SURFACE CHEMISTRY

LECTURE #1

5.0 INTRODUCTION

5.1 DEFINITION OF ADSORPTION AND RELATED TERMS :

(i) Adsorption : The phenomenon of increase in concentration at the surface due to molecular surface force is known as adsorption.

(ii) Adsorbate : The substances solids, gases or liquids which are adsorbed on the surface of adsorbent are called adsorbate.

(iii) Adsorbent : The solid or liquid substance on the surface of which adsorption take place is called adsorbent. Examples of adsorbents are **activated charcoal, Pt, Pd, Ni, Silica gel, gelatin, Al_2O_3, starch.**

(iv) Absorption : When a substance is uniformly distributed throughout the body of a solid or liquid, the phenomenon is called absorption.

(v) Sorption : It may be defined as the process in which both adsorption and absorption take place simultaneously.

Adsorption	Absorption
1. It involves higher concentration of the gas or liquid at the surface of a substance.	**1.** It involves uniform distribution of the molecular species throughout the bulk
2. It is rapid in the beginning and slows down near the equilibrium.	**2.** It occurs at a uniform rate.
3. It is a surface phenomenon.	**3.** It occurs throughout the bOdy of the material.
4. It is a fast process.	**4.** It is a slow process.

Mechanism of adsorption

Adsorption is due to the fact that the surface particles of the adsorbent are in different state than the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface, particles are not surrounded by atoms or molecules on all sides and hence they possess uribalanced or residual attractive forces.

(i) Adsorption is an exothermic process so $\Delta H = -ve$

(ii) Freedom of movement of gas molecules decreases so ΔS gas $= -ve$

(iii) Adsorption is a spontaneous process so $\Delta G = -ve$ but $\Delta S_{total} > 0$

Examples.

1. $H_2O_{(g)}$
   - → Anhy. $CaCl_2$ → Absorption
   - → Silica gel → Adsorption
2. $NH_{3(g)}$
   - → $H_2O_{(l)}$ → Absorption
   - → Charcoal → Adsorption
3. Ink
   - → Chalk → Absorption (water is absorbed)
   - → Chalk → Adsorption (ink is adsorbed)

4. When Charcoal is mixed with Methylene blue then its blue colour is adsorbed (adsorption) by charcoal and the dye becomes colourless.

5. When the Magneson reagent is mixed with white precipitate of $Mg(OH)_2$ blue colour is adsorbed by white precipitate (adsorption) of $Mg(OH)_2$

6. When charcoal is mixed in yellow sugar solution, then yellow colour is adsorbed by characoal and white coloured sugar solution is obtained (adsorption)

5.2 TYPES OF ADSORPTION

Depending upohthe nature of forces between molecules of adsorbate and adsorbent, adsorption is of two types.

Table : Comparison of Physi-sorption and Chemi-sorption

	Physical Adsorption	**Chemical Adsorption**
1.	It is caused by intermolecular van der Waal's forces.	It is caused by chemical bond formation.
2.	It is not specific.	It is highly specific.
3.	It is reversible.	It is irreversible.
4.	Heat of adsorption is low (– 20 to –40 kJ mol^{-1})	Heat of adsorption is high (–80 to –240 kJ mol^{-1})
5.	No appreciable activation energy is involved.	High activation energy is involved.
6.	It forms multimolecular layers on adsorbent surface under high pressure.	It forms unimolecular layer.
7.	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
8.	It decreases with increases of temperature.	It first increases then decreases with temperature.

5.3 FACTORS AFFECTING EXTENT OF ADSORPTION (x/m)

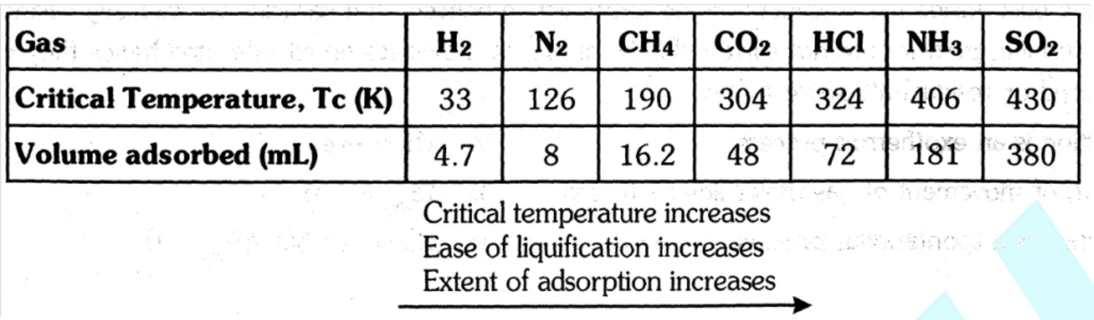
(i) Nature of adsorbent :

For Solids : Adsorption ∝ Surface area of adsorbent or free valency of the solid.

(ii) Nature of adsorbate:

For gases : Adsorption ∝ Critical temperature of gas (T_C)

Volume of gases at N.T.P. adsorbed by 1 g of Charcoal.

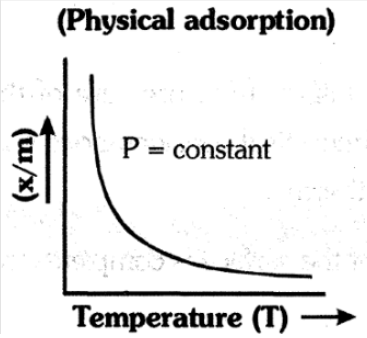


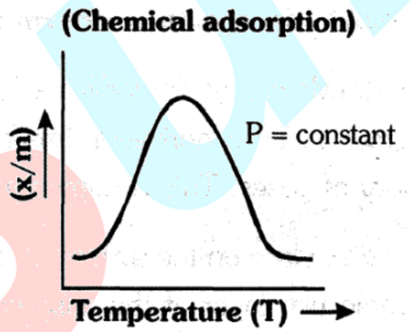
Gas	H_2	N_2	CH_4	CO_2	HCl	NH_3	SO_2
Critical Temperature, Tc (K)	33	126	190	304	324	406	430
Volume adsorbed (mL)	4.7	8	16.2	48	72	181	380

Critical temperature increases
Ease of liquification increases
Extent of adsorption increases →

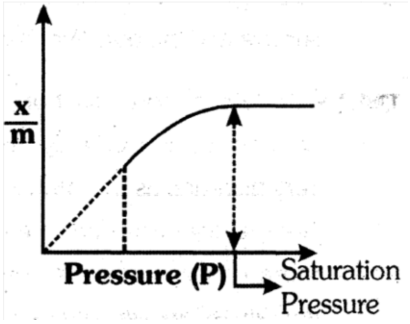
(iii) Effect of temperature : Adsobate + adsorbent *f* Adsorption, ΔH = –ve, exothermic process.

Normally adsorption decreases with temperature because adsorption is exothermic process. Physical adsorption shows regular decrease with temperature, but chemical adsorption first increases then decreases with temperature because it is specific, requires activation energy and in this process heat supplied may be used as its energy of activation.





(iv) Effect of Pressure : (Adsorption Isotherm)



The extent of the adsorption of a gas on a solid is generally expressed as $\frac{x}{m}$

Where:

x - Mass of adsorbate,
m - Mass of adsorbent

Theoretically $\frac{x}{m} \alpha P$

5.4 TYPES OF ADSORPTION ISOTHERM

(a) Freundlich adsorption isotherm : (Physical adsorption)

(i) Freundlich adsorption isotherm is obeyed by the adsorption where the adsorbate forms single layer on the surface of the adsorbent.

$\frac{x}{m} = kP^{\frac{1}{n}}$ Freundlich adsorption isotherm equation; $n \geq 1$

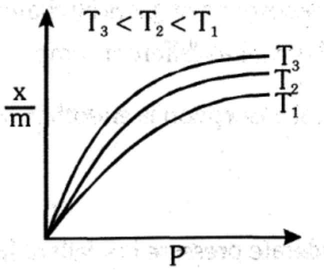
and in logarithmic form $\log\frac{x}{m} = \log k + \frac{1}{n}\log P$; $0 \leq \frac{1}{n} \leq 1$; in general $\frac{1}{n}$ is 0.1 to 0.5.

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

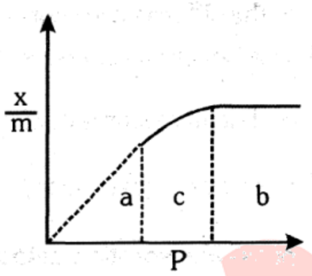
(ii) At low pressure, the extent of adsorption varies linearly with pressure $\frac{x}{m} \propto P$ …(a)

(iii) At high pressure, it becomes independent of pressure. $\frac{x}{m} \propto P^{\circ}$ ..(b)

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



Freundlich adsorption isotherm plot of x/m against P



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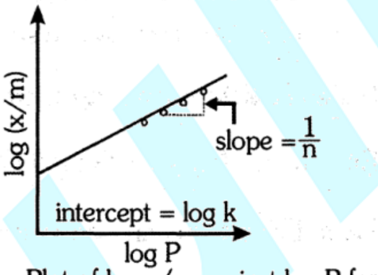


Plot of log x/m against log P for the adsorption of a gas on a solid

Adsorption in solutions (Liquid + Solid)

Ex. Dyes solution + Charcoal

$$\frac{x}{m} = K C^{\frac{1}{n}} \quad [C = \text{concentration of liquid}]$$

(b) The Langmuir adsorption isotherm :

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

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

(iii) Adsorption consists of two opposing processes, namely condensation of the gas molecules on the solid surface and evaporation (desorption) of the gas molecules from the surface back into the gaseous phase.

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

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

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

(vi) Adjacent adsorbed molecules do not interact but adsorbate molecules have equal ability to interact.

APPLICATIONS OF ADSORPTION

The phenomenon of adsorption finds a number of applications. Important ones are listed here:

(i) Gas masks : Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb. poisonous gases.

(ii) Removal of colouring matter from solutions : Animal charcoal removes colours of solutions by adsorbing coloured impurities.

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

- Generally adsorption is exothermic process but an example of chemical adsorption is endothermic.

  Ex. Glass + $H_2(g) \rightleftharpoons$ Glass/$H_2(g)$; ΔH = Positive [Exception]
- Freundlich adsorption isotherm explains physical adsorption upto moderate pressure but fails at high pressure.
- Occlusion → Adsorption of gases on metal surface voids is caned occlusion.

GOLDEN KEY POINTS

- Generally adsorption is exothermic process but an example of chemical adsorption is endothermic.

  Ex. Glass+ $H_2(g) \rightleftharpoons$ Glass/$H_2(g)$; ΔH = Positive [Exception]
- Freundlich adsorption isotherm explains physical adsorption up to moderate pressure but Jails at high pressure.
- Occlusion → Adsorption of gases on metal surface voids is called occlusion.

BEGINNER'S BOX-1

1. Which of the following is used to absorb water?

(1) Silica gel (2) Calcium acetate
(3) Hair gel (4) Anhydrous $CaCl_2$

2. The heat evolved in physisorption lies in the range (kJ/mol) of
(1) 20-40 (2) 40-100
(3) 100-200 (4) 200-400

3. Adsorbed acetic acid on activated carbon is
(1) Adsorbed (2) Absorber
(3) Adsorbent (4) Adsorbate

4. A plot of log ($\frac{x}{m}$) v/s log P for the adsorption of a gas on a solid gives a straight line with slope equal to
(1) $\frac{1}{n}$ (2) n (3) log k (4) k

5. The graph between log -m v/s log P is straight line inclined at ao. ang.l e 45° with, in.. terc.e pt 0.30. What will be rate of adsorption at pressure 0.4 atm.
(1) 0.4 (2) 0.6 (3) 0.8 (4) 0.9

6. 1 g of charcoal having surface area $3.02\times10^{2}m^{2}$ is mixed in 100 ml of 0.5 M acetic add solution; after few times concentrations of solution becomes1 0.49 M what will be surface area occupied one molecule of acetic acid ?
(1) 2×10^{-19} m^2 (2) 5×10^{-19} m^2 (3) 6×10^{20} m^2 (4) 10^{-3} m^2

5.5 COLLOIDAL SOLUTION

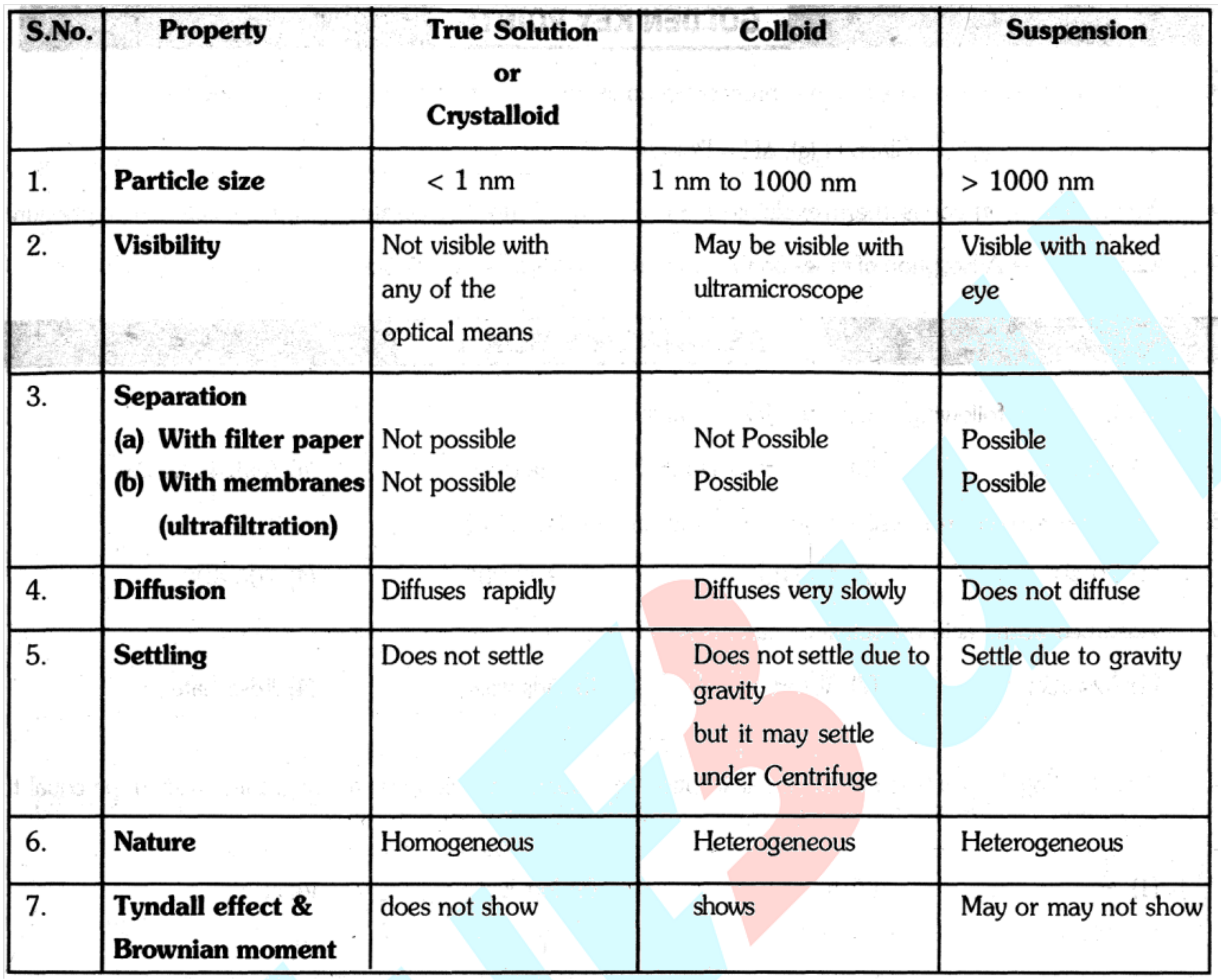
Thomas Graham (1861) studied the process of diffusion of dissolved substances through a parchment paper or an animal membrane and divided the substances into two classes :-
(1) Crystalloid (2) Colloid

But this classification soon proved to be wrong since a crystalloid could behave as a colloid under different conditions and vice-versa.

For example: NaCl behaves as a crystalloid in aqueous medium and behaves as a colloid in benzene medium, whereas soap behaves as a typical colloid in water and behaves as a crystalloid in alcohol.

So new classification was given based on the size of solute particles.

Table : Comparison of true solutions, colloids and suspension

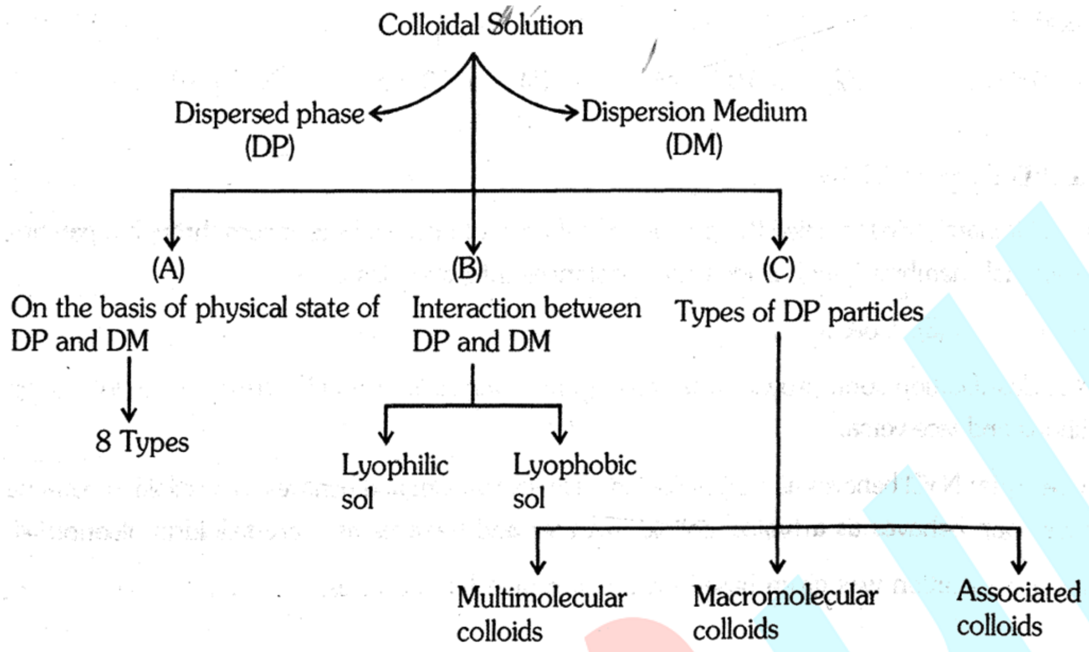


S.No.	Property	True Solution or Crystalloid	Colloid	Suspension
1.	**Particle size**	< 1 nm	1 nm to 1000 nm	> 1000 nm
2.	**Visibility**	Not visible with any of the optical means	May be visible with ultramicroscope	Visible with naked eye
3.	**Separation**			
	(a) With filter paper	Not possible	Not Possible	Possible
	(b) With membranes (ultrafiltration)	Not possible	Possible	Possible
4.	**Diffusion**	Diffuses rapidly	Diffuses very slowly	Does not diffuse
5.	**Settling**	Does not settle	Does not settle due to gravity but it may settle under Centrifuge	Settle due to gravity
6.	**Nature**	Homogeneous	Heterogeneous	Heterogeneous
7.	**Tyndall effect & Brownian moment**	does not show	shows	May or may not show

5.6 TYPES OF COLLOIDAL SOLUTIONS

A colloidal system is made of two phases. The substance distributed as the colloidal particles is called **Dispersed phase** or internal phase or the discontinuous phase. The continuous phase in which the colloidal particles are dispersed is called dispersion medium. for example-, for a colloidal solution of copper in water, copper particles constitute the dispersed phase and water the dispersion medium,

Depending on the dispersed phase or dispersion medium, colloidal solutions can be classified by 3 ways-



A. CLASSIFICATION OF COLLOIDAL SYSTEMS BASED ON DISPERSED PHASE AND DISPERSION MEDIUM

Dispersed phase	Dispersion medium	Type of Colloidal Solution	Example
Solid	Solid	Solid sol	Ruby glass (Gold dispersed in glass), Gem stones, Minerals
Solid	Liquid	**Sol**	Ink, Colloidal gold, Paints, Cell fluids, Silt
Solid	gas	Aerosol	Dust, Soot in air, smoke
liquid	Solid	**Gel**	Cheese, curd, Jellies, Boot polish, Opal, Butter
liquid	Liquid	**Emulsion**	Milk, Hair cream, **butter**, Cold Cream
liquid	gas	Aerosol	Fog, Mist, Clouds, Insecticide sprays
gas	Solid	Solid Sol	Cork, Pumice stone, Foam rubber, Bread, Cake
gas	Liquid	Foam	Whipped Cream, Shaving Cream, Soda water, Soap lather

A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular structure but colloidal solution is heterogeneous in nature.

Sol : If the colloidal system has the appearance of a fluid, then it is called a **Sol.** On the basis of dispersion medium different types of sols are possible.

S.N.	Dispersion medium	Name of solution
i.	Water	Hydrosol or aquasol
ii.	Benzene	Benzosol
iii.	Alcohol	Alcosol
iv.	Air	Aerosol

EMULSIONS:

Emulsions are liquid-liquid colloidal system They are of two types
(i) Oil dispersed in water (O/W type) (ii) Water dispersed in oil(W/O type)
In the first type water acts as a dispersion medium. Examples of this type of emulsions are **milk** and **vanishing** cream. In milk, liquid fat is dispersed in water.
In the second system, oil acts as dispersion Medium. Common examples of this type are **butter**, **cold cream**, and **cod liver oil** etc.
Emulsions of oil and water are unstable and sometimes they separate into two layers on standing. For stabilization of an emulsion, a third compenent called emulsifying agent is usually added. The emulsifying agent forms ill an interfacial film between suspended particles and the medium. The principal emulsifying agents for o/w emulsions are **proteins**, **gums, soaps**, etc. For w/o emulsion the principal emulsifying agents are **heavy metal salts of fatty acids, lon9 chain alcohol, lamp black.**

GELS:

A get is a jelly like colloidal system in which a liquid is dispersed in a solid medium. Gelatin can behave both as sol and gel. **Gels may be classified into two types -**
(a) Elastic gels : These are those which possesses the property of elasticity. They change their shape on applying force and return to original shape when the force is removed. Gelatin, starch and soaps are examples of substances which form elastic gels.
(b) Non - elastic gels : These are the gels which are rigid like Silica gel. These are prepared by appropriate chemical action. Thus silica gel is produced by adding concentrated hydrochloric acid to sodium silicate solution of the correct concentration.

(B) CLASSIFICATION BASED ON INTERACTION BETWEEN DISPERSED PHASE AND DISPERSION MEDIUM :

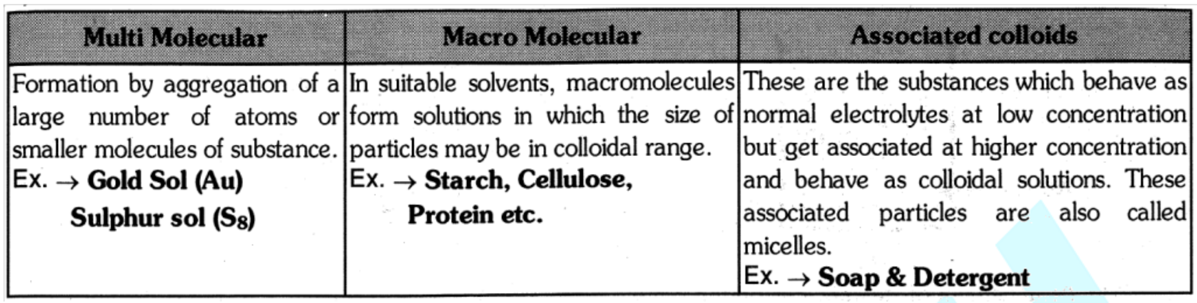
LYOPHILIC SOL AND LYOPHOBIC SOL

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion medium, are called lyophilic sols (Solvent - loving). For example - dispersion of gelatin, starch, gum and proteins in water.
Colloidal solutions in which the dispersed phase has no affinity or attraction for the medium or for the solvent are called Lyophobic colloidal (Solvent hating) solutions. Eg. : Metals and their sulphides.

Comparison of Lyophilic and Lyophobic sols

S.No	Property	Lyophilic sol (Emulsoid)	Lyophobic sol (suspensoid)
1	**Preparation**	Can be easily prepared by shaking or warming the substance with solvent	Can not be prepared easily Special methods are required
2	**Stability**	Are more stable	Are less stable
3	**Reversibility**	Are reversible	Are irreversible
4	**Viscocity**	Viscosity is much higher than that of solvent	Viscosity is nearly same as that of the solvent
5	**Surface tension**	Surface tension is usually low	Surface tension is almost same as that of solvent
6	**Hydration or solvation**	These are highly solvated as the particle have great affinity for solvent	These are less solvated as the particles have less affinity for the solvent
7	**Charge**	The particles have little charge or no charge at all	The particles carry a characteristic charge either positive or negative
8	**Visibility**	Particles can not be seen under microscope	Particles can be seen under microscope
9	**Coagulation or precipitation**	Precipitated by high concentration of electrolytes	Precipitated by low concentration of electrolytes
10	**Tyndall effect**	Less Scattering	More Scattering
11	**Migration in electric field**	May or may not migrate as they may or may not carry charge	Migrate towards anode or cathode as these particles carry charge
12	**General Example**	**Mostly of organic nature** Example : Gelatin, Starch, Gum, Albumin & Cellulose Solution	**Mostly of Inorganic nature** Example : Transition metal salt like Gold, As etc.

(C) ON THE BASIS OF TYPE OF DISPERSED PHASE



Multi Molecular	Macro Molecular	Associated colloids
Formation by aggregation of a large number of atoms or smaller molecules of substance. Ex. → **Gold Sol (Au)** **Sulphur sol (S_8)**	In suitable solvents, macromolecules form solutions in which the size of particles may be in colloidal range. Ex. → **Starch, Cellulose,** **Protein etc.**	These are the substances which behave as normal electrolytes at low concentration but get associated at higher concentration and behave as colloidal solutions. These associated particles are also called micelles. Ex. → **Soap & Detergent**

The negative ions aggregate to form a micllle of colloidal size. The negative ion has a long hydrocarbon chain and a polar group ($-COO^-$) at one end. In micelle formation, the long hydrocarbon chain (tail) which is insoluble in water is directed towards the centre while the soluble polar head is on the surface in contant with water. The charge on the moicelle is responsible for the stabnility of this system.

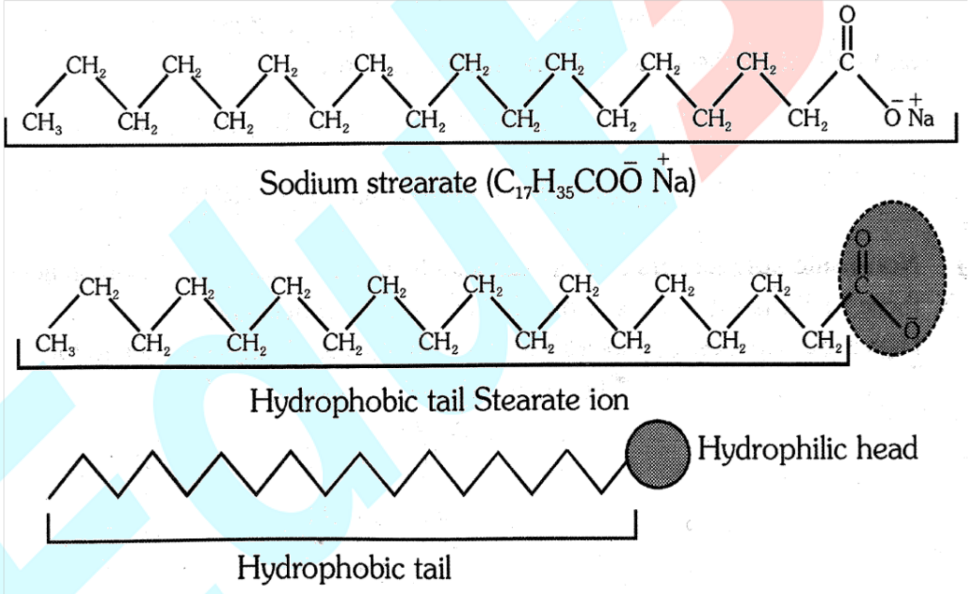
Critical Micelle concentration (CMC) :

The concentration above which associated colloids or Micelles are formed is called CMC,

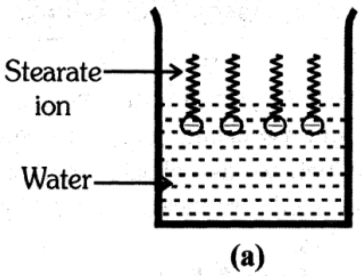
CMC of soap is 10^{-4} to 10^{-3} mol lit^{-1}

These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

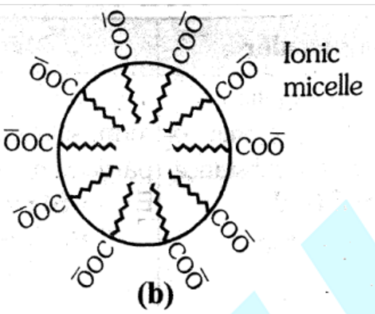
Kraft Tempearature (T_K) : Temperature above which Micelles are formed.



Hydrophobic and hydrophilic parts of stearate ion



(a) Arrangement of stearate ions on the surface of water at low concentrations of soap



(b) Arrangement of stearate ions inside the bulk of water (ionic micelle) at critical micelle concentrations of soap

NECESSARY AND SUFFICIENT CONDITION FOR MICELLE FORMATION ARE:-

(a) Compounds must have hydrophobic part means long chain alkyl group.

(b) Compounds must have hydrophillic part means $-SO_3^-$, $-COO^-$, $-\ddot{\underset{\cdot\cdot}{O}}-$, $-\overset{+}{N}R_3$ etc.

All these compounds which forms micelle are also known as surfactants. They are surface active agents which reduces surface tension.

SURFACTANTS :

Surfactants are those substances which are preferentially adsorbed at the interfaces like air-water, oil-water and solid-water interfaces. Thus, it is the sw:factant which is responsible for micellisation and emulsification.

Surfactants are divided into three categories:

(i) Catioqic surfactants :

Such substances on ionisation give a cation having hydrophobic and hydrophilic group, e.g., cetylpyridinium chloride.

Cetyltrimethyl ammonium chloride,	$C_{16}H_{33}(CH_3)_3\overset{+}{N}Cl^-$
Octadecyl ammonium chloride	$C_{18}H_{37}NH_3^+Cl^-$

Ionisation of these compounds may be represented as

$$C_{18}H_{37}NH_3^+Cl^- \xrightarrow{\text{Water}} \underset{\text{(Hydrophobic end)}}{C_{18}H_{37}NH_3^+} + \underset{\text{(Hydrophilicend)}}{Cl^-}$$

(ii) Anionic surfactants : Such substances give anion which act as surfactant

e.g. :- SodiumPalmitate $C_{15}H_{31}COONa$
Sodium Oleate $C_{17}H_{33}COONa$

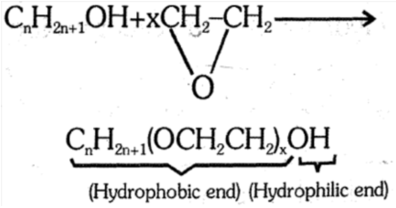
and salts of sulphonic acid having molecular formula

$C_nH_{2n+1}SO_3M$ where, $M^+ = Na, K^+, NH_4^+$, etc.

$$C_{15}H_{31}COONa \xrightarrow{\text{Water}} \underset{\text{(Hydrophobic end)}}{C_{15}H_{31}} + \underset{\text{(Hydrophilicend)}}{COO^-} + Na^+$$

(iii) Non-ionic surfactants : These surfactants do not ionise or dissociate in aqueous medium, but these molecules also have hydrophobic and hydrophilic end.

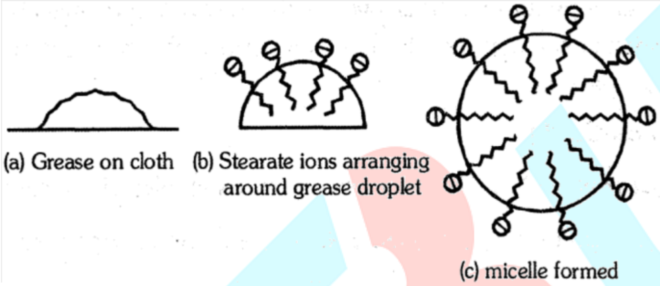
High molecular mass alcohol adds to several molecules of ethylene oxide to form hydroxy surfactant.



$$C_nH_{2n+1}OH + xCH_2-CH_2 \longrightarrow \underbrace{C_nH_{2n+1}(OCH_2CH_2)_x}_{\text{(Hydrophobic end)}}\underbrace{OH}_{\text{(Hydrophilic end)}}$$

CLEANSING ACTION OF SOAPS

The cleansing action of soap is due to fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of stearate ions in the oil droplet and hydrophilic part projects out of grease droplet like bristles. Thus soap helps in emulsification and washing away of oils and fats. The negatively charged sheath around the globules prevents them from coming together and forming aggregates.

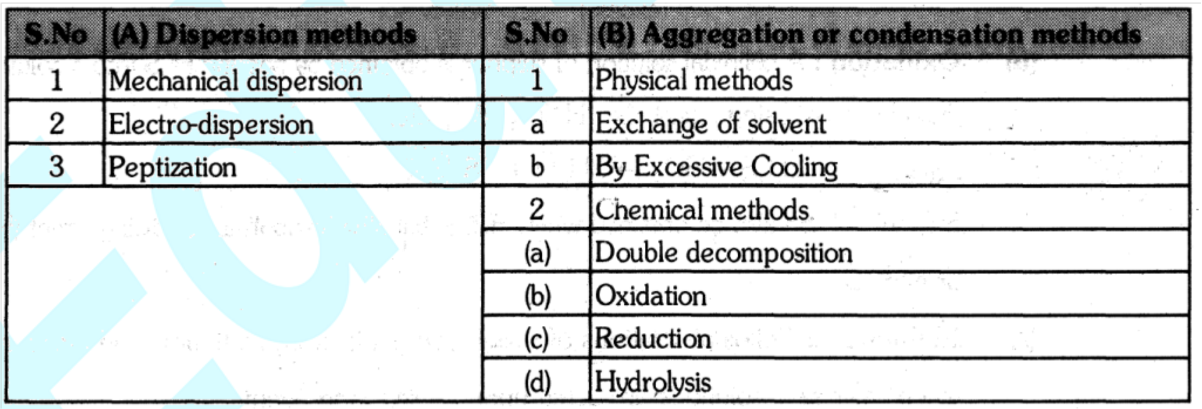

(a) Grease on cloth (b) Stearate ions arranging around grease droplet (c) micelle formed

5.7 METHODS OF PREPARATIONS

Lyophilic sols may be prepared by simply warming the solid with liquid dispersion medium eg. starch with water. On the other hand lyophobic sols have to be prepared by special methods. These methods fall into two categories –

(A) Dispersion Methods : In this larger macro sized particles are broken down to colloidal size

(B) Condensation Methods : In this colloidal sized particles are built up by aggregating single ions or molecules. This method is known as condensation method.



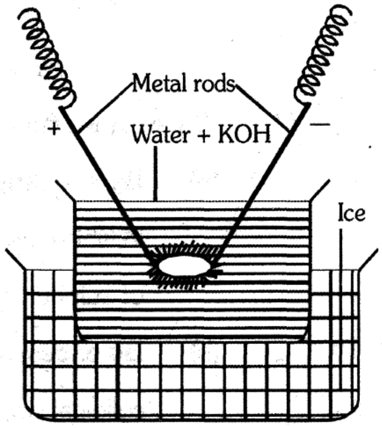
S.No	(A) Dispersion methods	S.No	(B) Aggregation or condensation methods
1	Mechanical dispersion	1	Physical methods
2	Electro-dispersion	a	Exchange of solvent
3	Peptization	b	By Excessive Cooling
		2	Chemical methods
		(a)	Double decomposition
		(b)	Oxidation
		(c)	Reduction
		(d)	Hydrolysis

(A) Dispersion Methods.

(i) Mechanical dispersion : The substance to be dispersed is grinded as finely as possible and then shaken with the dispersion medium to form a suspension. This suspension is passed through colloidal mill where the suceided particles are broken to produce particles of colloidal size.

Ex.: Ink, paints.

(ii) Electro-dispersion (Bredig's arc method):



Electro-dispersion

This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum etc. An arc is struck between the metal electrodes under the surface of water containing some stabilizing agent such as a trace of KOH. The water is cooled by immersing the container in a ice bath: The intense heat of the arc vaporizes some of the metal which condenses under cold water.

Ex. : Pt, Ag, Cu, Au, Ph Sol are prepared by this method.

(iii) Peptization (Peptization is a opposite process of coagulation)

The process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte. The electrolyte used is called a **Peptizing agent.**

FEW EXAMPLES OF SOLS OBTAINED BY PEPTIZATION :

(i) $AgI \downarrow + AgNO_3 \rightarrow [AgI]\ Ag^+ \text{ Ɱ } NO_3^-$

(ii) $AgI \downarrow + KI \rightarrow [AgI]\ I^- \text{ Ɱ } K^+$

(iii) $Fe(OH)_3 \downarrow + FeCl_3 \rightarrow [Fe(OH)_3]\ Fe^{3+} \text{ Ɱ } 3Cl^-$

(iv) $Fe(OH)_3 \downarrow + NaOH \rightarrow [Fe(OH)_3]OH^- \text{ Ɱ } Na^+$

(v) $CdS \downarrow + H_2S \rightarrow [CdS]\ S^{2-} \text{ Ɱ } 2H^+$

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

(B) Condensation methods

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

(Optional)

(a) Double decomposition : A 1% solution of arsenic oxide is prepared in hot water. The solution is cooled, filtered and is then gradually added to water saturated with hydrogen sulphide, then a stream of H_2S is passa:l through the solution. This is continued till an intense follow coloured solution is obtained.

$$\underset{}{As_2O_3} + \underset{\text{(excess)}}{3H_2S} \longrightarrow \underset{\text{Yellow sol}}{As_2S_3} + 3H_2O$$

(b) Oxidation : A colloidal solution of sulphur is obtained by passing H_2S into a solution of sulphur dioxide or oxidising agent Ex.: HNO_3, Br_2, Etc.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S \text{ (Sol)}$$

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

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

$$2AuCl_3 + 3SnCl_2 \longrightarrow 3SnCl_4 + 2Au\text{(Sol)}$$

(d) Hydrolysis : Colloidal solution of mqny.metal hydroxides are prepared by this method. Ferric hydroxide sol is prepared by the)tydrolysis of ferric chl6ride with boiling water.

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$

The hydroxide sol of Cr and AI can also be prepared by this method.

(2) Physical Methods :

(a) By exchange of solvent : when a true solution is mixed with an excess of some other solvent in which the solute is insoluble but solvent is soluble, a colloidal sol is formed. For eg. when a solution of sulphur in alcohol is mixed in excess of water, a colloidal solution of Sulphur is formed.

(b) By excessive cooling : Molecules of certain substantances condense together to form particles of colloidal size.

For Example : Colloidal sol of ice in an organic solvent like ether or chloroform may be prepared by freezing the mixture of water and the solvent.

BEGINNER'S BOX-2

1. The nature of colloidal solution obtained when excess $FeCl_3$ is added in precipitate of $Fe(OH)_3$?

(1) (+) vely charged (2) (–) vely charged

(3) No charge (4) All of above

2. Which of the following will form negatively charged colloidal solution ?

(1) 100 ml 0.1 M $AgNO_3$ + 100 ml 0.1 M KI

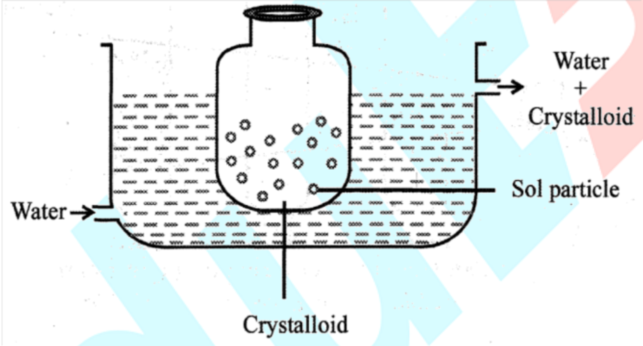
(2) 100 ml 0.2 M $AgNO_3$ + 100 ml 0.1 M KI

(3) 100 ml 0.1 M $AgNO_3$ + 100 ml 0.2 M KI

(4) 100 ml 0.2 M $AgNO_3$ + 200 ml 0.1 M KI

5.8 PURIFICATION OF COLLOIDAL SOLUTION :

(a) Dialysis :



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

(ii) Itsprinciple isbasedupon the fact that colloidal particles can not pass through a parchment or cellophane membrane while the ions of the electrolyte can pass through it.

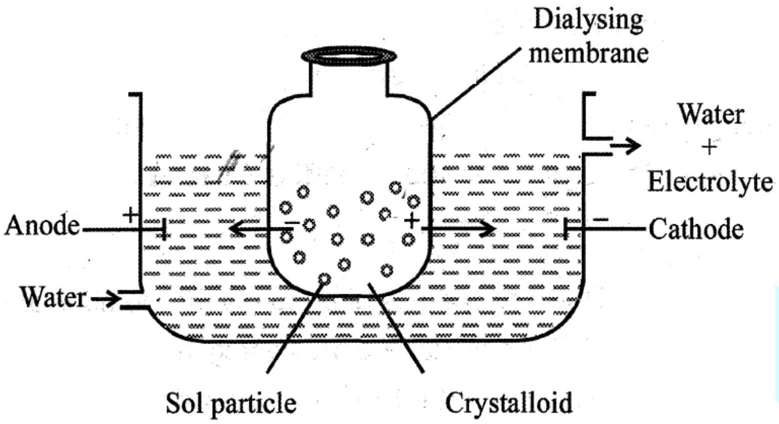
(iii) The impurities slowly diffuse out of the bag leaving behind pure colloidal solution

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

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

(vi) Prolonged dialysis can cause the colloid to coagulate.

(b) Electrodialysis



Process of dialysis can be made faster by applying an electric field if the dissolved substances in the impure colloidal solution is onfy an electrolyte.

(c) **Ultramfitration :**

(i) Sol particles directly pass through ordinary filter paper because their pores are larger than the size of sol particles.

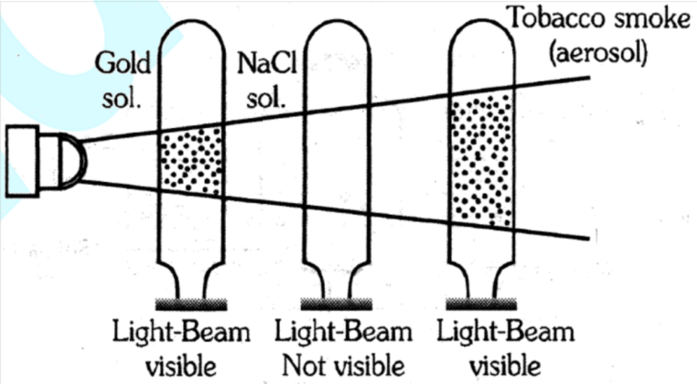
(ii) If the pores of the ordinary filter paper are made smaller by soaking the filter paper in a solution of gelatin or collodion and subsequently hardened by soaking in formaldehyde, the treated filter paper may retain colloidal particles and allow the true solution particles to escape. Such filter paper is known as ultrafilter and the process of separating colloids by using ultrafilters is known as ultrafiltration.

(iii) Collodion is a 4% solution of nitro cellulose in mixture of alcohol and ether.

5.9 PROPERTIES OF COLLOIDAL SOLUTIONS

(a) **Heterogenous :** Colloidal particles in a solution differ in sizes and are not homogeneously distributed through out the solution.

(b) **Vasibility :** Colloidal particles can not be seen with naked eyes or with the help of microscope. Colloidal particles, however scatter light and become visible as bright spots in a dark background when seen through a ultramicroscope. In 1903 Zsigmondy devised a microscope which is based on the principle of scattering of light by sol particles. A strong beam of light is focussed by a series of lenses in a vessel containing the sol. The colloidal solution is observed at right angle to the beam of light.



(c) **Filterability :** Colloidal particles pass through an ordinary filter paper but do not pass through parchment and other fine membranes.

(d) **Surface tension and viscosity :** For Lyophobic sols, surface tension and viscosity are not very different from.those of the medium, as there is very light interaction between the suspended particles and the medium. On the other hand Lyophilic sols show a pigh degree of solvation of the particles and therefore, the properties of the meclium are modified. Thus, the viscosity is much higher for the sol than for the medium. Furthermore the surface tension of the sol is lower than that of pure medium.

(e) **Colour :** The colour of colloidal solution depends on the wavelength of the light scattered by the dispersed particles. The wavelength of the scattered light again depends on the size and the nature of particles. For example the colour of silver sol changes with the particle (suspended) diameter in solution the colour of colloidal solution also change with the manner in which the observer receives the light. For ex. mixture of milk and water appears blue when viewed by reflected light gut red when viewed by transmitted light. finest gold sol is red in colour as size of particle increases it appears purple then blue and finally golden.

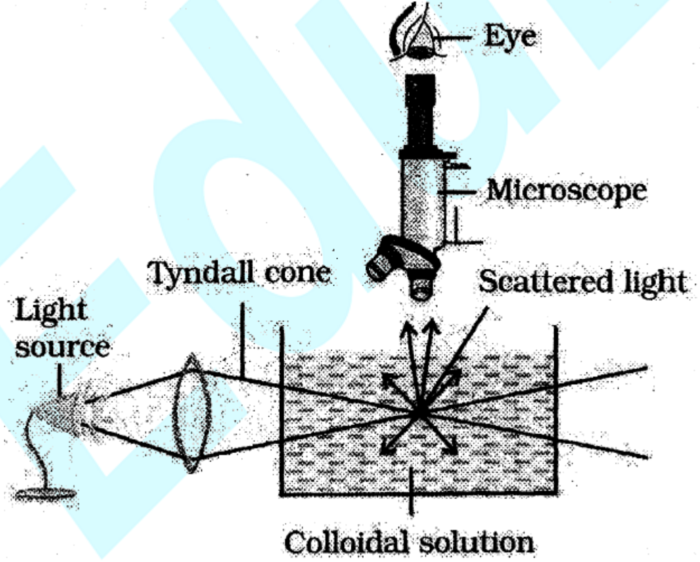
(f) **Colligative properties :**These properties depend on the number of solute particles in solution. In case of colloidal solutions, colloidal particles are the aggregates of ions or molecules and when compared to true solutions or normal solutions, the total no. of particles of solute in solution are very less due to large size and hence these solutions exhibit colligative properties to lesser extent.

(g) **Optical properties (Sols exhibits Tyndall effect) :** When a beam of light is passed through a sol and viewed at right angles, the path of the light shows up as a hazy beam of cone (illuminated path of bluish light). This was first observed by Faraday and later by Tyndall and is known as Tyndall effect. The same phenomenon is observed when a beam of sunlight enters a dark room through a small slit. When light is focussed on· a sol and observed perpendicular to the beam of light rays, a cone is seen which is called Tyndall cone.

Tyndall effecican be observed only when following two conditions can be sptisfied.

(i) Diameter of dispersed particle is not much smaller than wavelength of light used.

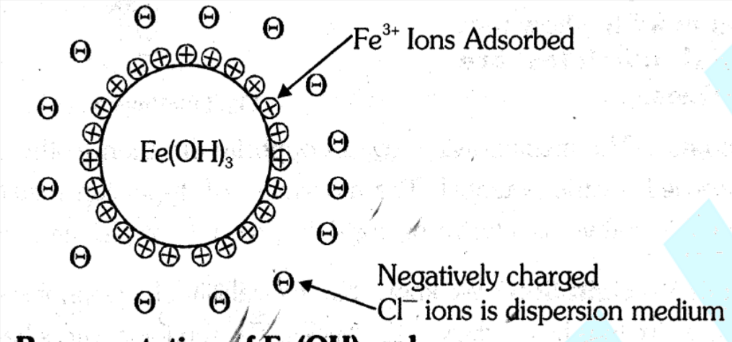
(ii) The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude.



(h) **Kinetic properties :** When a sol is examined with an ultramicroscope, the suspended particles are seen as shining of light. By following an individual particle, it is observed that the particle is in a state of continuous motion in zigzag path. The continuous rapid zigzag motion of a colloidal particle in the dispersion medium is called "Brownian movement or motion" (first observed by British botanist Robert Brown).

The Brownian movement has been explained to be due to the unbalanced bombardments of the colloidal particles by the molecules of dispersion medium.

(i) Charge on colloidal particles : Colloidal particles always carry an electric charge. The mutual forces of repulsion between similarly cruirged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the solution.



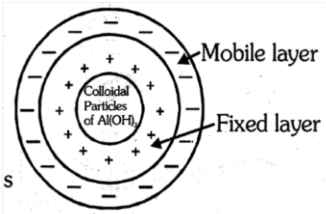
Representation of $Fe(OH)_3$ sol.

	Positively charged		Negatively charged
1.	Metallic hydroxides $Cr(OH)_3$, $Al(OH)_3$ & $Fe(OH)_3$ and hydrated metallic oxides $Al_2O_3.xH_2O$, $CrO_3.xH_2O$	1.	Metallic sulphides like As_2S_3, Sb_2S_3, CdS
2.	Basic dye in acidic medium stuff like:- Methylene blue sol	2.	Acid dye in basic medium stuff like:- Congo red sols
3.	Proteins in (acidic medium)	3.	Metal like – Au, Ag, Cu, Pt etc.
4.	**Haemoglobin (Hb)**	4.	Proteins in (basic medium), Sols of starch, gum, gelatin, clay & charcoal

NOTE : Blood is nbaturally occurring negatively charged colloid but haemoglobin (Hb) is a positively charged colloid.

ELECTRICAL DOUBLE LAYER

The combination .of the two layers of +ve and –ve charges around the sol particle is called **Helmholtz double layer**. According to modem view, the first layer of ions is firmly held and is termed as **Fixed layer** or **Compact layer** while the second layer is mobile which is termed as **Diffused layer.**



The diffused layer is only loosely attached to the particle surface and moves in the opposite direction under an applied electric field. The potential difference between the fixed layer and the diffused layer of opposite charge is called **Electrokinetic Potential or Zeta Potential**.

(j) **Electrophoresis :** If electric potential is applied across two platinum electrodes dipped in a colloidal solution, the colloidal particles move towards one or the other electrode, due to charge on them. The movement of sol particles under an applied electric potential is called "Electrophoresis". Depending upon the direction of movement of particles towards cathode or anode electrophoresis can be called 'Cataphoresis' or 'Anaphoresis'.

Electrophoresis provides an experimental proof to show that the colloidal particles are charged particles.

(k) **Electro osmosis :** The medium will move in opposite direction to the dispersed phase under the influence of applied electric potential. The movemen; of dispersion medium under the influence of applied potential is known as 'Electro-osmosis' .(In presence of plasma membrane)

(l) **Coagulation or Precipitation :** We know that the stability of a lyophobic sol is due to the adsorption of positive or negative ions by the dispersed particles.The repulsion forces between the charged particles do not allow them to settle. If somehow, the charge is removed there is nothing to keep the particles apart from each qther. In such cases they aggregate or flocculate and settle dowri under the action of gravity. The flocculation and settlirlg down of the dispersed phase particles is called· coagulation or precipitation. The precipitation can be brought about in five ways –

Coagulation of lyophobic Sol :

(i) By addition of electrolyte.
(ii) By electrophoresis.
(iii) By mixing two oppositely charged sols.
(iv) By boiling.
(v) By repeated dialysis

(i) **By addition of electrolytes :** When an electrolyte is added in excess to a sol, then the electrolyte furnishes both the type of ions in solution. The oppositely charged ions get adsorbed on the surface of colloidal particles. This causes neutralization and the size mass of colloidal particle increases and it becomes a suspended particle. Due to greater volume and greater mass these suspended particles settle down and coagulate. The ion responsible for neutralization of charge on the particle is called the flocculating ion.

Hardy Schulze Rule : This rule states that the precipitating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion.

The higher the valency of the flocculating ion, the greater is its coagulating power. Thus for the precipitation of As_2S_3 sol (–ve)the precipitating power of Al^{3+}, Ba^{2+}, and Na^+ ions is in the order

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

Similarly for precipitating $Fe(OH)_3$ sol (positive) the precipitating power of $[Fe(CN)_6]^{-3}$, SO_4^{2-} and Cl^- ions is in the order

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

The minimum concentration of an electrolyte in milli moles required to cause precipitation of 1 litre sol in two hours is called FLOCCULATION VALUE. The smaller the flocculating value, the higher will be the coagulating power of the ion.

(ii) By electrophoresis -During electrophoresis the charged sol particles migrate towards the electrode of opposite sign where they deposit their charge and then get coagulated (As neutral particles can aggregate and change to suspension particles.)

(iii) By mixing two oppositely charged sols -The coagulation of two sols of opposite charge can be effected by mixing them eg. $Fe(OH)_3$ (positive sol) and Arsenic sulphide (negative sol) when mixed neutralize each other, join and coagulate.

(iv) By boiling -Sols such as sulphur and silver halides dispersed in water get coagulated when boiled due to increased collisions between sol particles and water molecules, which removes the adsorbed charged layer from the sol and therefore the sol particles settle down.

(v) By repeated dialysis - When dialysis is repeated again and again then colloidal solution gets coagulated.

COAGULATION OF LYOPHIUC SOLS

Lyophilic sols are stable due to less charge and high solvation of th.e colloidal particles. When these two factors are removed, a lyophillic sol can be coagulated.

This is done (i) By adding electrolyte (ii) By adding suitable solvent.

When solvents such as alcohol and acetone are added to hydrophilic sol, the dehydration of dispersed phase occurs. Under this condition a small quantity of electrolyte can bring about coagulation.

BEGINNER'S BOX-3

1. $[Fe(OH)_3]\ Fe^{3+}$; can be coagulated easily by -

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

2. To coagulate $[AgI]\ Ag^+$; NO_3^- Sol; The decreasing order of coagulation power in following is -

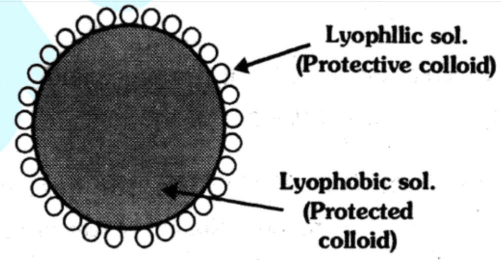
(a) NaCl (b) K_2SO_4 (c) $Ca_3(PO_4)_2$ (d) $K_4[Fe(CN)_6]$

(1) (a) > (b) > (c) > (d) (2) (d) > (c) > (b) > (a)

(3) (a) > (d) > (c) > (b) (4) (d) > (c) > (a) > (b)

5.10 PROTECTION OR PROTECTIVE ACTION :

Lyophobic sols are readily precipitated by adding small amounts of electrolytes. However, these sols are often stabilized by the addition of lyophilic sols.



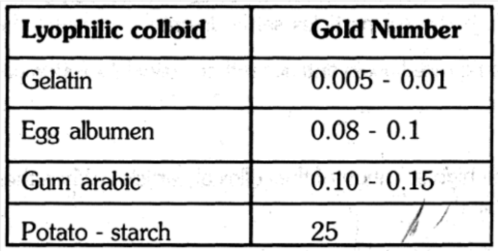
[Protection of lyphobic sol.]

The property of lyophilic sols to prevent the precipitation or coagulation of a lyophobic sol is called protection. The lyophilic sol used to protect a lyophobic sol from precipitation is referred to as a protective colloid lyophilic sols form a thin layer around lyophobic sol or around the ions furnished by electrolyte and therefore the coagulation can not take place (as the size does not increase much). **Gelatin, Albumin, Gum Arabia, Potato Starch** are some of the examples of **Protective colloids**. The lyophilic colloids differ in their protective power. The protective power is measured in terms of gold number.

"Gold number" introduced by Zsigmondy. The number of **milligrams** of a hydrophilic colloid that will just prevent the precipitation of 10 ml of standard gold sol on addition of 1 ml of 10% NaCl solution is known as **Gold number** of that protector (Lyophilic colloid).

The precipitation of the gold sol is indicated by a colour change from red to blue when the particle size just increases.

The **smaller the gold number** of a protective lyophilic colloid, **greater is its protection power**. **Gold Number** of some hydrophilic colloids.



Lyophilic colloid	**Gold Number**
Gelatin	0.005 - 0.01
Egg albumen	0.08 - 0.1
Gum arabic	0.10 - 0.15
Potato - starch	25

$$\text{Gold number} = 10 \times \frac{\text{Mass of lyophillic sol(mg)}}{\text{Volume of lyophobic sol(mL)}}$$

$$\text{Protection Capacity} \ \alpha \ \frac{1}{\text{(Gold number)}}$$

Gelatin and starch have the maximum and minimum protective powers respectively.

BEGINNER’S BOX-4

1. On adding 1mL solution of 10% NaCl to 10 mL gold sol in presence of 0.025 g starch so that coagulation is just prevented what will be gold number of starch.

(1) 0.25 (2) 2.5 (3) 25 (4) 0.025

2. Which one is a natural colloid?

(1) NaCl (2) Sugar (3) RCOONa (4) Blood

3. Collidal solution of silver can be prepared by

(1) Colloidal mill (2) Double decomposition method
(3) Bredig's Arc method (4) Electrodialysis

4. Medicines are more effective if they are used in

(1) Colloidal state (2) Solid state
(3) Solution state (4) None of these

5. Colloidal solution commonly used in treatment of skin diseases is

(1) Colloidal sulphur (2) Colloidal silver
(3) Colloidal gold (4) Colloidal antimony

5.11 APPLICATIONS OF COLLOIDS

Colloids are widely used in the industry. Following are some examples:

(i) Electrical precipitation of smoke : Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator11'is called Cottrell precipitator.

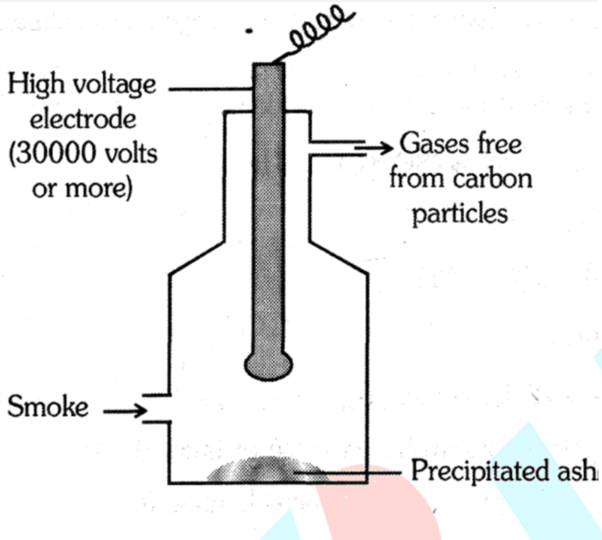


Fig : Cottrell smoke precipitator

(ii) Purification of drinking water : The water obtained .from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.

(iii) Medicines : Most of the medicines are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. Colloidal gold is used for intramuscular injection. Milk of magnesia, an emulsion, is used for stomach disorders. Colloidal medicines are more effective because they have large surface area and are therefore easily assimilated.

(iv) Tanning : Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning. Chromium salts are also used in place of tannin.

(v) Cleansing action of soaps and detergents : This has already been described.

GOLDEN KEY POINTS

- Colloidal solution of graphite in water is called **"Aquadag"** while that in **Oil** is called **Oildag**.
- Gold solution in water is called **Purple of cassius**.

5.12 CATALYST AND CATALYSIS :

Substances which accelerate the rate of a chemical reaction and themselves remain chemically and quqntitatively unchanged after the reaction are known as catalyst and the phenomenon is known as catalysis.

Catalysis can be broadly divided into two groups

(A) Homogeneous catalysis : When the reactants and the catalyst are in the same phase (i.e. liquid or gas), the process is said to be homogeneous catalysis.

Example:

(i) Lead chamber process : Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process

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

(ii) Inversion of cane sugar : In aqueous solution, it is catalysed by dilute acid (hydrogen ions)

$$C_{12}H_{22}O_{11}(aq) + H_2O(\lambda) \xrightarrow{H_2SO_4\,(aq)} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$

(iii) Hydrolysis of methyl acetate is catalysed by H^+ ion furnished by hydrochloric acid

$$CH_3COOCH_3(\lambda) + H_2O(\lambda) \xrightarrow{HCl(l)} CH_3COOH(aq)+CH_3OIH(aq)$$

(B) **Surface catalysis or heterogeneous catalysis :** The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis .

Example:

(i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt.

$$2SO_2(g) + o_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

(ii) Haber process for NH_3

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

(iii) Decomposition of H_2O_2

$$2H_2O_2(\square) \xrightarrow{Pt(s)} 2H_2O(\lambda) + O_2(g)$$

(iv) Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.

$$\text{Vegetable oil } (\lambda) + H_2(g) \xrightarrow{Ni(s)} \text{Vegetable ghee } (s)$$

(v) Synthesis of CH_3OH

$$CO(g) + 2H_2(g) \xrightarrow[ZnO-Cr_2O_3]{Cu} CH_3OH\ (\lambda)$$

SOME OTHER RELATED TERMS

(a) Promoters : Those substances which do not themselves act as catalysts but their presence increases the activity of catalyst are called catalytic promoters.

Example:

In Haber process for the synthesis of ammonia, Fe is catalyst while molybdenum (Mo) acts as a promoter

$$N_2(g) + 3H_2(g) \xrightleftharpoons[Mo(Promoter)]{Fe(catalyst)} 2NH_3(g)$$

(b) Inhibitors : The substance which decreases the rate of chemical reaction is called inhibitor. It increases the activation energy for the reaction.

Example:

$$Na_2SO_3 + \frac{1}{2}O_2 \xrightarrow{C_2H_5OH} Na_2SO_4$$

$$C_6H_5CHO + \frac{1}{2}O_2 \xrightarrow{\text{Diphenalamine}} C_6H_5COOH$$

- ♦ H_3PO_4, glycerol and acetamide decrease the rate of decomposition of hydrogen peroxide.

(c) Catalytic poison : The substance whose presence decreases or destroys the activity of a catalyst is called catalytic poison.

Example:

Carbon monoxide or H_2S act as poison for Fe catalyst in Haber process for manufacture of NH_3.

As_2O_3 acts as poison for Pt asbestos in contact process for H_2SO_4.

(d) Autocatalysts :

When one of the product of the reaction begin to act as a catalyst, it is called auto catalyst.

Example:

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

(Autocatalyst)

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

(Autocatalyst)

In the initial stage the reaction is slow but as soon as the product come into existence the reaction rate increases.

(e) Induced catalyst :

When a chemical reaction enhance, the rate of another chemical reaction it is called induced catalysis.

Example:

Sodium arsenite solution is not oxidised by air if however, air is passed through a mixture of Na_3SO_3 & Na_2SO_3, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus influences the oxidation of sodium arsenite.

$$Na_2SO_3 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4 \qquad Na_3AsO_3 + \frac{1}{2}O_2 \longrightarrow Na_3AsO_4$$

(f) General characteristics of catalysts :

(i) A catalyst remains unchanged in mass and chemical composition but can change their physical state.

(ii) Only a very small amount of catalyst is sufficient to catalyse a reaction.

(iii) A catalyst does not initiate a reaction.

(iv) When a catalyst is a solid, it is usually more efficient when used in finely divided form.

(v) Generally catalyst does not change the nature of products.

(vi) A catalyst does not change the equilibrium state of a reversible reaction but helps to decrease time to achive the equilibrium state or position of equilibrium.

(vii) Catalysts are generally specific in nature.

(viii) Catalyst can change rate constant of the reaction.

(ix) Catalysts participate in mechanism of reaction.

(x) Catalyst does not change enthalpy of reaction, free energy and entropy because they are state function.

(g) Theories of catalysis

(I) Intermediate compound formation theory : This theory explains homogeneous catalysis mainly. According to this theory, the catalyst combines with one of the reactants to give an intermediate compound. This intermediate compound reacts with the other reactants and gives the product and regenerates the catalyst in its original form. Thus the reactants do not directly combine with each other, instead they react through the catalyst which provides an alternative pathway which involves lesser energy of activation.

For example: The function of nitric oxide [NO] as a catalyst in the formation of SO_3 is explained as follows.

$$\underset{\text{(Catalyst)}}{2NO} + \underset{\text{(reactant)}}{O_2} \rightarrow \underset{\text{(Intermediate)}}{2NO_2} \quad ; \quad \underset{\text{(intermediate)}}{NO_2} + \underset{\text{(reactant)}}{SO_2} \xrightarrow[\text{reaction}]{\text{fast}} \underset{\text{(product)}}{SO_3} + \underset{\text{(catalyst regenerated)}}{NO}$$

(II) Adsorption theory : This theory explains the heterogeneous catalysis. The role of a solid catalyst in enhancing the reaction rate is explained on the basis of this theory in the following steps.

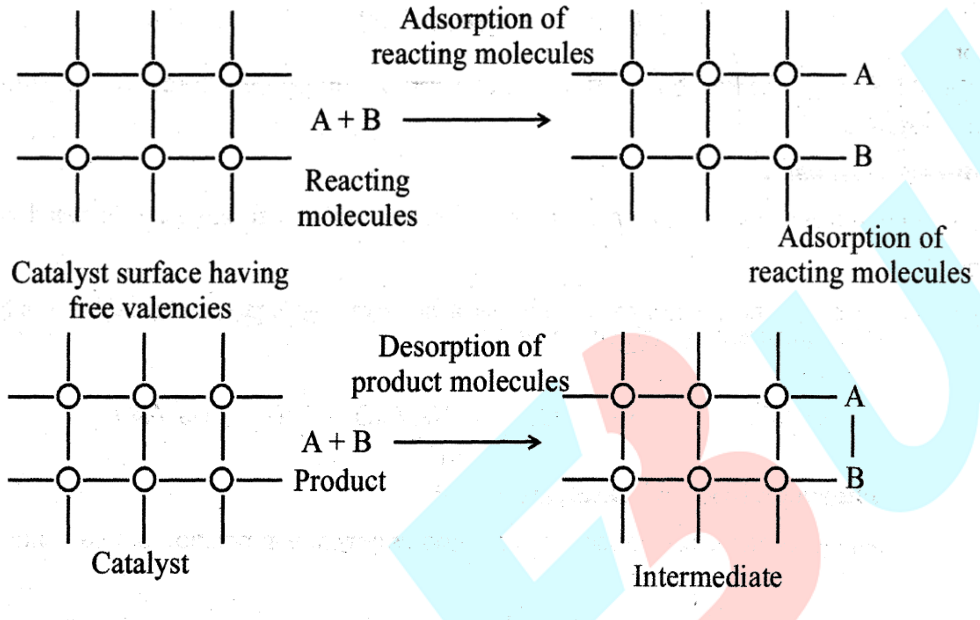


Fig. : Adsorption of reacting molecules, formation of intermediate and desorption of products

(i) The reactant molecules are adsorbed on the surface of the catalyst at adjacent points. Adsorption leads to higher concentration of the adsorbed reactant on the surface of a catalyst.

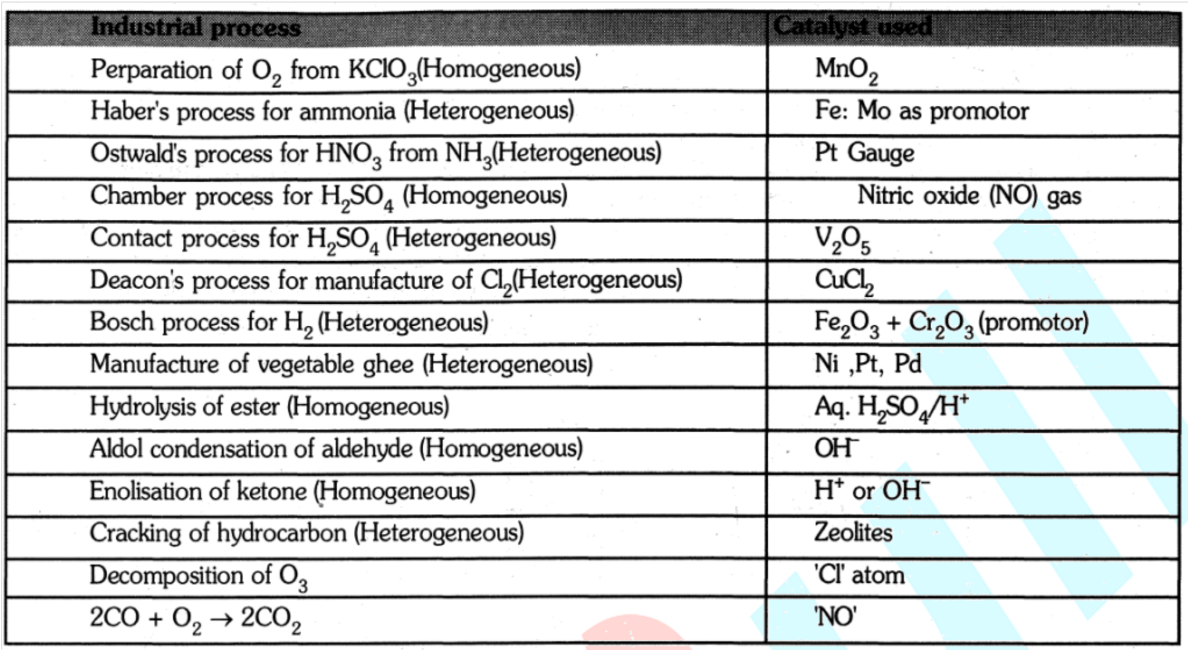
(ii) As adsorption is an exothermic process, the heat of adsorption provides the necessary activation energy for the chemical reaction to proceed.

(iii) The adsorbed reactant molecules are tied on the solid surface of the catalyst. The bonds between the atoms of chemisorbed reactant molecules are weakened. The reactant molecules of sufficient energy combine together and with the surface of the catalyst to form surface activated complex.

This adsorbed activated complex is decomposed to form products at a definite faster rate.

(iv) The product molecules rapidly leave the catalyst surface to make room for the other reactant molecules to get adsorbed. Thus the chemical combination between reactant molecules goes on at the surface of the catalyst at a much faster rate.

(h) Catalyst in Industry : Some of the important process and their catalyst are given in below.



Industrial process	Catalyst used
Perparation of O_2 from $KClO_3$(Homogeneous)	MnO_2
Haber's process for ammonia (Heterogeneous)	Fe: Mo as promotor
Ostwald's process for HNO_3 from NH_3(Heterogeneous)	Pt Gauge
Chamber process for H_2SO_4 (Homogeneous)	Nitric oxide (NO) gas
Contact process for H_2SO_4 (Heterogeneous)	V_2O_5
Deacon's process for manufacture of Cl_2(Heterogeneous)	$CuCl_2$
Bosch process for H_2 (Heterogeneous)	$Fe_2O_3 + Cr_2O_3$ (promotor)
Manufacture of vegetable ghee (Heterogeneous)	Ni ,Pt, Pd
Hydrolysis of ester (Homogeneous)	Aq. H_2SO_4/H^+
Aldol condensation of aldehyde (Homogeneous)	OH^-
Enolisation of ketone (Homogeneous)	H^+ or OH^-
Cracking of hydrocarbon (Heterogeneous)	Zeolites
Decomposition of O_3	'Cl' atom
$2CO + O_2 \rightarrow 2CO_2$	'NO'

(i) Zeolites (Shape selective catalyst) :

(i) The calatytic reaction that depends upon the pore structure of the catalyst & the size of the reactant is called shape selective catalysis. The pore size is generally in range 260-740 pm.

Ex. → Zeolite (honey comb - like structure).

Formula· of Zeolite is $Na_{x/n}$ $[(AIO_2)_x(SiO_2)_y]$ z H_2O

(ii) Zeolite is also called sodium alumino silicate, water softner & cationic exchanger (Exchange only cation from hard water).

(iii) Zeolite is 3D silicate.

(iv) Zeolite, before using as catalyst are heated in vacuum so that the water of hydration is lost and as a result Zeolite becomes porous.

♦ **Application of Zeolite :**

Normally used in petro chemical industries for cracking of hydrocarbon & isomerisation.

**$R - OH \xrightarrow{ZSM-5}$ gasoline (Petrol)

5.13 ENZVME CATALYSIS

(i) Enzymes are complex nitrogenous organic compounds which are produced from living plants and animals.

(ii) They are actually protein molecules of high molecular mass and form colloidal solutions in water.

(iii) They catalyse biochemical reactions.

Reactions catalyzed by enzymes :

Enzyme	**Source**	**Reaction**
(i) Invertase	Yeast	Sucrose → Glucose and Fructose
(ii) Zymase	Yeast	Glucose → Ethyl alcohol and carbon dioxide
(iii) Diastase	Malt	Starch → Maltose
(iv) Maltase	Yeast	Maltose → Glucose
(v) Urease	Soyabean	Urea → Ammonia and CO_2

(vi) Pepsin	Stomach	Proteins → Amino acid

Characteristics of enzyme catalysis :

(i) Highly efficient : One molecule of an enzyme may transform one million molecules of the reactant per minute.

(ii) Highly specific nature : One catalyst cannot catalyse more than one reaction.

(iii) Highly active under optimum temperature (298 K to 310 K)

(iv) Highly active under optimum pH (5 to 7)

(v) Increasing activity in presence of cofactor (Na^+, Mn^{2+}, Co^{2+}, Cu^{2+} etc.) and co-enzymes

Mechanism of enzyme catalysis (key lock theory) : There are number of active centres of definite shape present on the surface of colloidal particles of enzymes. The molecules of the reactant (substrate), which have complementary shape fit into these cavities just like a key fits into a lock. On account of the presence of active groups an activated complex is formed which then decomposes to yield the product.

$$\begin{array}{ccccccccc} \text{Enzyme} & & \text{Substrate} & & \text{Activated complex} & & \text{Enzyme} & & \text{Products} \\ E & + & S & \rightleftharpoons & [E-S] & \longrightarrow & E & + & P \end{array}$$

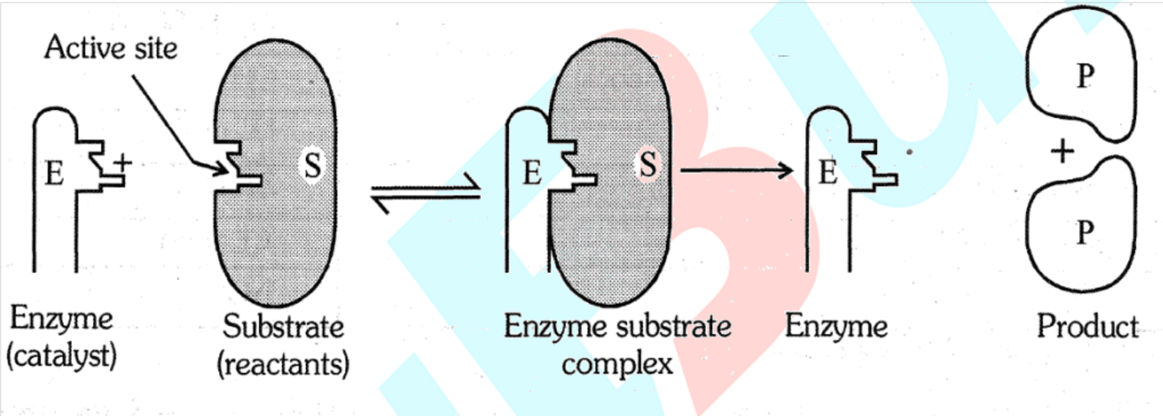


Fig : Mechanism of enzyme catalysed reaction

GOLDEN KEY POINTS

- The difference between inhibitors and poisons is that the catalytic inhibitor retards rate of reaction by itself while catalytic poison retards the rate of reaction by reducing the activity of catalyst.
- d-block metals are good catalysts, as they have higher surface area and unpaired d-electrons.

BEGINNER'S BOX-5

1. Catalytic poisons are

(1) Poison for catalyst	(2) Poison for reactant
(3) Poison for product	(4) None of these

2. A catalyst is more effective in

(1) Finely powdered state	(2) Colloidal state
(3) Rough surface	(4) All of these

3. Zeolites are

(1) Water softener (2) Catalyst

(3) Both (1) and (2) (4) Colloids

ANSWER KEY

BEGINNER'S BOX-1

1.	(4)	**2.**	(1)	**3.**	(4)	**4.**	(1)	**5.**	(3)	**6.**	(2)

BEGINNER'S BOX-2

1.	(1)	**2.**	(3)

BEGINNER'S BOX-3

1.	(4)	**2.**	(2)

BEGINNER'S BOX-4

1.	(3)	**2.**	(4)	**3.**	(3)	**4.**	(1)	**5.**	(1)

BEGINNER'S BOX-5

1.	(1)	**2.**	(4)	**3.**	(3)