Surface Chemistry

ADSORPTION

- **1.** Adsorption:- The phenomenon of increase in concentration at the surface due to molecular surface force is known as adsorption.
- 2. Adsorbate:- The substances, gases or liquids which are adsorbed on the surface of adsorbent are called adsorbate.
- **3.** Adsorbent:- The solid substance on the surface of which adsorption takes place is called adsorbent.

Examples of adsorbents are activated charcoal, Pt, Pd, Ni, Silica gel, gelatin, Al_2O_3 , starch.

- **4. Absorption:-** When a substance is uniformly distributed throughout the body of a solid or liquid, the phenomenon is called absorption.
- 5. Sorption:- It may be defined as the process in which both adsorption and absorption take place simultaneously.
- 6. **Desorption :** Removal of the adsorbed substance from surface.



	Adsorption	Absorption
1.	It involves higher concentration of the	1. It involves uniform distribution of the
	gas or liquid at the surface of a substance.	molecular species throughout the bulk
2.	It is rapid in the beginning and slows	2. It occurs at a uniform rate.
	down near the equilibrium.	
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 unbalanced or residual attractive forces.

Types of adsorption:- Depending upon the nature of forces between molecules of adsorbate and adsorbent, adsorption is of two types.

	Comparison of physi-sor	ption and chemi-sorption
	Physical Adsorption	Chemical Adsorption (Activated ad.)
1.	It is caused by intermolecular vander 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	Heat of adsorption is high. -200 to -400 kJ/mol
5.	No appreciable activation energy is involved.	High activation energy is involved.
6.	It forms multimolecular layers on adsorbent surface	It forms unimolecular layer.
	under high pressure.	

Special point : Chemical Adsorption is endothermic \rightarrow Ex. : Glass + H₂ gas [Exception]

FACTOR EFFECTING RATE OF

ADSORPTION

(1) Nature of adsorbent :

Adsorption ∞ Surface area of adsorbent or free valency of the solid.(So, powdered form of adsorbent is more effective)

(2) Nature of adsorbate:

(A) A dsorption of Gas: Adsorption $\propto T_c$ of gas (B) Adsorption from solution: Adsorption \propto Concentration of solute in the solution.

Volume of Gas	Volume of Gases at N. T. P. adsorbed by 1 g of Charcoal at 288 K							
Gas	\mathbf{H}_{2}	N ₂	CO	CH ₄	CO ₂	HCl	NH ₃	SO ₂
Critical Temperature, T _c (K)	33	126	134	190	304	324	406	430
Volume adsorbed (mL)	4.7	8.0	9.3	16.2	48	72	181	380

Critical temperature increase Ease of liquification increase Extent of adsorption increase

(3) Effect of temperature :

Adsorbate + Adsorbent \implies Adsorption, $\Delta H = -ve$, exothermic process.

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



(4) Effect of Pressure:- Adsorption Isotherm.

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

Where :



Types of adsorption isotherm :

(i) Freundlich adsorption isotherm (Physical adsorption) :

Adsorbent-Solid,



According to this $\left|\frac{x}{m} = Kp^{n}\right|$ (i) K & n are constants. Value of K & n depends on nature of adsorbent & nature of adsorbate.

According to this $\frac{x}{m}$ increase with increase of P but at high pressure $\frac{x}{m}$ becomes constant. When taping logarithm of equation.

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



In solution (liquid + solid)

Ex.: dyes solution + Charcoal

$$\frac{x}{m} = KC^{\frac{1}{r}}$$

$$C = (Conc^n of liquid)$$

(ii) Langmuir adsorption isotherm (Chemisorption, unilayer adsorption) :

Langmuir 1916 postulated that :

- 1. The gases being adsorbed cannot form a layer more than a single molecule in depth.
- 2. There in no interaction between the adjacent adsorbed molecules.
- 3. A dynamic equilibrium exists between the adsorbed molecules and the free gas molecules.
- 4. The adsorption sites are equivalent in their ability to adsorb particels.

The constants a and b are characteristic of a particular system at a particular temperature.



For Solid + Liquid

Applications of adsorption :-

- (1) Production of high vaccum
- (2) Gas masks
- (3) Humidity control
- (4) Removal of colouring matter from solution
- (5) Heterogeneous catalysis
- (6) Seperation of inert gases
- (7) Softening of hard water
- (8) De ionisation of water
- (9) In curing diseases
- (10) Cleansing agents
- (11) Froth floatation process
- (12) Adsorption indicators
- (13) Chromatographic analysis

CATALYSIS

The phenomenon in which the rate of a reaction is altered (increased or decreased) by the presence of a substance (Catalyst) is known as catalysis.

Catalytic reactions are divided into two types.

(a) Homogeneous catalysis

- (b) Heterogeneous catalysis
- (a) Homogeneous catalysis:- When the reactants and the catalyst are in the same physical state, i.e. in the same phase, it is called homogeneous catalysis. For example:-
- (i) Lead chamber process:- In this process for the manufacture of sulphuric acid (H_2SO_4) , NO (gas) is used as a catalyst.

 $2SO_{2}(g) + O_{2}(g) \xrightarrow{No(g)} 2SO_{3}(g)$

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

 $\begin{array}{c} C_{12}H_{22}O_{11}+H_2O \xrightarrow{H_2SO_4(aq)} C_6H_{12}O_6 + C_6H_{12}O_6\\ Sucrose & Glucose & Fructose \end{array}$

- (b) Surface catalyst or Heterogeneous catalysis:-When the catalyst and the reactants are not in the same physical state i.e. not in the same phase, it is called heterogeneous catalysis. For example.
- (i) Decomposition of $H_2O_2(\ell)$:

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

(ii) Habers process for NH_3

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

(ii) Synthesis of CH_3OH

$$CO(g) + 2H_2(g) \xrightarrow{Cu}_{ZnO-Cr_2O_3} CH_3OH(\ell)$$

TYPES OF CATALYSIS

(i) Positive catalysts

(iii)Autocatalysts

Catalysts are divided into four types.

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(ii) Negative catalysts(iv) Induced catalyst
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 (i) Positive catalysts:- The substance which increase the rate of a reaction are known as positive catalyst. It decreases the energy of activation for the reaction. For example:-

 $\begin{array}{ll} 2\text{KClO}_{3}\left(s\right) & \xrightarrow{\text{MnO}_{2}\left(s\right)} & 2\text{KCl}\left(s\right) + 3\text{O}_{2}(g) \\ \text{N}_{2} + 3\text{H}_{2} & \xrightarrow{\text{Fe}\left(s\right)} & 2\text{NH}_{3}\left(g\right) \end{array}$

(ii) Negative catalysts: - The substance which decreases the rate of chemical reaction is called negative catalyst or inhibitor. It increase the activation energy for the reaction. For example.

$$Na_{2}SO_{3} + \frac{1}{2}O_{2} \xrightarrow{C_{2}H_{5}OH} Na_{2}SO_{4}$$

$$C_{6}H_{5}CHO + \frac{1}{2}O_{2} \xrightarrow{Di Phenylamine} C_{6}H_{5}COOH$$

(iii) Autocatalysts:- When one of the products of the reaction begins to act as a catalyst, it is called autocatalyst. For example. In the initial stages the reaction is slow but as soon as the products come into existence the reaction rate increases

(iv) Induced catalyst:- When a chemical reaction enhances the rate of another chemical reaction it is called induced catalysis. For example:-

Soduim arsenite solution is not oxidised by air. If however, air is passed through a mixture of $Na_3AsO_3 \& Na_2SO_3$, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus influences the oxidation of sodium arsenite.

$$Na_{2}SO_{3} + \frac{1}{2}O_{2} \rightarrow Na_{2}SO_{4}$$

Sod. sulphite air Sod. sulphate.
$$Na_{3}AsO_{3} + \frac{1}{2}O_{2} \rightarrow Na_{3}AsO_{4}$$

Sod. arsenite air Sod. aresenate

Promoters:- Those substance which do not themselves act as catalysts but their presence increases the activity of a catalyst are called catalytic promoters or catalyst for a catalyst. Example:-

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

 $N_{2}(g) + 3H_{2}(g) \xrightarrow{Fe(Catalyst)} 2NH_{3}(g)$

Catalytic Poison:- The substance whose presence decreases or destroy the activity of a catalyst is called catalytic poison. For example:- Carbon monoxide or H_2S in hydrogen gas, acts as a poison for Fe catalyst in the Haber process for NH_3 , As_2O_3 acts as poison for Pt asbestos in contact process for H_2SO_4

Inhibitors:- Those substances which retard rate of a chemical reaction are known as inhibitor. For example:

 $H_{3}PO_{4}$, glycerol or acetamide decrease the rate of decomposition of hydrogen peroxide.

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 catalysts does not change the equilibrium state of a reversible reaction but helps to achieve the equilibrium state or position of equilibrium in lesser time.
- (vii) The catalysts is generally specific in nature.
- (viii) Change rate constant of reaction.
- (ix) Does not change free energy of reaction.
- (x) Participate in mechanism of reaction.

THEORIES OF CATALYSIS

Intermediate compound formation theory:-This theory explains homogeneous catalysis mainly. According to this theroy, 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.

 $NO_2 + SO_2 \xrightarrow{fast} SO_3 + NO$ intermediate reactant product catalyst regenerated

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.

- 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 nescessary 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.

	Catalysts in Industry:- Some of the important proc	esses and their catalyst are given below.
	Industrial process	Catalyst used
1.	Perparation of O_2 from KClO ₃ (Homo)	MnO ₂
2.	Haber's process for ammonia (Hetero)	Fe: Mo as promoter
3.	Ostwald's process for HNO ₃ from NH ₃ (Hetero)	Pt Gauge
4.	Chamber process for H_2SO_4 (Homo)	Nitric oxide (NO) gas
5.	Contact process for H_2SO_4 (Hetero)	V ₂ O ₅
6.	Deacon's process for manufacture of Cl_2 (Hetero)	CuCl ₂
7.	Bosch process for H_2 (Hetero)	$Fe_2O_3 + Cr_2O_3$ (promoter)
8.	Manufacture of vegetable ghee (Hetero)	Ni, Cu as promoter
9.	Hydrolysis of ester (Homo)	aq H ₂ SO ₄
10.	Aldol condensation of aldehyde (Homo)	-OH
11.	Enolisation of ketone (Homo)	H ⁺ or –OH
12.	Cracking of hydrocarbon (Hetero)	Zeolites
13.	Decomposition of O ₃	'Cl' atom
14.	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	'NO'

ZEOLITE (Shape selective catalyst) :

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

Ex. \rightarrow Zeolite (honey comb – like structure)

- 2. Zeolite is also called sodium alumino silicate, water softner & cationic exchanger (Exchange only cation from hard water).
- 3. Zeolite is 3d silicate.
- 4. 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 $__{ZSM-5}$ gasoline (Petrol)

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 :-

(i) Crystalloid (ii) 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	True Solution Colloid					
		or						
		Crystalloidal						
(i)	Particle size	$< 10^{-7} \text{cm or } 10 \text{\AA}$	10^{-7} to 10^{-5} cm	$> 10^{-5} \text{ cm or } 10^{3} \text{\AA}$				
		or $1 \text{ m}\mu$ or $< 1 \text{ nm}$	or 10Å to 10³Å	or 100 mµ				
			or 1mµ to 100 mµ	or > 100 nm				
			or 1 nm to 100 nm					
(ii)	Visibility	Not visible with any of	Visible with	Visible with naked				
		the optical means	ultramicroscope	eye				
(iii)	Seperation							
	(a) with filter	Not possible	Not Possible	Possible				
	paper							
	(b) with	Not possible	Possible	Possible				
	membranes							
(iv)	Diffusion	Diffuses rapidly	Diffuse very slowly	Does not diffuse				
(v)	Settling	Does not settle	Does not settle but it	Settles under				
			may settle under	gravity				
			Centrifuge					
(vi)	Nature	Homogeneous	Heterogeneous	Heterogeneous				
(vii)	Tyndall effect &	does not show	shows	May or may not show				
	Brownian moment							
	1	Crystalloidal particles	Colloidal particles	Suspensions				
		00000	0 0 0 0					
		00000	0000					
		Smaller particles < 10Å	Particles size 10Å to 10 ³ Å	Particles having size bigger than 1000Å				

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 physical states of dispersed phase or dispersion medium, colloidal solutions are of eight types

CLASSIFICATION OF COLLOIDAL SYSTEMS BASED ON DISPERSED PHASE						
AND DISPERSION MEDIUM						
Type of Colloidal	Dispersed	Dispersion	Example			
Solution	phase	medium				
Foam	gas	Liquid	Whipped Cream, Shaving Cream, Soda water			
Solid Foam	gas	solid	Cork, pumice stone, Foam rubber			
Liquid Aerosol	liquid	gas	Fog, mist, clouds, insecticide sprays.			
Emulsion	liquid	liquid	milk, hair cream, *butter, cold cream.			
Gel	liquid	solid	butter, cheese, curd, Jellies, boot polish			
Smoke (aerosol)	solid	gas	dust, soot in air			
Sol (liquid)	solid	liquid	ink, colloidal gold, paints, cell fluids.			
Solid sol	solid	solid	Ruby glass (gold dispersed in glass), alloys			
			gem stones, minerals.			

A colloidal dispersion of one gas in another is not possible since the two gases would give a homogenous molecular structure.

CLASSIFICATION OF COLLOIDAL SYSTEMS :

(1) Classification based on appearance :- 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 sol are possible.

S.No. Dispersion medium Name of solution

- 1. Water Hydrosol or aquosol
- 2. Benzene Benzosol
- 3. Alcohol Alcosol
- 4. Air Aerosol.

The colloidal systems which have more rigid structures are called Gel. Gelatin behaves both as a sol and a gel.

(2) Classification based on interaction of phases :-

LYOPHILIC AND LYOPHOBIC SOLS

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion phase, are called lyophilic sols (solvent - liking). 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 Lyphobic colloidal (Solvent hating) solutions.

	COMPARISION OF LYOPHOBIC AND LYOPHILIC 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	viscocity is much higher	viscocity is nearly same			
		than that of solvent	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	These are highly solvated	These are less solvated as			
	solvation	as the particles have great	the particles have less			
		affinity for solvent	affinity for the solvent			
7.	Charge	The particles have little	The particles carry a			
		charge or no charge at all	characteristic charge either			
			positive or negative			
8.	Visibility	Particles can not be seen	Particles can be seen under			
		under microscope	microscope			
9.	Coagulation or	Precipitated by high	Precipitated by low			
	precipitation	concentration of electrolytes	concentration of electrolytes			
10.	Tyndall effect	Less Scattering	More Scattering			
11.	Migration in	may or may not migrate	migrate towards anode or			
	electric field	as they may or may not carry charge.	cathode as these particles carrry charge			
12.	General Example	Mostly of organic nature	Mostly of Inorganic nature			
		Ex. Gelatin, Starch, Gum,	Ex. Transiton metal salt in water.			
		Albumin & Cellulose Solution	Gold, As etc.			

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 macrosized 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.

Surface Chemistry

Dispersion method

- 1. Mechanical dispersion 2. Electro-dispersion
- 3. Ultrasonic dispersion 4. Peptization

Aggregation or condensation method

- 1. By condensing vapours
- 2. Exchange of solvents (Physical method)
- 3. Change of physical state (Physical method)
- 4. Chemical methods
 - (a) Double decomposition (b) Oxidation
 - (c) Reduction (d) Hydrolysis

DISPERSION METHODS

1. 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 suspended particles are broken to produce particles of colloidal size.

2. 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 vapourises some of the metal which condenses under cold water.

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

3. DISPERSION BY ULTRASONIC



Quartz generator

Fig. Prep. of Hg sol. by ultrasonc vibrations.

Claus prepared mercury sol by subjecting Hg to sufficiently high frequency ultrasonic vibrations as shown in fig. The ultrasonic vibrations produced by the generator spread through the oil and strike the vessel containing Mercury under water. This produces clouds of Mercury which form the Mercury sol.

4. PEPTIZATION

The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed peptization. The electrolyte used is called a **Peptizing agent.**

A. few examples of sols obtained by peptization are :

- (i) Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution at once forms a dark reddish brown colloidal solution. Ferric chloride acts as a peptizing agent.
- (ii) Freshly precipitated silver chloride can be converted into a colloidal solution by adding a small amount of hydrochloric acid.
- (iii) Cadmium sulphide can be peptized with the help of hydrogen sulphide.

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.

Surface Chemistry

CONDENSATION METHODS

- (1) Physical Methods :
- (a) By condensing vapours : Sols of Sulphur and Mercury can be formed by passing the vapours of Sulphur and Mercury in cold water containing some NH_4NO_3 .
- (b) 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 poured in excess of water, a colloidal sol of sulphur is formed.
- (c) By excessive cooling : Molecules of certain substances condense together to form particles of colloidal size. For eg. colloidal sol of ice in an organic solvent like ether or chloroform may be prepared by freezing the mixture of water and the solvent.

(2) Chemical method :

The chemical method 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 :

(a) Double decomposition (i) Arsenic sulphide sol: 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, whilst a stream of H_2S is being passed through the solution. This is continued till an

 $As_2O_3 + 3H_2S \longrightarrow As_2S_3$ (Yellow Sol) + $3H_2O$

intense yellow coloured solution is obtained.

(b) **Oxidation** - A colloidal solution of sulphur is obtained by passing H_2S into a solution of sulphur dioxide or oxidising agent Ex. : HNO₃, Br₂, Etc.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$
 (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.

 $2\text{AuCl}_3 + 3\text{SnCl}_2 \rightarrow 3\text{SnCl}_4 + 2\text{Au}$ Sol.

(d) **Hydrolysis :-** Colloidal solution of many metal hydroxides are prepared by this method. Ferric hydroxide sol is prepared by the hydrolysis of ferric chloride with boiling water.

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

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

- * Purification of Colloidal Solⁿ-
 - (1) Dialysis
 - (2) Ultrafiltration
 - (3) Ultracentrifugation

PROPERTIES OF COLLOIDAL SOLUTIONS

- 1. Heterogenous Colloidal particles in a solution differ in sizes and are not homogenously distributed through out the solution.
- 2. Visibility 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.



- **3.** Filterability Colloidal particles pass through an ordinary filter paper but do not pass through parchment and other fine membranes.
- 4. Surface tension and viscocity For Lyophobic sols, surface tension and viscocity are not very different from those of the medium, as there is very slight interaction between the suspended particles and the medium. On the other hand Lyophilic sols show a high degree of solvation of the particles and therefore, the properties of the medium are modified. Thus, the viscocity is much higher for the sol than for the medium. Furthermore the surface tension of the sol is lower than that of pure medium.
- 5. Colour The colour of hydrophobic sol 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.
- 6. 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 colloidal solutions are very less and hence these solutions exhibit colligative properties to lesser extent.
- 7. Optical properties Sols exhibit 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.



8. Kinetic properties - When a sol is examined with an ultramicroscope, the suspended particles are seen as shining specks of light. By following an individual particle, it is observed that the particle is in a state of continuous motion in zig-zag path. The continuous rapid zig-zag 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 particles by the molecules of dispersion medium.

9. Charge on colloidal particles -



Representation of Fe(OH)₃ Sol.

Colloidal particles always carry an electric charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity. This gives stability to the sol. The charge is due to the preferential adsorption of either positive or negative common ion present in excess.

Adsorg	Adsorption of charge :						
AgI	+	KI	\longrightarrow	AgI / I [_]	(Negative Sol)		
				(Excess)			
AgI	+	AgNO ₃	\longrightarrow	AgI/Ag^{+}	(Positive Sol)		
				(Excess)			
FeCl ₃	+	H ₂ O	\longrightarrow	$\operatorname{Fe(OH)}_{3}/\operatorname{Fe}^{+3}$	(Positive Sol)		
FeCl ₃	+	NaOH	\longrightarrow	$\operatorname{Fe(OH)}_3/\operatorname{OH}^-$	(Negative Sol)		
SnO ₂	+	$4\mathrm{H}^{+}$	\longrightarrow	$Sn^{+4} + 2H_2O$;	$\mathrm{SnO}_2/\mathrm{Sn}^{\mathrm{+4}}$	(In acidic medium)(Positive Sol)	
SnO ₂	+	20H-	\longrightarrow	$SnO_3^{2-} + H_2O;$	$\mathrm{SnO}_2/\mathrm{SnO}_3^{2-}$	(In basic medium)(Negative Sol)	

	A list of common sols with the type of charge on their particles.						
	Positively charged	Negatively charged					
1.	Metallic hydroxides	Metallic sulphides like As_2S_3 , Sb_2S_3 , CdS					
	e.g. Cr(OH) ₃ , Al(OH) ₃ & Fe(OH) ₃						
2.	Basic dye stuff example -	Acid dye stuff example - Congored sols					
	Methylene blue sol	Metal like – Au, Ag, Cu, Pt etc.					
3.	Proteins in acidic medium	Proteins in basic medium					
		Sols of starch, gum, gelatin, clay & charcoal					

ELECTRICAL DOUBLE LAYER

The surface of a colloidal particle acquires a +ve/ve charge by selective adsorption of a layer of positive /negative ions around it. This layer attracts counter ions from the medium which form a second layer of –ve/+ve charges. The combination of the two layers of +ve and –ve charges around the sol particle was called **Helmholtz double layer**. According to modern view, the first layer of ions is firmly held and is termed **Fixed layer** while the second layer is mobile which is termed as **Diffused layer**.



[Helmholtz double layer]

The combination of the compact and diffused layer is referred as the **Stern double 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**.

10. Electrophoresis - If electric potential is applied across two platinum electrodes dipping 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.** 11. Electro osmosis - The medium will move in opposite direction to the dispersed phase under the influence of applied electric potential. The movement of dispersion medium under the influence of applied potential is known as 'Electro - osmosis'.(In presence of plasma membrane)

12. 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 other. In such cases they aggregate or flocculate and settle down under the action of gravity.

The flocculation and settling down of the discharged sol particles is called coagulation or precipitation. The precipitation can be brought about in five ways-

- (a) By addition of electrolyte.
- (b) By electrophoresis.
- (c) By mixing two oppositely charged sols.
- (d) By boiling.
- (e) By repeated dialysis

(a) 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 neutralisation and there by the size and mass of colloidal particle increases and it becomes a suspension particle. Due to greater volume and greater mass these suspension particles settle down i.e they coagulate. The ion responsible for neutralisation 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 precipitating 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 $[Fe(CN)_6]^{-3}$, SO₄²⁻ 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 2 hours is called FLOCCULATION VALUE. The smaller the flocculating value, the higher will be the coagulating power of the ion.

(b) By Electrophoresis -

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

(c) By mixing two oppositely charged sols -

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

(d) By boiling -

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

(e) By repeated dialysis - On continuous dialysis, besides the electrolytic impurities the adsorbed ions are also removed and so the sol gets precipitated.

COAGULATION OF LYOPHILLIC SOLS

Lyophilic sols are stable due to charge and solvation of the 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 occur. Under this condition a small quantity of electrolyte can bring about coagulation.

13. Protection or Protective action.

Lyophobic sols are readily precipitated by small amounts of electrolytes. However, these sols are often stablized by the addition of Lyophilic sols.



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" 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
Protection Capacity ∞ ——	1

 $\frac{Pachy \propto}{Pr \text{ otection Number (Gold number)}}$

Gelatin and starch have the maximum and minimum protective powers.

Congo rubin Number – Ostwald introduced congo rubin number to account for protective power of colloids. It is defined as the amount of protective colloids in milligrams which prevents colour change red to violet in 100 ml of 0.01% congorubin dye to which 0.16 g equivalent of KCl is added.

EMULSIONS

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These are liquid-liquid colloidal systems There are two types of Emulsions -

- (i) Oil dispersed in water (O/W types)
- (ii) Water dispersed in oil (W/O types)
- * In the first type water acts as 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** and **Cold cream**.
 - Emulsions of oil and water are unstable and sometimes they seperate into two layers on standing. For stabilisation of an emulsion, a third component called emulsifying agent is usually added. The emulsifying agent form an interfacial film between suspended particles and the medium. The Principal agent for o/w emulsions are proteins, gums, soaps, etc. for w/o emulsion the principal emulsifying agents are heavy metal salts of fatty acids, long chain alcohols etc.

Assoicated Colloids [Micelles]

Substances whose molecules aggregate to form particles of colloidal dimensions are called associated colloids. The molecules of soaps and detergents are usually smaller than the colloidal particles. However, In concentrated solutions, these molecules associate and form aggregates of colloidal size. These aggregates of soaps or detergent molecules are called Micelles. Soaps and detergents are strong electrolytes and gives ions when dissolved in water

 $C_{17}H_{35}COONa \longrightarrow C_{17}H_{35}COO^{-} + Na^{+}$ Soap



SOLID CIRCLE () REPRESENTS POLAR GROUP (COO-Na⁺) WAVY LINE (~~) REPRESENTS NON-POLAR GROUP (R-)

The negative ions aggregate to form a micelle 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 it directed towards the centre while the soluble polar head is on the surface in contact with water. The charge on the micelle is responsible for the stability of this system.

GELS

A gel is a jelly like colloidal system in which a liquid is dispersed in a solid medium.

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 eg. 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.

Properties of Gels :

- 1. **Hydration :** A completely dehydrated elastic gel can be regenereted by adding water to it.
- 2. Swelling : Partially dehydrated elastic gels imbibe water when immersed in the solvent. This results in increase in volume of the gel which is called swelling.
- **3. Syneresis :** Inorganic gels on standing, loose water and shrink. This process is called syneresis.
- **4. Thixotropy :** Some gels revert to liquid sols on agitation. This reversible sol-gel transformation is called Thixotropy.

Types of colloids according to their size						
Multi Molecular	Macro Molecular	Associated colloids				
Formation by aggregation of	Formation by aggregation	These are the substances				
a large number of atoms or	of big size molecules.	which behave as normal elec-				
smaller molecules of substance.	These are polymers with high	trolytes at low concentration				
$Ex. \rightarrow \textbf{Gold, Sol, Sulphur sol}$	molecular mass	but get associated at higher				
(Au) (S ₈)	Ex. \rightarrow Starch, Cellulose,	concentration and behave as				
	Protein etc.	colloidal solutions. These				
		associated particles are also				
		called micelles.				
		Ex. → Soap & Detergent				

APPLICATIONS OF COLLOIDS

Colloids play an important role in our daily life and industry. Some of the important applications of colloids are listed below -

- 1. Food.
- 2. Medicines.
- 3. Paints.
- 4. Electrical precipitation of smoke.
- 5. Purification of sewage water.
- 6. Formation of Delta
- 7. Purification of blood .
- 8. Tanning . Animal leather (skin) is soft due to the presence of very fine globules of oils and fats in the pores of skin. These globules are colloidal in nature. When this soft leather (skin) is placed in salt water, these globules of oils and fats coagulate and settle down in water. Now when the animal hides are dried they become hard. This process of making soft leather to hard leather by dipping it in salt water is called Tanning. Usually chromium salts are used for tanning.

- **9.** Adsorption indicators: Surface of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein etc. In the case of precipitation titration of AgNO₃ versus NaCl the indicator is adsorbed at the end point producing a characteristic colour on the precipitate.
- **10. Industrial products**. Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc are all colloidal solutions.
- Colloidal solution of graphite in water is called "Aqua dag" while that in Oil is called Oil dag.
- **12.** Gold solution in water is called **Purple of cassius**.
- **13**. Colloidion is cellulose nitrate & ethyl alcohol colloidal solution.

Artificial rain :

Can be caused by spraying oppositely charge dust or fine sand or precipitate like AgI (AgI has a crystal structure similar to ice)

Critical Micelle concentration (CMC) :

The concentration at which associated colloids or Micelles are formed is called CMC.

Kraft Temperature (T_K) : Temperature at which Micelles are formed.