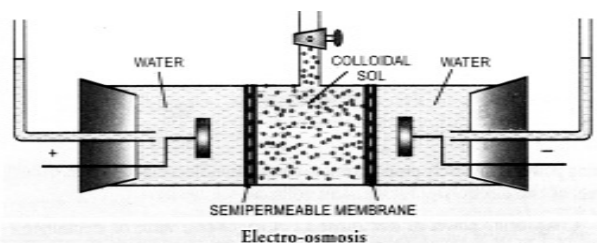
4.11 Stability of sols

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

4.11.1 Stronger repulsive forces between the similarly charged particles : All colloidal particles in any sol possess similar charge. Therefore, due to the electrostatic repulsion these are not able to come closer and form aggregates. Thus stronger repulsive forces between the similarly charged particles in a sol promote its stability.

4.11.2 Particle-solvent interactions : Due to strong particle-solvent (dispersion medium) interactions, the colloidal particles get strongly solvated. Due to solvation, the effective distance between the colloidal particles increases, and therefore, the Vander Waal's force of attraction decreases. As a result, the particles are not able to form aggregates. Lyophilic sols are mainly stabilized by solvation effects due to strong interactions between the sol particles and the dispersion medium.

4.12 Coagulation or Flocculation or Precipitation

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

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

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

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

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

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

4.12.6 Hardy schulze rule :

The coagulation capacity of different electrolytes is different. It depends upon the valency of the active ion are called flocculating ion, which is the ion carrying charge opposite to the charge on the colloidal particles. *Greater the valency of the active ion or flocculating ion, greater will be its coagulating power*".

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

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

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

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

4.12.7 Coagulation or flocculation value :

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

or

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

Thus , a more efficient flocculating agent shall have lower flocculating value.

FLOCCULATION VALUES OF SOME ELECTROLYTES

Sol	Electrolyte value (mM)	Flocculation	Sol	Electrolyte	Flocculation value (mM)	
As_2S_3 (–vely charged)	NaCl	51.0	Fe(OH)$_3$ (+vely charged)	KCl	9.5	
	KCl	49.5		BaCl$_2$	9.3	
	CaCl$_2$	0.65		K$_2$SO$_4$	0.20	
	MgCl$_2$	0.72		MgSO$_4$	0.22	
	MgSO$_4$	0.81				
	AlCl$_3$	0.093				
	Al$_2$(SO$_4$)$_3$	0.096				
	Al(NO$_3$)$_3$	0.095				

Note : Coagulating value or flocculating value $\propto \dfrac{1}{\text{coagulating power}}$.

4.12.8 Coagulation of lyophilic sols : There are two factors which are responsible for the stability of lyophilic sols. These factors are the **charge** and **solvation of the colloidal particles**. When these two factors are removed, a lyophilic sol can be coagulated. This is done by **adding electrolyte** and by **adding suitable solvent**. When solvent such as alcohol and acetone are added to hydrophilic sols the dehydration of dispersed phase occurs. Under this condition a small quantity of electrolyte can bring about coagulation.

4.13 Protection of colloids and Gold number

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

"The phenomenon of preventing the coagulation of a lyophobic sol due to the addition of some lyophilic colloid is called sol protection or protection of colloids." The protecting power of different protective (lyophilic) colloids is different. The efficiency of any protective colloid is expressed in terms of *gold number.*

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

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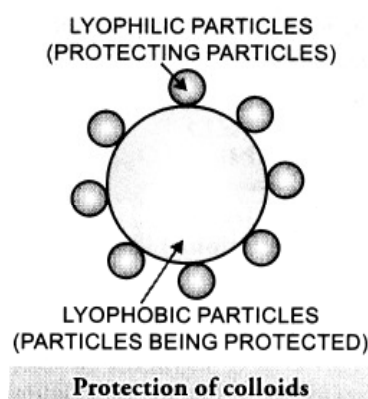
Thus, smaller is the gold number, higher is the protective action of the protective agent.

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

GOLD NUMBERS OF SOME HYDROPHILLC SUBSTANCES

Sr. No.	Hydrophilic substance	Gold number	Hydrophilic substance	Gold number
1.	Gelatin	0.005-0.01	Sodium oleate	0.4 – 1.0
2.	Sodium caseinate	0.01	Gum tragacanth	2
3.	Haemoglobin	0.03-0.07	Patato starch	25
4.	Gum arabic	0.15-0.25		

The protective colloids play very significant role in stabilisation of the non–aqueous dispersions, such as paints, printing inks etc.

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

4.14 Application of colloids

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

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

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

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

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

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

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

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

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

4.14.8 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.

5. EMULSIONS

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

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

Oil droplets
Water
Oil in water
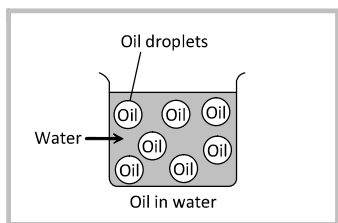
5.1 Types of Emulsion

Depending upon the nature of the dispersed phase, the emulsions are classified as;

phase, the emulsions are classified as;

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

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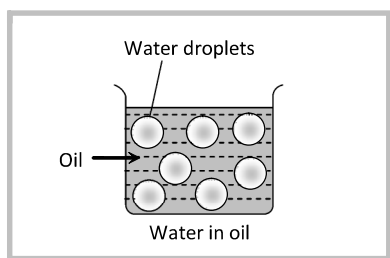
5.1.2 Water-in-oil emulsion (W/O) : The emulsion in which water forms the dispersed phase, and the oil acts as the dispersion medium is called a water-in-oil emulsion. These emulsion are also termed **oil emulsions. Butter** and **cold cream** are typical examples of this types of emulsions. Other examples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

5.2 Preparation of Emulsions

Emulsions are generally prepared by vigorously agitating a mixture of the relevant oil and water by using either a high speed mixer or by using ultrasonic vibrators. The emulsions obtained by simple mechanical stirring are unstable. The two components (oil and water) tend to separate out. To obtain a stable emulsion, a suitable stabilizing substance is generally added. The stabilizing substance is called *emulsifier or emulsifying agent.* The emulsifier is added along with the oil and water in the beginning. For Examples : *s*ubstances which can act as emulsifiers are soaps, detergents, long chain sulphonic acid, lyophilic colloids like gelatin, albumin, casein etc.

5.3 Nature of emulsifier

Different emulsifiers may act differently in the case of a particular emulsion.

For example,

◆ Sodium oleate is used to prepare oil-in-water (O/W) emulsions.

◆ Magnesium and calcium oleates are used to prepare water-in-oil (W/O) emulsions. When calcium oleate is added to an emulsion stabilized by sodium oleate, the stability of the system decreases. At a certain ratio of $Na^+ : Ca^{2+}$, the oil-in-water emulsion becomes unstable. If the Ca^{2+} ions concentration is increased further very quickly, then the reversal of the emulsion type occurs, that is the oil-in-water emulsion gets converted into a water-in-oil type.

5.4 Identification of emulsions

Several methods are available to find out whether an emulsion is of the oil-in-water type or of the water-in-oil type emulsion. An emulsion can be identified as follows.

5.4.1 Dilution test : Add water to the emulsion. If the emulsion can be diluted with water this means that water acts as the dispersion medium and it is an example of oil-in-water emulsion. In case it is not diluted, then oil acts as dispersion medium and it is an example of water-in-oil emulsion.

5.4.2 Dye test : An oil soluble suitable dye is shaken with the emulsion. If colour is noticed on looking at a drop of the emulsion, it is oil-in-water type emulsion. In case the entire background is coloured, it is an example of water-in-oil type.

5.4.3 Conductivity test : Add small amount of an electrolyte (e.g. *KCl*) to the emulsion. If this makes the emulsion electrically conducting , then water is the dispersion medium. If water is not the dispersed phase.

5.5 Properties of emulsion

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

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

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

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

5.6 Applications of emulsions

5.6.1 Concentration of ores in metallurgy

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

5.6.3 Cleansing action of soaps.

5.6.4 Milk, which is an important constituent of our diet an emulsion of fat in water.

5.6.5 Digestion of fats in intestine is through **emulsification**.