

# COLLOIDS

Coll Sol

An ordinary solution consists of a solvent and solute: The particles of the solute are usually small molecules or ions. These solute particles dispersed throughout the solvent. e.g. when sugar or common salt is added to water a true solution is formed. On the other hand when substances like sand, powdered-glass etc are added to water, they settle down. The mixture of sugar or salt and water is said to be homogeneous, while the mixture of clay and water is said to be heterogeneous. Such a solution of water and sand or clay is called coarse suspensions. Between these two extremes of true solutions and coarse suspension exist solutions called colloidal solutions having properties in between them.

## DEFINITION

A colloidal solution is defined as a heterogeneous system consisting of two phases ① A dispersed phase which consists of the colloidal particles and ② a dispersion medium e.g. Indian ink, the milk, the dispersion of Sulphur, Starch, Gum in water, and blood serum are all examples of colloids. Thomas Graham (1861) studied the diffusion of different substances in solutions through membranes and found that some had high rate of diffusion while the other had very low rate of diffusion. According to the rates of diffusion Graham classified all substances into two groups, the crystalloids and colloids.

The first group of substances are comparatively of low molecular weight e.g. Salt, urea, and sugars. The particles



such substances exist as ions or molecules in solution and are very mobile. Thus they diffuse through the membrane quickly. These substances can be crystallized readily from solution and hence were called crystalloids. The other group of substances like proteins, tanin, albumin, gelatine, starch, or glue move relatively slowly and show little or no tendency to diffuse across the membrane were termed colloids. The particles of colloidal substance are much larger. They may aggregates to hundreds of ordinary sized molecules or even a single large or macromolecule (e.g. protein). A colloids are dispersions of small particles of one material in another. Small means around or less than 100 nm in diameter. They are aggregates of numerous atoms or molecules which are too small to be seen with an ordinary optical microscope. They pass through most filter papers but can be detected by light scattering, sedimentation and osmosis. Some distinctive properties of colloids are given and compared with true solutions and coarse suspensions in table.

Properties	True Solution	Colloidal dispersion	Coarse Suspension
1) Size of Particles	0.1 - 1.0 nm	$10^{-10} - 10^3$ nm	$\geq 10^3$ nm
2) Phase	One-Phase system	Two-Phase system	Two Phase system
3) Shape	—	Linear, Coiled, Rod, shaped, ellipse, or flat plates.	Irregulars
4) Visibility	Molecules or ions invisible in electron microscope.	Particles visible in electron microscope but invisible in ordinary microscope.	Particles visible to naked eye

PROPERTIES		TRUE SOLUTIONS	COLLOIDAL DISPERSION CHARGE SUSPENSIONS
1) Charge on Particles		Positive or negative ions or neutral molecules.	Positively or negatively charged particles
2) Diffusion		Diffuse rapidly through membrane	Diffuse slowly or have no tendency to diffuse through membrane.
3) Aggregates	molecules contain $2 - 10^3$ atoms	Particles composed of $10^3 - 10^6$ atoms	Particles composed of more than $10^6$ atoms
4) Dispersion of light	Do not scatter light	Scattering of light	Scatter and reflect light.
5) Filterability	Pass through ultra-filters.	Particles can pass through an ordinary filter paper, but are retained by ultra-filters	Particles can not pass through ordinary filter paper.
6) Effect of gravity	No effect	Do not settle down under the influence of gravity	Settle down under influence of gravity.
7) Examples	Salt, urea, or Sugar Solutions	Milk, rubber, Soap, mist, fog etc	Mud or Sand Suspension

## CLASSIFICATION OF COLLOIDS

A Colloidal System is made up of two phases a dispersed phase and the dispersion medium. Since both the dispersed phase and the dispersion medium may be Solid, Liquid or Gas. Colloidal Solutions may be classified according to the state of the two phases to yield the nine types of Colloidal Systems as given in table. Actually there are eight types of Colloidal Systems. Since Colloidal System of two gases cannot exist, because they are incapable of producing two phases.

DISPERSED PHASE	DISPERSION MEDIUM	NOMENCLATURE	EXAMPLES
1- Gas	Gas	-	Unknown
2- Gas	Liquid	Foam	Whipped Cream, Soap lather.
3- Gas	Solid	Solid foam	→ Pumic. Stone, foam rubber
4- Liquid	Gas	AeroSol	Fog, mist, Cloud
5- Liquid	Liquid	Emulsion	Oil in water, milk.
6- Liquid	Solid	Gel or Jelly	Jellies, butter
7- Solid	Gas	Smoke	Cheese.
8- Solid	Liquid	Sol	smokes, dust, iodine vapours in air.
9- Solid	Solid	Solid Sol	AgCl, Au, As <sub>2</sub> S <sub>3</sub> , Cr S in H <sub>2</sub> O Alloys, Ruby glass mixed crystals, gems

# SOLS

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Sols are colloidal systems in which a solid is dispersed in a liquid. If the dispersion medium is water, they are termed as HydroSols or Aquasols. When the dispersion medium is alcohol or benzene, the sols are referred to as "Alcosols" and Benzosols respectively.

Sols can be subdivided into two classes.

(i) LYOPHILIC SOLS (SOLVENT-LOVING)

(ii) LYOPHOBIC SOLS (SOLVENT-HATING)

(A) LYOPHILIC SOLS

Lyophilic sols are those colloidal dispersions in which the dispersed phase exhibits a definite affinity or attraction for the dispersion medium or the solvent. When lyophilic sols are precipitated, they can easily be converted back into sols by the addition of the dispersed medium and are therefore termed as reversible sols. Lyophilic sols are more stable than the lyophobic sols. The examples of lyophilic sols are dispersion of starch, gum, gelatin, and proteins in water.

(B) LYOPHOBIC SOLS

Lyophobic sols are those dispersions in which the dispersed phase has no attraction for the dispersed medium or solvent.

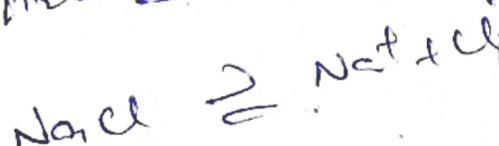
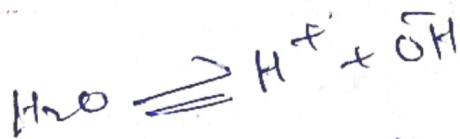
Lyophobic sols can readily be precipitated from the colloidal solution and they cannot be easily converted back into the colloidal solutions by the addition of the dispersion medium and are therefore termed irreversible sols. Lyophobic sols are not very stable. The examples of lyophobic sols are dispersion of gold, iron(III) hydroxide and sulphur in water.

For dispersions in water, the term Hydrophilic and Hydrophobic are used instead of the generalized terms lyophilic and lyophobic.

## Properties of Lyophobic and Lyophilic Sols.

(6)

Properties	Lyophobic Sols	Lyophilic Sols
(1) Visibility in ultramicroscope	The Particles are easily be detected in the ultramicroscope.	The Particles cannot be readily detected in the ultramicroscope.
(2) Charge on Particles	Particles carry positive or negative charge.	Particles may have little or no charge at all.
(3) Solvation	No Solvation of Particles	Particles are generally solvated.
(4) Tyndall Effect	Exhibit Tyndall effect	Do not exhibit tyndall effect.
(5) Migration in electric field	Particles migrate to either anode or cathode.	Particles migrate to anode or cathode or remain stationary.
(6) Precipitation by electrolytes	Precipitated by low concentration of electrolyte	Precipitate by high concentration of an electrolyte
(7) Viscosity	Viscosity almost the same as of the dispersion medium itself.	Viscosity higher than dispersion medium.
(8) Surface Tension	Similar to that of dispersion medium	Generally lower than that of dispersion medium.



# Preparation Of Sol's

(7)

Lyophilic Sol's can be prepared by simply warming the solid with the liquid dispersion medium e.g gelatin, gum, starch yield Sol's on simply warming with water. On the other hand, Lyophobic Sol's are prepared by special methods. These methods are divided into two groups.

(A) DISPERSION METHOD

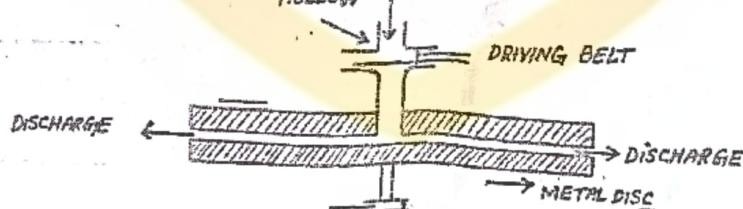
(B) CONDENSATION OR AGGREGATION METHODS

(A) DISPERSION METHOD

In which large macro-sized particles are broken down to colloidal size.

(i) MECHANICAL DISPERSION USING COLLOIDAL MILL

The substance to be dispersed is suspended in the dispersion medium in the form of coarse particles. Then this suspension is fed into a colloidal mill. The mill consists of two steel plates nearly touching each other and rotating in opposite directions with high speed. The coarse particles are reduced to colloidal size and are then dispersed in the liquid to give Sol. Colloidal graphite (a lubricant) and printing inks are made by this method.

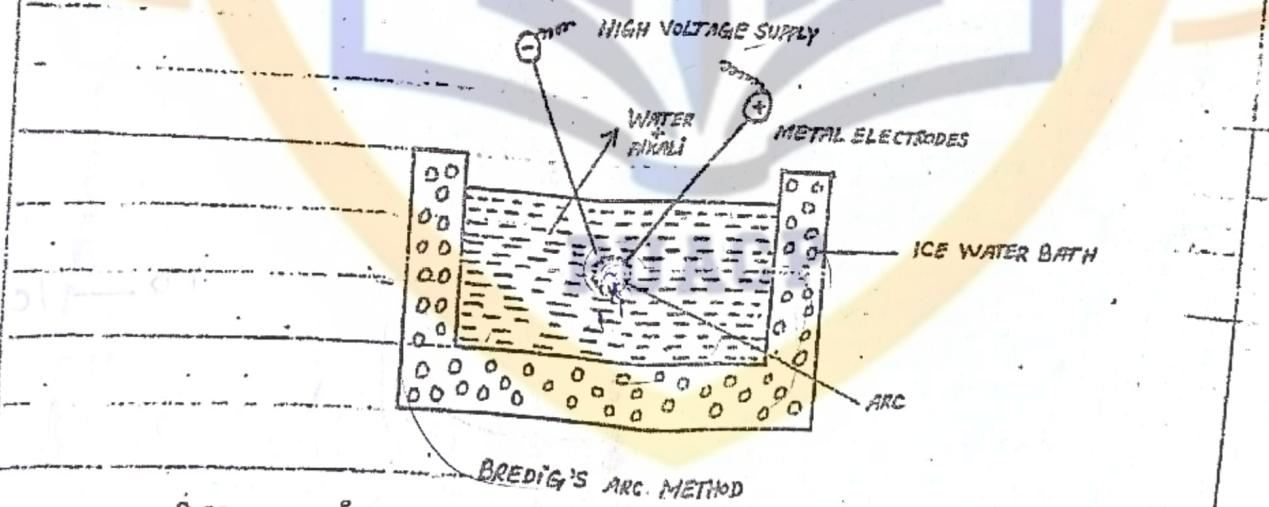


A COLLOIDAL MILL

### (2) ELECTRO-DISPERSION (BREDIG'S ARC METHOD)

(8)

This method involves both dispersion and condensation. Process in this method, an electric arc is struck beneath conductivity. Water between the two electrodes of a metal to be dispersed. The water is kept cold by immersing the container in ice cold water. The intense heat of the arc turns some of the metal into vapours which are immediately condensed by the surrounding ice-cold water to give particles of colloidal size. A small quantity of alkali ( $KOH$ ) is added to water to stabilize the sol. Since the metal has been ultimately converted into sol particles (via metal vapour, this method is treated as dispersion) it is used for preparing hydrosols of metals e.g. Silver, gold, lead, copper and platinum. Non-metal sols can be made by suspending coarse particles of the substance in the dispersion medium and striking an arc between iron electrodes.



### (3) PEPTIZATION

Peptization is the reverse process of coagulation.

The dispersal of a precipitated material into colloidal solution by the action of an electrolyte in solution is called peptization. The electrolyte is called a peptizing agent. Some freshly precipitated ionic solids are dispersed into colloidal solution.

in water by the addition of small amounts of electrolytes, particularly those containing a common ion. The precipitate absorbs the common ion and electrically charged particles then split from the precipitate as colloidal particles. Freshly prepared precipitate of ferric hydroxide on treatment with a small amount of solution (peptizing agent) forms a dark reddish brown sol. In the preparation of lyophilic sols, such as glue, gum, gelatin, starch, etc., in dispersion medium water itself act as a peptizing agent.

#### (B) CONDENSATION OR AGGREGATION METHOD.

In which colloidal sized

particles are built up by aggregating single ions or molecules.

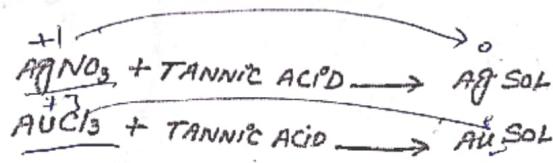
The essential principle of these methods is that the ions or molecules originally present in a true solution are converted into insoluble colloidal size particles by means of a chemical reaction. The unwanted ions (spectator ions) present in the sol are removed by dialysis as these ions may eventually coagulate the sol.

The more important methods for preparing hydrophobic sols are given below.

#### (i) REDUCTION

Metal sols are generally obtained by the reduction of dilute solution of their salts or oxides of metal with some reducing agent usually organic reducing agents like tannic acid.

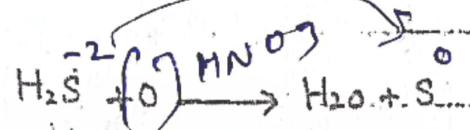
Silver sols and gold sols can be obtained by treating dilute solution of silver nitrate or gold chloride with tannic acid as reducing agent



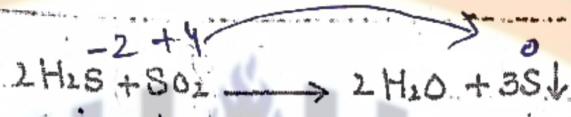
## (ii) OXIDATION

(10)

A milky sulphur sol is frequently formed during qualitative analysis, by the action of hydrogen sulphide with an oxidizing agent such as nitric acid or ferric ions.



A Sulphur Sol Can be Prepared by Passing  $\text{H}_2\text{S}$  into a Solution of Sulphur dioxide.



## (iii) HYDROLYSIS

Sols or the hydroxides of weakly electro positive metals such as Fe, Cr, Al, Sn etc are prepared by hydrolysis of their salts in aqueous solution. For example sol of ferric hydroxide is prepared by the addition of a few  $\text{cm}^3$  of 33%  $\text{FeCl}_3$  solution to a large volume of boiling water with constant shaking.



The neutral solution of  $\text{FeCl}_3$  used as a reagent in the laboratory becomes dark red on standing. The change in colour is due to the formation of ferric hydroxide sol by partial hydrolysis.

## (iv) DOUBLE DECOMPOSITION

An arsenious sulphide sol is prepared

by passing a slow stream of  $\text{H}_2\text{S}$  gas through a cold solution of arsenious sulphide



The excess of hydrogen sulphide is removed by passing a stream of hydrogen

#### iv) CHANGE OF SOLVENT

(11)

it is a general principle that if a substance A is soluble in B, but is insoluble in C, A will form a colloidal suspension, when a solution of A in B is added to an excess of C. The two solvents B and C should be miscible. Thus a Sulphur sol can be prepared by adding a saturated solution of Sulphur in alcohol to water.

#### PURIFICATION OF SOLS

The sol obtained by the methods stated above contains besides the colloidal particles, appreciable amounts of electrolyte. To obtain the pure sol this electrolyte has to be removed.

The purification of sols can be accomplished by three methods.

(A) DIALYSIS

(B) ELECTRODIALYSIS

(C) ULTRAFILTRATION

(A) DIALYSIS

The process of removing ions (or molecules) from a sol by diffusion through a permeable membrane is termed as Dialysis.

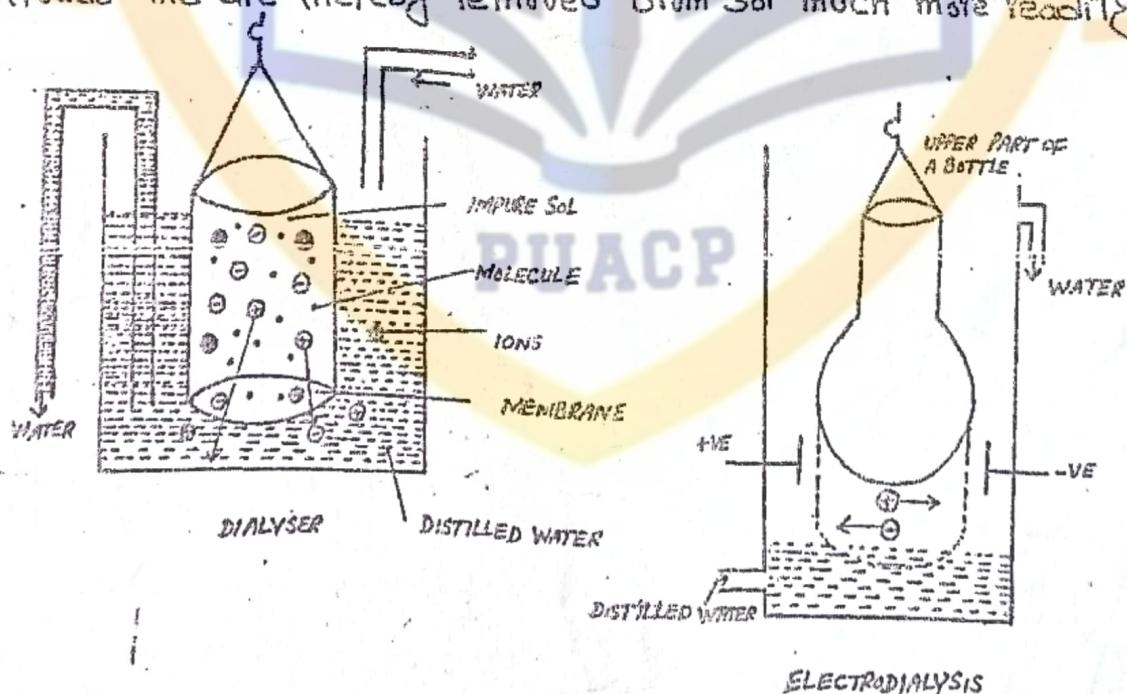
The apparatus used for dialysis is called Dialysis. Different forms (cylinder, bag, or thimble) and a number of dialysing materials have been used for the purification of sol. Parchment paper, Cellophane sheet, cellulose acetate and animal bladder are used for membranes of dialysers. Ordinary dialyser consists of a cylindrical vessel closed at one end with the membrane. The sol to be dialysed is placed in the cylinder which is then suspended in a large dish containing distilled water. On

→ Privileged Contact with the distilled water. The ions in solution pass through the membrane into water, but the colloidal particles unable to pass through the membrane are retained to yield a pure sol.

The distilled water is renewed from time to time, but it is preferable to use a continuous flow of water, as dialysis is greatly accelerated thereby. Dialysis is a slow process and takes a long time for completion.

### (B) ELECTRODIALYSIS

The process of dialysis can be accelerated to facilitate the rapid diffusion of the electrolyte through the membrane under the influence of an electric field and process is then called electrodialysis. Two electrodes are placed in outer vessel containing water outside the membrane containing the sol and electrolyte. When potential difference is applied across the membrane, ions in the sol move faster towards the opposite electrodes and are thereby removed from sol much more readily.



# PROPERTIES OF SUSPENSIONS

(13)

## (1) FILTERABILITY.

The Colloidal Particles can easily pass through an ordinary Filter Paper, while Coarse Particles cannot do so. Colloidal Particles are generally removed by ultrafilters.

## (2) INFUSIBILITY

The Colloidal Particles have little Power of diffusion, chiefly because of their large size as Compared to Solute Particles in Solution.

## (3) HETEROGENITY

The Colloidal System is heterogeneous in nature. The Colloidal Particles invisible under the ordinary microscope are visible under the ultra-microscope, while the molecules or ions of true solution are invisible in ultramicroscope or even in an electron microscope.

## (4) COLOUR

The Colour of Sol depend on the wavelength of the light scattered by dispersed Particles. The wavelength of the scattered light depends on the size and nature of Particles. Thus Sulphur Sol with different Particle Size shows different Colour either bright yellow or light yellow.

## (5) SURFACE TENSION AND VISCOSITY

The Surface tension and Viscosity of Sols depend on whether the Sols are Hydrophobic or Hydrophilic. For Hydrophobic Sols density, surface tension and viscosity are not very different from those of medium. This is so because there is very slight interaction between, suspended Particles and medium. On the other hand Hydrophilic Sols show a high degree of solvation of the Particles and as a result, the

Physical properties are modified. Thus the viscosity is much higher for the sol than for the medium. Furthermore the surface tension of the sol is generally lower than that of the pure medium.

### (6) SOLS EXHIBIT TYNDALL EFFECT

The phenomenon of the scattering of light by the sol particles is called Tyndall effect. The illuminated beam or cone formed by the scattering of light by the sol particles is called the Tyndall beam or Tyndall Cone. True solutions do not show Tyndall effect. Since ions or molecules are too small to scatter light. The amount of light scattered depends on three factors (A) Fourth power of the wavelength of the incident light ( $\lambda^4$ ), (B) The difference between the refractive index of the particles and that of medium. (C) The size and the shape of particles.)

### (7) VISIBILITY

Sol particles can be seen with an electron microscope. The particles have been found to be spherical, rod-like or long filaments. Gold sol particles are observed in an electron microscope having size 0.1 nm.

### (8) BROWNIAN MOVEMENT

The continuous rapid zig-zag movement excited by colloidal particles in the dispersion medium is called Brownian movement. Brownian movement is due to the bombardment of the colloidal particles by molecules of medium. The movement of the particles is caused by unequal number of molecules of the medium striking it from opposite directions. When more molecules strike the particle on one side than on another side, the direction of movement is changed. Thus a zig-zag motion of the colloidal





Partic<sup>le</sup>s can be observed through an ultra microscope. True solutions and suspensions do not exhibit Brownian movements. The Brownian movement is, in part, responsible for the stability of colloidal dispersion, as it counteracts the force of gravity acting on the sol particles.

#### (10) COLLIGATIVE PROPERTIES

Sols show colligative properties as lowering of vapour pressure, depression in freezing point, boiling point elevation and osmotic pressure, but the effect observed are very much smaller than for true solutions. In fact, with the exception of osmotic pressure, the effect are partially negligible. The osmotic pressure of sol is usually very low than that of a true solution having the same concentration.

The colligative properties depend on number of particles present whether in a true solution or in a colloidal solution. It is to be expected that a colloidal particle is an aggregate of about 1000 molecules as they exist in a true solution i.e. the number of particles present in a sol will be  $1/1000$  of that present in a true solution having same concentration. Hence colligative effects will be reduced by the same amount. Such a decrease in number of particles lead to practically no observable difference between colligative properties of sol and true solution with the exception of osmotic pressure. Since the osmotic pressure, being larger in magnitude than others, still clear and obvious, although considerably reduced below that of true solution of the same concentration.

#### (10) ELECTRICAL CHARGE

The sol particles carry an electrical charge. All the suberruent particles possess either a positive or negative charge. The charge on the particles mainly responsible for the stability of sols.

- The mutual force of repulsion between similarly charged particles prevent them from aggregating and settling under action of gravity.
- The sol particles acquire charge by preferential adsorption of positive or -ve ions, on the surface of the particles from dispersion medium. For example, a Ferric hydroxide sol particles acquire a positive charge because they adsorb common ion  $\text{Fe}^{3+}$  from dispersion medium. Arsenious sulphide sol particles acquire a negative charge since they adsorb the common ion  $\text{S}^{2-}$  (from  $\text{H}_2\text{S}$ ) from the dispersion medium.

### (11) ELECTROPHORESIS OR CATAPHORESIS

Since colloidal particles are charged and when placed in an electric field these particles migrate either towards the cathode or anode depending upon their charges. This migration of electrically charged sol particles under the influence of an applied electric field is called cataphoresis or electrophoresis.

Since different colloidal species in a mixture migrate at different rates, electrophoresis may be employed for their separation. For this reason, electrophoresis is used extensively for the fractionation and analysis of proteins, nucleic acids, polysaccharides, and other complex substances of biological interest and activity.

### (12) ELECTRO-OSMOSIS

The movement of the dispersion medium under the influence of an applied electric field is called electro-osmosis. A sol is electrically neutral. Therefore, the dispersion medium carries an equal but opposite charge to that of the dispersed particles. If sol particles are kept stationary by some suitable means, the dispersion medium would move to the electrodes of opposite sign under the influence of an applied electric field.

The phenomenon of electro-osmosis is used technically in removal of water from peat, in dewatering moist clay and in dry-dyeing dye pastes.

## (25) PRECIPITATION OR COAGULATION OF SOLS

(17)

The stability of a sol is mainly due to electric charge on sol particles. For lyophobic sols, the stability is due to their electric charge but for lyophilic sols, stability is both due to their electric charge and their high hydration (solvation). Removal of charge in lyophobic sols would lead to precipitation of sols, while to precipitate a lyophilic sol, both the charge and solvation must be removed. The flocculation (or aggregation) and settling down of the discharged sol particles is called coagulation or precipitation of sol. The precipitation of a lyophobic sol can be brought about by in four ways: by addition of electrolytes, by electrophoresis, by mixing two oppositely charged sols, by boiling.

## (26) PROTECTION

The stability of lyophobic sols can be increased by the addition of more stable lyophilic sol like gelatin or albumin. These lyophilic substances are absorbed on surface of the lyophobic particles by electrostatic force or sometimes by chemical interaction, thus converting the lyophobic sol into one with more lyophilic character and as a result the sol acquire greater resistance to precipitation. The property of lyophilic sols to prevent the precipitation of a lyophobic sol is called protection.

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~~Light related properties~~

## OPTICAL PROPERTIES OF SOLS 118

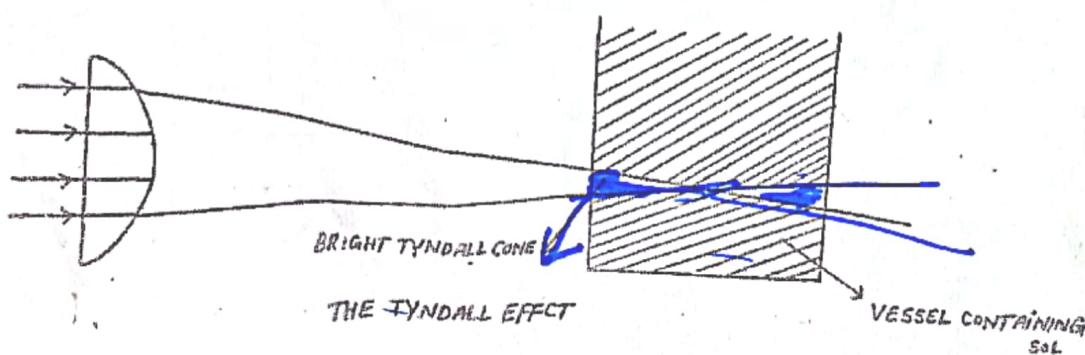
### TYNDALL EFFECT → based on light scattering

Colloidal Particles are too small to be seen in the microscope. Nevertheless their presence can be made evident by optical means.

If a strong beam of light is passed through a medium which is optically clear. That is it contains no particles larger than about  $10^{-7}$  cm in the path of the light. Cannot be easily detected if particles of larger e.g. Colloidal Size are present however, they will scatter the light and as a result the beam is rendered visible. The phenomenon of the scattering of light by the sol particles is called "Tyndall Effect". The illuminated beam or cone formed by the scattering of light by the sol particles is called the "Tyndall beam" or "Tyndall Cone".

When a beam of light enters a dark room through a small hole the dust particles floating in air scatter the beam, is rendered visible when viewed at right angle.

Similarly when a strong beam of light is passed through a sol. The sol particles absorb light energy and part of the incident light is scattered in all directions and as a result hazy beam or cone of illuminated particles appears. Since colloidal dispersions with their large particle are good scatters of light, and they exhibit Tyndall effect on passage of light which can readily be observed and measured.

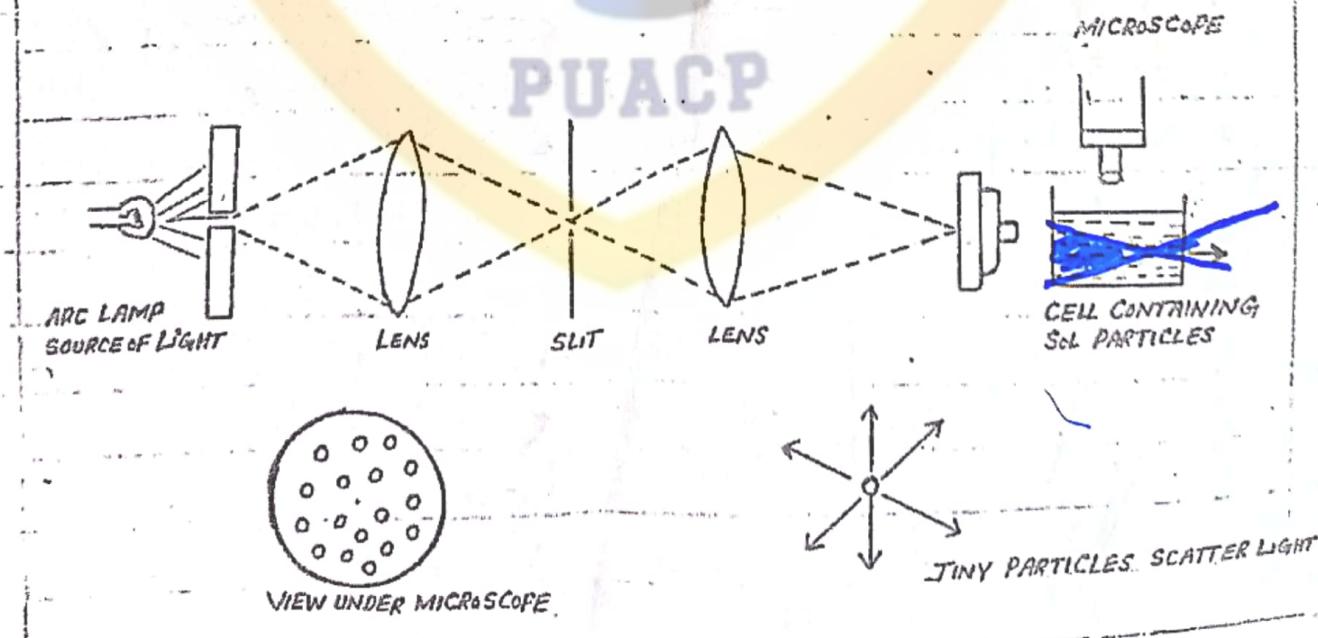


Tiny solutions do not show Tyndall effect since ions or molecules are too small to scatter light. The amount of light scattering depends on three factors.

- i) The fourth power of the reciprocal of the wavelength ( $\lambda$ ) of the incident beam of light ( $1/\lambda^4$ )
- ii) The difference in the refractive index of the particles and that of the medium.
- iii) The size and shape of the particle.

Zsigmondy (1903) used the Tyndall Phenomenon to set up an apparatus called Ultra microscope in order to investigate scattering of light by Sol Particles in dispersion medium.

When a strong beam of light usually from an electric arc lamp passes through several lenses and a slit and enters the cell containing Sol, the Sol is viewed through a microscope placed at right angle to the path of light since colloidal particles scatter light in all directions, it enters the microscope and tiny bright colloidal particles are observed moving about chaotically (zigzag) against a dark background.



## DETERMINATION OF PARTICAL SIZE

(20)

The general theory of light scattering by isotropic, noninteracting, spherical particles of any uniform size was developed by Gustav Mie in 1906. Although the mathematical results of the theory are very complex they can nevertheless be summarized as follows.

Suppose that unpolarized incident light of wave length  $\lambda_0$  in vacuum and initial intensity  $I_0$  is passed through a dispersion and suppose, further, that the intensity of light scattered at any angle  $\theta$  to the direction of primary beam is  $I_\theta$ . Mie theory predicts, then, that the ratio  $I_\theta = \frac{I_\theta}{I_0}$  will be function of  $\theta$ ,  $m$ , and the diameter  $\alpha = \pi D/\lambda_m$  where  $D$  is diameter of the scattering particles and  $\lambda_m$  is the wave length of the light in the medium. The two wave lengths  $\lambda_m$  and  $\lambda_0$  are related by the equation.

$$\lambda_m = \frac{\lambda_0}{n_0} \quad (1)$$

The same conclusion applies to the vertical component of  $I_\theta$ , namely  $I_{\theta v}$ . Since both  $I_\theta$  and  $I_{\theta v}$  depend on  $D$ , they can both be employed to determine particle size of colloidal dispersions by means of light scattering. Total light scattered light also depends on  $m$  and  $\alpha$ , and hence this quantity can be used as well as to find  $D$ .

Of the various means by which  $D$  can be obtained we shall discuss only two methods:-

- (A) The minimum intensity method
- (B) Transmission method

## Minimum INTENSITY METHOD

(21)

Dispersions with particle size larger than about  $1800\text{ \AA}$  in diameter exhibit minima or minima and maxima in the intensity of the vertical component of the scattered light i.e. in plots of  $I_{90} \text{ vs } \theta$ . Recently Maron and Elder showed on the basis of Mie theory and experimentally, that the angular positions of the first minimum,  $\theta_1$  are related to  $D$ ,  $d_m$  and values of  $m$  between 1.00 and 1.55 by equation

$$\frac{D}{d_m} \sin \frac{\theta_1}{2} = 1.002 - 0.347m \quad (2)$$

Consequently, when  $m$  and  $d_m$  are known and  $\theta_1$  is measured for a dispersion,  $D$  can then be calculated by means of equation 2.

Equations similar to (2) are obeyed also by higher minima as well as maxima and hence these can be used as well to determine  $D$ .

Table (A) shows some particle diameters obtained in this manner for several latex dispersions of butadiene-styrene ( $m=1.17$ ) and polystyrene  $m=1.10$  in water

LATEX NO	$m$	$d_m(\text{\AA})$	$\theta_1$	$D(\text{\AA})$
580-G	1.20	3017 3253	94.5° 108	2630 2600
10713	1.17	3253 4049	66 85	3920 3980
497	1.17	3253 4094	43 53	5820 5810
197	1.17	3253 4094	38 48	6550 6600
597	1.17	4094 4330	31 33	10060 10010

TABLE-A PARTICLE DIAMETERS OF LATTICES OBTAINED BY  
MINIMUM INTENSITY METHOD

## THE TRANSMISSION METHOD

(22)

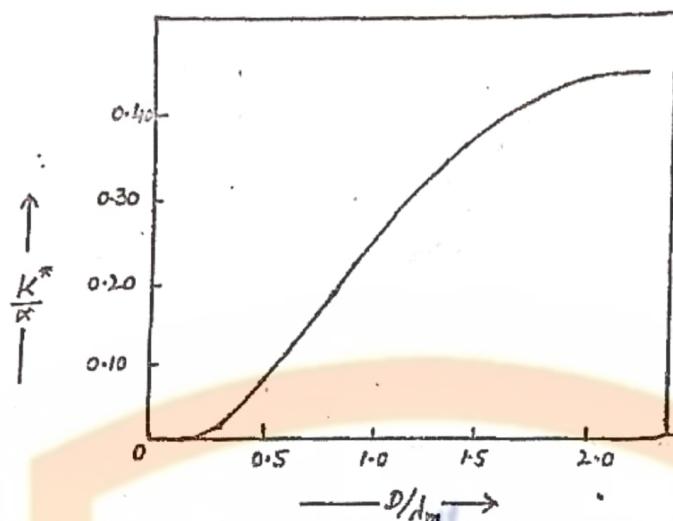
- This method is based on application of Mie theory to the total intensity of scattered light. When light of wavelength  $\lambda$  and intensity  $I_0$  is passed through a dispersion contained in a cell of length  $l$ , the intensity of the transmitted light is reduced to  $I$  by scattering. The relation between  $I$  and  $I_0$  is given by

$$T = \frac{l}{\lambda} \ln \frac{I_0}{I} \quad \dots \quad (3)$$

- where  $\eta$  is the turbidity of the dispersion. Again if we let  $C$  be the concentration of scattering particles in grams per cc and  $\rho$  their density. The Mie theory predicts that

$$\left( \frac{2e dm}{3\pi} \right) \left( \frac{T}{C} \right)_0 = \frac{K^*}{\alpha} \quad \dots \quad (4)$$

- where  $K^*$  is a quantity called the scattering coefficient of the particles. The zero subscript on  $T/C$  indicates that this ratio has to be plotted against  $C$  and extrapolated to  $C=0$  in order to eliminate any interactions among the particles. All the quantities on left-hand side of equation (4) are experimentally measurable, and hence  $\frac{K^*}{\alpha}$  can be found. Again  $\frac{K^*}{\alpha}$  is a function of  $m$  and  $\alpha$  which can be calculated from Mie theory. At any constant value of  $m$ ,  $\frac{K^*}{\alpha}$  as a function of  $D/dm$  is given by a curve such as shown in figure. Consequently, once  $\frac{K^*}{\alpha}$  is found experimentally it can be used with the plot for the appropriate  $m$  value to find  $D/dm$  and then  $D$ .



MIE THEORY PLOT OF  $\frac{K^*}{K}$  VS  $\frac{D}{D_m}$  FOR  $m = 1.20$

$D (A^\circ)$	LATEX 243 $m = 1.15$	LATEX G-S $m = 1.17$	LATEX 580-G $m = 1.20$
7000	905	3660	2570
7500	920	3680	2640
8000	921	3660	2630
8500	919	3670	2640
9000	919	3710	2620
9500	931	3670	2620
10000	905	3770	2590
AVERAGE	$917 \pm 7$	$3690 \pm 30$	$2620 \pm 20$

TABLE - PARTICLE DIAMETERS OF SYNTHETIC LATTICES OBTAINED  
BY TRANSMISSION METHOD

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Session 2001-02

UNIVERSITY OF THE PUNJAB

## OTHER METHODS FOR DETERMINATION OF PARTICLE SIZE

Another means of getting at the size and shape of disperse particles is the electron microscope. In this instrument a beam of electrons is used instead of ordinary light to observe and photograph of colloidal particles. In figure (A) is shown an electron Photomicrograph of synthetic rubber latex particles whose average diameter is 2300 Å. With suitable enlargement of such photomicrographs magnification as high as 100,000 diameters have been obtained.

FIG - ELECTRON PHOTOMICROGRAPH OF SYNTHETIC RUBBER LATEX PARTICLES

In certain systems, such as synthetic rubber latexes, particle size can also be determined by adsorption methods. These involve titration of the colloid with a soap solution until the surface of the particles is covered with a monolayer of soap. From the amount of soap required per unit weight of disperse phase and the area occupied by a soap molecule on the surface then is calculated the average diameter of the particles.

## KINETIC PROPERTIES OF SOLS

(25)

The Properties of Sols which can be discussed conveniently under this heading are diffusion, Brownian motion, and sedimentation.

### DIFFUSION

Graham observed that Colloidal Particles diffuse much more slowly than Solutes in the Solution. Albert Einstein and others showed that it is possible to derive an expression for the diffusion of Colloidal Particles in a medium provided it is assumed that the Van't Hoff equation for osmotic pressure applies, and that the Colloid Particles are spherical and large compared with the molecules of medium. With these assumptions the equation for the diffusion coefficient  $D_f$  i.e. the number of moles of Colloid diffusing across unit area per unit time under a concentration gradient of 1 mole per centimeter, follows the

$$D_f = \frac{RT}{N} \left( \frac{1}{6\pi\eta r} \right) \quad (1)$$

where

$R$  = Gas Constant in ergs mole<sup>-1</sup> degree<sup>-1</sup>

$T$  = Absolute temperature

$N$  = Avogadro's number

$\eta$  = The viscosity of medium in Poises

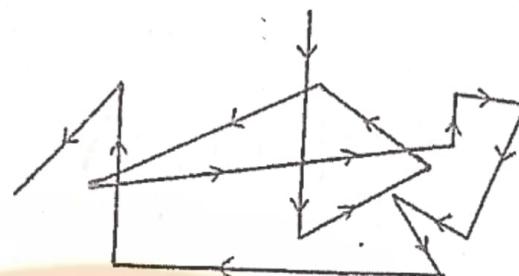
$r$  = Radius of the colloidal Particles in Centimeters

Above equation has been found to hold well for various types of dispersions

### BROWNIAN MOVEMENT

The English botanist, Robert Brown (1827) observed under a microscope that Pollen grains and other microscopic particles

Suspended in water show a ceaseless, unpredictable and chaotic motion. If a single particle is observed, it is seen to move in a continuous series of short, straight paths as indicated in figure below:



#### SUCCESSIONAL MOVEMENT OF A SINGLE PARTICLE IN A COLLOIDAL DISPERSION

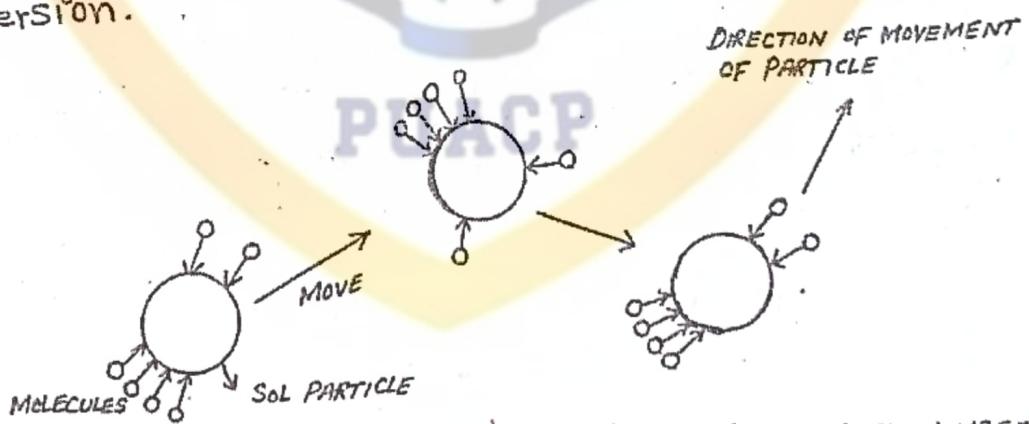
This movement was later named Brownian movement. Brownian concluded that the movement of the suspended particles was not dependent on the currents in the liquid or gas, not on their mutual attraction or repulsion, neither on the gradual evaporation of the liquid nor on the action of capillary forces, but was a property of particles themselves. Wiener (1863)

Presented the correct interpretation of the Brownian motion.

He pointed out the motion is caused by the molecules of the liquid, it will be interesting to recall from the study of the kinetic theory of and the study of liquids that molecules in the gaseous and liquid states are in constant motion, travelling in straight lines until they collide with some other molecules. The kinetic energy of a molecule has a certain average value which is a function of its mass and speed at a given temperature. The bombardment of the colloidal particles by the molecules of the medium results in their acquiring the same kinetic energy as that of the bombarding molecules. The higher the temperature, the more vigorous is the movement and hitting by the molecules if the colloidal particle is in the large size range (diameter).

more than 5 micron)  $1\text{ micron} = \mu = 10^{-6}\text{ metre}$ . it is always receiving thousands and millions of blows from all sides. The resultant of these countless hits from all sides is that the particle does not move, if however the particle is small enough, it gets a stronger blow from one side than from the other. Thus the probability of unequal bombardment of a colloidal particle increases as the size of particle decreases and the particle moves in the direction of resultant blows. Changes in the direction result when the number of bombardments on one side becomes momentarily larger than the bombardments from the other side and also on collision with other particles. Thus a zigzag motion of the colloidal particle can be observed through ultramicroscope.

The Brownian movement of colloidal particles is an important factor in causing them to remain suspended indefinitely instead of settling under the influence of gravitation. Hence, it accounts in part, for the permanence of colloidal dispersion.



THE BOMBARDMENT ON THE SIDES OF THE COLLOIDAL PARTICLES BY UNEQUAL NUMBER OF MOLECULES OF THE MEDIUM

The validity of this explanation of Brownian motion is borne out by mathematical considerations again due to Einstein. He showed that on the basis of assumptions

(20)

Mentioned in connection with diffusion, the diffusion coefficient of a colloid should be related to the average displacement,  $\Delta$ , produced by Brownian movement in time  $t$  along  $x$ -axis. The relation between  $D_f$  and  $\Delta$  is

$$D_f = \frac{\Delta^2}{2t} \quad \dots \quad (1)$$

Eliminating  $D_f$  between equation (1) and (2).

$$\frac{\Delta^2}{2t} = \frac{RT}{N} \left( \frac{1}{6\pi\eta r} \right)$$

$$\Delta^2 = \frac{RT}{N} \left( \frac{t}{3\pi\eta r} \right)$$

- This equation was used by Perrin in his classical experiments on suspensions of gamboge and mastic in water.
- For the determination of Avogadro's number.

## SEDIMENTATION OF SUSPENSIDS

Although colloidal dispersions may be stable over long periods of time, sometimes years, they nevertheless tend to settle out slowly under the influence of gravity on prolonged standing. The rate of settling can usually be followed quite readily, for the boundary between clear medium and sol. is, as a rule quite distinct. From the observation of such rates it is possible to arrive at the dimensions of the suspended particles and their masses.

Consider a tube such as shown in fig. containing a disperse phase of density  $\rho$  suspended in a medium of density  $\rho_m$  and viscosity  $\eta$ . If  $e$  is greater //



that  $e_m$ , the particle will be displaced upward. Any particle of radius  $r$  tending to settle under gravity will be opposed by frictional force of medium. Now, when equilibrium is established between these two forces spherical particle will fall according to Stokes's law with a constant velocity  $v$  given by

$$v = \frac{2r^2 g (e - e_m)}{9\eta} \quad (1)$$

where  $g$  is the acceleration of gravity. Since  $v$  at a point such as  $Z$  from the top  $A$  is obviously  $\frac{dz}{dt}$ , the rate at which the height of level  $B$  changes with time equation (1) may be written as

$$\frac{dx}{dt} = \frac{2r^2 g (e - e_m)}{9\eta} \quad (2)$$

on integrating this equation between limits  $x_1$  at  $t_1$  and  $x_2$  at  $t_2$ , we obtain,

$$\int_{x_1}^{x_2} dx = \frac{2r^2 g (e - e_m)}{9\eta} \left. dt \right|_{t_1}^{t_2}$$

$$|x|_{x_1}^{x_2} = \frac{2r^2 g}{9\eta} (e - e_m) |t|_{t_1}^{t_2}$$

$$(x_2 - x_1) = \frac{2r^2 g}{9\eta} (e - e_m) (t_2 - t_1) \quad (3)$$

By knowing  $e$ ,  $e_m$  and  $\eta$  and by measuring the distances  $x_1$  and  $x_2$  at two different times  $t_1$  and  $t_2$ . It is possible to calculate from equation (3) the radius

Q. Settling Particle. Once the radius is known, the mass of a single particle follows from  $m = \frac{4}{3} \pi r^3 e$  and the molar weight of the disperse phase from  $M = Nm$ . Unless the suspended particles are large, sedimentation under gravity is an extremely slow process. However it is possible to accelerate greatly by means of ultracentrifuge. An ultracentrifuge is essentially a very-high-speed centrifuge in which the centrifugal force of rotation is substituted for the force of gravity. By whirling colloidal dispersions in cells placed in specially designed rotors, accelerations as high as one millions times that of gravity has been achieved. Under these conditions even finely dispersed sols can be sedimented in a relatively short time. To observe the rate of settling optical methods have been developed which permit photographing the level of the sol at various stages of settling without stopping the ultracentrifuge.

Since the acceleration of a centrifugal field at a distance  $z$  from the axis of rotation is  $\omega^2 z$ , where  $\omega$  is the angular velocity of rotation in radians per second. Putting this quantity in equation (2) in place of  $g$  gives immediately the rate of settling, namely,

$$\frac{dx}{dt} = \frac{2r^2 \omega^2 z (e - e_m)}{9\eta} \quad (4)$$

By separating variables and integrating between the same limits as before, we have

$$\int_{x_1}^{x_2} \frac{dx}{x} = \frac{2r^2 \omega^2}{9\eta} (e - e_m) \int_{t_1}^t dt$$

$$\left| \ln \frac{x_2}{x_1} \right| = \frac{2 r^2 w^2}{9 \eta} (e - e_m) \left| \frac{t}{t_1} \right|^{\frac{1}{2}} \quad (31)$$

$$\ln x_2 - \ln x_1 = \frac{2 r^2 w^2}{9 \eta} (e - e_m) (t_2 - t_1)$$

or  $\ln \left( \frac{x_2}{x_1} \right) = \frac{2 r^2 w^2}{9 \eta} (e - e_m) (t_2 - t_1) \quad (5)$

Through equation (5)  $r$  may again be calculated from the values of  $x$  and  $t$  at two stages of the sedimentation and from a knowledge of the speed of rotation of the ultracentrifuge  $w$ . This procedure for obtaining  $r$  and therefore from the molar weight of a suspensoid is called the sedimentation velocity method.

An alternate procedure for obtaining these quantities is the sedimentation equilibrium method. If a suspensoid is whirled sufficiently long in an ultracentrifuge a stage is reached at which the sol. no longer settle. At this point an equilibrium is reached between the rate of sedimentation and the rate at which the suspended particles tend to diffuse back into the more dilute portions of a cell against the centrifugal force. By equating these two rates, it is possible to arrive at the distribution of concentration with distance in various parts of the sedimentation cell. This distribution is given by the relation.

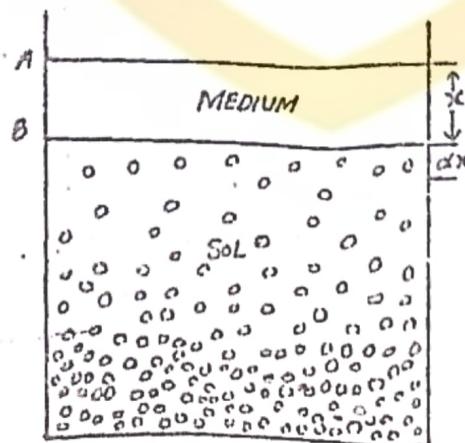
$$\ln \frac{C_2}{C_1} = \frac{M w^2 (e - e_m) (x_2^2 - x_1^2)}{2 R T P} \quad (6)$$

where  $C_1$  and  $C_2$  are the concentrations of colloid at levels  $x_1$  and  $x_2$  while  $M$  is the molecular weight of the colloid.

By determining the concentrations  $C_1$  and  $C_2$  at the two levels  $x_1$  and  $x_2$  in the settling cell at sedimentation equilibrium,  $M$  can easily be calculated from equation ④. Equation (5) is applicable to dilute dispersions of uniform spherical particles while equation ⑥ applies to dilute dispersions of particles of any shape so long as they are all of the same size. When the particles are non-spherical a more involved analysis of the sedimentation velocity data is required. Again, when systems are heterogeneous in particle size, it is possible by sedimentation studies to determine the particle size distribution for the systems. Most of the sedimentation studies have been made on proteins in aqueous solution and on other substances of biological interest. Some results obtained are given.

Protein	$M$ (g/mole)
Trypsin	15,000
insulin	46,000
urease	480,000
Rabbit virus	47,000,000

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SEDIMENTATION UNDER GRAVITY

# ELECTRICAL PROPERTIES OF SOLS

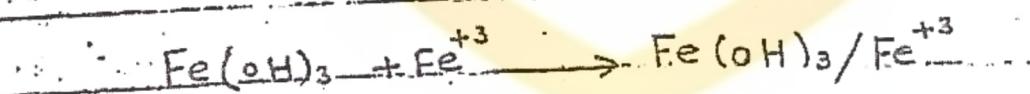
(33)

Hydrophilic Sol's are much stable than hydrophobic Sol's. One of the reason is that there is a strong force of attraction between Hydrophilic Sol Particles and dispersion medium. On the other hand hydrophobic Sol's are less stable. So it is useful to discuss the electrical properties of hydrophobic Sol here. All the suspended particles posses either a positive or negative charge. The charge on the particles is mainly responsible for the stability of sols, since the mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity.

The Sol Particles acquire charge by the following ways.

## 1. PREFERENTIAL ADSORPTION OF IONS

The charge on colloidal particles in some cases results from adsorption of either positive or negative ions from the medium in which they are prepared e.g. Ferric chloride Sol Particles acquire a positive charge because they absorb the common ion  $\text{Fe}^{+3}$  (from  $\text{FeCl}_3$  used in the preparation of the sol) from the dispersion medium.

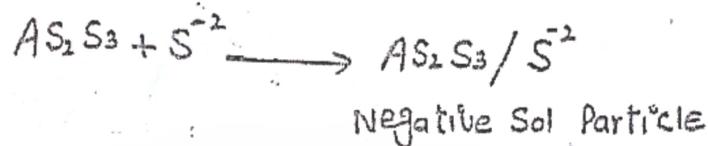


Positive Ferrichydroxide Sol

Since the sol as a whole is neutral, the charge on the particles is counterbalanced by another charged ions termed as "Counterions" (in this case  $\text{Cl}^-$ ) furnished by electrolyte in the medium.

(2\*)

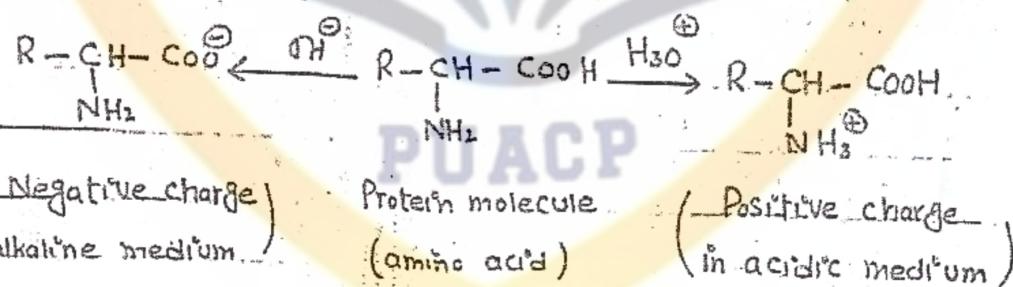
Similarly Arsenious sulphide Sol Particles acquires a negative charge since they absorb the common ion  $S^{2-}$  (from  $H_2S$ ) from the medium)



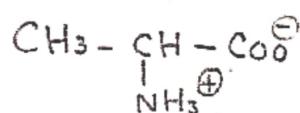
## 2) DUE TO THE PRESENCE OF ACIDIC AND BASIC GROUP

The charge in case of Proteins, amino acids, poly Peptides etc can be explained due to the presence of acidic (such as  $-COOH$  or  $-OH$ ) and basic (such as  $-NH_2$ ;  $-NH$ ) groups in the molecules.

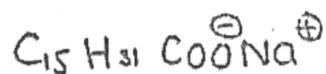
In acidic Solution the molecules will have Positive charge due to the Protonation of the basic groups, while in alkaline Solution the molecules will be negatively charged due to Ionization of the acidic group as shown in the following scheme.



It is clear that the charge in such cases is a function of pH of the medium. The pH at which the net charge on the molecule is zero is called Isoelectric Point. The molecules at the iso electric point exist as zwitterion

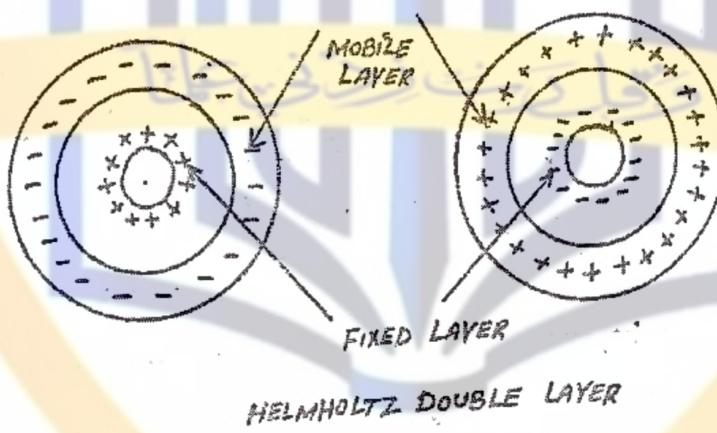


In the case of Soaps, the charge on the particles is due to ionization of molecule e.g.



### HELMHOLTZ AND ELECTRICAL DOUBLE LAYERS

The surface of colloidal particles acquires a positive or negative charge by selective adsorption of a layer of positive or negative ions around it. This layer attracts counterions from the medium which forms a second layer of opposite charges. The combination of two layers of positive and negative charges around the Sol particle is called Helmholtz Double Layer.

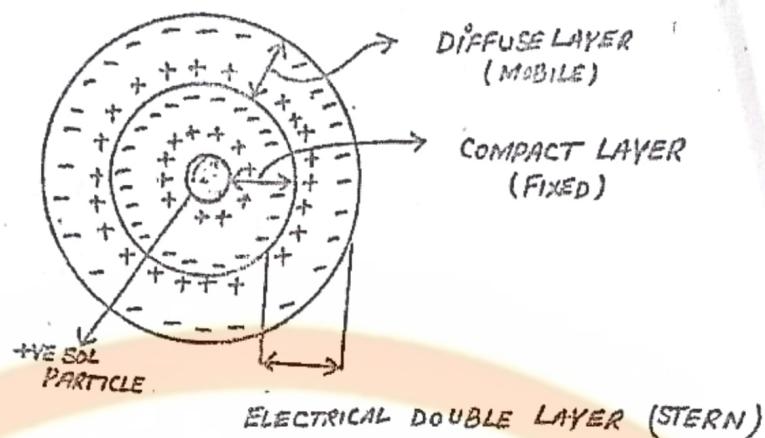


Helmholtz thought that the charges next to the particle surface were fixed while the compensating charge along with the medium (liquid) were mobile. More recent considerations have shown that the double layer is made of

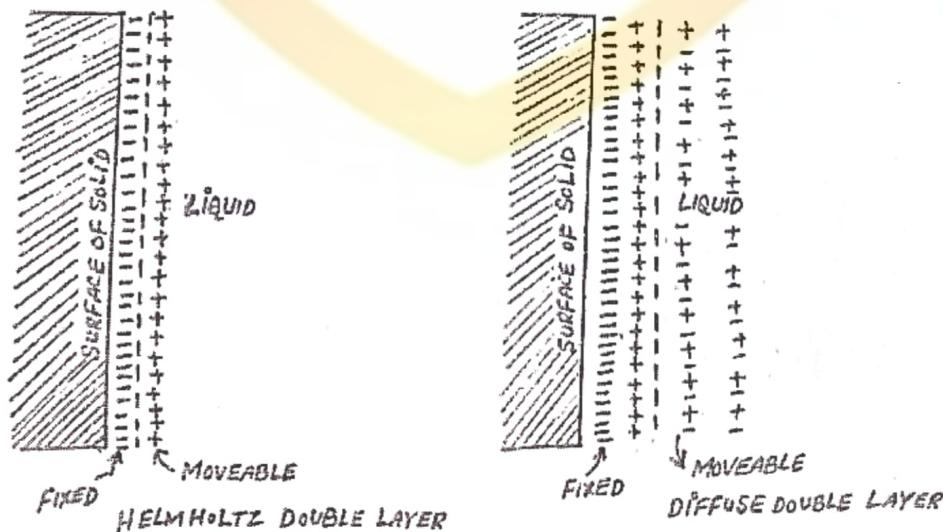
(A) A compact layer of positive and negative charges which are fixed firmly on to particle surface

(B) A diffuse layer of counterions dispersed into the medium containing opposite ion.

The combination of the compact and diffuse layer is referred to as the Stern Double layer



Any solid in contact with a liquid tends to develop a difference in potential across the interface between the two. Thus, when water is brought into contact with a glass surface, the latter adsorbs hydroxyl ions and becomes negatively charged with respect to the water. To counterbalance this charge, hydrogen ions are attracted to the surface to form a double layer of charges with the negative charges on the glass and positive charges in the water immediately adjacent to these as shown in figure. Such an arrangement of charges called Helmholtz double layer leads to a difference of electric potential between the solid and liquid.



HEMHOLTZ AND DIFFUSE LAYERS

The diffuse layer is only loosely attached to the particle surface and moves in the opposite direction under the applied electric field. Because of the distribution of the charge around the particle, there is a difference in potential between the compact layer and the bulk of solution across the diffuse layer. This is called the electrokinetic or zeta potential. Zeta potential accounts for the electrical properties such as

- (A) Cataphoresis or electrophoresis
- (B) Electro-osmosis of colloids
- (C) Streaming potential
- (D) Sedimentation potential

The magnitude of the zeta potential can be determined with the help of these properties.

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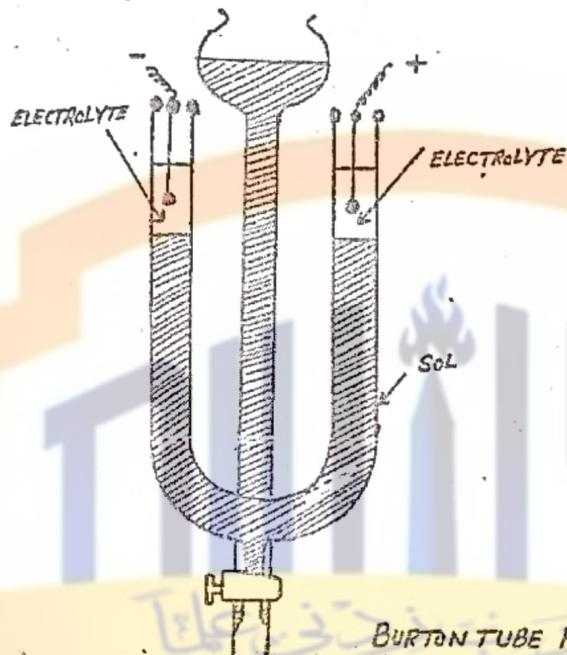


## ELECTROPHORESIS OR CATAPHORESIS

The migration of electrically charged colloidal particles

Under an applied electric potential is called electrophoresis.

This effect can be followed readily in the apparatus shown in figure called Burton tube



BURTON TUBE FOR ELECTROPHORESIS

This apparatus consists of a U-tube fitted with a stopcock for drainage and a funnel-shaped filling tube with stopcock (not shown) attached to the back of U-tube. A solution of some suitable electrolyte of lower density than the sol is first placed in the tube, and the sol next introduced through the funnel so as to displace the electrolyte upward and produce sharp boundaries in the two arms. Electrodes are then inserted as shown, and connected to a source of potential, such as high voltage battery. When the colloidal particles are negatively charged it is observed that the level of the sol falls gradually on the negative electrode side and rise simultaneously on the positive side i.e. the colloidal particles move toward the



Positive electrode. Conversely, when the particles are positively charged, the reverse occur. If the electrophoresis is permitted to proceed until the appropriate electrode is reached, the sol will discharge and precipitate.

By noting whether colloid particles migrate in an electric field and the direction of migration, it is readily possible to determine whether the particle in a given colloid are charged and what is the sign of charge. Through such means it has been established that hydrophobic colloids are specific in their adsorption of either positive or negative ions. Thus sulphur, metallic sulfide and noble metal sols are negatively charged. On the other hand metal oxide sols, such as iron and aluminum oxide, are positively charged. This same specificity of charge is observed also with some hydrophilic sols. However, with certain sols of the latter type, particularly the proteins, the sign of charge depend on the pH of the solution. Above a certain pH value, characteristic for each sol, the particles are negatively charged, while below this pH they have a positive charge. At the pH value in question called the isolectric point, the particles are uncharged and consequently do not migrate in an electric field. As a rule the isolectric point does not come at a definite pH but covers a pH range being, for instance, 4.1 - 4.7 for casein from human milk, and 4.5 - 5.3 for hemoglobins from various sources.

Electrophoresis can also be utilized for quantitative measurements of the rate with which colloid particles migrate. By determining the time necessary for a sol to migrate a definite distance under a potential difference applied

- Positive electrode. Conversely, when the particles are positively charged, the reverse occur. If the electrophoresis is permitted to proceed until the appropriate electrode is reached, the sol will discharge and precipitate.

- By noting whether colloid particles migrate in an electric field and the direction of migration, it is readily possible to determine whether the particle in a given colloid are charged and what is the sign of charge. Through such means it has been established that hydrophobic colloids are specific in their adsorption of either positive or negative ions. Thus sulphur, metallic sulfide and noble metal sols are negatively charged. On the other hand, metal oxide sols, such as iron and aluminum oxide, are positively charged. This same specificity of charge is observed also with some hydrophilic sols. However, with certain sols of the latter type, particularly the proteins, the sign of charge depend on the pH of the solution. Above a certain pH value, characteristic for each sol, the particles are negatively charged, while below this pH they have a positive charge. At the pH value in question called the isolectric point, the particles are uncharged and consequently do not migrate in an electric field. As a rule the isolectric point does not come at a definite pH but covers a pH range being, for instance, 4.1 - 4.7 for casein from human milk, and 4.5 - 5.3 for hemoglobins from various sources.

Electrophoresis can also be utilized for quantitative measurements of the rate with which colloid particles migrate. By determining the time necessary for a sol to migrate a definite distance under a potential difference applied

Over a given length of conducting Path, the electrophoretic mobility can be calculated i.e the rate in Centimeters per second under a Potential drop of one volt per centimeter. Such Calculations show that the migration velocities of Colloidal Particles are not much different from those of ions under the same conditions, and are of the order of  $10$  to  $60 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1} \text{ Volt}^{-1}$ . Since different Colloidal species in a mixture migrate at different rates, electrophoresis may be employed for their separation. For this reason electrophoresis is used extensively for the fractionation and analysis of proteins, nucleic acids, polysaccharides, and other complex substances of biologic interest and activity.



## ELECTRO-Osmosis

(41)



The movement of the dispersion medium under influence of an applied electric field is called electro-osmosis (osmosis = diffusion through porous membrane).

A sol is electrically neutral. Therefore, the dispersion medium carries an equal but opposite charge to that of the dispersed particles. If sol particles are kept stationary by some suitable means, the dispersion medium would move to the electrode of opposite sign under the influence of an applied electric field. Electro-osmosis is a direct consequence of the existence of zeta potential between the sol particles and the medium.

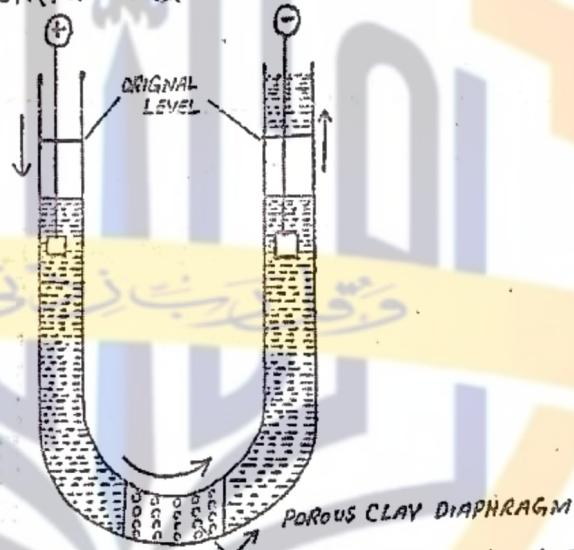


FIG - ELECTRO-OSMOSIS

The phenomenon of electroosmosis can be observed by fixing a porous diaphragm made of colloidal particles (dispersed phase) such as moist clay in a U-tube containing the dispersion medium water. When an electric current is applied across the two platinum electrodes immersed in water on each side of clay (dispersed phase), the dispersion medium (water) is observed to move towards one or the other electrode as shown in fig. The direction of flow of the dispersion medium (water) depends on the charge of the colloid. The phenomenon of electro-osmosis is used technically in the removal of water from peat, in dewatering moist clay and drying dye pastes.

## STABILITY OF SOLS

The stability of hydrophobic sols can be increased by the addition of more stable hydrophilic sol like gelatin or albumin. These hydrophilic substances are absorbed on the surface of the hydrophobic particles by electrostatic force or sometimes by chemical interaction. Thus converting the hydrophobic sol into one with more hydrophilic character, and as a result the sols acquire greater interaction to precipitation.

The property of hydrophilic sols to prevent the precipitation of a hydrophobic sol is called protection. The hydrophilic sol used to protect a hydrophobic sol from precipitation is commonly called a protective colloid. If a little gelatin (protective colloid) is added to a gold sol (hydrophobic sol) it is no longer precipitated on the addition of NaCl solution. In hydrophilic colloids, on the other hand charge removal may decrease stability, but it does not necessarily lead to precipitation. This fact is well illustrated by proteins at their isoelectric point, where the particles are uncharged. Although in this state the protein dispersions are least stable, they don't always precipitate because they are still protected by a surrounding layer of water. However, as soon as this layer is removed by some appropriate means, coagulation takes place, and the protein settles as a precipitate.

**PUACP**

The hydrophilic colloids differ widely in their power of protection. The protective power of different colloids is measured in terms of Gold Number as introduced by Zsigmondy.

The Gold Number is defined as the number of milligrams of a hydrophilic colloid that will just prevent the precipitation of  $10\text{ cm}^3$  of a gold sol on the addition of  $1\text{ cm}^3$  of 10 per cent Sodium Chloride Solution.

The smaller the gold number of a hydrophilic colloid, the greater

is, the its Protective Power. The gold numbers of a few hydrophilic colloids are given in table. (43)

Gold numbers of some hydrophilic colloids.

TABLE - GOLD NUMBERS OF SOME HYDROPHILIC COLLOIDS

LYOPHILIC SOL	GOLD NUMBER
GELATIN	0.005 - 0.01
CASEIN	0.01 - 0.02
HAEMOGLOBIN	0.03 - 0.07
EGG ALBUMIN	0.08 - 0.01
DEXTRIN	6 - 20
POTATO STARCH	20 - 25

The action of protective colloids play an important part in many biological systems, it is made use of in a number of biological preparations and pharmaceutical products. Argyrol a colloidal silver and silver oxide have pronounced antibacterial properties

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## Precipitation Or Coagulation Of Sol's

The stability of a sol is mainly due to the electric charge on Sol Particles. For lyophobic sols, the stability is due to their electric charge but for lyophilic sols stability is both due to their electric charge and their high hydration (Solvation). Removal of charge in lyophobic sols would lead to precipitation of sols, while to precipitate a lyophilic sol, both the charge and solvation must be removed.

The flocculation (or aggregation) and settling down of the discharged sol particles is called coagulation or precipitation of sol.

The precipitation of a lyophobic sol can be brought about in four ways as given below.

(A) BY ADDITION OF ELECTROLYTES

(B) BY ELECTROPHORESIS

(C) BY MIXING TWO OPPositELY CHARGED SOLS

(D) BY BoILING

### (A) BY ADDITION OF ELECTROLYTES

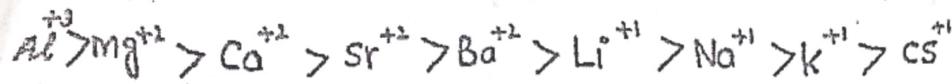
When excess of an electrolyte

is added to a sol the dispersed particles are precipitated. The electrolyte furnished both positive and negative ions in the medium. The sol particles adsorb the oppositely charged ions and get neutralized. The electrically neutral particles then aggregate and settle down as precipitate. The amount of electrolyte required to precipitate a given sol depends on the nature of both the sol and the electrolyte added.

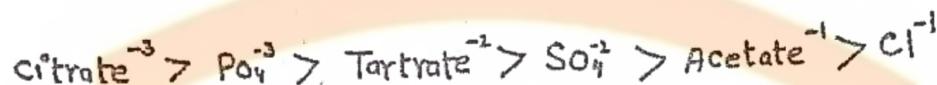
### HARDY-SCHUIZE RULE

He states that the ion which is effective in causing precipitation of a sol is the one carrying opposite charge to that of the colloidal particles and the precipitating effect increase markedly with increasing valency of ion, the higher the valency of the ion, the greater is the precipitating power. Thus for precipitating  $As_3S_3$  sol (negatively charged)

the precipitating power of various ions is given by lyotropic series, in which the ions are arranged in order of decreasing precipitating effectiveness. For cations this series gives



Similarly for precipitating  $Fe(OH)_3$  sol (positively charged) the precipitating power of various anion is given by



However this order is not always valid. Depending on the nature of the colloid being precipitated, the relative position of various anions and cations may be changed.

The minimum amount of an electrolyte required in millimoles to bring about the precipitation  $dm^{-3}$  (per litre) of the sol in two hours is called the precipitation or flocculation value. The smaller the precipitation value the higher the precipitating power of an ion.

FERRIC HYDROXIDE SOL (POSITIVE)		ARSENIOUS SULPHIDE SOL (NEGATIVE)	
ELECTROLYTE	CONCENTRATION MILLIMOLES/LITRE	ELECTROLYTE	CONCENTRATIONS MILLIMOLES/LITRE
NaCl	9.3	NaCl	51
KCl	9.0	KCl	50
KI	16.2	HNO <sub>3</sub>	50
BaCl <sub>2</sub>	9.6	HCl	31
K <sub>2</sub> SO <sub>4</sub>	0.20	MgCl <sub>2</sub>	0.72
MgSO <sub>4</sub>	0.22	CaCl <sub>2</sub>	0.65
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.19	ZnCl <sub>2</sub>	0.65
K <sub>3</sub> Fe(CN) <sub>6</sub>	0.095	AlCl <sub>3</sub>	0.093

From the table it is evident that, although some specificity does exist, the precipitating action of various electrolytes depends essentially on the valence of the anions in the positive sol and on the valence cations in the negative sol. Furthermore, the precipitating power of an electrolyte increases very rapidly with increase in the valence of the anion or cation, the ratio for the mono, di- and tri-valent anions or cations are approximately 1:40:90 for  $\text{Fe(OH)}_3$  sol and 1:70:500 for  $\text{As}_2\text{S}_3$  sol. From the table, it may be seen that  $\text{Al}^{+3}$  ions in alums, are very effective and are used in styptic pencils for congealing of blood. When river water containing colloidal clay flows into the sea, it induces coagulation and delta formation takes place.

#### (B) BY ELECTROLYSIS

In electrophoresis, the charged sol particles migrate to electrodes of opposite sign under influence of an electric field. As the charged particles come in contact with the electrodes the particles are discharged and are precipitated.

#### (C) BY MIXING OF TWO OPPositELY CHARGED SOL

When two sols of opposite charges are mixed together in different proportions, their mutual precipitation can be affected. Ferric hydroxide (+ve sol) and arsenious sulphide (-ve sol) form such a pair and when mixed in the correct proportions they are precipitated.

#### (D) BY BoILING

Sols such as Sulphur and Silver halides dispersed in water may be coagulated by boiling.

#### PRECIPITATION OF LYOPHILIC SOLS

Precipitation in lyophilic sols may be brought about when solvents such as alcohol or acetone, which have a high affinity for water are added to a lyophilic sol. The disperse phase undergoes dehydration to yield particles whose stability is now only due to their charge. A small amount of electrolyte added to this sol in this condition produces ready precipitation.