Surface Chemistry

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1. Surface Chemistry

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1.1 Absorption and Adsorption:

There are many properties of matter, which are related to their surface. Such properties become predominant if the substance is in finely divided form or its surface is rough. Under these conditions the surface area increases enormously and large amount of material is present in the surface. The surface related properties of matter are adsorption, colloidal state and emulsions. There are residual forces acting along the surface of liquids and solids. Due to residual forces, the surface of a solid (or a liquid) has a tendency to attract and retain molecules of other species with which it is brought into contact. Concentration of these species is more at the surface than in the bulk of the solid or liquid. The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid (or liquid) is known as adsorption. Solid, particularly when finely divided, have a large surface area, hence this behaviour is predominant on solid surfaces. The solid that takes up a gas or vapour or a solute from solution, is called the adsorbent while the gas or the solute, which is held to the surface of the solid is called the adsorbate. If the concentration of a substance at the surface of another substance is more than in the bulk of the adjoining phases, it is called positive adsorption. If the concentration of a substance at the surface of another substance is less than in the bulk of the adjoining phases, it is called negative adsorption. This type of adsorption takes place only in case of solutions. The removal of the absorbed substance from a surface is called desorption. When equilibrium is reached,

Rate of adsorption = Rate of desorption

1.1.1 Difference between Adsorption and Absorption:

Adsorption is different from absorption. Absorption of a substance A by a substance B means that A is uniformly distributed all over B. Adsorption on the other hand, means that A is present on the surface of B, but the concentration of A in parts of B away from the surface is negligible. In some cases, adsorption and absorption take place simultaneously and it is difficult to determine the relative extent of adsorption and adsorption. The term sorption is widely used in such cases.

Sr. No.	Adsorption	Absorption
1.	It is surface phenomenon.	It is bulk phenomenon.
2.	Adsorbate is accumulated at the surface.	The substance getting absorbed is uniformly distributed throughout the bulk of the substance.

Sr. No.	Adsorption	Absorption
3.	The rate of adsorption is very rapid in the beginning. The rate however decreases gradually until equilibrium is reached	Absorption proceeds at a steady rate.

1.1.2 Types of Adsorption:

Depending upon the nature of forces between the adsorbate (solute) and adsorbent (solvent) molecules, adsorption can be classified into two groups:

a. Physical adsorption
b. Chemical adsorption.

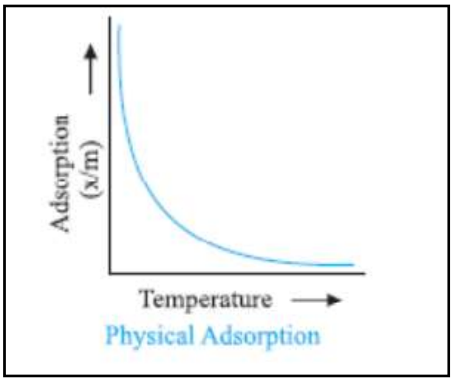
Sr. No.	Physical adsorption	Chemical adsorption
1.	It is caused by intermolecular van der Waal's forces.	It is caused by chemical bond formation.
2.	It is not specific and is reversible.	It is highly specific and is irreversible.
3.	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. which form compounds with the adsorbent exhibit chemisorption.
4.	Heat of adsorption is low and is negative.	Heat of adsorption is high and is negative.
5.	Low temperature is favourable. It decreases with the increase of temperature.	High temperature is favourable. It increases with the increase of temperature.
6.	No appreciable activation energy is involved.	High activation energy is involved.
7.	High pressure is favourable. Decrease of pressure cause desorption.	High pressure is favourable. Decrease of pressure does not causes desorption.
8.	It depends on the surface area. It increases with the increase of surface area.	It also depends on the surface area. It with increase of surface area.
9.	It forms multi-layers on adsorbent surface under high pressure	It forms unimolecular layer.

1.1.3 Factors Affecting Adsorption:

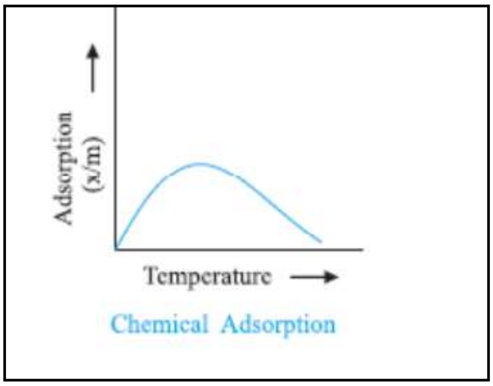
The extent of adsorption of a gas on the surface of a solid depends on the following factors:

a. **Nature of gas:** Since physical adsorption is non-specific in nature, any gas will be adsorbed on the surface of a solid to some extent or other. However, under any given conditions of temperature and pressure, easily liquefiable gases such as NH_3, CH_4, HCl, CO etc. are adsorbed more than permanent gases like O_2, N_2 etc. Chemisorption is specific in nature. Therefore, only those gases will be adsorbed which form chemical bonds with it.
b. **Nature of solid:** Activated charcoal is the most common adsorbent for easily liquefiable gases. Poisonous gases such as CH4 and CO fall in this group. Therefore, it is used in gas masks. Other gases such as O2, H2 and N2 adsorb more on metals such as Ni, Pt and Pd.
c. **Specific area of solid:** Specific area of an adsorbent is the surface area available for adsorption per gm of adsorbent. Greater the specific area of an adsorbent, greater will be the adsorption. The specific area of an adsorbent can be increased by making the surface rough. The pores must be large enough to allow penetrations of gas molecules.
d. **Pressure of gas:** As physical adsorption is reversible, it is accompanied by decrease in pressure. Therefore, it is expected that at a given temperature the extent of adsorption will increase with the increase of pressure of the gas.
e. **Temperature:** As adsorption is accompanied by release of heat energy, so in accordance with LeChatelier's principle, the increase of temperature should decrease the extent of adsorption. This has indeed been found to be so. A plot of x/m vs temperature at constant pressure is called adsorption isobar.

In the case, physical adsorption x/m decreases with increase of temperature whereas in the case of chemisorption, x/m initially increases with temperature and then decreases. The initial increase is due to the fact that chemisorption requires activation energy.



Physical Adsorption



Chemical Adsorption

f. **Activation of solid:** Activation of adsorbent means increasing its absorbing power. This is increased by increasing specific area either by making the surface rough or by breaking the solid into smaller particles. But care must be taken so that particles do not become very small then inter-particle spaces will be too small to allow penetration of gas molecules.

Adsorbing power of an adsorbent can be increased by:

a. By making the surface of the adsorbent rough.
b. By subdividing the adsorbent into smaller pieces or grains.
c. By removing gases already absorbed.

A. Adsorption from Solution:

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. The litmus solution when shaken with charcoal becomes colour less.

The following observations have been made in the case of adsorption from solution phase:

a. The extent of adsorption decreases with the increase of temperature.
b. The extent of adsorption increases with the increase of surface area of the adsorbent.
c. The extent of adsorption depends on the concentration of the solute in solution.
d. The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

The adsorption of a solute from solutions is very similar to the adsorption of a gas on the surface of a solid. Therefore, Freundilich adsorption isotherm is applicable even in the adsorption from solutions. If C is the concentration of a solution in mol L^{-1}, then extent of adsorptions (x/m) is given by,

$$\frac{x}{m} = k(C)^{\frac{1}{n}}$$

Taking log on both sides we get : $\log \frac{x}{m} = \log k + \frac{1}{n} \log C$

Graph of log x/m vs log C is a straight line with a slope of (1/n).

B. Applications of Adsorption:

The phenomenon of adsorption finds a numbers of applications. Some of them are:

a. Activated charcoal is used in gas masks to remove poisonous gases such as carbon monoxide, methane etc. Animal charcoal is used to remove colouring matter from cane-sugar juice in the manufacture of sugar.
b. Ion exchange resin is used to remove hardness of water.
c. Several organic compounds are purified by chromatographic adsorption.
d. Silica gel is used for removing and controlling humidity.
e. The catalytic effect of a number of catalysts, like spongy iron in the manufacture of ammonia and nickel, platinum or palladium in the reduction of unsaturated hydrocarbons, is based on the principle of adsorption.

f. Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.
g. Control of humidity: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.
h. Heterogeneous catalysis: Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H2SO4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.
i. Separation of inert gases: Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.
j. In curing diseases: A number of drugs are used to kill germs by getting adsorbed on them.
k. Froth floatation process: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent
l. Adsorption indicators: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.
m. Chromatographic analysis: Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

1.2 Colloidal State:

Thomas Graham classified the soluble substances into two categories depending upon the rate of their diffusion through animal and vegetable membranes or parchment paper. He observed that certain substances diffuse freely through the membrane, whereas others do not diffuse.

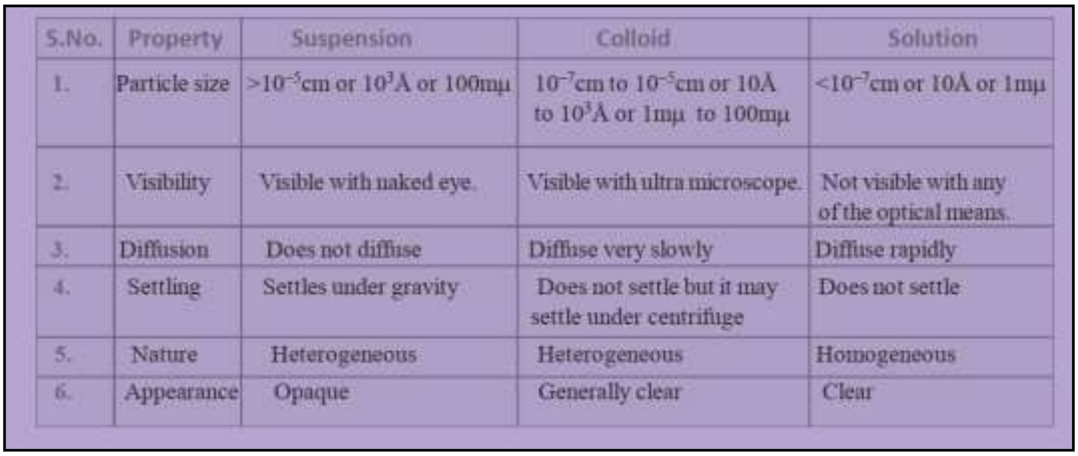
The former type of substances on account of their crystalline nature like common salt, sugar, urea, etc., were named crystalloids while the second type of substances were termed as colloids (Greek word, kola, meaning glue-like).

All inorganic acids, bases and salts and organic compounds such as sugar, urea, etc., were included in crystalloids while substance such as starch, gelatine, gums, silicic acid, etc., belonged to the colloidal group.

1.2.1 Types Colloidal Solutions:

A. Classification on the basis on the size of the particle of the colloids: The nature of a substance whether crystalloid or colloid depends upon the size of the **Solute** particles.

When the size of solute particles lies between 1 nm to 100 nm it behaves Like a colloid. If size of solute particles is greater than 100 nm, it exists as suspension and if particle size is less than 1 nm it exists as a true solution.



S.No.	Property	Suspension	Colloid	Solution
1.	Particle size	$>10^{-5}$cm or 10^3Å or 100mμ	10^{-7}cm to 10^{-5}cm or 10Å to 10^3Å or 1mμ to 100mμ	$<10^{-7}$cm or 10Å or 1mμ
2.	Visibility	Visible with naked eye.	Visible with ultra microscope.	Not visible with any of the optical means.
3.	Diffusion	Does not diffuse	Diffuse very slowly	Diffuse rapidly
4.	Settling	Settles under gravity	Does not settle but it may settle under centrifuge	Does not settle
5.	Nature	Heterogeneous	Heterogeneous	Homogeneous
6.	Appearance	Opaque	Generally clear	Clear

B. Classification on the basis on the physical state of dispersed phase and dispersion medium: Colloidal solution is heterogeneous in nature and always consists of at least two phases-namely disperse phase and dispersion medium. The component present in small proportion and consisting of particles of colloidal dimensions is called disperse phase. The medium in which colloidal particles are dispersed is called dispersion medium. The two phases can be solid, liquid or gas. There are eight different types of colloidal solutions.

Disperse phase	Dispersion medium	Common name	Example
Solid	Solid	Solid sol	Alloys
Solid	Liquid	Sol	Au sol
Solid	Gas	Aerosol	Smoke
Liquid	Solid	Gels	Cheese
Liquid	Liquid	Emulsion	Milk
Liquid	Gas	Liquid aerosol	Mist, Cloud
Gas	Solid	Solid foam	Pumice stone
Gas	Liquid	Foam	Soap lather

If colloidal solution has fluid like appearance it is called sol. The dispersion medium in such cases is generally liquid. Depending upon the nature of medium, colloids are sometimes given special names.

For example:

Dispersion medium	Name of the sol
Water	Hydrosol
Alcohol	Alcosol
Benzene	Benzosol
Gases	Aerosol

C. Classification on the basis of interaction between different phases: Depending upon the nature of interaction between phase and dispersion medium, colloids are classified as:

a. **Lyophillic colloids:** The disperse phase has great affinity for dispersion medium. In such cases the disperse phase does not easily get precipitated and the colloids are quite stable. The solids obtained after evaporation of the medium can be easily brought back to the colloidal state by shaking the solids with the dispersion medium. The colloides are thus reversible, e.g., gum, gelatin, starch, proteins and certain polymersin organic solvents. If water is used as the dispersion medium the colloid is called hydrophilic colloid.
b. **Lyophobic colloids:** The disperse phase has little affinity for the dispersion medium. These sols are relatively less stable. They can be easily precipitated by addition of small amount of electrolyte. Once the sol is precipitated, it cannot be easily brought back to the colloidal state. They are thus irreversible, e.g., gold sol and sulphur sol, etc. If water is used as the dispersion medium. The sol is called hydrolyophobic colloid.

Sr. No	Property	Lyophilic Sols	Lyophobic Sols
1.	Surface tension	Lower than that of the medium.	Same as that of the medium.
2.	Viscosity	Much higher than that of the medium.	Same as that of the medium.
3.	Reversibility	Reversible	Irreversible
4.	Stability	More stable	Less stable
5.	Visibility	Particles can't be detected even under ultramicroscope.	Particles can be detected under ultramicroscope.
6.	Migration	Particles may migrate in either direction or do not migrate in an electric field.	Particles migrate either towards cathode or anode in an electric field.
7.	Action of electrolyte	Addition of smaller quantity of electrolyte has little effect.	Coagulation takes place.
8.	Hydration	Extensive hydration takes place.	No hydration takes place

D. Classification on the basis of the particles of the dispersed phase

Sr. No.	Multimolecular Colloids	Macromolecular Colloids	Associated Colloids
1.	They are formed by the aggregation of a large number of atoms or	They are molecules of large size, e.g., polymers like rubber,	They are formed by the aggregation of large no. of ions in

Sr. No.	Multimolecular Colloids	Macromolecular Colloids	Associated Colloids
	molecules generally have diameters less than 1nm, e.g., sols of gold, sulphur.	nylon, starch, proteins etc.	conc. solution e.g., soap sol.
2.	Their molecular masses are not very high.	They have high molecular masses.	Their molecular masses are generally high.
3.	Their atoms or molecules are held together by weak van der Waal's forces.	They usually have lyophobic character.	Their molecules contain both lyophillic and lyophobic groups

1.2.2 Preparation of Colloidal Solutions:

Different type of methods are used for the preparation of lyophobic and lyophilic sols:

a. **Preparation of lyophilic sols:** The colloidal solutions of lyophilic colloids like starch, glue, gelatine, etc., can be readily prepared by dissolving these substances in water either in cold or on warming. Solutions of colloidal electrolytes such as soaps and dye stuffs can also be prepared similarly.

b. **Preparation of lyophobic sols:** To get a substance in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension (1Å to 103Å) or increasing the size of molecular particles as to form larger aggregates. In some cases, a third substance is usually added to increase the stability of the sol. These substances are called stabilizers. Thus, there are two ways by which the lyophobic sols can be prepared.

A. Dispersion methods:

By splitting coarse aggregates of a substance into colloidal size.

B. Condensation methods:

By aggregating very small particles (atoms, ions or molecules) into colloidal size.

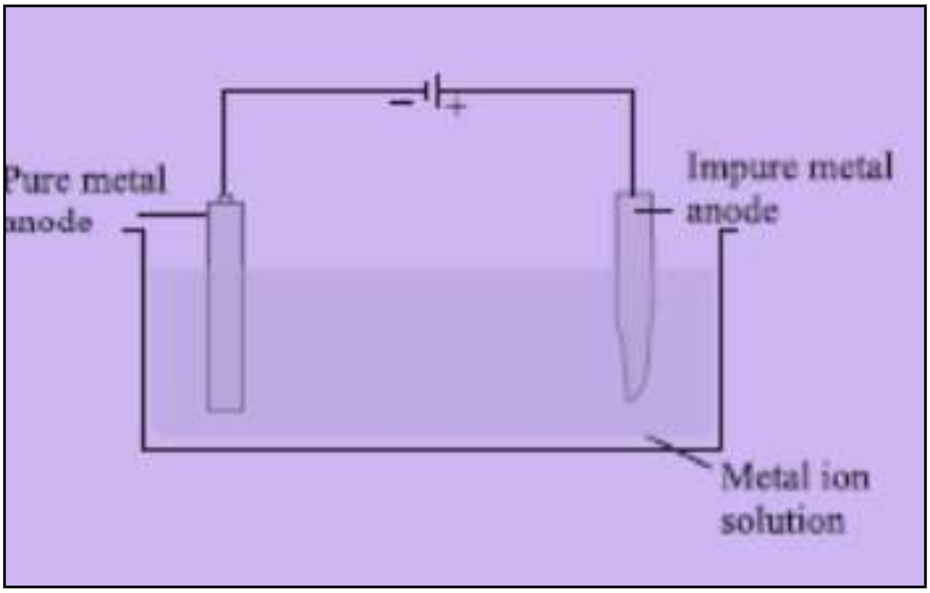
Sr. No	Dispersion Methods	Condensation Methods
1.	Mechanical dispersion	Exchange of solvents
2.	Electro-dispersion	Change of physical state

Sr. No	Dispersion Methods	Condensation Methods
3.	Peptization	Chemical methods: a. Double decomposition b. Oxidation c. Reduction d. Hydrolysis

A. Dispersion Methods:

a. **Mechanical dispersion:** Solid material is first finely ground by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the colloid mill. The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution. Colloidal graphite (a lubricant) and printing ink are made by this method. Tannin is used as a stabilizer in the preparation of colloidal graphite and gum arabic in lampblack colloidal solution (Indian ink)

b. **Electrical disintegration or Bredig's arc methods:** This process involves dispersion as well as condensation. Colloidal solutions of metals such as gold, silver, copper, platinum etc., can be prepared by this method. In this method electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vaporises some of the metal, which then condenses to form particles of colloidal size.



c. **Peptization:** This is a process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte. The electrolyte used for this purpose is called peptizing agent. This method is generally applied to convert fresh precipitate into colloidal solutions because such precipitates are simply aggregates of colloidal particles held by weak forces.

Causes of Peptization:

During peptization, the precipitate adsorbs one of the ion of the electrolyte on its surface. The adsorbed ion is generally common with those of precipitate. This causes the development of positive or negative charge on the precipitates, which ultimately breaks into particles of colloidal dimensions.

For example, when freshly precipitated ferric hydroxide is shaken with aqueous solution of ferric chloride (peptizing agent) it adsorbs Fe3+. Similarly, a precipitate of AgCl on shaking with dilute solution of AgNO3 adsorbs Ag+ ion and get peptised to colloidal particles of the type [AgCl]Ag+. In some cases, peptization can also be achieved by organic solvents. For example, cellulose nitrate is peptised by ethanol. The colloidal solution of cellulose nitrate in ethanol is called ‘collodion’.

B. Condensation Methods:

a. **By exchange of solvent:** If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility in water. Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.
b. **By change of physical state:** Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabilizer (an ammonium salt or a citrate).
c. **Chemical methods:** The chemical method involves chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of super-saturation is produced but the actual precipitationis avoided.

- **Double Decomposition:** A colloidal solution of arsenic sulphide is obtained by passing hydrogen sulphide into solution of arsenic oxide in distilled water.

$$As2O3 + 3H2O \longrightarrow As2S3\text{(yellow sol)} + 3H2O$$

Sols of silver halide are obtained by mixing dilute solutions of silver salts and alkali metal halides in equivalent amounts.

$$NaCl + AgNO3 \longrightarrow AgCl + NaNO3$$

- **Oxidation:** A colloidal solution of sulphur can be prepared by passing hydrogen sulphide into a solution of sulphur dioxide in water or through a solution of an oxidising agent like bromine water or nitric acid.

$SO2 + 2H2S \longrightarrow 2H2O + 3S\text{ (sol)}$

Sulphur sol can also be obtained when H2S is bubbled through an oxidising agent (bromine water or nitric acid).

- **Reduction:** A colloidal solution of a metal like silver, gold or platinum can be prepared by the reduction of its salt solution with a suitable reducing agent such as stannous chloride, formaldehyde, hydrazine etc.

$$2AuCl3 + 3SnCl2 \longrightarrow 2Au \text{ (Gold Sol)} + 3SnCl4$$

$$4AgCl + N2H4 \longrightarrow 4Ag \text{ (Silver sol)} + N2 + 4HCl$$

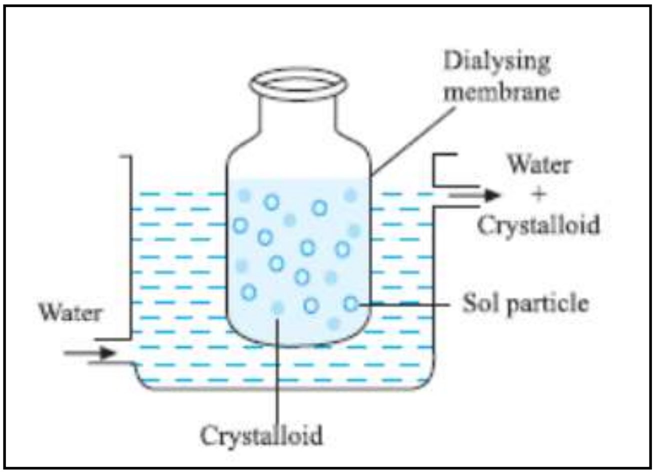
- **Hydrolysis:** By this method hydroxide sols of less electropositive metals like Fe, Al or Sn are prepared. A red sol of ferric hydroxide is obtained by the hydrolysis of ferric chloride with boiling water.

$$FeCl3 + 3H2O \longrightarrow Fe(OH)3 \text{ (Red sol)} + 3HCl$$

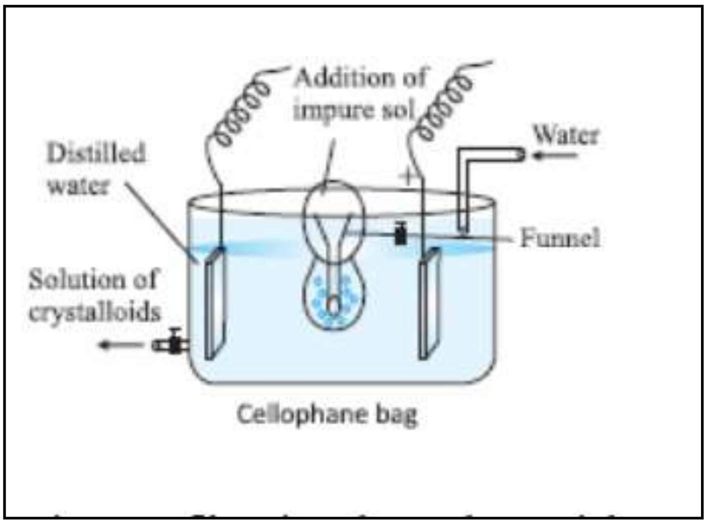
1.2.3 Purification of Colloidal Solutions:

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. The process used for reducing these impurities to a requisite minimum is known as purification of colloidal solution. The purification of colloidal solution is carried out by the following methods:

a. **Dialysis:** It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Since particles in true solution (ions or smaller molecules) can pass through animal membranes (bladder) or parchment paper or cellophane sheet but colloidal particles do not, the above can be used for dialysis. The apparatus used for this purpose is called dialyser. A bag of suitable membrane containing the colloidal solution suspended in a vessel through which fresh water is continuously flown. The molecules and ions diffuse through the membrane into the outer colloidal solution are left behind



b. **Electro-dialysis:** Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only electrolyte. The process is then named electro-dialysis. The colloidal solution is placed between two electrodes while pure water is taken in a compartment on each side. The ions present in the colloidal solution migrate out to the oppositely charged electrodes.



1.3 Ultra Filtration:

In this method, colloidal solutions are purified by carrying out filtration through special type of graded filter papers called ultra-filters. These filter-papers are made from ordinary filter paper by impregnating them with colloidon solution and subsequently hardened by soaking in formaldehyde and finally drying it. These filter papers allow the electrolytes to pass through them but not the colloidal particles. The ultra-filtration is generally a slow process and can be hastened by the application of suction. The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

Ultra Centrifugation:

In this method, the colloidal solution is placed in a high-speed ultracentrifuge. On centrifuging the colloidal particles settle down. The impurities remain in the dispersion medium and are removed by decantation. The settled colloidal particles are shaken with water containing peptizing agent to form the colloidal Solution again.

1.3.1 Properties of Colloidal Solutions:

The characteristic properties of colloidal solutions are as given below:

a. **Heterogeneous Nature:** A colloidal solution is heterogeneous in nature. It consists of two phases namely the dispersed phase and the dispersion medium

b. **Visibility:** Colloidal particles are too small to be seen with naked eye. But they become visible as bright sports against dark background when viewed through an ultra-microscope due to scattering of light caused by them.

c. **Filterability:** The size of solute particles is smaller than the pore size of filter paper and therefore, they can readily pass through a filter paper. Colloidal particles, however cannot pass through ultra-filters, parchment paper or animal membrane.

d. **Surface tension and viscosity:** The surface tension and viscosity of lyophobic sols are not very different from those of the dispersion medium. On the other hand, lyophilic sols show higher viscosity and lower surface tension in comparison to the dispersion medium.

e. **Colligative Properties:** A colloidal solution has very small value of mole fraction of dispersed phase due to high average molecular mass of the colloidal particles. As a result all the colligative properties, colloidal solutions have quite low values when compared to true solutions, having same concentration. However, the low osmotic pressure of a colloidal solution is measurable and can be used to determine the molecular weight of colloidal particles.

f. **Tyndall Effect:** Scattering of light by the colloidal particles present in a colloidal solution is known as Tyndall effect and is caused by the scattering of blue part of light by the colloidal particles.

If a strong beam of light is passed through a colloidal solution placed in a dark place, the path of the beam gets illuminated. The illuminated path of beam is called Tyndall Cone. The scattering is caused if the size of particles is of the order of wavelength of light.

The same effect is not observed when the light is passed through a true solution as the size of solution particles is too small to cause any scattering. Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied:

- The diameter of the dispersed particles is not much smaller than the wavelength of the light used.
- The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude. This condition is satisfied by lyophobic sols. The lyophilic sols show little or no Tyndall effect as there is very small difference in the refractive indices of the dispersed phase and the dispersion medium.

g. **Brownian movement:** The colloidal particles of a colloidal solution when viewed through an ultra-microscope show a constant zig-zag motion. This type of motion was first observed by Robert Brown and hence known as Brownian movement. It is caused by the uneven impacts of the particles of the dispersion medium on the colloidal particles. As the size of the particles increases, the probability of uneven impacts decreases and the Brownian movement becomes slow. When the dispersed particles acquire the dimensions of suspension, no Brownian movement is observed. This motion is independent of the nature of the colloid but depends on the size of the particles and the viscosity of solution. Smaller the size and lesser the viscosity, faster is the motion. The motion becomes intense at high temperature.

1.4 Catalysis:

Catalysis is the phenomenon by which rate of a chemical reaction is changed due to the participation of a substance called a catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself. A catalyst may participate in multiple chemical transformations.

Potassium chlorate, when heated strongly decomposes slowly giving dioxygen. The decomposition occurs in the temperature range of 653-873K.

$$2KClO3 \rightarrow 2KCl + 3O2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473-633K and also at a much accelerated rate. The added manganese dioxide remains unchanged with respect to its mass and composition. In a similar manner, the rates of a number of chemical reactions can be altered by the mere presence of a foreign substance.

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Characteristics of Catalytic Reactions:

- The catalyst remains unchanged in amount and chemical composition at the end of the reaction; it may, however, undergo considerable change in physical form
- The reaction of a catalyst is specific to a large extent. Thus, the decomposition of KClO3 is catalyzed by MnO2 but not by platinum.
- The catalyst does not initiate a reaction; it merely accelerates the reaction that is already occurring. A catalyst does not alter the final state of equilibrium in a reversible reaction.

A certain minimum energy must be possessed by the reactants, so that they may react and produce the products. This is called the activation energy (E) a for the reaction. A catalyst is said to lower the activation energy and thus increase the rate of the reaction. Thus, a catalyst increase the rate of a reaction by providing a pathway whose activation energy is lower than the activation energy of the uncatalyzed reaction. Promoters are substance that increase the catalytic activity, even though they are not catalysts by themselves. For example, in Haber's process for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as catalyst.

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

1.4.1 Type of Catalysis:

a. **Positive Catalysis:** The catalyst increases the rate of reaction.

Example : $2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$ (Contact process)

$C_2H_4 + H_2 \xrightarrow[\Delta]{Ni} C_2H_6$ (Ethane)

b. **Heterogeneous Catalysis:** A catalytic process in which the catalyst and the reactants are in different phases is called heterogeneous catalysis. This process is also called contact or surface catalysis.

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

(ii) $2SO_2(g) + O_2(g) \xrightarrow{Pt.asbestos} 2SO_3(g)$

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

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

Example:

- **General Principle of Catalysis:**

It is not possible to give a uniform explanation of the mechanism of the phenomenon of catalysis as catalytic reaction are of varied nature. However, two broad theories of catalytic action have been proposed. First theory, known as intermediate compound formation theory, explains successfully the homogeneous catalysis.

The second theory termed as adsorption theory explains the heterogeneous catalysis.

a. **Intermediate Compound formation Theory:** According to this theory, the catalyst first forms an intermediate compound with one of the reactants. The intermediate compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.
b. **Adsorption Theory:** This theory explains the mechanism of heterogeneous catalysis. The old point of view was that when the catalyst is in solid state and the reactions are in gaseous state or in solutions, the molecules of the reactants are adsorbed on the surface of the catalyst. The increased concentration of the reactants on the surface influences the rate of reactions. Adsorption being an exothermmic process, the heat of adsorption is taken up by the surface of the catalyst, which is utilised in enhancing the chemical activity of the reacting molecules. The view does not explain the specificity of a catalyst. The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst.

The mechanism involves five steps:

a. Diffusion of reactants of the surface of the catalyst.
b. Some form of association between the catalyst surface and the reactants occurs. This is as sumed to be adsorption.
c. Occurrence of chemical reaction on the catalyst surface.
d. Desorption of reaction products away from the catalyst surface.
e. Diffusion of reaction products away from the catalyst surface.

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2. A Review on Combinatorial Chemistry

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Abstract:

The use of combinatorial chemistry techniques has been explored as an alternative to conventional approaches for the synthesis of compounds in the drug discovery process. This technique is the starting point for the development of synthesis concepts that were intended to cover and explore the chemical space without having to prepare every individual compound. Combinatorial Chemistry technologies were developed in response to the increased screening capacities that are available when drug discovery changed its screening paradigm from a pharmacology-based approach to target oriented lead finding. This article will illustrate technique used in combinatorial chemistry, some of the advances made in recent years and their application in the synthesis of different peptides, oligosaccharides and other molecules.

Keywords:

Combinatorial Chemistry, synthesis, solid phase, solution phase.

2.1 Introduction:

Combinatorial Chemistry is a technology for synthesizing and characterizing collections of compounds and screening them for useful properties was conceived about 20 years ago. Initially, the field focused primarily on the synthesis of peptide and oligonucleotide libraries in the 1990s, the focus of the field changed predominantly to the synthesis of small, drug like Organic compounds. And many pharmaceutical companies and biotechnology firms now use it in their drug discovery efforts. The drug discovery process became a highly parallel one, in which hundreds or even thousands of structures could be synthesized at one time. Sometime high throughput screening (HTS) has been performed for their in vitro assays, running assays in 96 well microtiter plates and by using laboratory robotics for pipetting and analysis.

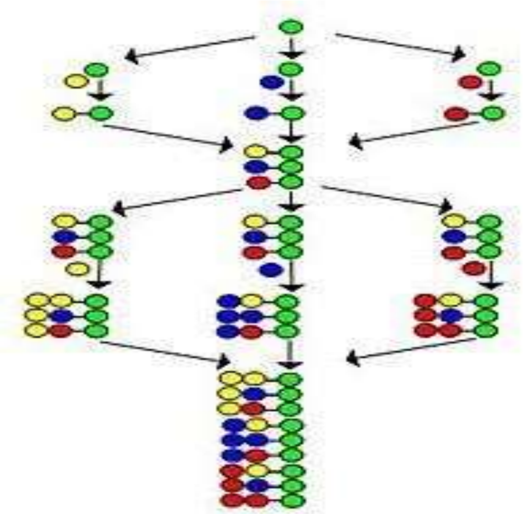
The main purpose of computer assisted combinatorial chemistry is to generate thousands structurally diverse compounds as libraries, maximising their diversity, which are then considered in an experimental parallel automated synthesis and screening on the basis of their properties. The key issue is to integrate all important steps of CC/CT in a single, multidisciplinary approach.

- The multipin procedures introduced by Geysen and his collegues – was used for the parallel synthesis of arrays of peptides. It is now considered as the prototype of the powerful automatic machines now capable of preparing hundreds of different kinds of individual compounds in parallel.

- The " portioning - mixing method invented by Furka & his collegues – was developed to enable the users to prepare millions of new peptides in only a couple of days; also for synthesizing organic libraries.

Several others techniques developed for synthesis of large new compounds at a time were the biological method of preparation of peptide libraries, the light- directed spatially addressable parallel chemical synthesis. Researchers continue find ways to further enhance the capabilities of combinatorial chemistry, including these developments: A growing trend toward the synthesis of complex natural-product-like libraries, including the carbohydrate-based libraries, An increased focus on “phase trafficking” techniques are used for integrating synthesis with purification, Novel strategies for purification and analysis, such as the combinatorial use of supercritical fluid chromatography And the application of combinatorial chemistry to new targets, such as nuclear receptors. The goal of combinatorial chemistry able to synthesis, purify, chemically analyze, and biologically test all the structures in the library, using as few synthetic experiments as possible.

Combinatorial chemistry was first applied to the synthesis of peptides. In 1963 Merrifield introduced the efficient synthesis of peptides on a solid supports or resin. Combinatorial chemistry is of two types: first is solid phase combinatorial chemistry and second is solution phase combinatorial chemistry. Many countries have emphasized the urgent need to get acquainted with Combinatorial Technologies in order to enable local enterprises to remain competitive and economically viable in the coming decades and gain expertise on application practices of combinatorial technology. In view of global competition, CC/CT together with molecular modeling may be considered as powerful tools for the implementation and/or the increase of a country is capabilities in drug design, agro chemistry, new materials and new catalysts. The above considerations become even more significant if it is taken into account that many countries have abundant natural resources which are presently well below their proper exploitation. Combinatorial chemistry can enhance the potential of these resources.



Definition:

Combinatorial chemistry is one of the important new methodologies developed by researches in the pharmaceutical industry to reduce the time &costs associated with producing effective & Competitive new dugs. Modern combinational chemistry involves both the synthesis & screening of large sets of compounds called libraries. The libraries themselves can be always of individual compounds or mixtures. When two reactants, A &B combines, A is actually a mixtures of five components while B may be a composite of ten, so on complete of reaction, a mixture of 50 different compounds will be produced.

Combinatorial chemistry is one of the important new methodologies developed by academics & researchers in the pharmaceutical, agrochemical and biotechnology industries to reduce the time & costs associated with producing effective, marketable, & competitive new drugs. Simply put, scientists use combinatorial chemistry to create large population of molecules, or libraries that can be screened efficiently en masse. By producing larger diverse compound libraries, companies increase the probability that they will find novel compounds of significant therapeutic & commercial values. The field represents a convergence of chemistry & biology, made possible by fundamental advances in miniaturizations, robotics, and receptor development.

While combinatorial chemistry can be explained simply, its application can take a variety of forms, each requiring a complex interplay of classical organic synthesis techniques rational drug design strategies, robotics, scientific information management.

2.2 Synthetic Methods in Combinatorial Chemistry:

The various methods as used for synthesis of compounds in combinatorial chemistry. They all.

- Parallel synthesis leading to individual compounds.
- Combinatorial synthesis of mixtures.

Methods is which the no: of synthesized compounds remain constant in the consecutive series of coupling steps. These methods termed parallel procedures, are suitable for preparing series of individual compounds. They includes…….

1. Portioning mixing (PM) synthesis
2. Parallel Synthesis methods

2.2.1 The Portioning – Mixing Synthesis:

The portioning mixing method is based as Merrifield's solid phase procedure:

In solid phase combinatorial chemistry, reagents or products are attached to solid supports such as polystyrene beads—is the most traditional form of phase trafficking. In solid-phase organic synthesis, it’s easy to purify products by filtration, it’s possible to do mix-and-split synthesis (a technique used to make very large libraries), excess reagents can be used to drive reactions to completion, and syntheses can be automated easily. Solid phase chemistry has some advantages over the solution-phase. First, in solid-phase synthesis, large excesses of reagents can be used to drive reactions to completion; these excess reagents can then be removed at the end of the reactions by filtration and washing. Second, because of easy separation of reagents and products, solid phase chemistry can be automated more easily than solution chemistry. Separation of compounds bound to the solid support from those in solution is accomplished by simple filtration.

Solid support used in Solid phase synthesis:

Most solid state combinatorial chemistry is conducted by using polymer beads ranging from 10 to 750 μm in diameter. The solid support must have the following characteristics for an efficient solid-phase synthesis:

a. Physical stability and of the right dimensions to allow for liquid handling and filtration;
b. Chemical inertness to all reagents involved in the synthesis;
c. An ability to swell while under reaction conditions to allow permeation of solvents and reagents to the reactive sites within the resin;
d. Derivatization with functional groups to allow for the covalent attachment of an appropriate linker or first monomeric unit.

The compounds to be synthesized are not attached directly to the polymer molecules. They are usually attached by using a linker moiety that enables attachment in a way that can be easily reversed without destroying the molecule that is being synthesized and allow some room for rotational freedom of the molecules attach to the polymer.

Types of solid that are used:

a. **Polystyrene resins** in this Polystyrene is cross linked with divinyl benzene (about 1% crosslinking). polystyrene resin are suitable for nonpolar solvents.
b. **Tenta Gel resins** Polystyrene in which some of the phenyl groups have polyethylene glycol (PEG) groups attached in the para position. The free OH groups of the PEG allow the attachment of compounds to be synthesized. PEG Containing resins are suitable for use in polar solvents.
c. **Polyacrylamide resins** like super blue these resin swell better in polar solvent, since the contain amide bonds, more closely resemble biological materials.
d. **Glass and ceramic beads** these type of solid supports are used when high temperature and high pressure reaction are carried out.

Linkers used in solid phase synthesis:

To support the attachment of a synthetic target, the polymer is usually modified by equipping it with a linker. Linker must be stable under the reaction conditions, but they must be susceptible to a cleavage. Some specialized linker have been developed to meet particular reaction or product conditions this type of linker is known as traceless linkers, it can be cleaved from the resin with no residual functionality left.

This type of linkers allows the attachment of aryl and alkyl products that do not have OH or NH functionality example of these linker include silyl group (-Si(CH3)2) that is sensitive to acid and can be cleaved to give un substituted phenyl or alkyl product.

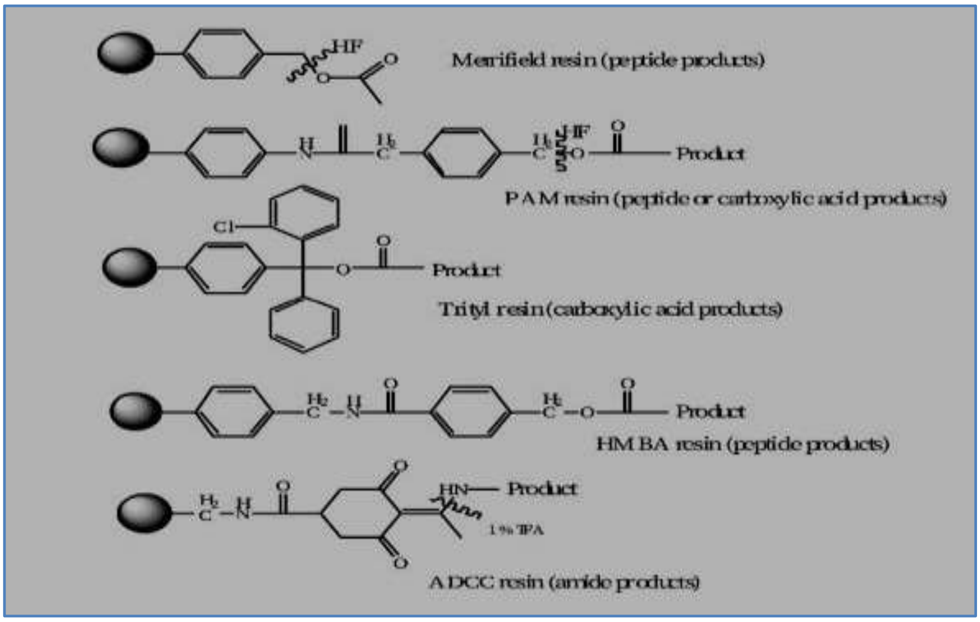
A new class of linkers was developed known as safety-catch linkers which is inert to synthetic condition and chemically transformed to allow final liberation of the product from the resin.

Now a ultraviolet light sensitive protecting groups are used, like affymax group is used in the synthesis of carboxylic acid and carboxamide products. Some groups have used linkers that can only be cleaved by enzymes.

A novel linker possessing selenocyanate and masked carboxylic acid was developed for the solid-phase synthesis of dehydropeptides. This linker was used to demonstrate the synthesis of the model compound of RGD-conjugated dehydropeptide.

Oxabicyclo norbornenes constitute a convenient and readily cleaved linker for solid-phase organic synthesis. A simple and inexpensive furfuryl- substituted resin has been shown to capture and release maleimide dienophiles under conditions compatible with intermediate synthetic steps.

A new linker based on a chroman system is developed for the side-chain anchoring of Arg and other guanidine-containing molecules. The system is compatible with the Fmoc/tBu solid-phase strategy, because the release of the final product is achieved by treatment with TFA in the presence of Scavengers.

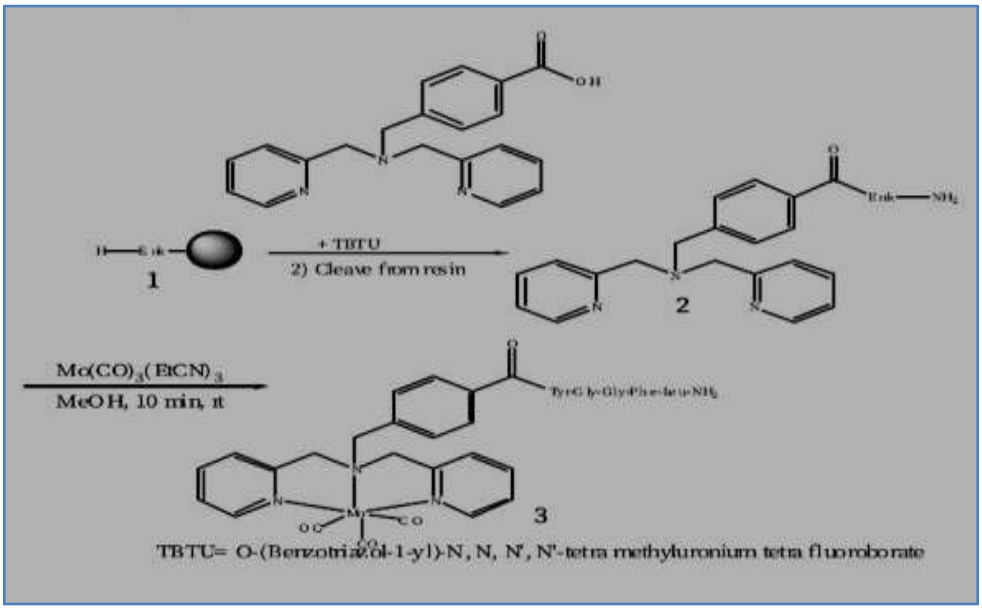


2.2.2 Application of solid phase synthesis:

A. Solid-Phase Synthesis of Peptide –Metal-Complex Conjugates:

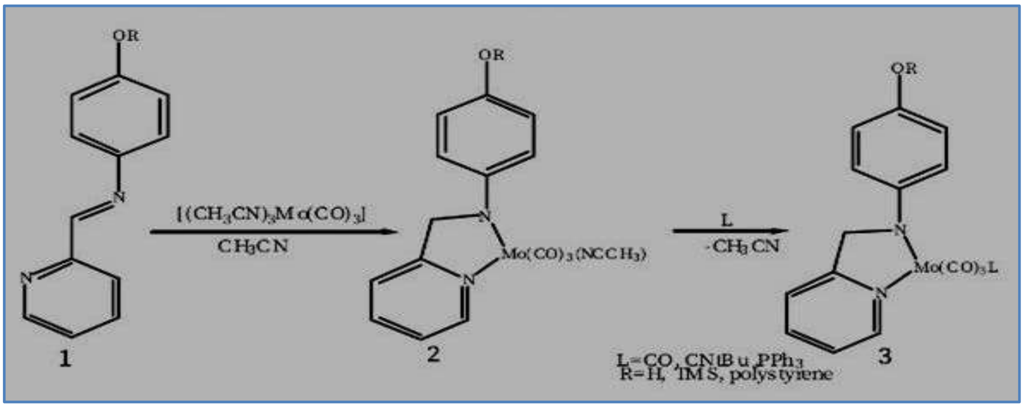
Solid-phase synthesis of inorganic complexes was established by Heinze, Metzler-Nolte, Reedijk and others. Coordination and organometallic chemistry on solid-phase were typically studied in the context of catalyst performance. Recently, solid-phase synthesis using insoluble resins as solid support was used to synthesize metal complexes based on peptide backbone ligands. These coordination compounds find applications in biochemistry as well as in medicinal chemistry. Resin-bound chelates were prepared in such a manner that upon the addition of suitable metal salts the target metal complexes were selectively released from the resin and used.

a. Synthesis of Bis(2-picolyl)amine (bpa) molybdenum conjugate: In case when the attachment of a metal complex to the peptide on the solid support is not desirable, e.g. with radioactive metal isotopes, an innocent anchoring group can be attached to the peptide during solid-phase synthesis. The ligand– peptide conjugate is then cleaved from the resin, purified and the metal label is only added in solution immediately prior to use of the bioconjugate.



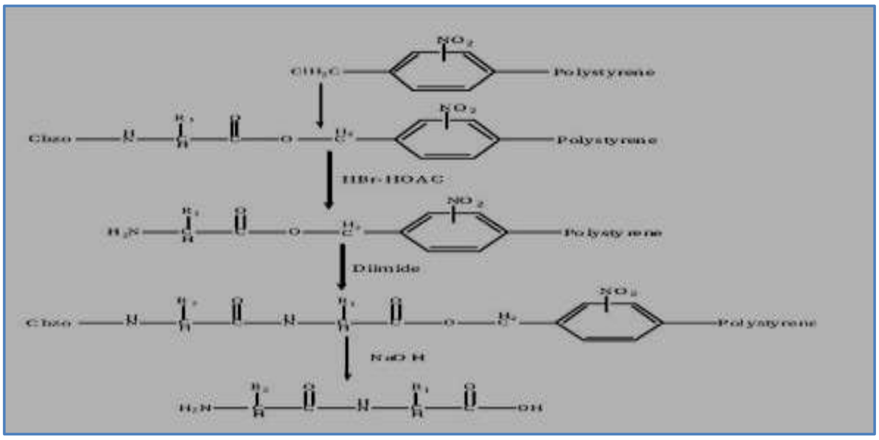
TBTU= O-(Benzotriazol-1-yl)-N, N, N', N'-tetra methyluronium tetra fluroborate

b. Bidentate Schiff base metal conjugates: A solid-phase synthesis approach for molybdenum carbonyl complexes was developed by Heinze. neither peptide coupling nor metallated amino acids are used, because it illustrates that complex organometallic transformations are possible on solid support. A specific resin and linker system allows coordination under solid-phase reaction conditions and the cleavage of the metal complex from the solid support. Bidentate Schiff base **1** was used as the ligand. The phenolic hydroxyl group allows the attachment to the solid support. A silyl ether based linker was chosen due to its stability under basic and acidic conditions and the possibility to cleave with fluoride ions, which are expected to be unreactive towards most metal complexes. In solution high temperature and rather harsh oxidative reaction conditions are necessary to synthesize the desired tricarbonyl compounds. Such harsh conditions have to be avoided in solid-phase chemistry with polystyrene resins as the molybdenum precursors can react with the aromatic residues of the support. Heinze and co- workers used [(CH3CN)3Mo(CO)3] as a Mo(CO)3 source and under mild reaction conditions the intensely blue coloured complexes **2** and **3** formed rapidly and having excellent yields. However, acetonitrile, a rather poor solvent for resin swelling, had to be used in a mixture with toluene. The cleavage was performed with tetra-*n*-butylammonium fluoride in dichloromethane and resulted in deeply coloured solutions of the deprotonated complexes.



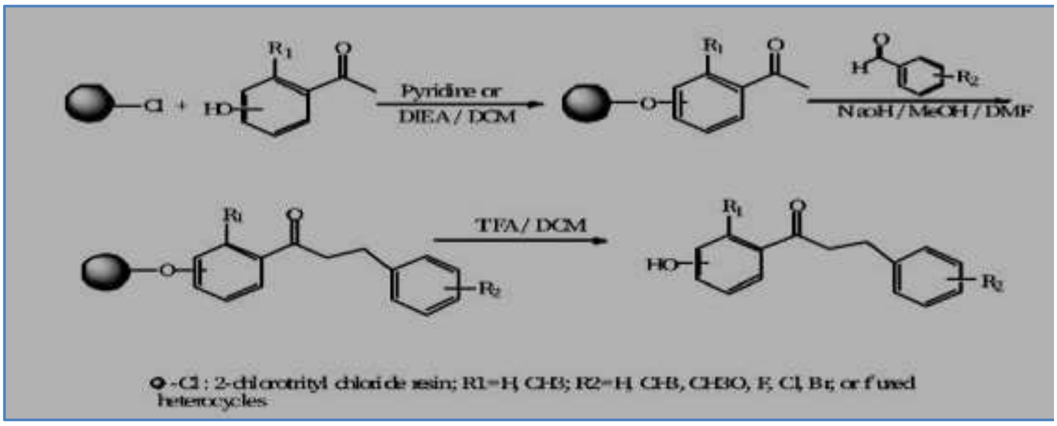
B. Synthesis of a Tetra-peptide:

A new approach to the chemical synthesis of polypeptides was investigated. It involved the stepwise addition of protected amino acids to a growing peptide chain which was bound by a covalent bond to a solid resin particle. This provided a procedure whereby reagents and by-products were removed by filtration, and the recrystallization of intermediates was eliminated. The advantages of the new method were speed and simplicity of operation. The feasibility of the idea was demonstrated by the synthesis of the model tetrapeptide L-leucyl-L-alanylglycyl-L-valine. To provide a point of attachment for the peptide the polystyrene resin was partially chloromethylated. The product was then nitrated or brominated. The resulting substituted chloromethyl polystyrene was treated with the triethylammonium salt of the first protected amino acid in the proposed peptide chain to give a substitute dbenzyl ester linkage. This was the stable covalent bond which held the growing peptide chain in the solid phase on the supporting resin. Protecting group which was used throughout the syntheses to be reported was the carbobenzoxy group. It was selected because it could be removed readily and completely by hydrogen bromide in glacial acetic acid stituted carbobenzoxy-L-valyl polymer even in 10% HBracetic acid there was also considerable loss of ester. After nitration the rate of removal of carbobenzoxy was decreased, but the loss of ester was reduced to a very small level. With 30% HBr the carbobenzoxy group was removed in **2** to **4** hr., while the ester cleavage remained low level for at least **6** hr.



C. Solid Phase Synthesis of Chalcones by Claisen-Schmidt Condensations:

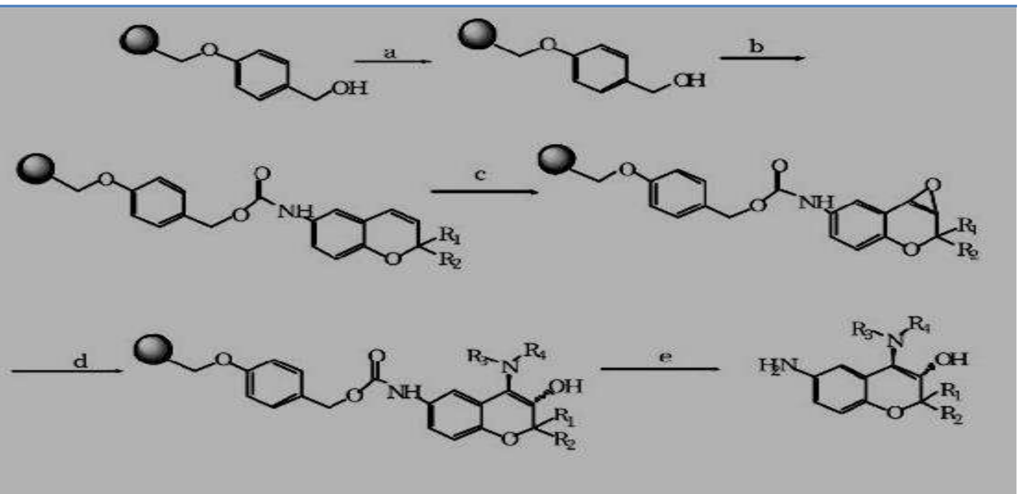
In order to accelerate the development of relatively inexpensive antimalarials that are effective against chloroquine-resistant strains of Plasmodium falciparum, a methodology for the solid phase synthesis of chalcone (l, 3-diphenyl- 2-propen-lone) analogues reasonably having high yields and purity. In a manual peptide synthesis vessel a mixture 3- or 4-hydroxyacetophenone and 2- chlorotritylchloride resin (l00 mg, l.l-l.6 mmol/g) in anhydrous dichloromethane (3 mL) was shaken for l h at room temperature. Resin was washed with DMF (3x), MeOH (2x) and DCM (3x) and dried in vaccum. The resin-attached aldehydes (l eq.) or methyl ketones (l eq.) were condensed with either substituted methyl ketones (l0 eq.) or substituted aldehydes (l0 eq.) with NaOH (0.1 eq.) in l0% MeOH-DMF (3 mL total) at room Temperature for 24 h. Resins were washed in the same sequence as the first step described above. The product was cleaved with TFA/DCM at room temperature for 20 min. Determination of product purity is done by HPLC.



D. Synthesis of Benzopyran Derivatives Using Two-Phase Solvents system:

Solid-phase organic synthesis has emerged as a powerful technique in generating combinatorial libraries of small organic molecules which is useful for drug discovery. Heterocyclic compounds provide scaffolds on which pharmacophores can be arranged to yield potent and selective drugs. A variety of heterocycles have been synthesized on solid support. A successful application of the epoxides **4** to generate the 3-hydroxy-4-amino substituted benzopyran library. We selected the Wang resin **1** as a polymer support, the hydroxy group of the Wang resin is useful in the introduction of 6-aminochromenes **6** through the carbamate linker which also serves as an efficient protection group for the amino group against the subsequent oxidation and alkylation reactions.

The benzopyran derivatives **6** were finally liberated from the resin by trifluoroacetic acid (TFA). In the first step, the 4-nitrophenyl carbonate resin **2** was prepared by adding pyridine in CH2Cl2 to the Wang resin 1 in the presence of p- nitrophenyl chloroformate in CH2Cl2. The reaction of carbonate resin **2** with 6- amino-2,2-dimethyl chromene and Ndiisopropylethylamine (DIPEA) in N, N dimethylacetamide (DMA) afforded the carbamate resin 3 and the progress of the reaction was verified by the complete disappearance of the carbonate peak at 1760 cm-1 in the IR. It was found that the two-phase solvent system comprised of chloroform and saturated aqueous NaHCO3 was quite satisfactory. Under this condition the desired epoxide resin was obtained in good yield. We assumed that the success of this reaction was due to the basic aqueous solution’s ability to remove excess m-chlorobenzoic acid quite effectively. The hydroxyl compounds 6 can also be used for further combination with acylating agents to preparing diverse chemical libraries for biological evaluation.



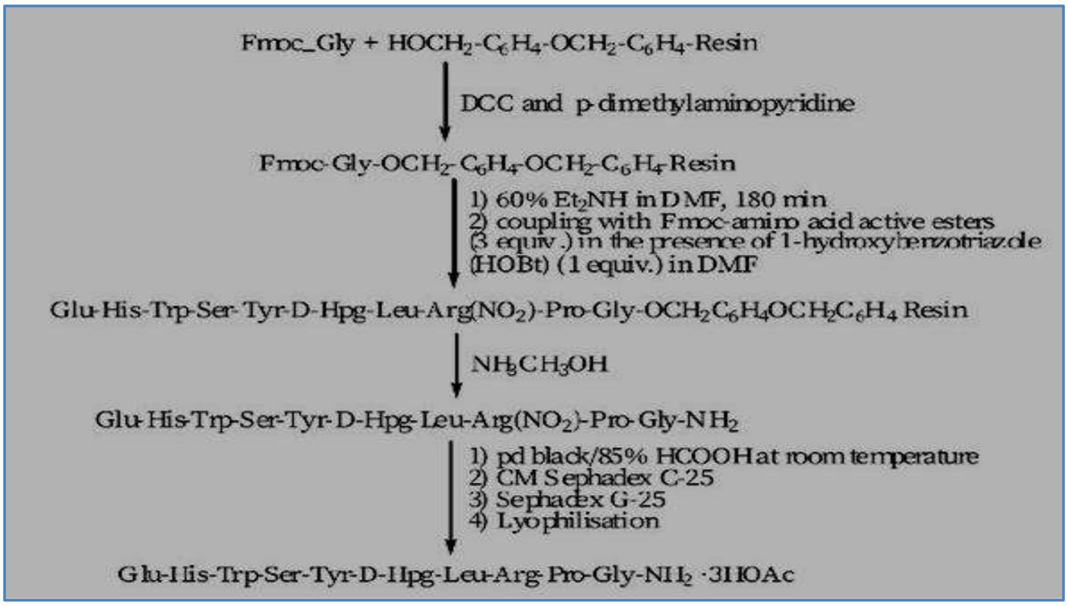
(a) p-nitrophenyl chloroformate, pyridine, CH_2Cl_2; (b) 6-amino-2,2-dimethyl chromene 7, DIPEA, DMA; (c) m-CPBA, $CHCl_3$: sat. aqueous $NaHCO_3$ (9 : 1); (d) 2 equiv. $Mg(ClO_4)_2$, 4 equiv. R_3R_4NH, CH_3CN; (e) TFA : CH_2Cl_2 (1 : 3), 4, 5, and 6 are racemates

E. Synthesis of luteinizing hormone releasing hormone analogues using 9- fluorenyl-methyloxycarbonyl amino acid:

Synthesis of the hypothalamic hormone, luteinizing hormone releasing hormone (LHRH) and its agonists and antagonists by using acid labile protecting groups like Boc, Z, etc., for a-amino or side-chain protection generally involves final treatment with anhydrous liquid hydrogen fluoride leading to contamination of the final product with closely related impurities there by necessitating extensive purificaiton. In solid phase synthesis of peptides, use of base labile 9 fluorenylmethyloxycarbonyl (Fmoc) group for Na-protection would allow milder conditions to be employed during the synthesis in addition to the requirement of minimal side-chain protection and this strategy was followed for the synthesis of LHRH analogues. The purity of the final peptides was demonstrated by paper chromatography on Whatman No. 1 chromatography paper strips by ascending method by using the following solvent systems:

A.*n*-BuOH-HOAc-H2O (4:5:5, upper phase, v/v)

B. *n*-BuOH-HOAc-H2O-pyridine (30:6:24:20, v/v)

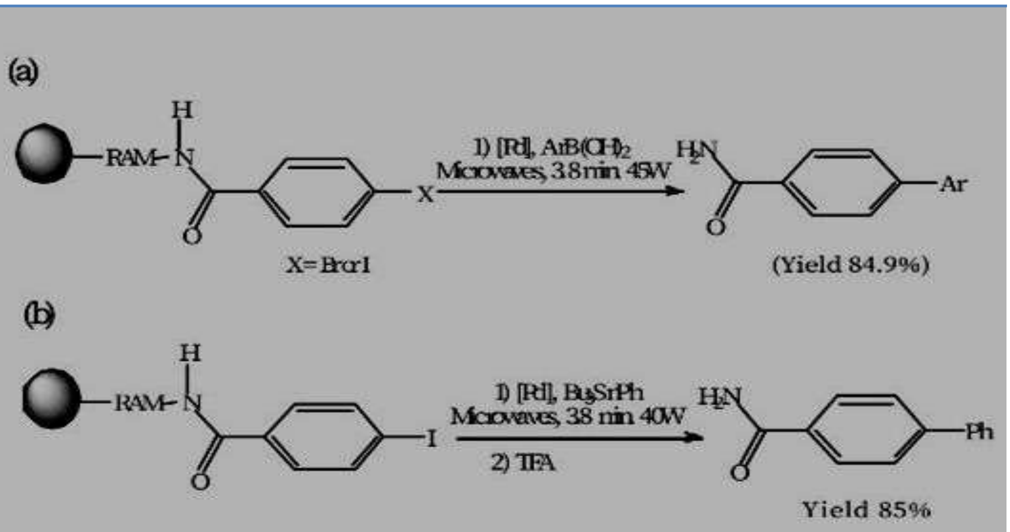


F. Microwave–assisted combinatorial synthesis:

The combination of microwave power to solid phase synthesis is quite logical. Rate accelerations and high loadings for several solid-phase protocols have been reported with reaction time being reduced in some cases from hours to a few minutes.

The combination of solid phase synthesis and microwave heating is receiving attention and this combination has enormous potential for better results Larhardetal. have demonstrated that highly useful Suzuki and Stille reactions could be conducted under flash-heating conditions using a single mode cavity and would afford better yields.

They reported microwave-assisted palladium-catalyzed coupling of aryl and heteroaryl boronic acids with iodo- and bromo-substituted benzoic acids, anchored to Tenta Gels RAM, provided high isolated yields of coupled products after a reaction time of 3.8 min. Suzuki and Stille reactions worked readily on a polymeric support consisting of a benzoic acid linked to Rinkamide on polyethylene glycol (PEG) grafted polystyrene (TentaGel). The polymer was found to be stable under these harsh conditions.

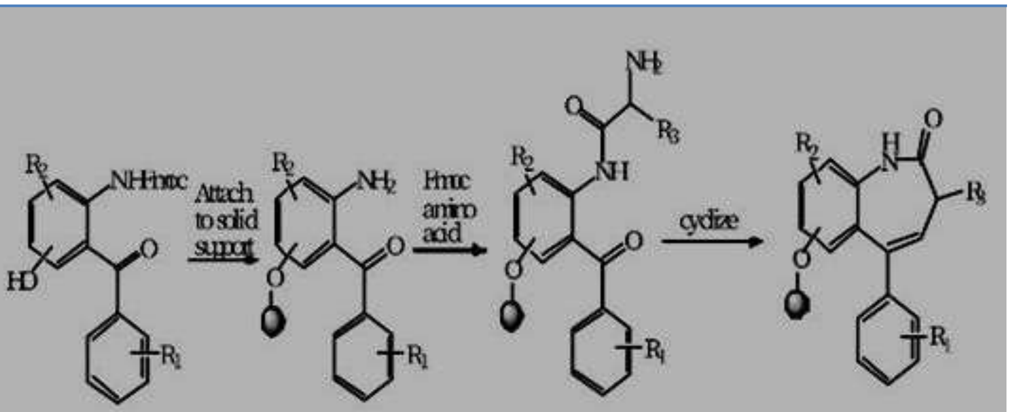


(a) Suzuki coupling on Solid-Phase Assisted by Microwave Irradiation (b) Microwave assisted stille reaction on polymer tethered 4-iodobenzoic acid

G. Synthesis of 1, 4 benzodiazepines:

The choice of benzodiazepines was inspired because of the medicinal importance of these materials and their resemblance to peptides.

Here the library was constructed by a combination of three reactants. In the synthesis 1, 4 benzodiazepines Fmoc is used as a common protecting group and detachment of solid support is done by tetrafluoroacetic acid.



Features:

a. **Efficiency:** It can be seen that starting with a single substance, the no: of compounds is tripled after each coupling step. First 3 x 1 = 3 resin bound dipeptides, then 3 x 9 = 27 resin bound tripeptides & finally 3 x 27 = 81 tetrapeptides are formed. If a 20 different amino acids are used in the synthesis, the no. of peptides in each coupling step is increased by a factor of 20. The total no: of the synthesized peptides can be expressed by a simple formula 20', when n is the no. of amino acids.
b. **Formation of all possible sequence combinations:** Consecutive execution of the three simple operations (portioning, coupling, mixing) ensures with mathematical accuracy – the formation of all possible sequence combinations of amino acid building blocks used in the synthesis. This combinatorial principle embodied in PM synthesis captured the imagination of many researchers & had a profound effect on the development of the field.
c. **Formation of compounds in one-to-one molarities:** It is very important to prepare libraries in which the constituents are present in equal molar quantities. Otherwise, a low activity component, if present in a large amount, may show a stronger effect than a highly active component present lower quantity. The PM method was designed to comply with requirement of 1:1 molar ratio. Before each round of couplings, the resin is thoroughly mixed, then divided into homogenous equal portions. This ensures that the previously formed peptides are present in equimolar quantities in each portion.
d. The PM synthesis determination of the structure of the various organic compds is not as simple as sequencing peptide, the bead are usually encoded. The building blocks of the encoding tags are attached to the beads in parallel with the organic building blocks of the library. Two types of encoding are:
e. **Encoding with sequence:** When encoding by sequences, the encoding tags are peptides or oligo nucleotides. Their sequences encode both identity of the organic reagents coupled to the bead & the order of coupling. The white, black, gray & white square encode the organic reagents represented by white, black & gray circles & their white – black. Gray – white coupling order.
f. **Binary coding:** In binary encoding system the coding units are halobenzenes carrying a varying length hydrocarbon chain attached to the bead through a cleavable space. It is simply their presence which codes for the organic building blocker & their position.
g. Reducing the No. of the varied amino acids:
h. Reducing the No. of varied positions:

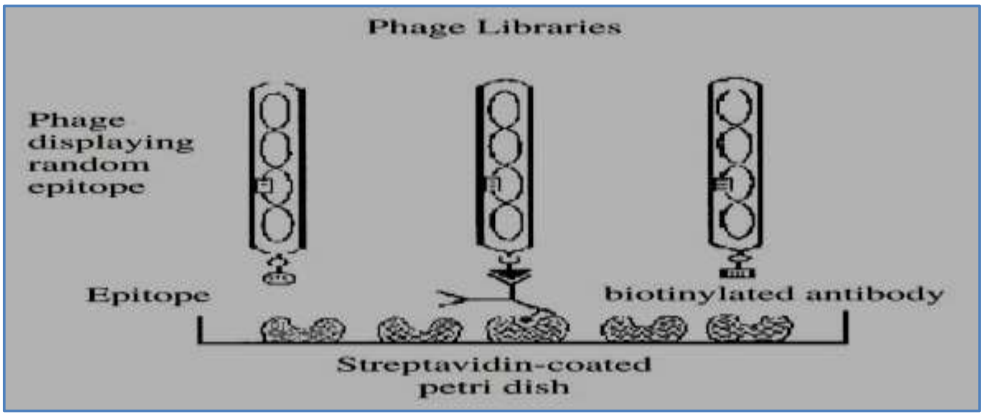
The Mixed Reagen Method of The Synthesis of Combinatorial Liberties.

Combinatorial peptide libraries can be prepared by using mixture of amino acids in the acylation step of the solid phase synthesis. Although the method is even more efficient than PM procedure, it has serious disadvantages. The one to one molar ratio of the formed compound cannot be assured due to the differences in the coupling rates of amino acids. There differences can in part be compensated by proper adjustment of the concentration of amino acids in the coupling mixtures. The method has been applied mainly in preparation of peptides libraries, but non peptide libraries have also been sythesized. Because mixtures of reactants are used in couplings, at the end of the synethsis of all library components are present on every bead. This means that only mixtures can be prepared by their method.

2.3 The Biologycal Method:

Biological methods for library preparation are mainly limited to peptide or oligonucleotide libraries. For peptide libraries, methods are based on the construction of a pool of clones each one expressing a different peptide on its surface. The peptides are fused to proteins normally expressed on the surface of the microorganism used. Phage display libraries are the most commonly used. Screening is accomplished by incubation of the target molecule, adsorbed to a solid support, with the phage population. Active phages will bind the target even after extensive washing steps. Target-bound phages are isolated and propagated by infection of *E. coli* and subjected to an additional round of adsorption to the immobilized target.

This procedure increases both the number of active phages and the stringency of selection, since harsher condition may be employed in the washing steps to reduce the number of non-specifically bound phages. As for the case of synthetic libraries, iterative cycles of adsorption, washing, elution and propagation in *E. coli* are performed to enrich the phage population in the active or in few active sequences. Active phages may then be subjected to DNA sequencing in order to decode the active peptide sequence. The use of biological display libraries for the isolation of peptide ligands is an interesting alternative to chemical libraries. Since 1985. when this technique was first published, many fields of research have benefited from its use. Web resources relevant to Combinatorial Chemistry and Combinatorial Technologies. There is a sort of information explosion accompanying the development of Combinatorial Chemistry and Combinatorial Technologies and an almost exponential growth of publications and patents in the field. At the same time, several web sites have been established providing updated information.



2.4 Solution Phase Combinatorial Chemistry:

Most ordinary synthetic chemistry takes place in solution phase. The use of solution phase techniques has been explored as an alternative to solid-phase chemistry approaches for the preparation of arrays of compounds in the drug discovery process. Solution-phase work is free from some of the constraints of solid-phase approaches but has disadvantages with respect to purification.

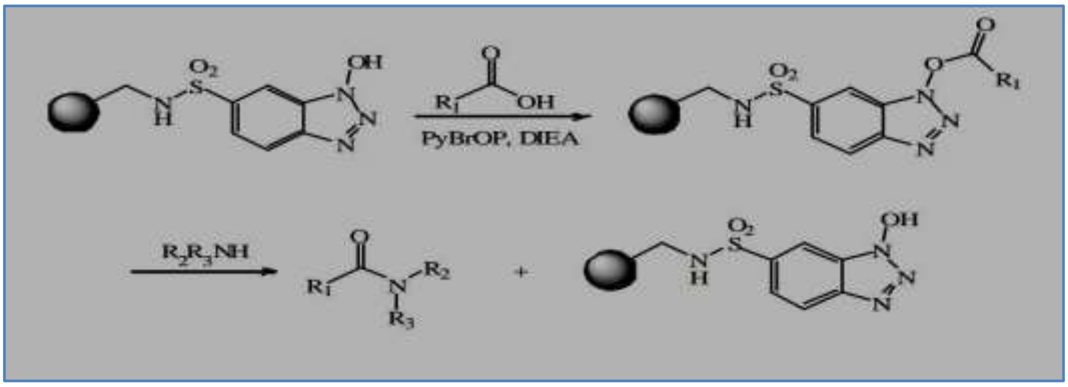
In solution phase synthesis we use soluble polymer as support for the product. PEG is a common vehicle which is used in solution phase synthesis it can be liquid or solid at room temperature and show varying degrees of solubility in aqueous and organic solvent. By converting one OH group of PEG to methyl ether (MeO-PEG- OH) it is possible to attached a carboxylic acid to the free OH and use in solution phase combinatorial synthesis. Another common support which is used in solution phase synthesis is liquid Teflon consisting mainly of long chain of (-CF2-) groups attached to a silicon atom. When these phases are used as a soluble support for synthesis the resulting product can be easily separated from any organic solvent.

A. Synthesis of Polymer by Solution Phase Combinatorial Chemistry: Tartar and co workers reported the synthesis of polymer supported

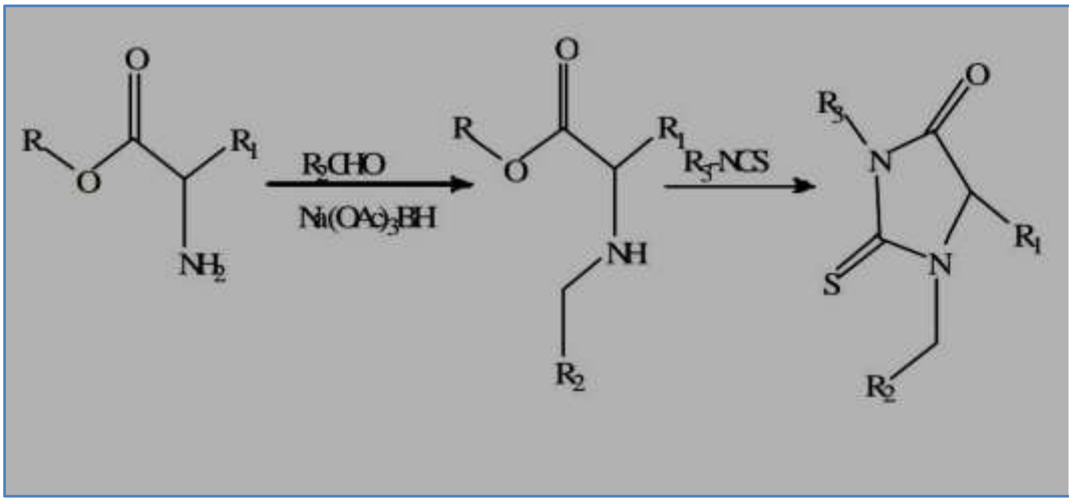
1-hydroxybenzotriazole. Reaction of the reagent with a carboxylic acid in the presence of an activating agent afforded the polymer bound activated ester which was reacted with amines to liberate the amide in solution.

Supported electrophilic, nucleophilic or ionic reagents used to remove impurities from solution have been termed scavenger reagents; polymer supported quenching reagents (PSQ) or complementary molecular reactivity/ molecular recognition polymer (CMR/R polymer). Use of such reagents provides a versatile counterpart to the approach. Booth and Hodges utilized a high loading amine resin derived from chloromethylpolystyrene and tris (2- aminoethyl) amine in the preparation of ureas, thioureas, sulphonamides and amides.

B. Synthesis of Thiohydantoins:



Sim and Ganesan developed a one-pot three component synthesis of thiohydantoins using the reductive amination of amino esters with aromatic aldehydes and sodium triacetoxyborohydride followed by the reaction with an isocyanate in the presence of triethylamine. The thiohydantions were isolated by an aqueous work-up protocol which incorporated the addition of glycine to convert unreacted reagents into water soluble materials. The methodology was used in the preparation of an array of 600 discrete compounds.



C. Solution Phase Synthesis of Biologically Important Oligosaccharides:

We departed from the traditional goal of oligosaccharide total synthesis striving for maximum convergency and followed a linear synthesis approach based on monosaccharide building blocks.

Using this method similar to that practiced for peptides and oligonucleotides we assembled several complex structures.

a. **Synthesis of High Mannose Structures of HIV gp120:** We completed the synthesis of a series of highly branched mannosides found on gp120 of HIV. Two different trisaccharides, a hexa-, and a nonasaccharide were prepared in conjugatable form. These structures were used to investigate the interaction of cyanovirin-N, a highly potent topical anti-HIV agent, with gp120. In collaboration with Barry O’Keefe (NCI) and Angela Gronenborn (NIH) isothermal calorimetry and high-field NMR were used to establish the minimal binding sequence and to map the binding site on the protein.
b. **Synthesis of Oligosaccharide Antigens Involved in Cancer and Bacterial Infections:** Cell surface carbohydrates act as biological markers for various tumors and are involved in bacterial and parasitic infections. Specific carbohydrate structures are found on particular cell populations and may be used to induce a specific immune response. These complex structures require reliable methodologies for their assembly. The Lewis antigens, a class of glycosphingolipids, are essential for cellular adhesion and recognition. In addition to their role in normal cellular adhesion processes such as the inflammatory response they have been implicated in many types of cancer and bacterial infections. We developed new synthetic routes for the modular assembly of the Lewis antigens as demonstrated on the example of H-type II that lend themselves to automation. Other tumor-associated antigens including Gb3 have also been prepared.

The oligosaccharides obtained from these syntheses are currently being attached to surfaces to enable rapid screening of carbohydrate-protein interactions.

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3. Preparation and Purification of Colloids

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Introduction:

Colloids are an important part of our everyday life and play an important role in the fields of agriculture, medicine, biology, industries, etc. Proteins, starch, gelatin, jellies, milk, curd, cheese, paints, varnishes, alloys, smoke, clouds, fog, volcanic dusts, etc. are familiar examples of different types of colloids. Hence a knowledge and understanding of colloidal chemistry is essential.

A *colloidal solution* or *colloidal dispersion* is a mixture of two substances in which one substance is present in form of finely divided particles (with diameter lying between 10–2000 Å) that are dispersed in the other substance.

Thus, a colloidal solution is a two phase system. The substance present as minute particles forms the discontinuous phase called the *dispersed phase* while the substance in which the particles are dispersed forms the continuous phase, referred to as the *dispersion medium*. For example- in a colloidal solution of gold in water, the gold particles constitute the dispersed phase and water forms the dispersion medium. Both the dispersed phase and dispersion medium can either be a solid or a liquid or a gas. So there are eight different types of colloidal systems.

Out of the different types of colloidal systems, the three main types are –

a. *Sols* in which a solid is dispersed in a liquid. For e.g.- proteins, paints, gold sol, arsenious sulphide sol, etc.
b. *Emulsions* in which both the dispersed phase and the dispersion medium are liquids. For e.g.- milk, cod-liver oil, butter, etc.
c. *Gels* in which a liquid is dispersed in a solid. For e.g.- gelatin, jellies, silica gel, etc.

In this chapter, methods for the preparation of sols, emulsions and gels will be discussed along with the techniques used for the purification of sols.

3.1 Preparation of Colloids:

A colloidal solution is intermediate between a true solution and a suspension. This is because the diameter of the dispersed particles in a colloidal system is more than that of the solute particles in a true solution (with diameter between 1-10 Å) but smaller than that of a suspension (with diameter of more than 2000 Å). Hence the main consideration in preparation of colloidal solutions is that the dispersed particles should be in the size range of 10-2000 Å.

3.1.1 Sols:

A colloidal system in which the dispersed phase is a solid and the dispersion medium is a liquid is called *sol*. When the dispersion medium is water, the sol is known as *hydrosol* and if it is alcohol or benzene or any other organic solvent, the sol is named *alcosol* or *benzosol* or *organosol* respectively.

On the basis of the affinity of the dispersed phase for the dispersion medium, sols have been divided into two categories:

a. **Lyophilic sols** (*liquid loving*) in which the dispersed phase exhibits strong affinity for the dispersion medium. For e.g.- proteins, gum in water. If water is the dispersion medium, lyophilic sols can also be termed as hydrophilic sols.
b. **Lyophobic sols** (*liquid hating*) in which the dispersed phase has no affinity for the dispersion medium. For e.g.- gold sol, ferric hydroxide sol, etc. When water is the dispersion medium, the lyophobic sols are also called hydrophobic sols.

Due to the difference in the affinity between the two phases in the lyophilic and lyophobic sols, different methods are employed for their preparation.

3.2 Prepartion of Lyophililc Sols:

In lyophilic sols (also called *intrinsic colloids*) the dispersed phase shows strong affinity for the dispersion medium. Hence they can be easily prepared by simply mixing the solid (to be dispersed) with the suitable liquid acting as the dispersion medium.

In some instances slight warming may also be required to obtain the sol. These sols are stable and, therefore, addition of stabilizers is not required during their preparation. They are reversible in nature, since on evaporation of the dispersion medium, the residue left can again be converted into colloidal state by addition of the liquid.

Some examples of lyophilic sols are: starch, gelatin, acacia in water, rubber in benzene, etc.

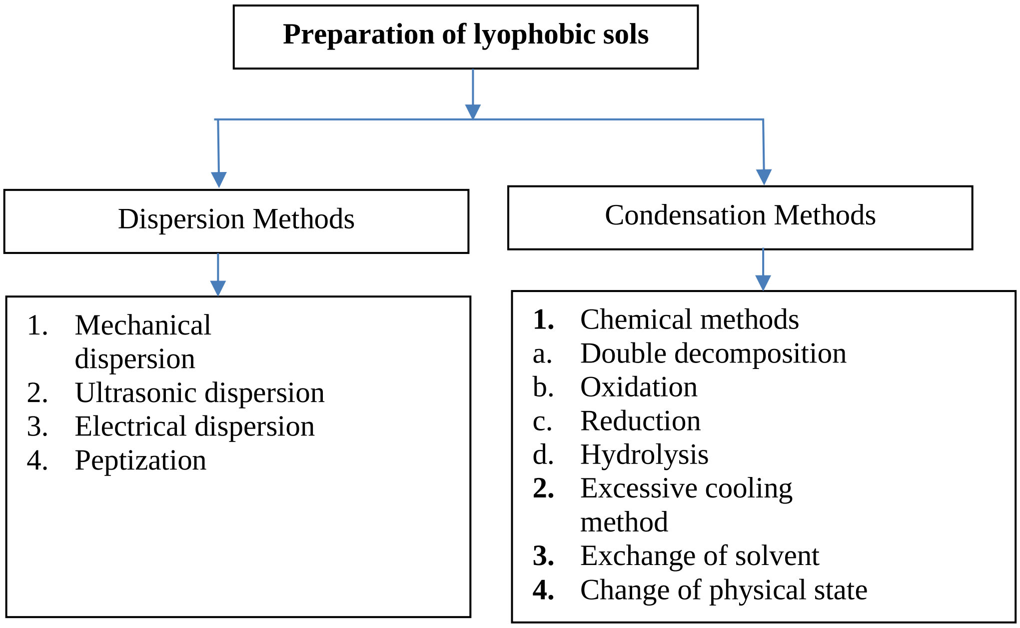
Preparation of Lyophobic Sols:

Lyophobic sols (also called *extrinsic colloids*) cannot be prepared by simply mixing the solid with the liquid medium since there is hardly any affinity between the dispersed phase and the dispersion medium.

They are comparatively unstable and hence require stabilizing agents at the time of preparation. They are irreversible in nature which means that once the dispersion medium is evaporated, the residue left cannot be converted again into sol by addition of the liquid.

Therefore, special techniques are employed for the preparation of lyophobic sols. The methods for their preparation have been divided into two categories:

1. **Dispersion methods:** They involve breaking down of bigger sized particles of a substance into smaller particles of colloidal dimensions. The colloidal particles obtained are stabilized by the addition of a stabilizing agent.
2. **Condensation / Aggregation methods:** In these methods, particles of colloidal size are built by the aggregation of a large number of atoms or molecules.



3.2.1 Dispersion Methods:

The different types of dispersion methods used for the preparation of lyophobic sols are:

A. Mechanical dispersion:

In this technique the substance (to be dispersed) is first ground by usual methods to obtain smaller sized particles. It is then mixed with the dispersion medium to get a suspension. This suspension, together with a stabilizing agent, is then passed through a *colloidal mill* (Figure 3.1).

The colloidal mill, also known as *disc mill,* consists of two heavy metal discs placed one above the other and separated by a very small distance. These discs are capable of rotating at a very high speed (about 7000 revolutions per minute) in opposite directions. The powerful shearing force breaks the suspended particles into colloidal sized particles and thus a sol is obtained.

Some examples: Colloidal solutions of printing inks, paints, varnishes, etc. are prepared by this method.

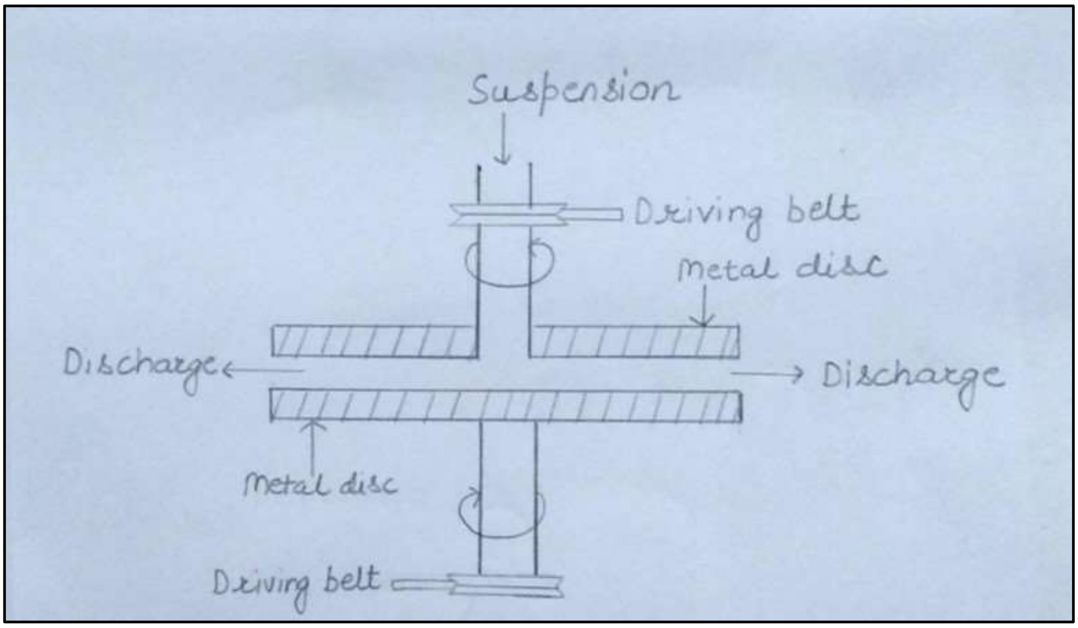


Figure 3.1: Colloidal Mill

B. Ultrasonic Dispersion:

This method involves the use of high intensity ultrasonic waves and it has been effectively used for the preparation of some sols. Ultrasonic waves refer to ultrasound waves with a frequency of 20 KHz and above (more than the upper limit of human audible range). The ultrasonic waves are usually generated by '*Piezoelectric oscillator'* method in which a piezoelectric crystal (such as a quartz crystal) converts electrical energy (electric current) into mechanical energy (sound waves). These waves can also be produced by '*Magnetostriction oscillator*' method which involves the use of a ferromagnetic rod of nickel or iron which is magnetized. Due to magnetization there is a small change in the dimensions of the rod which then undergoes rapid vibrations, thereby generating the ultrasonic waves.

Ultrasonic vibrations can transform a coarse suspension into colloidal dimensions. When ultrasonic waves enter the liquid (dispersion medium), they propagate through the liquid by creating alternate compression (contraction) and rarefaction (expansion) cycles (Figure 3.2). This produces a negative pressure in the medium which breaks the liquid into voids, which then form small sized bubbles or cavities. This is called cavitation. The cavities expand and contract with the compression and rarefaction cycles. They continue to grow in size and after attaining a critical size they implode with the surrounding liquid rushing into them. When the cavity collapses violently near a solid surface, high speed jets of liquid with velocity as high as 400 km / hour are formed.

The potential energy of the cavity gets converted into the kinetic energy of the liquid jet. These jets strike the solid surface with great impact. A tremendous shearing force is generated which disrupts the solid and converts it into a colloidal dispersion.

Examples: Claus prepared mercury sol by this method. Also sulphides and metal oxides can be dispersed into colloidal state by this technique.

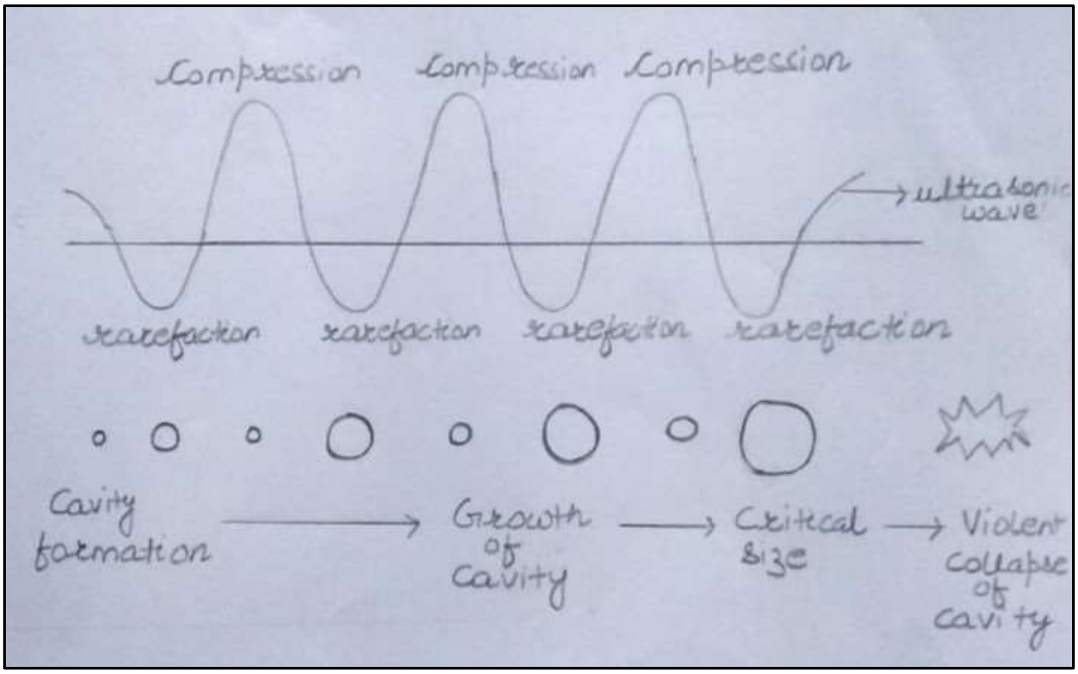


Figure 3.2: Principle of Ultrasonic Cavitation

B. Electrical Dispersion (Bredig's arc method):

G. Bredig introduced this method in 1898. This technique is used to prepare sols of metals in water (also called hydrosols). Two electrodes of the metal, whose sol is to be prepared, are dipped in *de-ionized* water containing traces of an alkali (KOH). The water is kept cold by immersing the container in an ice bath (Figure 3. 3). The electrodes are connected to a high voltage source. An electrical arc is struck between the two electrodes. The intense heat produced turns some part of the metal into vapours which are immediately condensed by the surrounding ice cold water to give aggregates of colloidal size. Traces of electrolyte added to water (KOH) help in stabilization of the sol.

Examples: Hydrosols of gold, silver, platinum, copper, etc. are prepared by this method.

This technique of electrical dispersion has also been modified to prepare organosols of metals and non-metals. In the modified method, electrodes usually made of iron or aluminium (which do not disintegrate) are employed. The material to be dispersed is suspended in form of granules in the dispersion medium (an organic medium) and an arc is struck between the electrodes. It is noteworthy that this electrical method involves both dispersion as well as condensation processes. The atoms of the metal in vapour state condense to form aggregates of colloidal size but since the process is initiated using bulk metal, hence it is regarded as a dispersion method.

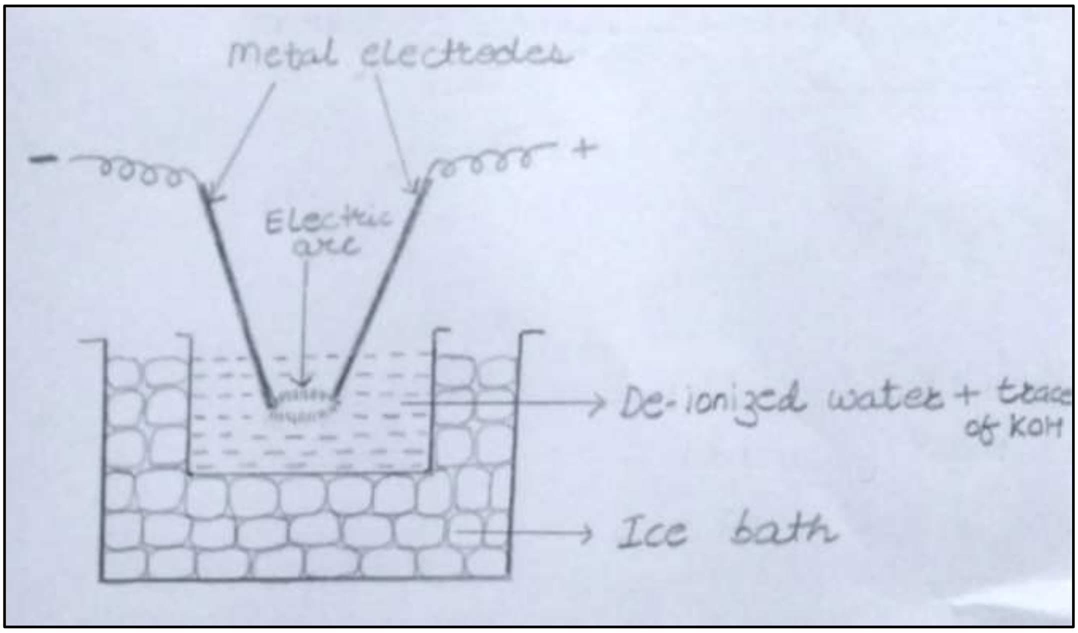


Figure 3.3: Bredig's arc method

D. Peptization: Certain freshly prepared precipitates such as silver chloride, ferric hydroxide, etc. can be converted into their colloidal solutions in water by the addition of a small amount of a suitable electrolyte. The electrolyte which is added should have an ion common with the precipitate which is to be dispersed. The precipitate preferentially adsorbs one of the ions of the electrolyte which is chemically closely related to it. As a result the particles of the precipitate acquire a positive or negative charge depending on the charge of the ion that has been adsorbed. Due to the presence of similar type of charges, the particles of the precipitate repel each other and are pushed apart. They separate out as colloidal sized particles and in this way a stable sol is formed.

The process of disintegration of a freshly prepared precipitate into particles of colloidal size by the addition of a small amount of a suitable electrolyte is called peptization. The electrolyte used for this purpose is called peptizing agent. Peptization is the reverse process of coagulation.

Some examples of sols prepared by peptization are:

Reddish brown colloidal solution of ferric hydroxide ($Fe(OH)_3$) is obtained on the addition of a small amount of ferric chloride ($FeCl_3$) to a freshly prepared precipitate of ferric hydroxide. Ferric chloride acts as the peptizing agent (with Fe^{+3} ions being in common with the precipitate) and the peptization action is due to the preferential adsorption of ferric ions.

$$\underset{\text{Precipitate}}{Fe(OH)_3} + Fe^{+3} \rightarrow \underset{\text{Reddish brown sol}}{Fe(OH)_3 . Fe^{+3}}$$

- **Formation of $Fe(OH)_3$ sol by peptization:**

Precipitate of silver chloride (Ag^+Cl^-) yields a sol on the addition of a small amount of hydrochloric acid which acts as the peptizing agent (Cl^- ion being in common with the precipitate). Colloidal solution is obtained due to the preferential adsorption Cl^- ions.

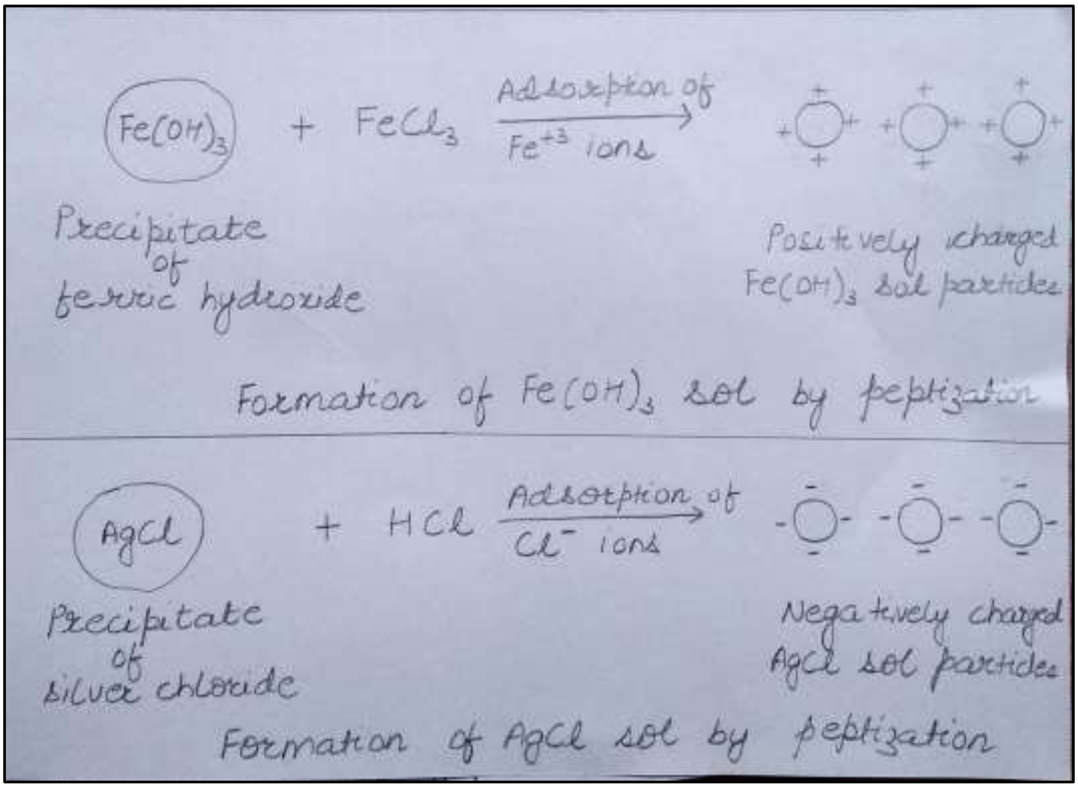
$$\underset{\text{Precipitate}}{AgCl} \quad + \quad Cl^- \quad \rightarrow \quad \underset{\text{Sol}}{AgCl.\,Cl^-}$$

- **Formation of AgCl sol by peptization:**

Silver chloride precipitate can also undergo peptization on addition of a small amount of a dilute solution of silver nitrate. Silver ions, being in common, are preferentially adsorbed by the precipitate.

$$\underset{\text{Precipitate}}{Ag\,Cl} \quad + \quad Ag^+ \quad \rightarrow \quad \underset{\text{Sol}}{AgCl.\,Ag^+}$$

Cadmium sulphide (CdS) precipitate can be converted into a sol by the addition of hydrogen sulphide (sulphide ions being in common are adsorbed).



Sol of aluminium hydroxide ($Al(OH)_3$) can be obtained by the addition of a small amount of dilute hydrochloric acid to a freshly prepared precipitate of aluminium hydroxide. The action of hydrochloric acid on $Al(OH)_3$ yields Al^{+3} ions that are preferentially adsorbed.Sometimes repeated washing of the precipitate also causes peptization. For example- when freshly prepared precipitates such as that of $Al(OH)_3$, $BaSO_4$ or CuS are repeatedly washed with distilled water, their colloidal solutions in water are obtained.

3.2.2 Condensation / Aggregation Methods:

The principle of condensation methods is that the materials from which the lyophobic sol is to be prepared are present initially in true solution as ions or molecules and they are then converted into particles of colloidal size, by aggregation, using different chemical reactions and methods. These reactions are strictly carried out under controlled conditions of concentration, temperature, order of mixing, etc. that allow the formation of colloidal solutions only but prevent the further growth of the colloidal particles and their subsequent precipitation.

The various types of condensation methods that are commonly used are as follows:

A. Chemical Methods:

Different types of chemical reactions have been used for the preparation of lyophobic sols.

a. Double Decomposition: Various colloidal solutions have been prepared through this reaction. Some examples are as follows:

a. A yellow coloured stable sol of arsenious sulphide (As_2S_3) is prepared by slowly passing hydrogen sulphide gas through a cold solution of arsenious oxide in water.

$$As_2O_3 + 3H_2S \rightarrow \underset{\text{Yellow sol}}{As_2S_3} + 3H_2O$$

The H_2S gas is continuously passed till the yellow colour of sol attains maximum intensity. However, excess of hydrogen sulphide (an electrolyte) is removed either by boiling or by passing in a stream of purified hydrogen or nitrogen or carbon dioxide.

b. On mixing a very dilute solution of ferric chloride and potassium ferrocyanide, a prussian blue sol of ferric ferrocyanide is obtained.

$$3\,K_4Fe(CN)_6 + 4FeCl_3 \rightarrow \underset{\text{Prussian blue sol}}{Fe_4[\,Fe(CN)_6]_3} + 12KCl$$

The ionic impurities formed in this reaction are removed by the process of dialysis (discussed later in the chapter).

c. Mercuric sulphide sol is obtained by passing H_2S gas through a solution of mercuric cyanide.

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

d. Silver halide sols can be obtained by mixing dilute solutions of an alkali halide and a silver salt.

$$AgNO_3 + NaX \rightarrow \underset{\text{Sol}}{AgX} + NaNO_3$$

(X= Cl, Br, I)

b. Oxidation: Certain Sols have been prepared *via* oxidation reactions. For instance:

a. On exposing an aqueous solution of hydrogen sulphide to air, sol of sulphur is obtained as a result of an oxidation reaction.

$$2H_2S + O_2 \rightarrow \underset{\text{Sulphur sol}}{2S} + 2H_2O$$

Sulphur sol can also be obtained by passing H_2S gas through an oxidizing agent such as a solution of sulphur dioxide or bromine water or nitric acid, etc.

$$2H_2S + SO_2 \rightarrow \underset{\text{Sulphur sol}}{3S} + 2H_2O$$

$$H_2S + Br_2 \rightarrow \underset{\text{Sulphur sol}}{S} + 2HBr$$

$$H_2S + 2HNO_3 \rightarrow \underset{\text{Sulphur sol}}{S} + 2NO_2 + 2H_2O$$

b. Selenium sol can be prepared in the same manner by the oxidation of hydrogen selenide solution.

$$2H_2Se + O_2 \rightarrow \underset{\text{Selenium sol}}{2Se} + 2H_2O$$

c. Iodine sol is obtained by the reaction of iodic acid with hydroiodic acid.

$$5HI + HIO_3 \rightarrow \underset{\text{Iodine sol}}{3I_2} + 3H_2O$$

c. Reduction: Metal sols such as silver, gold, platinum, palladium, iridium, copper, lead, etc. can be obtained by the reduction of the solutions of their soluble salts or oxides. For this purpose, reducing agents that are employed are non- electrolytes.

Some examples of the commonly used reducing agents are: formaldehyde, tannic acid, phenyl hydrazine, hydroxylamine, stannous chloride, hydrogen, phosphorus, carbon monoxide.

Some examples of sols prepared by this method are:

a. Silver sol is obtained by the reduction of silver nitrate with tannic acid.

$$AgNO_3 + \text{tannic acid} \rightarrow Ag\ (\text{sol})$$

b. Gold sol has been prepared by the reduction of gold salts, *viz*, gold (III) chloride with stannous chloride.

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

The colloidal gold particles obtained by this reaction are adsorbed on to stannic hydroxide (hydrated stannic oxide) formed by the hydrolysis of $SnCl_4$.

$$SnCl_4 + 4H_2O \rightarrow Sn(OH)_4 + 4HCl$$

The gold sol, thus obtained, has a purple colour and it is called *purple of cassius* (after the name of Andreas Cassius of Leyden who discovered it in 1685). The intensity of the sol colour correlates with the concentration of gold present. Purple of cassius is quiet expensive and is used to make ruby glass, fine potteries, miniature paintings, etc.

Gold sol can also be prepared by the reduction of a gold salt with formaldehyde.

$$2AuCl_3 + 3HCHO + 3H_2O \rightarrow \underset{\text{Gold sol}}{2Au} + 3HCOOH + 6HCl$$

In another method, gold sol has been readily obtained by the reduction of chloroauric acid solution (having traces of potassium carbonate) with formaldehyde. In this reaction, first chloroauric acid reacts with potassium carbonate to yield potassium aurate.

$$HAuCl_4 + 2K_2CO_3 + H_2O \rightarrow Au(OH)_3 + 2CO_2 + 4KCl$$

$$2\,Au(OH)_3 + K_2CO_3 \rightarrow 2KAuO_2 + CO_2 + 3H_2O$$

The above solution is heated and a dilute formaldehyde solution is added to it. Reduction occurs and gold sol is obtained.

$$2KAuO_2 + 3HCHO + K_2CO_3 \rightarrow \underset{\text{Sol}}{2Au} + 3HCOOK + KHCO_3 + H_2O$$

c. Platinum sol has been prepared by the reduction of its salt solution with a suitable reducing agent.

$$PtCl_2 + SnCl_2 \rightarrow Pt\,(sol) + SnCl_4$$

d. Hydrolysis: Sols of hydroxides of weakly electropositive metals such as aluminium, iron, chromium, tin, thorium, zirconium, etc. have been prepared by hydrolysis of aqueous solutions of their salts. The solutions of these metal salts undergo appreciable hydrolysis since the bases corresponding to the metals are weak. Hydrolysis is a type of a double decomposition reaction with water acting as one of the reactants.

For example: Red sol of ferric hydroxide is obtained on adding a small amount of ferric chloride solution drop by drop to hot water.

$$FeCl_3 + 3H_2O \rightarrow \underset{\text{Red sol}}{Fe(OH)_3} + 3HCl$$

In this reaction ferric chloride also acts as a stabilizer. The ferric ions (Fe^{+3}) furnished by $FeCl_3$ solution, are adsorbed on the surface of the particles of $Fe(OH)_3$ which, resultantly acquire a positive charge.

Presence of similar charge on the particles develops repulsion between them and hence prevents their coagulation. This confers stability to the sol. Purification of sol and removal of HCl formed in the reaction is done by dialysis.

B. Excessive cooling method:

This technique has been used to obtain a colloidal solution of ice in organic solvents such as chloroform or ether. The process involves freezing a solution of water in the organic solvent. Due to freezing the molecules of water, that can no longer be held in solution, separately combine to form bigger particles of colloidal dimensions.

C. By exchange of solvents: Colloidal solutions of many substances can be prepared by exchange of solvents. The process involves taking the solution of the substance (to be dispersed) in one solvent and then pouring it into another solvent in which the substance is comparatively less soluble (or sparingly soluble). For instance:

a. When an alcoholic solution of sulphur is poured in excess of water, a colloidal solution of sulphur in water is obtained. Sulphur is present in molecular form in alcohol but due to its insolubility in water, the molecules precipitate out as colloidal particles in water.
b. Phenolphthalein, used as an indicator in acid- base titrations, is used in form of its alcoholic solution since it is soluble in alcohol but not in water. Therefore, when water is added to a solution of phenolphthalein, a milky liquid is formed which is actually a colloidal solution of phenolphthalein in water.

D. By change of physical state: Colloidal solutions of some elements such as mercury and sulphur have been obtained by this technique. In this method, the vapours of the element are passed through cold water containing a suitable stabilizer (for e.g.- an ammonium salt or a citrate).

3.3 Purification of Sols:

The sols prepared by the methods discussed above usually contain impurities, particularly that of electrolytes. Presence of small amount of electrolytes stabilizes the sol but their excess concentration renders the sol unstable. Hence elimination of these impurities by suitable means is necessary. Some commonly used methods for purification of sols are: *Dialysis*, *Electrodialysis*, *Ultra-filtration* and *Ultracentrifugation*.

A. Dialysis:

The process of separating colloidal particles from dissolved ions or molecules of smaller dimensions (crystalloids) by diffusion through a semi- permeable membrane is called dialysis and the membrane used for this purpose is called dialyser

The technique of dialysis was first employed by British Chemist, Thomas Graham in 1861. The principle of this technique is that while ions or molecules (crystalloids) can easily diffuse through parchment and other fine membranes, the colloidal particles (being bigger in size) cannot do so readily. Hence crystalloids, present as impurities in sol, easily pass through the dialyser but the colloidal particles are retained (due to their very slow rate of diffusion).

Parchment paper is commonly used in dialysis. In addition to it, other membranes that can be used are of cellophane, cellulose nitrate and cellulose acetate. The membranes can be employed in form of a bag or an elongated tube.

The simplest dialyser consists of a bag made of parchment or cellophane in which the colloidal solution to be purified is taken (Figure 3.4). The bag is suspended in a wider vessel containing distilled water. The crystalloids present as impurities in the colloidal solution diffuse out into the surrounding water in the vessel while the colloidal particles remain in the bag. Thus the sol is purified. Accumulation of crystalloids in water may lead to back diffusion, hence the distilled water in the wider vessel is periodically renewed. But it is more preferred to maintain a continuous flow of water in the vessel.

This is achieved by allowing water to enter the vessel from an inlet near the bottom and allowing it to leave from an outlet near the top of the vessel. This accelerates the process of diffusion as the concentration of crystalloids in the surrounding water remains practically zero. This concentration gradient, in turn, favours the fast diffusion of ions or molecules into the surrounding water.

For example: Ferric hydroxide sol prepared by hydrolysis (by addition of ferric chloride solution to hot water) is purified by this method. For the stability of this sol, it is necessary to remove HCl (an electrolyte) formed in the reaction.

Hence, the impure sol of ferric hydroxide is subjected to dialysis. After sometime the entire HCl diffuses into the surrounding water and pure reddish sol of $Fe(OH)_3$ is left in the bag.

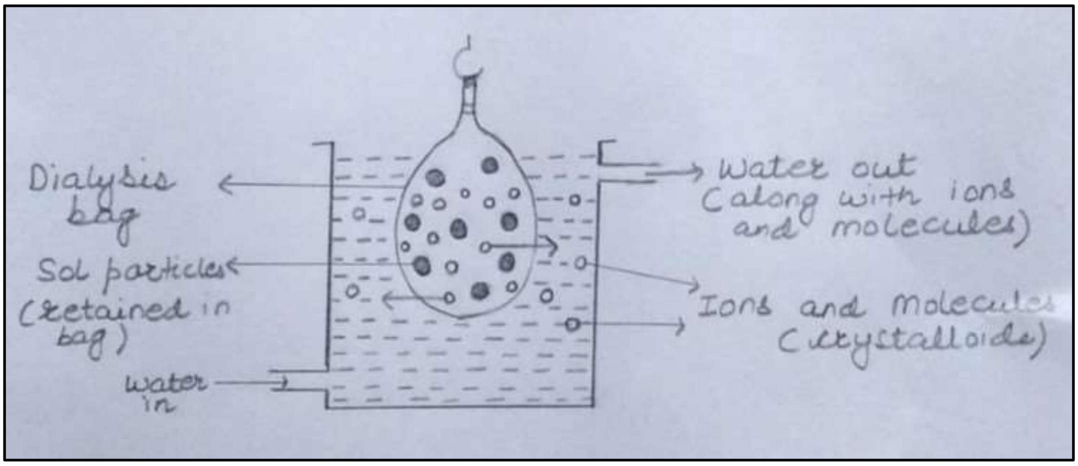


Figure 3.4: Dialysis

B. Electrodialysis:

The process of dialysis is very slow. However, it can be accelerated by the application of an electric field. This process is referred to as electrodialysis. In this method, two metal screens supporting the dialysing membranes are placed in a container (Figure 3.5). The colloidal solution, to be purified, is placed between the two membranes.

On the other side of each dialysing membrane is a compartment filled with pure water. Required potential is applied between the two metal screens. Under the influence of the electric field, the ions of the electrolyte (present as impurities) migrate towards the oppositely charged electrode while the colloidal particles are retained. Thus the process of dialysis is triggered. The water in the compartments is renewed frequently or continuously.

It is important to note that electrodialysis can be used only for the removal of electrolytic impurities and cannot be used if non-electrolytic impurities such as sugar, urea, etc. are present.

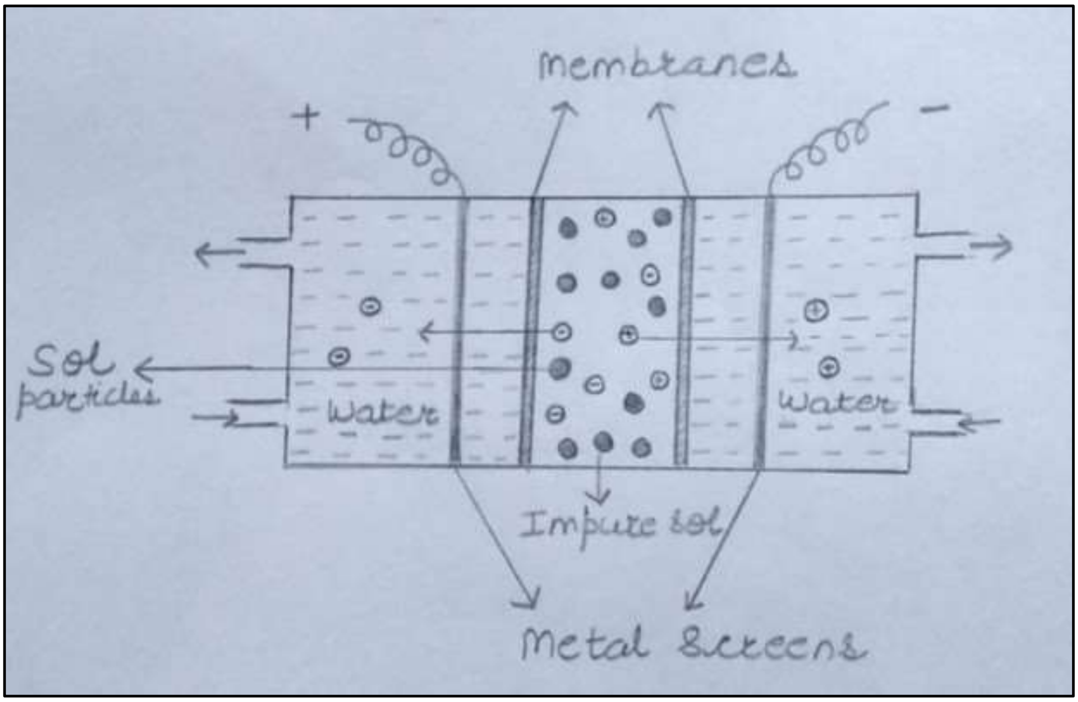


Figure 3.5: Electrodialysis

D. Ultra-filtration:

Ultra-filtration is a type of filtration through a semipermeable membrane in which separation is facilitated by pressure acting as the driving force. For purification of sols by this method, specially prepared filter papers called ultra-filters are employed.

The pore size of ordinary filter papers is larger than the size of colloidal particles. Hence if a sol is filtered through ordinary filter paper, the colloidal particles will also pass through it along with smaller sized solutes and solvent. However the size of these pores can be reduced by soaking the filter papers in a solution of gelatin or collodion (syrupy solution of 4% nitrocellulose in alcohol and ether) or a regenerated cellulose such as cellophane. The papers are then hardened by dipping them in formaldehyde solution and subsequently drying them. As a result the pore size of papers becomes small enough to hold back the colloidal particles. Such treated filter papers are called ultra-filters.

On filtering the impure sol through ultra-filters, the smaller sized impurity particles and solvent pass through it while the larger colloidal particles are retained on the ultra-filter paper. The colloidal particles on the paper can be redispersed into a fresh dispersion medium to obtain pure sol.

Filtration through ultra-filters is slow. To speed up the process, pressure is applied (either on the side of the sol or on the filtrate side by using a suction pump) to drive the filtration of solutes, hence the name ultra-filtration (Figure 3.6). The ultra-filters are quiet delicate and fragile, therefore, they are usually supported on a wire mesh and then used.

It may also be noted that ultra-filters with different pore sizes can also be prepared by soaking the filter papers in solutions of collodion of different concentrations. By using a series of graded ultra-filters, not only the colloidal solution can be purified, but it can also be separated into fractions having colloidal particles of different sizes.

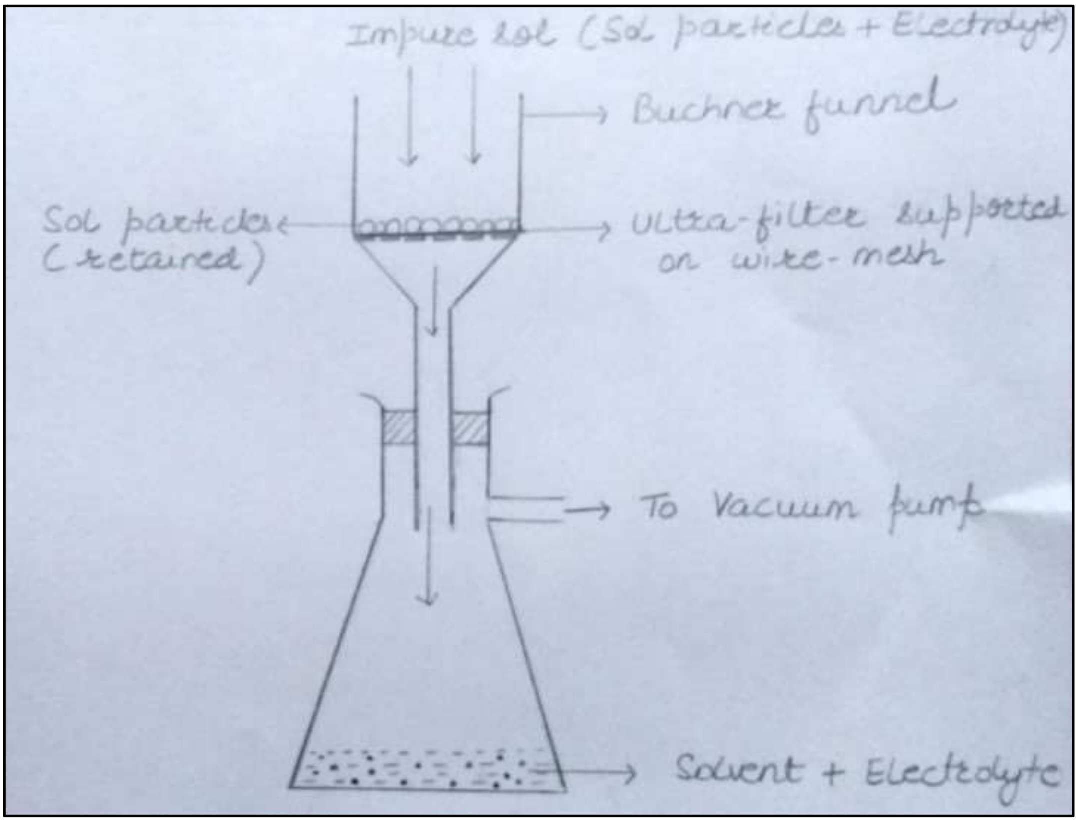


Figure 3.6: Ultra-filtration

C. Ultracentrifugation:

The colloidal particles are always in a constant state of random and zigzag motion in the dispersion medium. Normally they remain suspended in the medium and the process of their settling down is very slow. But it can be enhanced by the application of centrifugal force.

Ultracentrifugation is a method of separating impurity particles from colloidal particles in the sol (according to the difference in their densities and / or particle size) by applying centrifugal force that is generated by spinning the colloidal solution around an axis (in a rotor) at a very high speed. The denser colloidal particles settle at the bottom while the lighter impurities remain suspended in the solution. In this purification process, the impure colloidal solution or sol is taken in a centrifuge tube and placed inside an ultracentrifuge. The rotor of the ultracentrifuge is spun at a very high speed (15000 revolutions per minute or more) about the central axis, thus generating the centrifugal force.

The colloidal particles being more dense, settle at the bottom of the tube and form the sediment while the impurities remain in the supernatant solution. This supernatant is called centrifugate (Figure 3.7).

The settled colloidal particles are removed from the tube and again dispersed into a fresh dispersion medium to get pure sol.

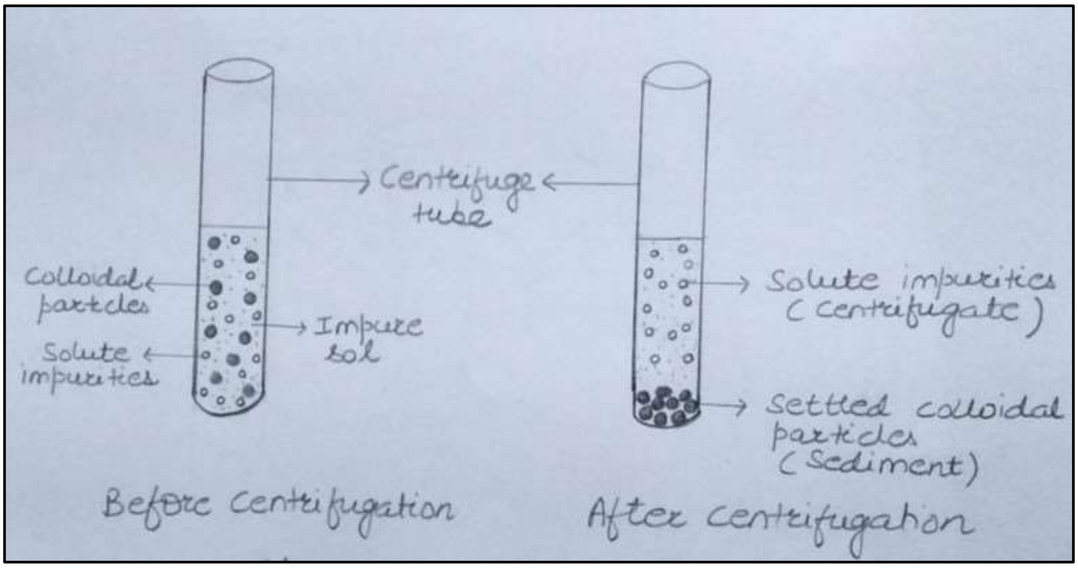


Figure 3.7: Ultracentrifugation of impure sol

3.4 Emulsions:

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

In an emulsion, small droplets of one liquid are dispersed in another immiscible liquid. Normally, one of the two liquids is water and the other liquid, which is insoluble in water, is called oil.

Accordingly, emulsions are of two types:

a. **Oil- in –Water type (O/W type)** in which oil is the dispersed phase (internal or discontinuous phase) and water is the dispersion medium (external or continuous phase). For example- milk (with droplets of liquid fat dispersed in water), vanishing cream, etc.
b. **Water- in – Oil type (W/O type)** in which water forms the dispersed phase and oil forms the continuous phase (dispersion medium). For example- cod liver oil, butter, etc.

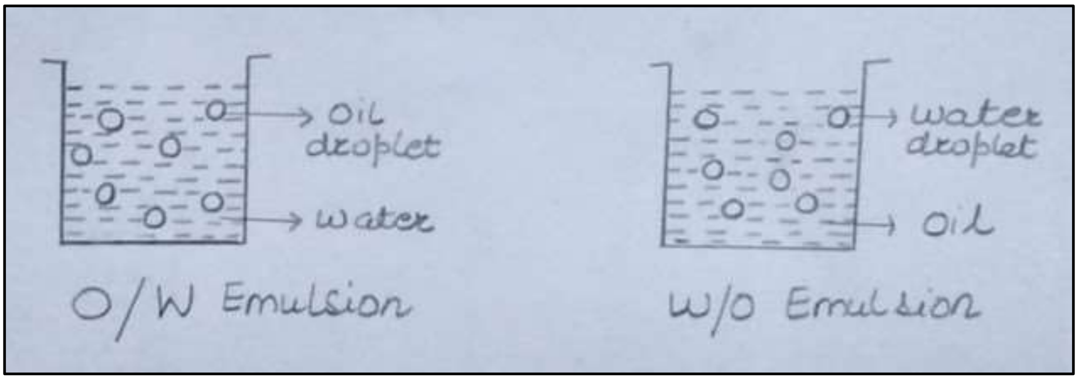


Figure 3.8: Two types of emulsions

- **Emulsification and Emulsifiers:**

The process of dispersing one liquid in a second immiscible liquid, thus forming an emulsion, is called *emulsification*. An emulsion which is obtained by simply mixing and agitating together the two immiscible liquids is unstable. On standing, the liquids separate into two layers. To obtain a stable emulsion, it is essential to add a small amount of a third substance known as *emulsifier* or *emulsifying agent* or *stabilizing agent*. Emulsifiers are broadly of three types:-

a. Certain long chain compounds with polar groups such as soaps, long chain sulphonic acids and sulphates.
b. Lyophilic substances such as proteins, gum, agar-agar.
c. Some insoluble powders such as lead sulphate, calcium carbonate, clay, carbon black, etc.

Role of Emulsifiers: Emulsifiers provide stability to an emulsion. They form a protective film around the droplets of the dispersed phase and thus stabilize the emulsion by reducing the surface tension at the oil-water interface. The protective barrier around the droplets keeps them separated and prevents their coalescence.

- **Preparation of Emulsions:**

Most emulsions are prepared by mixing the two liquids along with a suitable emulsifier and then agitating the mixture by passing it through a counter rotatory agitator or a homogenizer or a colloidal mill. One of the two liquids, as decided by the emulsifier, breaks down under the shearing forces to form droplets which get dispersed in the other liquid, thus forming an emulsion.

The type of emulsion obtained depends on the nature of the emulsifier used. According to the Bancroft's rule "*the phase in which the emulsifier is more soluble forms the continuous phase*". Hence water soluble emulsifiers tend to give O/W emulsions while oil soluble emulsifiers give W/O emulsions.

Griffin proposed a numerical scale, called Hydrophilic-lipophilic balance (HLB) which helps in predicting the type of emulsion that an emulsifier will produce. HLB is the balance of the size and strength of the hydrophilic and lipophilic moieties present on the emulsifier molecule. The HLB scale ranges from 0 - 20. If the HLB number of an emulsifier is in the range of 3.5 – 6 (indicating lipophilic nature), it is more suitable for use in W/O emulsion but if the HLB number is in the range of 8 -18 (indicating hydrophilic nature), the emulsifier is commonly used for O/W emulsions.

Examples: Acacia gum, whey protein are used as emulsifiers for O/W emulsions and emulsifiers such as lamp black (or soot), polyglyceryl oleate are used for W/O emulsions.

3.5 Gels:

The colloidal system in which a liquid is dispersed in a solid is called gel. Some common examples of gel are: gelatin, jellies, fruit jams, curd, agar-agar, shoe-polish, silica gel, alumina gel, etc. It is observed that on cooling a warm solution of gelatin, it sets into a semi-solid mass (a gel). In the similar way, many lyophilic sols and some lyophobic sols of sufficiently high concentration, on coagulation under certain conditions, change into a semi-rigid and jelly like mass which encloses the whole liquid present in the sol.

This process of transforming a sol into a gel is called gelation. Some common lyophilic sols which convert into a gel are- gum arabic, agar-agar, starch, etc. Lyophobic sols that can undergo gelation are- silicic acid, ferric hydroxide, ferric phosphate sols, etc.

Based on their properties, gels have been divided into two categories:

a. **Elastic Gels:** These gels possess the property of elasticity. On partial dehydration, they form an elastic solid which readily converts into the original form by addition of water followed by slight warming, if necessary. Examples of elastic gels are gelatin, agar-agar, starch, etc.
b. **Non-Elastic Gels:** These gels do not possess the property of elasticity. On dehydration, they become glassy or change into a powder which cannot be converted back into the original gel by addition of water followed by warming. Silica gel, alumina gel are examples of non-elastic gels.

A. Preparation of Gels:

The following methods can be used for the preparation of gels:

- **By cooling sols of moderate concentration:** As discussed above, certain hydrophilic sols of moderate concentration, that have been prepared in hot water, change into a gel on cooling. In such sols, the particles are highly hydrated. On cooling, they come closer and cluster together to form larger aggregates which eventually form a semi-solid framework that encloses the entire dispersion liquid (Figure 3.9). This results in the formation of a semi - solid rigid mass with gel structure. For example- gels of gelatin, agar-agar, etc. can be prepared by this method.

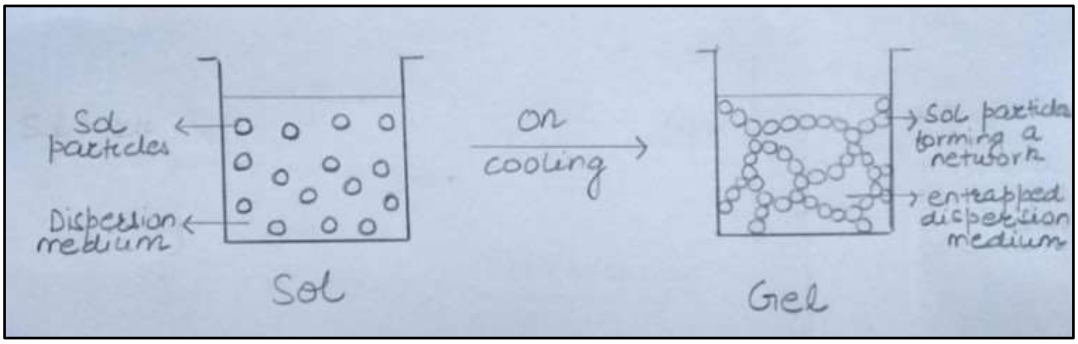


Figure 3.9: Formation of gel from sol

- **By double decomposition:** This method is used to prepare hydrophobic gels such as silicic acid (silica gel) and aluminium hydroxide (alumina gel).

For preparation of silica gel, hydrochloric acid is added to an aqueous solution of sodium silicate. Highly hydrated silicic acid is precipitated which on standing changes into a gel.

$$Na_2SiO_3\,(aq.) + 2HCl \rightarrow \underset{\text{Hydrated silicic acid}}{H_2SiO_3.nH_2O\downarrow} + 2NaCl$$

In the similar way, alumina gel can be prepared by mixing solutions of sodium hydroxide and aluminium chloride of suitable concentrations. As a result, an extensively hydrated precipitate of aluminium hydroxide is obtained which on standing sets into a gel.

$$AlCl_3 + 3\,NaOH \rightarrow \underset{\text{Hydrated aluminium hydroxide}}{Al\,(OH)_3.nH_2O\downarrow} + 3\,NaCl$$

- **By change of solvents:** Certain hydrophobic gels have been prepared using this method. For example- When ethyl alcohol is rapidly added to an aqueous solution of calcium acetate of adequate concentration, the salt separates out to form a colloidal solution. When allowed to stand, it sets into a semi- rigid gel of calcium acetate enclosing the entire alcohol.

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4. Properties of Colloidal Solutions

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Introduction:

Colloid science concerns systems in which one or more of the components has at least one dimension within the nanometre (10^{-9}m) to micrometre ($l0^{-6}$m) range. The adjective 'micro-heterogeneous' provides an appropriate description of most colloidal systems as they consist of a dispersed phase (or discontinuous phase) distributed uniformly in a dispersion medium (or continuous phase). The range of colloidal systems of practical importance and their processes is vast. They have special properties which are of great practical importance, and they were appropriately described by Ostwald as lying in the World of Neglected Dimensions. A full understanding of the properties of colloids calls upon a wide range of physical and chemical ideas, while the multitude of colloidal systems presented to us in nature, and familiar in modern society, exhibit a daunting complexity.

A detailed and fundamental theoretical understanding of colloidal behavior is possible only through a thorough knowledge of broad areas of physics, chemistry, mathematical physics, biological structures, and biological processes. On the experimental side there is an ever-increasing emphasis on the application of modern physical techniques to colloidal problems. Colloid science is truly an interdisciplinary subject.

In this chapters an attempt is made to summarize the basic concepts related to properties of colloidal solutions which can help readers to get an insight of colloid science.

4.1 Nature:

Colloidal solutions are heterogenous and polydispersed in nature. They consist of two phases: Dispersed phase and dispersion medium where the molecules or particles vary in size.

4.2 Particle Shape:

Colloidal particles can be classified according to shape as corpuscular, laminar, spherical, or linear (Figure 4.1). Many colloidal systems contain spherical or nearly spherical particles. Emulsions, latexes, liquid aerosols, etc., contain spherical particles. Certain protein molecules are approximately spherical. The crystallite particles in dispersions such as gold and silver iodide sols are sufficiently symmetrical to behave like spheres. Corpuscular particles which deviate from spherical shape can often be treated theoretically as ellipsoids of revolution. Many proteins approximate this shape. Iron (III) oxide and clay suspensions are examples of systems containing plate-like particles. High-polymeric material usually exists in the form of long thread like straight or branched-chain molecules.

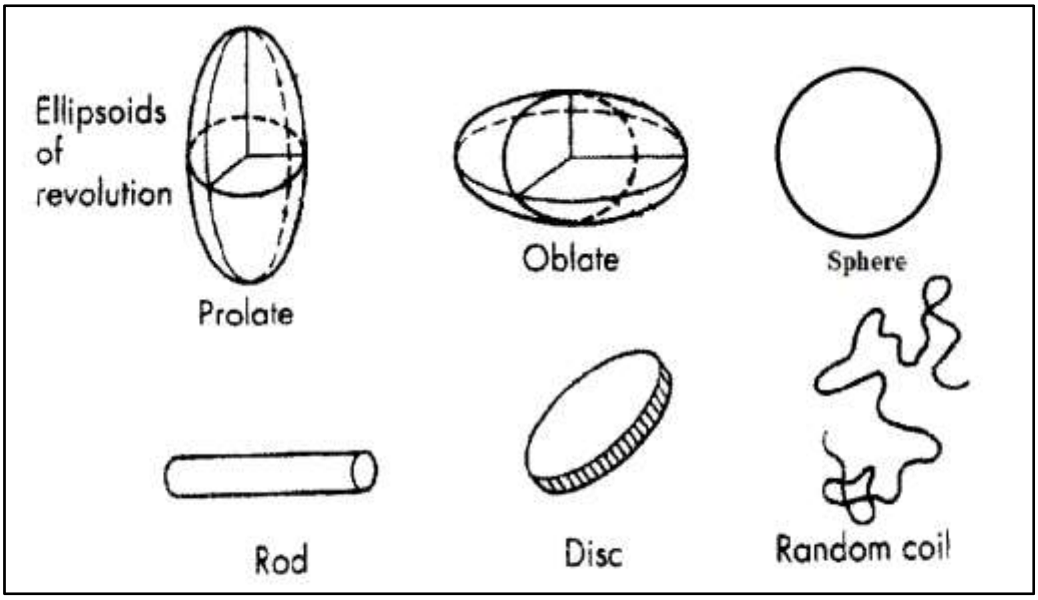


Figure 4.1: Some model representations of colloidal particles.

When particles aggregate together, many different shapes can be formed. These do not necessarily correspond to the shape of the primary particles.

4.3 Filterability:

Colloids can easily pass-through filter papers but can not diffuse through parchment or other fine membranes due to their particle size, which is smaller than pore size of filter paper and larger than pore size of fine membranes.

4.4 Visibility:

Colloidal particles cannot be seen through naked eyes or ordinary microscope due to their exceedingly small size. The shortest wavelength in visible spectra is about 4000 Å. Hence, we cannot see any object less than 200µm and colloidal particles have sizes less than 200µm.

Recently new techniques like Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and Scanning Transmission Electron Microscope (STEM) are used to determine the size and shape of colloidal particles.

4.5 Kinetic Properties:

In this section we will try to understand the properties of colloidal particles related to their movement. Colloidal particles exhibit movement under different circumstances, it could be random, or it could be due to various factors like gravitational field, electrical environment, concentration gradient, etc. (Figure 4.2).

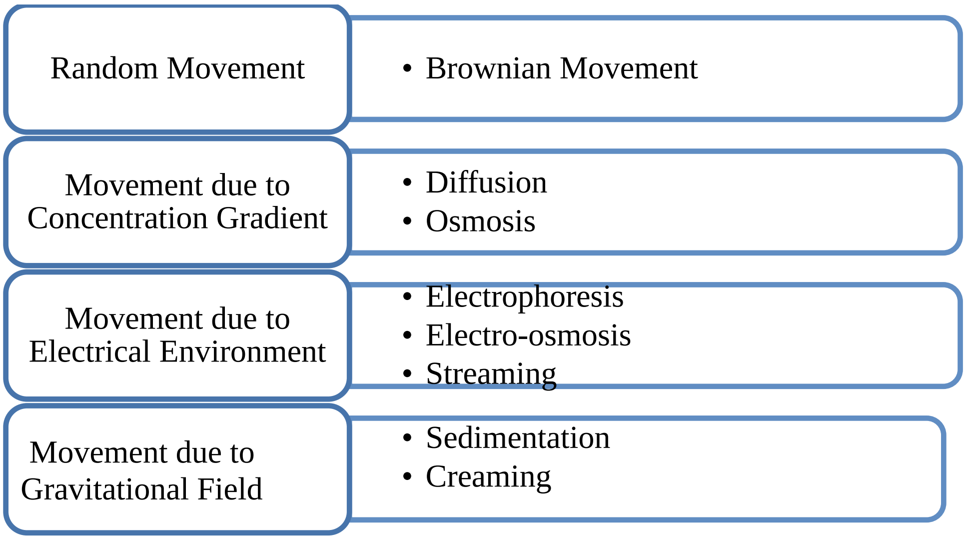


Figure 4.2: Kinetic properties of colloidal solutions

Here, we will cover Brownian movement, diffusion, and various osmotic phenomena. Next, we will briefly deal with sedimentation and creaming in a gravitational field. We will discuss electro-kinetic properties like, electrophoresis, electro-osmosis, and streaming potential in detail in a different section.

4.5.1 Brownian Motion:

In 1827, Robert Brown, an English botanist first observed the random stepwise or zig-zag movement of colloidal particles (Figure 4.3). It was later named after him as Brownian motion and provided early evidence for the molecular kinetic theory. It was interpreted as arising from the random bombardment of the molecules of the surrounding dispersion medium on the particles of dispersed phase. Now, the questions that arise here are, what will be the speed of colliding particles, are the collisions occurring at constant speed, what will be the impact of collision on the direction of motion of particle?

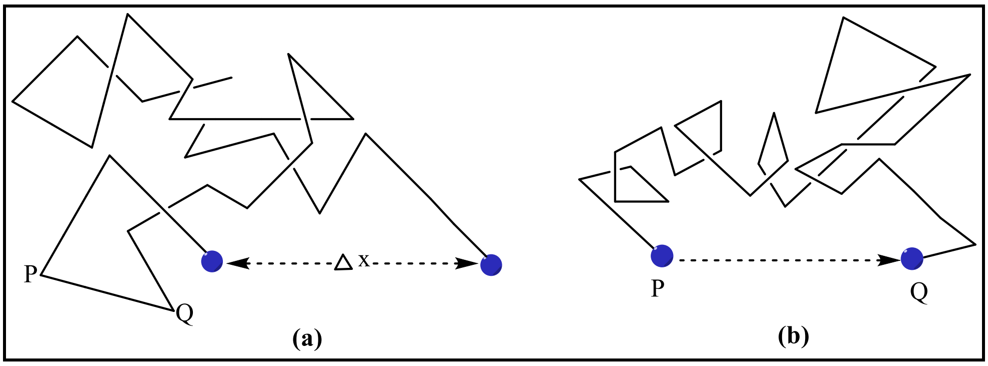


Figure 4.3: Schematic representation of the zig-zag stepwise path executed by a particle doing Brownian motion. **(a)** After successive time intervals δt, the particle is shown at a

position with the total displacement Δx after a time Δt. **(b)** If δt is longer than the gap between collisions of molecules of the medium with the particle, then each of the steps in (a), e.g., PQ, is itself comprises an array of random substeps executed on a shorter timescale, as represented in (b). The shorter δt will result in more fine-grained representation of the motion.

To answer these questions, one must understand that the molecules of the medium immediately adjacent to the particles can move randomly in any direction and their speeds are distributed according to the Maxwell-Boltzmann law. The impact of the collision on the colloidal particle is determined by the force acting upon its surface and it is proportional to both the velocity of the molecules of dispersion medium and the frequency with which they are colliding with the particles of dispersed phase. The later is proportional to the local density of the molecules within one free path of the surface. Since the local density and molecular velocity in a liquid fluctuates, the force on unit area of particle surface will also fluctuate. At any instant, the particle will feel a net force arising due to the imbalance of forces on various parts of its surface [Figure 4.4(a)]. Thus, the direction and magnitude of the resultant force will vary randomly from instant to instant, resulting in a zig-zag motion of the particle.

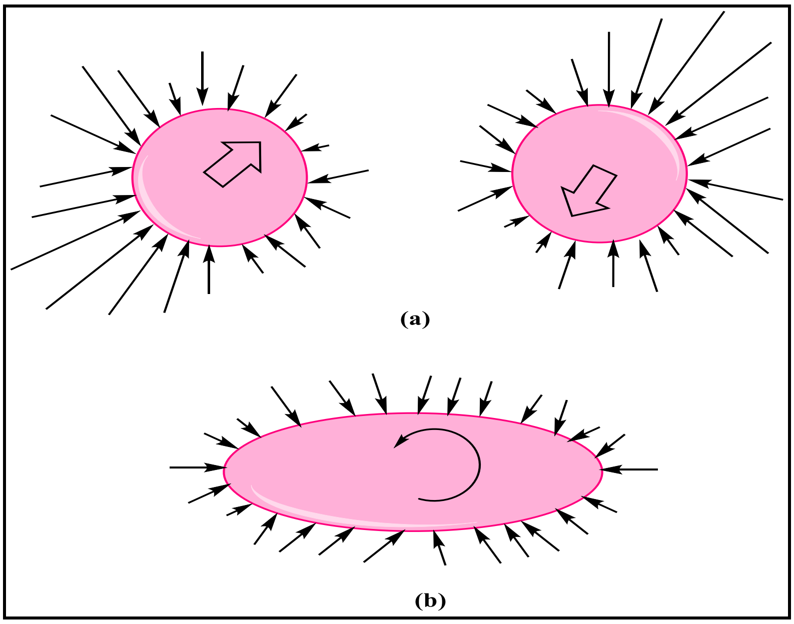


Figure 4.4: (a) Resultant force on a particle arising due to the random forces caused by the bombardment of molecules of the dispersion medium; the direction and magnitude of the resultant force vary randomly from instant to instant. **(b)** Rotational Brownian motion of a non-spherical particle.

To understand Brownian motion more clearly one must consider the equation of motion of the particle facing randomly varying instantaneous forces (Langevin, 1908). The resultant motion of this force is opposed by the resistance arising from viscous forces, which is proportional to the velocity of the particle. Solution of this equation leads to an expression for the mean square velocity of a large number of particles.

According to the principle of equipartition of energy, the mean square velocity is equal to 3kT/m, where m is the mass of the particle. This can lead to the mean Brownian displacement $\overline{\Delta x}$ of a particle from its original position after a time Δt and is given by:

$$\overline{\Delta x^2} = (2kT/B)\ \Delta t, \qquad (1)$$

where B is the viscous friction coefficient. Considering colloidal particles to be spherical we can use Stokes' equation which will relate B to the viscosity of the medium (η) and the radius of the particle (r):

$$B = 6\pi\eta r, \qquad (2)$$

hence

$$\overline{\Delta x^2} = (kT/3\pi\eta r)\ \Delta t, \qquad (3)$$

$$\overline{\Delta x} = \{(kT/3\pi\eta r)\ \Delta t\}^{1/2}, \ (4)$$

Note that the mass of the particle does not appear openly in equation (3), but the mean square displacement is proportional to the reciprocal of its radius and hence to the reciprocal of the cube root of its volume. This means that the smaller the particle the more extensive the Brownian motion. We also observe the important result from equation (4), that the mean displacement is proportional to the square root of the time.

Now imagine if the particles are non-spherical then what will happen? To answer this one must consider that in this case, firstly, the simple form of Stokes' equation will not be applicable, and secondly, the unsymmetrical forces applied on the particle by molecules of dispersion medium cause the particles to rotate. This phenomenon is called Brownian rotation or rotational diffusion where particles undergo rotational motion rather then translational motion [Figure 4.4(b)].

In conclusion, Brownian motion is a three dimensional 'random walk' taken by the particles due to random collisions with molecules of medium and is consisted of a sequence of steps whose directions being chosen at random without being affected by the direction of the preceding step.

4.5.2 Diffusion:

In colloidal solutions diffusion occurs as a consequence of Brownian motion. Let us consider consider a thin sheet which initially contains c^0 particles in unit volume [Figure 5 (a)] and observe the distribution of these particles after a time Δt. They will have spread out in both directions.

Random walks follow the square root of time (See equation 4) as compared to linear or ballistic walks which directly follow time thus, the chance that a given particle will have reached a distance Δx is proportional to $\Delta t^{1/2}$.

On observing the graph between distance covered Δx and concentration c we will find that the sharp initial concentration peak will spread out into a broad peak, which has the shape of a Gaussian probability curve [Figure 4.5 (b)].

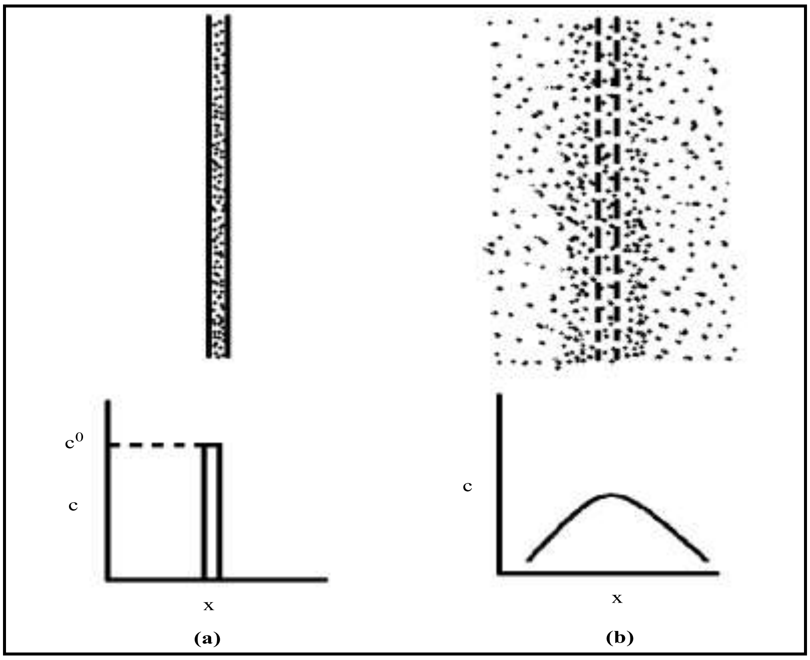


Figure 4.5. Diffusion of particles from a thin sheet at a concentration c^0 **(a)** at zero time, **(b)** after a time interval.

Consider a plane AB (Figure 4.6) passing through a dispersion and separating regions of concentration c_1 and c_2, where $c_1 > c_2$. Let the average Brownian displacement of a given particle perpendicular to AB in time Δt be $\overline{\Delta x}$.

For each particle, this displacement has equal probability of being 'left to right' or 'right to left'. The net mass of particles displaced from left to right across unit area of AB in time Δt is, therefore given by :

$$m = \frac{(c_1 - c_2)\overline{\Delta x}}{2} = \frac{(c_1 - c_2)\overline{\Delta x^2}}{2\overline{\Delta x}} \qquad 5$$

If $\overline{\Delta x}$ is small,

$$\frac{(c_1 - c_2)}{\overline{\Delta x}} = -\frac{\partial c}{\partial x} \qquad 6$$

Therefore,

$$m = -\frac{1}{2}\frac{\partial c}{\partial x}\overline{\Delta x^2} \qquad 7$$

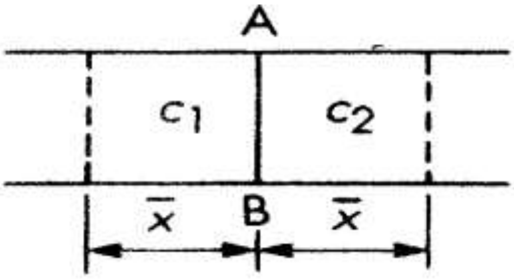


Figure 4.6: Diffusion across the plane AB passing through a dispersion and separating regions of concentration c_1 and c_2, where $c_1 > c_2$.

Now, as we know that diffusion is the tendency for molecules to migrate from a region of high concentration to a region of lower concentration and is a direct result of Brownian motion. Fick's first law of diffusion states that the mass of substance dm diffusing in the x direction in a time Δt across an area A is proportional to the concentration gradient $\partial c/\partial x$ at the plane in question:

$$dm = - DA \frac{\partial c}{\partial x} dt \qquad 8$$

Where D, denotes diffusion constant, it is a constitutive parameter that describes the constitution of the diffusing system. The minus signs in equation 6, 7, and 8 denote that diffusion takes place in the direction of decreasing concentration.

If the diffusion taking place in unit area ($A = 1\ m^2$) then

$$dm = - D \frac{\partial c}{\partial x} dt$$

$$m = - D \frac{\partial c}{\partial x} t \qquad 9$$

On comparing equations 7 and 9 we will get

$$-\frac{1}{2}\frac{\partial c}{\partial x}\overline{\Delta x^2} = - D \frac{\partial c}{\partial x} t$$

$$\overline{\Delta x} = (2Dt)^{\frac{1}{2}} \qquad 10$$

The above interpretation of diffusion is based on a molecular model of Brownian motion and follows broadly the arguments of Einstein (1905). On comparing equation 10 with equation 4 we can get the value of diffusion constant D, which agrees with Stokes-Einstein Equation.

$$(2Dt)^{\frac{1}{2}} = \{(kT/3\pi\eta r)\,\Delta t\}^{1/2}$$

$$D = \frac{kT}{6\pi\eta r} \qquad 11$$

4.5.3 Osmosis:

The phenomenon of osmosis is another example in which molecules flow from a location of higher chemical potential to a region of lower potential. In an osmotic experiment a sample of dispersion in compartment II is separated from pure medium in compartment I by a semi-permeable membrane which allows passage of molecules of the medium but is completely impermeable to particles of the suspension (Figure 4.7).

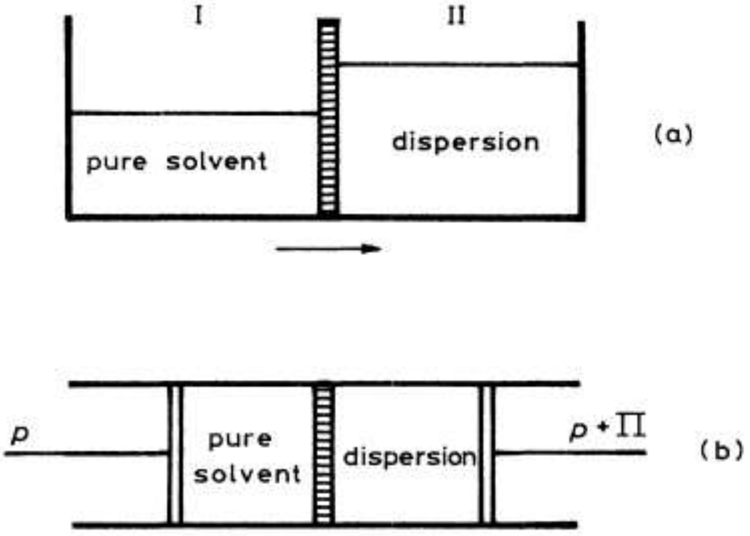


Figure 4.7: Osmosis. (a) Dispersion separated from pure solvent by a semi-permeable membrane. Solvent molecules diffuse into the dispersion. (b) Osmotic equilibrium is set up when an excess pressure Π is applied to the dispersion to stop the flow of solvent through the membrane.

The tendency to equalise chemical potentials (and, hence, concentrations) on either side of the membrane results in a net diffusion of solvent across the membrane. The counter-pressure necessary to balance this osmotic flow is termed the osmotic pressure (Π).

Osmosis can also take place in gels and constitutes an important swelling mechanism. The osmotic pressure Π of a solution is described in general terms by the virial equation:

$$\Pi = cRT\left(\frac{1}{M} + A_2c + A_3c^2 + \ldots\right) \qquad 12$$

where c is the concentration of the solution (expressed as mass of solute divided by volume of solution), M is the molar mass of the solute, and A_2, A_3, etc., are constants.

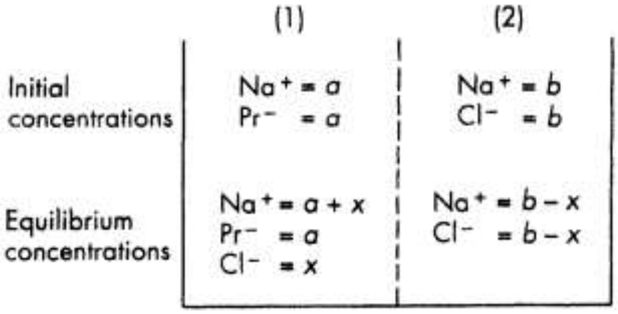
Therefore,

$$M = \frac{RT}{\lim\limits_{c \to 0} \Pi / c} \qquad 13$$

Hence, in principle, the molar mass of the particles can be calculated from measurements of osmotic pressure (Π) as a function of concentration in an extremely dilute suspension. However, in practice, the magnitude of osmotic pressure (Π) is so small for particulate dispersions that osmometry does not provide a useful route to particle size determination. It is nevertheless used for the determination of the molar mass of macromolecules.

A. Donnan Equilibrium:

A somewhat more complex situation arises when osmotic equilibrium is set up between solutions containing both non-diffusible and (inevitably) diffusible ionic species. Gibbs predicted and later Donnan demonstrated that if the non-diffusible ions are located on one side of a semipermeable membrane, the distribution of the diffusible ions become unequal and when equilibrium is attained, the diffusion is greater on the side of the membrane containing the non-diffusible ions. This distribution can be calculated thermodynamically, although a simpler kinetic treatment will suffice. Let us assume a simple example in which equal volumes of solutions of the sodium salt of a protein (PrNa, non-diffusible ionic species) and of sodium chloride (diffusible ionic species) with respective equivalent concentrations *a* and *b* are initially separated by a semipermeable membrane, as shown in Figure 4.8.



	(1)	(2)
Initial concentrations	$Na^+ = a$ $Pr^- = a$	$Na^+ = b$ $Cl^- = b$
Equilibrium concentrations	$Na^+ = a + x$ $Pr^- = a$ $Cl^- = x$	$Na^+ = b - x$ $Cl^- = b - x$

Figure 4.8: The Donnan membrane equilibrium

To maintain overall electrical neutrality Na^+ and Cl^- ions must diffuse across the membrane in pairs. Now, assume that *x* amount of Na^+ and Cl^- ions diffused from compartment (2) to (1) till equilibrium is reached. Thus, equilibrium concentrations in compartment (1) will be,

Concentration of $Na^+ = a + x$

Concentration of $Pr^- = a$

Concentration of $Cl^- = x$

And in compartment (2) will be,

Concentration of $Na^+ = b - x$

Concentration of $Cl^- = b - x$

Now, one must keep in mind the rate of diffusion in any particular direction will depend on the probability of an Na^+ and a Cl^- ion arriving at a given point on the membrane surface simultaneously. This probability is proportional to the product of the Na^+ and CI^- ion concentrations (strictly, activities), so that,

$$\text{rate of diffusion from (1) to (2)} = k(a+x)\,x$$

$$\text{rate of diffusion from (2) to (1)} = k(b-x)^2$$

At equilibrium, these rates of diffusion are equal i.e.,

$$(a + x)\,x = (b-x)^2 \tag{14}$$

$$x = \frac{b^2}{a+2b} \tag{15}$$

At equilibrium, the concentrations of diffusible ions in compartments (1) and (2) are $(a+2x)$ and $2(b-x)$, respectively, so,

$$\text{Excess diffusible ion concentration} = (a+2x) - 2(b-x)$$

$$= (a-2b+4x) \tag{16}$$

Substituting value of x from equation 15 in equation 16,

$$\text{Excess diffusible ion concentration} = a^2/(a+2b) \tag{17}$$

Clearly, due to unequal ion transfer a pressure difference will be established and under these circumstances' equilibrium involves not only the establishment of a pressure difference but also an electrical potential difference across the membrane, which is given by,

$$\psi^2 - \psi^1 = \left(\frac{RT}{F}\right) ln\left(\frac{x_{Na}^1}{x_{Na}^2}\right) = \left(\frac{RT}{F}\right) ln\left(\frac{x_{Cl}^2}{x_{Cl}^1}\right) \tag{18}$$

Where,

ψ^1 = electric potential developed in compartment (1)

ψ^2 = electric potential developed in compartment (2)

F = Faraday ((96 487 coulombs mo1^{-1})

x^1 = number of diffusible ions in compartment (1)

x^2 = number of diffusible ions in compartment (2)

Thus, three effects are observed:

- An osmotic pressure is set up.
- There is a net transfer of salt into the compartment containing the non-diffusable ion. This applies whether this ion is an anion or a cation.
- An electrical potential difference (membrane potential) is set up across the membrane.

4.5.4 Sedimentation and Creaming:

If the particles of a colloidal dispersion have different density from that of the medium then, they will tend to either sink (sediment), if they are denser than the medium, or rise to the surface (cream), if they are less dense due to the gravitational force. In either case a concentration gradient of particles is produced to restore a uniform concentration. Thus, gravitational forces are opposed by diffusion, and a steady state is set up in which the two processes are in balance. We can express the gravitational force as $-(\rho_p - \rho_m)v g$, where ρ_p and ρ_m are the densities of particle and medium, respectively, and v is the volume of a particle. The driving force for diffusion is (dμ/dh) where (dμ/dh) represents change in chemical potential with changing height. Hence in the steady state,

$$-(\rho_p - \rho_m)v g = (d\mu/dh) = kT(d\ln c/dh) \qquad 19$$

Where, c = Concentration of the dispersion

$$kTd\ln c = -(\rho_p - \rho_m)mgdh \qquad 20$$

Integrating this equation between a height h^0 and $h^0 + \Delta h$ we obtain,

$$c/c^0 = \exp[-(\rho_p - \rho_m)v g\Delta h/kT \qquad 21$$

The above argument brings out very clearly the way in which physicochemical equilibrium is achieved by the balance between the effects of potential energy (gravitational energy here) and thermal energy (represented here by diffusion or Brownian motion).

The experimental test of equation 21, and of 3, was first carried out by Perrin (1908) in his classical work on the sedimentation of gamboge particles in the Earth's gravitational field. This relationship is now widely applied in two main areas, first, to determine particle sizes of exceedingly small particles and, secondly, to study both the diffusion and molar mass of macromolecules by increasing the gravitational force using a centrifuge (or ultracentrifuge).

4.6. Electrical Properties:

4.6.1 Charge on Colloids:

When brought in to contact with polar medium, most substances acquire a surface electric charge, may be due to ionisation, ion adsorption, or ion dissolution. This surface charge influences the distribution of nearby ions in the polar medium as counterions (ions of opposite charge) are attracted towards the surface and co-ions (ions of like charge) are repelled away from the surface. Now this, along with the mixing tendency of thermal motion, results in the formation of an electric double layer made up of the charged surface and an excess of counter-ions over co-ions distributed in a diffuse manner in the polar medium. Hence, the theory of the electric double layer gives an insight about distribution of ions and, the magnitude of the electric potentials occurring in the locality of the charged surface. It is important to understand this concept as it provides an understanding of electrokinetic behaviour and stability of charged colloidal systems.

A. Origin of Charge:

The charge on colloidal surface can be acquired either by ionization, adsorption, dissolution, or presence and orientation of dipoles. We will now discuss the detailed account of the origin of charge on colloidal surface.

a. Ionisation:

Several colloidal solutions acquire their charge through the direct ionisation of their surface groups in polar media. Proteins represent a perfect case in this scenario as they gain their charge in aqueous medium due to ionization of carboxyl and amino groups into COO^- and NH_3^+ ions. The ionisation of such colloidal particles and their net molecular charge, depends strongly on the pH of the solution. For example, in acidic medium, a protein molecule will be positively charged while in basic medium it will be negatively charged (Figure 4.9). The pH at which the net charge (and electrophoretic mobility) is zero is called the iso-electric point.

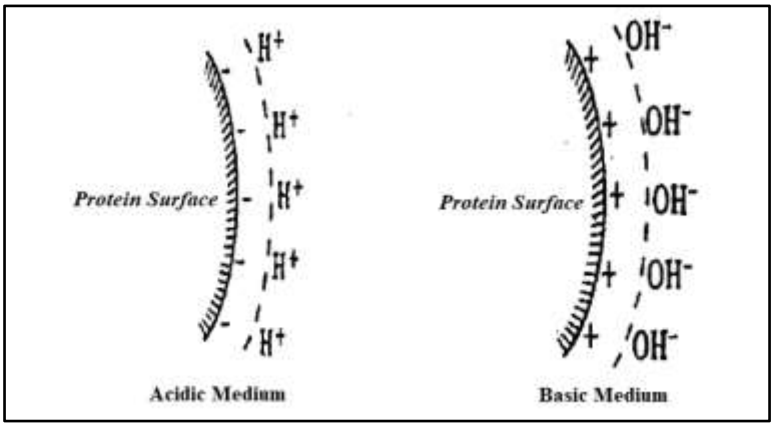


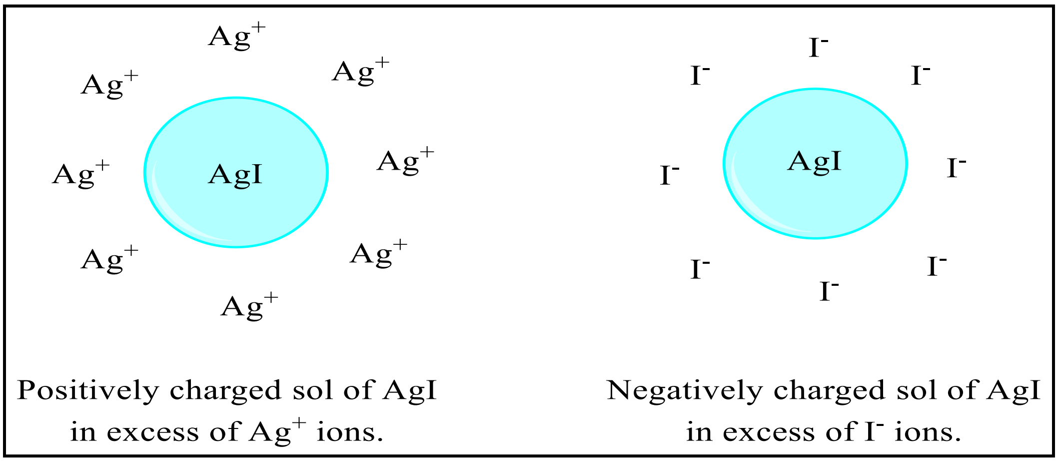
Figure 4.9: Origin of Charge in proteins due to ionization of surface groups.

b. Ion Adsorption:

A net surface charge can also be attained by the unequal adsorption of oppositely charged ions which results in either positive or negative surface excess concentrations. Surfaces which are already charged (e.g., by ionisation) usually show a preferential tendency to adsorb counter-ions, especially those with a high charge number. It is possible that a reversal of charge will be observed because the charge will be determined by adsorbed counter-ions. Interestingly, the surfaces in contact with aqueous media are more often negatively charged than positively charged. This is a consequence of the fact that cations are usually more hydrated than anions and so have the greater tendency to reside in the bulk aqueous medium, whereas the smaller, less hydrated, and more polarising anions have the greater tendency to be specifically adsorbed. Hydrocarbon oil droplets and even air bubbles suspended in water and in most aqueous electrolyte solutions have negative electrophoretic mobilities (i.e., they migrate towards the anode under the influence of an applied electric field). This net negative charge is explained in terms of negative adsorption of ions. Hydrated (e.g., protein and polysaccharide) surfaces adsorb ions less readily than hydrophobic (e.g., lipid) surfaces.

c. Ion Dissolution:

Ionic substances can acquire a surface charge by virtue of unequal dissolution of the oppositely charged ions of which they are composed. For example, silver iodide particles in aqueous suspension are in equilibrium with a saturated solution of which the solubility product, $a_{Ag^+}a_{I^-}$, is about 10^{-16} at room temperature. With excess I^- ions, the silver iodide particles are negatively charged; and with sufficient excess Ag^+ ions, they are positively charged (Figure 4.10). The zero point of charge is not at pAg 8 but is displaced to pAg 5.5 (pI 10.5), because the smaller and more mobile Ag^+ ions are held less strongly than the I^- ions in the silver iodide crystal lattice. The silver and iodide ions are referred to as *potential-determining* ions since their concentrations determine the electric potential at the particle surface. Silver iodide sols have been used extensively for testing electric double layer and colloid stability theories.



Positively charged sol of AgI in excess of Ag^+ ions.

Negatively charged sol of AgI in excess of I^- ions.

Figure 4.10: Surface charge due to Ion dissolution

d. Adsorption and Orientation of Dipoles

Net surface charge may not be affected by adsorption of dipolar molecules, but the orientation of dipolar molecules layer at the surface may make a significant contribution to the nature of the electric double layer.

4.6.2 Electrical Double Layer:

The electric double layer can be considered as consisting of two regions: 'an inner region which may include adsorbed ions, and a diffuse region in which ions are distributed according to the influence of electrical forces and random thermal motion. The diffuse part of the double layer will be discussed first.

Quantitative treatment of the electric double layer represents an extremely difficult and, in some respects, unresolved problem. The requirement of overall electroneutrality is, for any dividing surface, the charge density (charge per unit area) must be $+\sigma$ and $-\sigma$ on the opposite sides of the surface. Therefore, it dictates, that the magnitude of σ will depends on the location of the surface. Surface location is not a straightforward matter because of the geometric and chemical heterogeneity of the colloidal solutions. It follows, furthermore, that electric double-layer parameters (potentials, surface charge densities, distances) are not agreeable to unmistakeable definition. Despite this, various simplifications and approximations were made to develop double-layer theory at a high level of sophistication and usefulness. The simplest quantitative treatment of the diffuse part of the double layer is that due to Gouy (1910) and Chapman (1913), which is based on the following model:

- The surface is assumed to be of infinite extent, flat, and uniformly charged.
- The ions in the diffuse part of the double layer are assumed to be point charges distributed according to the Boltzmann distribution.
- The solvent is assumed to influence the double layer only through its dielectric constant, which is assumed to have the same value throughout the diffuse part.
- A single symmetrical electrolyte of charge number z will be assumed. This assumption facilitates the derivation while losing little owing to the relative unimportance of co-ion charge number.

Let the electric potential be ψ_0 at a flat surface and ψ at a distance *x* from the surface in the electrolyte solution. Taking the surface to be positively charged (Figure 4.11) and applying the Boltzmann distribution, Poisson’s equation, and Debye-H*ü*ckel approximation we will finally get,

$$\psi_0 = \sigma_0 / \varepsilon\, \kappa \qquad \text{(at low potential)} \quad 22$$

Where,

ψ_0 = Surface Potential

σ_0 = Charge Density

ε = Permittivity

κ = Debye's Length (represents distance of ions from charged surface)

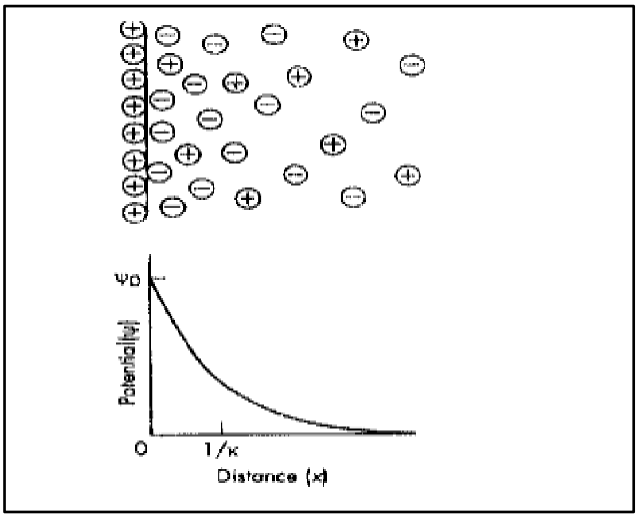


Figure 4.11: Schematic representation of a diffuse electric double layer (Gouy and Chapman model).

Therefore, the surface potential ψ_0, depends on both the surface charge density σ_0 and (through κ) on the ionic composition of the medium. If the double layer is compressed (i.e., κ increased), then either σ_0 must increase, or ψ_0 must decrease, or both.

The above treatment of the diffuse double layer assumes point charges in the electrolyte medium, however, in many colloidal systems, the double layer is created by the preferential adsorption of potential-determining ions. For example, the potential ψ_0 at the surface of a silver iodide particle depends on the concentration of silver (and iodide) ions in solution. Here, the finite size of the ions will, however, limit the inner boundary of the diffuse part of the double layer since the centre of an ion can only approach the surface to within its hydrated radius without becoming specifically adsorbed. In such cases, unfortunately, the Debye-Hückel approximation is often not applicable.

Stern (1924) proposed a model in which the double layer is divided into two parts separated by a plane (the Stern plane) located at about a hydrated ion radius from the surface and considered the possibility of specific ion adsorption (Figure 4.12). Specifically adsorbed ions are those which are attached (albeit temporarily) to the surface by electrostatic and/or van der Waals forces strongly enough to overcome thermal agitation. The centres of any specifically adsorbed ions are in the Stern layer- i.e., between the surface and the Stern plane. Ions with centres located beyond the Stern plane form the diffuse part of the double layer, for which the Gouy-Chapman treatment outlined before, is applicable.

The potential changes from ψ_0 (the surface or wall potential) to ψ_d (the Stern potential) in the Stern layer, and decays from ψ_d to zero in the diffuse double layer.

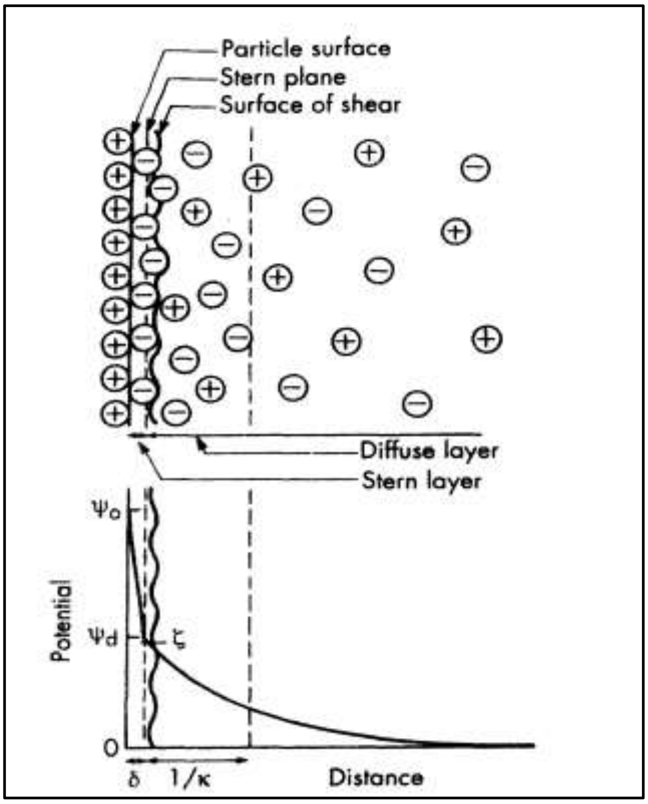


Figure 4.12 Schematic representation of the structure of the electric double layer according to Stern's theory

Estimation of Stern potential (ψ_d) can be done from electrokinetic measurements. Electrokinetic behaviour (discussed in the following sections of this chapter) depends on the potential at the surface of shear (surface of the tightly bound layer) which is located somewhere between the charged surface and the electrolyte solution. This potential of the surface of shear is called the electrokinetic or ζ (zeta) potential. The exact location of the shear plane (which is a region of rapidly changing viscosity) is another unknown feature of the electric double layer. To understand surface of shear one must understand that in addition to ions in the Stern layer, a certain amount of solvent will probably be bound to the charged surface and form a part of the electrokinetic unit. It is, therefore, reasonable to suppose that the shear plane is usually located at a small distance further out from the surface than the Stern plane and that ζ is, in general, marginally smaller in magnitude than ψ_d (see Figures 11). In tests of double-layer theory it is customary to assume ψ_d and ζ as identical, and the bulk of experimental evidence suggests that errors introduced through this assumption are generally small, especially at lyophobic surfaces. Any difference between ψ_d and ζ will clearly be most pronounced at high potentials ($\zeta = 0$ when $\psi_d = 0$), and at high electrolyte concentration (compression of the diffuse part of the double layer will cause more of the potential drop from ψ_d to zero to take place within the shear plane). The adsorption of non-ionic surfactant would result in the surface of shear being located at a relatively large distance from the Stern plane and a zeta potential significantly lower than ψ_d.

4.6.3 Electrokinetic Phenomena:

Electrokinetic is the general description applied to four phenomena (electrophoresis, electro-osmosis, streaming potential, sedimentation potential) which arise when attempts are made to cut off the mobile part of the electric double layer from a charged surface. If an electric field is applied tangentially along a charged surface, a force is exerted on both parts of the electric double layer.

The charged surface (plus attached material) tends to move in the appropriate direction, while the ions in the mobile part of the double layer show a net migration in the opposite direction, carrying solvent along with them, thus causing its flow.

On the contrary, an electric field is created if the charged surface and the diffuse part of the double layer are made to move relative to each other.

Among all the electrokinetic phenomena, electrophoresis has the greatest practical applicability and has been studied extensively in its various forms, whereas electro-osmosis and streaming potential have been studied to a moderate extent and sedimentation potential rarely, owing to experimental difficulties.

A. Electrophoresis:

Electrophoresis can be understood as the movement of a charged surface plus attached material (i.e., dissolved, or suspended material) relative to stationary liquid by an applied electric field.

The electrophoretic effect can be studied by a simple apparatus shown in Figure 4.13. It consists of a U-tube provided with a stopcock through which it is connected to a funnel shaped reservoir. The reservoir is filled with a reasonable quantity of sol and a small amount of water is placed in the U-tube.

Then, the stopcock is slightly opened to gradually raise the reservoir which leads to introduction of the sol into the U-tube. The water is displaced upwards, producing a sharp boundary in each arm. 50 to 200 volts of voltage is then applied using the platinum electrodes, immersed in water layer only.

The movement of the particles can easily be followed by observing the position of the boundary by means of naked eyes or a lens or a cathetometer. When the particles are positively charged, the boundary on the positive electrode side is seen to move down, and that on the negative electrode side to move up, showing that the particles move toward the negative electrode.

Thus, by noting the direction of motion of particles in the electric field it is possible to determine the sign of the charge carried by the particles. Determination of the rate at which colloidal particles migrate in an electric field can also be done using this technique. This rate is expressed in terms of electrophoretic mobility of colloidal particles.

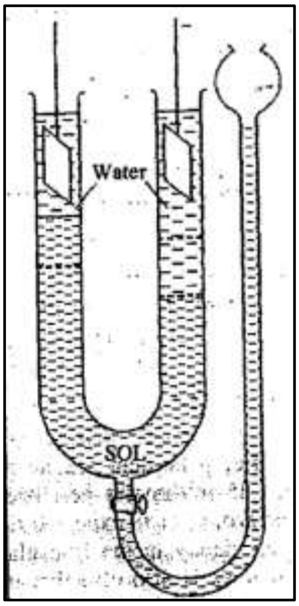


Figure 4.13: Apparatus to study Electrophoresis

The electrophoretic mobility of colloidal particles is defined as the distance travelled by them in one second under a potential gradient of 1 Volt per centimetre. It has been found that the electrophoretic mobility is of colloidal particles are of the same order as those of ions under similar conditions, that is, of the order of $(10 – 60) * 10^{-5}$ cm /s/Volt/cm.

Since different colloidal materials have different mobilities it is possible to separate them from one another from their mixtures. This method has been used for the fractionation of proteins, polysaccharide, nucleic acids, and other complex substances.

B. Electro-Osmosis:

The movement of dispersion medium relative to a stationary charged surface (e.g., a capillary or porous plug) by an applied electric field (i.e., the complement of electrophoresis) is known as electro-osmosis. The pressure necessary to counterbalance electro-osmotic flow is termed the electro-osmotic pressure.

A simple apparatus for studying electro-osmosis is shown in Figure 4.14. The colloidal system is placed in the central compartment A. Compartment A is separated from the compartments B and C, filled with water, by the dialysing membranes M and M’. The water in the compartments B and C also extends to the side tubes. T and T’, as shown. Now, the movement of colloidal particles is restricted by the membranes, therefore, when a potential difference is applied across the electrodes held close to the membranes in the compartments B and C, the water begins to move. If the particles carry negative charge, the water will carry positive charge, therefore, it will start moving towards the cathode and hence the level of water in the side tube T’ would be seen to rise. Similarly, if the particles carry positive charge, the water, which now carries negative charge, will start moving towards the anode and the level of water in the side tube T would start rising.

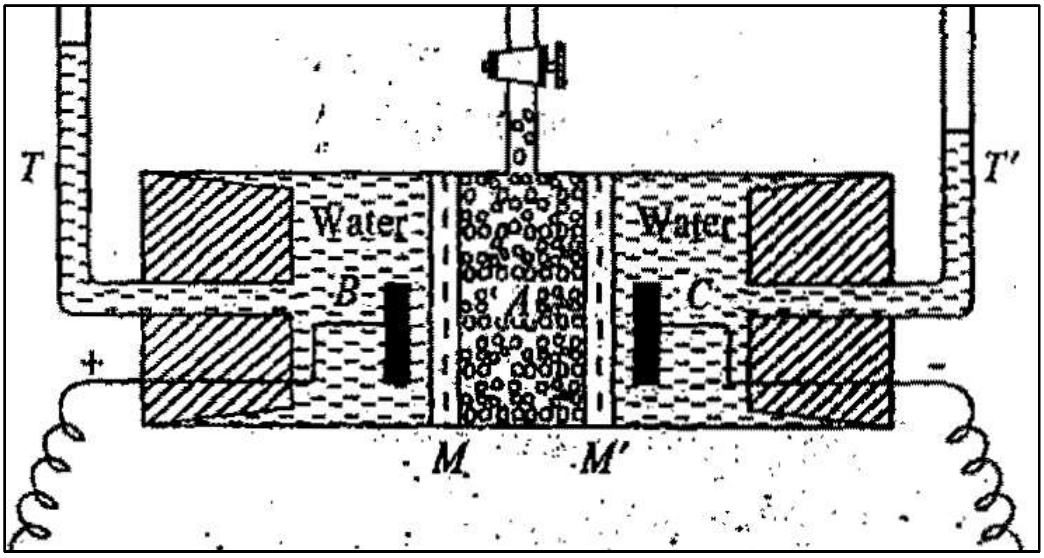


Figure 4.14: Apparatus to study Electro-Osmosis

C. Streaming Potential:

The electric field which is created when liquid is made to flow along a stationary charged surface (i.e., the opposite of electro-osmosis) is called streaming potential.

The development of a streaming potential when an electrolyte is forced through a capillary or porous plug is, in fact, a complex process as charge and mass transfer were occurring simultaneously by several mechanisms.

The liquid in the capillary or plug carries a net charge (that of the mobile part of the electric double layer) and its flow gives rise to a streaming current which consequently generates a potential difference. This potential opposes the mechanical transfer of charge by either back conduction (ion diffusion) or by electro-osmosis (in a much less extent). The transfer of charge due to these two effects is called the leak current, and the measured streaming potential relates to an equilibrium condition when streaming current and leak current cancel each other.

Figure 4.15 depicts a suitable apparatus for studying streaming potentials. A high-resistance voltmeter must be used to minimise current drain. Most of the difficulties associated with streaming potential measurement originate at the electrodes. A superimposed asymmetry potential often develops; however, it can be made to reinforce and oppose the streaming potential by reversing the direction of liquid flow.

The streaming current can be measured if the high-resistance voltmeter is replaced with a microammeter of low resistance compared with that of the plug. An alternating streaming current can be generated by forcing liquid through the plug by means of a reciprocating pump. The main advantage of studying alternating rather than direct streaming currents is that electrode polarisation is far less likely.

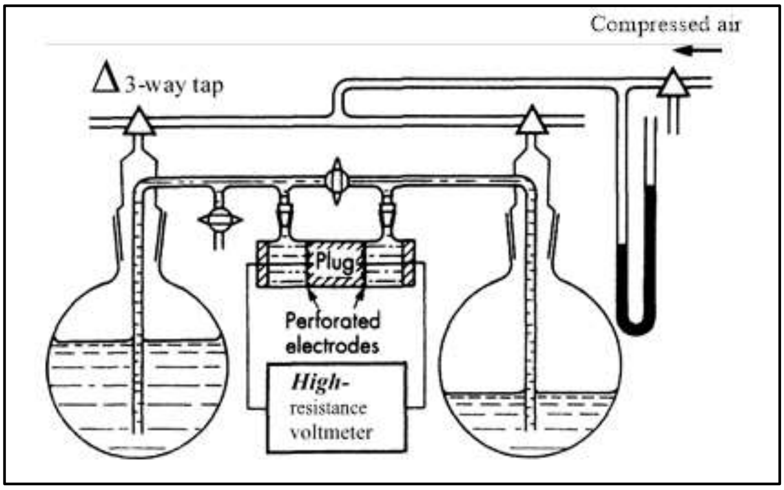


Figure 4.15: A Streaming potential apparatus

D. Sedimentation Potential:

Sedimentation potential can be considered as the opposite of electrophoresis. It can be explained as the phenomena where electric field is created by movement of charged particles relative to stationary medium. Sedimentation potential is studied rarely because of the experimental complexities.

4.6.4 Electrokinetic Theory:

Electrokinetic phenomena are only related to the nature of the mobile part of the electric double layer and may, therefore, be interpreted only in terms of the zeta potential or the charge density at the surface of shear. No direct information is given about the potentials ψ_0 and ψ_d (although, as already discussed, the value of ζ may not differ substantially from that of ψ_d), or about the charge density at the surface of the material in question.

Electrokinetic theory involves both the theory of the electric double layer and that of liquid flow and is quite complicated. In this section the relation between electrokinetically determined quantities (particularly electrophoretic mobility) and the zeta potential will be considered.

For curved surfaces, the shape of the double layer can be described in terms of the dimensionless quantity '$\kappa\alpha$', which is the ratio of radius of curvature to double-layer thickness. When $\kappa\alpha$ is small, a charged particle may be treated as a point charge; when $\kappa\alpha$ is large, the double layer is effectively flat and may be treated as such.

Henry derived a general electrophoretic equation for conducting and non-conducting spheres which takes the form,

$$u_E = \frac{\zeta\varepsilon}{1{\cdot}5\eta}[1 + \lambda F(\kappa\alpha)] \qquad 23$$

Where,

u_E = electrophoretic mobility of the particle

ζ = zeta potential

ε = permittivity of the electrolyte medium

η = viscosity of the medium

λ = overall conductivity of the system

Here, $F(\kappa\alpha)$ varies between zero for small values of $\kappa\alpha$ and 1.0 for large values of $\kappa\alpha$ and $\lambda = (k_0 - k_1)/(2\,k_0 + k_1)$, where k_0 is the conductivity of the bulk electrolyte solution and k_1 is the conductivity of the particles. For small $\kappa\alpha$ the effect of particle conductance is negligible. For large $\kappa\alpha$ the Henry equation predicts that λ should approach -1 and the electrophoretic mobility approach zero as the particle conductivity increases; however, in most practical cases, 'conducting' particles are rapidly polarised by the applied electric field and behave as non-conductors. For non-conducting particles (λ = *l/2)* the Henry equation can be written in the form,

$$u_E = \frac{\zeta\varepsilon}{1{\cdot}5\eta} f(\kappa\alpha) \qquad 24$$

where $f(\kappa\alpha)$ varies between 1.0 for small $\kappa\alpha$ (H$\ddot{u}$ckel equation, $u_E = \frac{\zeta\varepsilon}{1{\cdot}5\eta}$) and 1.5 for large $\kappa\alpha$ (Smoluchowski equation, $u_E = \frac{\zeta\varepsilon}{\eta}$). Zeta potentials calculated from the H$\ddot{u}$ckel equation (for $\kappa\alpha$ = 0.5) and from the Smoluchowski equation (for $\kappa\alpha$ = 300) differ by about 1 percent from the corresponding zeta potentials calculated from the Henry equation.

The Henry equation is based on several simplifying assumptions:

- The Debye-Huckel approximation is made.
- The applied electric field and the field of the electric double layer are assumed to be simply superimposed.
- ε and η are assumed to be constant throughout the mobile part of the double layer.

4.7 Stability:

The stability of a colloidal system is described by particles staying suspended in solution and depends on the interaction between the particles. These include van der Waals, and electrostatic interactions as they both contribute to the overall free energy of the system. Ideally, lyophobic sols are stabilised entirely by electric double-layer interactions and, as such, present colloid stability at its simplest whereas the stability of the lyophilic colloids depends upon both the electrical charge and solvation. To cause precipitation of the dispersed particles it is necessary that they coalesce into large aggregates.

Since in a lyophobic sol, the charge on all the colloidal particles is of the same sign, the repulsive forces prevent the particles from approaching sufficiently close to one another and to coalesce and coagulate. The magnitude of the repulsive forces depends upon the magnitude of the surface charge and the thickness of the electrical double layer. These factors also determine the value of the zeta potential which governs the stability of the colloidal system. If ζ is small, the resultant potential energy is negative so that the van der Waals attraction predominates over the electrostatic repulsion and the sol coagulates rapidly.

On the other hand, in the case of lyophilic sols, solvation plays a particularly important role. Since the colloidal particles are enclosed in a solvent 'cage', the cage serves as a barrier preventing the particles from coalescing to form aggregates. Thus, whereas in the case of lyophobic sols, removal of electrical charge may easily bring about coagulation, in the case of lyophilic colloids, the charge removal may not necessarily result in coagulation though it may decrease the stability of the sol.

4.7.1 Dlvo Theory of The Stability of Lyophobic Colloids:

This theory, involving the concept of zeta potential, was developed by the Russian scientists D. Derjaguin and L.D. Landau, and independently, by the Dutch scientists E. Verwey and J.T.G. Overbeek. According-to this theory, there is a balance' between the repulsive interactions between the charges of the electrical double layers on neighboring particles and the attractive van der Waals interactions between the molecules in the particle. The repulsive potential energy of the double layer on particles each of radius *r* is given by,

$$V_{rep} = \frac{Ar^2\zeta^2}{R} e^{-s/r_D} ; \qquad r << r_D \qquad 25$$

Where A is a constant, ζ is the zeta potential, R is the separation of the centers, s is the separation of the surfaces of the two particles (s = R - 2 *r* for spherical particles of radius *r*) and r_D is the thickness of the electrical double layer. Equation 25 holds for a thick double layer ($r << r_D$). For a thin double layer ($r >> r_D$),

$$V_{rep} = \frac{Ar\zeta^2}{2} \ln(1 + e^{-s/r_D}) ; \qquad r >> r_D \qquad 26$$

The potential arising from the attractive interaction is given by,

$$V_{att} = -B/s \qquad 27$$

where B is another constant.

Treating the electrical double layer as a simple electrical condenser, the zeta potential ζ; is given by the expression,

$$\zeta = 4\pi\eta u \,/\, \varepsilon_r \qquad 28$$

where η and ε_r, are the viscosity and the dielectric constant respectively, of the dispersion medium and u is the mobility of the colloidal particles.

For water as the dispersion medium, ζ; is found to lie between 0·03 and 0·06 V. The value of ζ; decreases when an ion of opposite charge to that of the colloidal particle is adsorbed. This reduces the mutual repulsion between the similarly charged colloidal particles. As a result, the colloidal particles easily come closer to one another to coalesce and form bigger aggregates which lies outside the colloidal range.

4.7.2 Coagulation of Colloidal Solutions:

A most important physical property of colloidal dispersions is the tendency of the particles to aggregate. This phenomenon of changing colloidal state to a suspended state is known as coagulation, flocculation, or precipitation of colloidal solutions. Encounters between particles dispersed in liquid media occur frequently and the stability of a dispersion is determined by the interaction between the particles during these encounters.

A. Coagulation of Lyophobic Colloids:

Coagulation can occur due to several reasons but in case of lyophobic sols, the most important way of coagulation is by small amounts of added electrolyte. The added electrolyte causes a compression of the diffuse parts of the double layers around the particles and may, in addition, exert a specific effect through ion adsorption into the Stern layer. The sol coagulates when the range of double-layer repulsive interaction is sufficiently reduced to permit particles to approach close enough for van der Waals forces to predominate. The critical coagulation concentration (c.c.c.) or flocculation value of an electrolyte (i.e., the minimum concentration of the electrolyte which is just sufficient to coagulate a lyophobic sol to an arbitrarily defined extent in an arbitrarily chosen time) shows considerable dependence upon the charge number of its ions oppositely charged to the coagulating sol. In contrast, it is practically independent of the specific character of the various ions, the charge number of the co-ions and the concentration of the sol, and only moderately dependent on the nature of the sol. These generalisations are illustrated in Table 1 and are known as the Schulze-Hardy rule. Thus, according to Hardy Schulze rule, greater the valency of the active ion or flocculating ion, greater will be its coagulating power." In nutshell, Hardy Schulze law states:

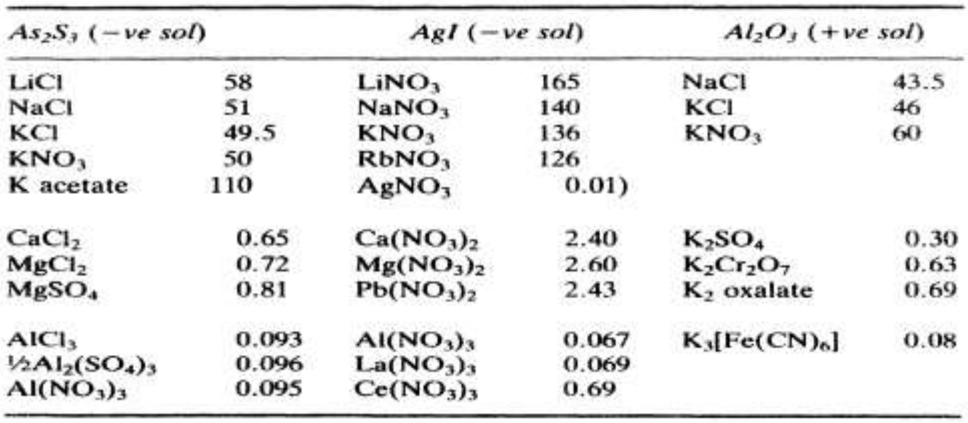
- The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.
- Coagulating power of an electrolyte is directly proportional to the valency of the active ions (ions causing coagulation).

For example, to coagulate negative sol of As_2S_3, the coagulation power of different cations has been found to decrease in the order as, $Al^{3+} > Mg^{2+} > Na^+$ (See Table 4.1)

Similarly, to coagulate a positive sol such as Al_2O_3, the coagulating power of different anions has been found to decrease in the order as, $[Fe(CN)_6]^{4-} > SO_4^{3-} > Cl^-$ (See Table 4.1)

Such arrangement of ions to represent their coagulating power against oppositely charged sols is known as lyotropic series or Hofmeister series. One must remember, more the coagulating power of the oppositely charged active ion smaller will be its flocculation value.

Table 4.1: Critical coagulation concentrations / Flocculation value (in millimoles per dm^3) for lyophobic sols.



As_2S_3 (−ve sol)		*AgI (−ve sol)*		*Al_2O_3 (+ve sol)*	
LiCl	58	$LiNO_3$	165	NaCl	43.5
NaCl	51	$NaNO_3$	140	KCl	46
KCl	49.5	KNO_3	136	KNO_3	60
KNO_3	50	$RbNO_3$	126		
K acetate	110	$AgNO_3$	0.01)		
$CaCl_2$	0.65	$Ca(NO_3)_2$	2.40	K_2SO_4	0.30
$MgCl_2$	0.72	$Mg(NO_3)_2$	2.60	$K_2Cr_2O_7$	0.63
$MgSO_4$	0.81	$Pb(NO_3)_2$	2.43	K_2 oxalate	0.69
$AlCl_3$	0.093	$Al(NO_3)_3$	0.067	$K_3[Fe(CN)_6]$	0.08
½$Al_2(SO_4)_3$	0.096	$La(NO_3)_3$	0.069		
$Al(NO_3)_3$	0.095	$Ce(NO_3)_3$	0.69		

The other means to attain coagulation of lyophobic colloids are by electrophoresis, by mixing equal quantities of oppositely charged sols (mutual coagulation), by boiling, by persistent dialysis, or by mechanical means like using vibrations, ultrasound, etc.

B. Coagulation of Lyophilic Colloids:

Majorly two factors are responsible for the stability of lyophilic sols: charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. Although, solvation plays more important role in stability of lyophilic colloids. Thus, addition of only small amount of electrolyte is not sufficient to coagulate the lyophilic sols. Unlike lyophobic colloids, they are required in much higher concentration (usually of the order of 1 M) for coagulation. Here, coagulation does not occur due to the neutralization of charge on the particles. The electrolyte binds with water and get hydrated, due to which polymer molecules in the lyophilic sol get dehydrated. This dehydration ultimately leads to coagulation. Similarly when solvent such as alcohol and acetone are added to hydrophilic sols the dehydration of dispersed phase occurs resulting in coagulation.

4.7.3 Protection of Colloids:

Addition of a lyophilic colloid to a lyophobic colloid, leads to the lesser sensitivity of the later towards the precipitating action of an electrolyte. This is expressed by saying that the lyophilic colloid protects a lyophobic colloid from precipitation by the action of electrolytes.

Substances such as gum acacia, gelatin, gum tragacanth, etc., are known as protective colloids as they probably get adsorbed on the solid surface in the form of loops wherein water gets trapped. The loops prevent the approach of particles to cause coagulation.

Zsigmondy gave quantitative treatment known as gold number of a protective colloid which represents stabilizing action of the protective colloids. The gold number is defined as the largest number of milligrams of a protective colloid which, when added to 10 mL of a special standard gold sol, just fails to prevent the colour change from red to blue upon the addition of one mL of 10 percent sodium chloride solution (Table 4.2). It must be emphasized that the protective action of a lyophilic sol depends upon several factors such as sol dispersity, the molar mass of the lyopbilic sol, the pH of the solution at which the experiment is carried out, and so on.

Table 4.2: Gold Number of some hydrophilic substances

Hydrophilic substance	Gold number	Hydrophilic substance	Gold number
Gelatin	0.005 - 0.01	Sodium oleate	0.4 – 1.0
Sodium caseinate	0.01	Gum tragacanth	2
Hamoglobin	0.03 – 0.07	Potato starch	25
Gum arabic	0.15 – 0.25		

Overall, stability of colloids depends upon the long-range van der Waals attractive forces between the particles, as they are the principal cause of aggregation. To counteract these and promote stability, equally long-range repulsive forces are required. Solvation tends to be too short-range; however, the molecular ordering associated with solvation can propagate several molecular diameters into the liquid phase and may exert some influence on stability.

The principal stabilising options are electrostatic (i.e., the overlap of similarly charged electric double layers) and polymeric. Polymeric and/or surfactant additives can influence stability by a variety of mechanisms and the overall situation is often overly complicated.

4.8 Optical Properties:

When a beam of light is directed at a colloidal solution or dispersion, some of the light may be absorbed (colour is produced when light of certain wavelengths is selectively absorbed), some is scattered, and the remainder is transmitted undisturbed through the sample. Light scattering results from the electric field associated with the incident light inducing periodic oscillations of the electron clouds of the atoms of the material in question - these then act as secondary sources and radiate scattered light.

4.8.1 The Tyndall Effect-Turbidity:

It was observed by Tyndall, in 1869, that when a beam of light is passed through a true solution, it cannot be seen unless the eye is placed directly in its path. However, when the same beam of light is passed through a colloidal dispersion, it becomes visible as a bright streak. This phenomenon is known as the Tyndall effect and the illuminated path (streak of light) is known Tyndall cone (Figure 4.16).

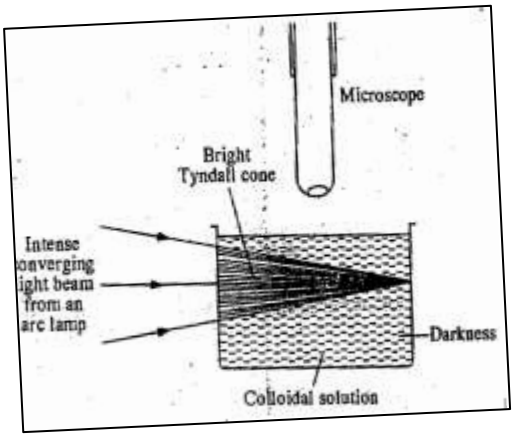


Figure 4.16: Tyndall effect

All materials are capable of scattering light (Tyndall effect) to some extent. The noticeable turbidity associated with many colloidal dispersions is a consequence of intense light scattering. A beam of sunlight is often visible from the side because of light scattered by dust particles. Solutions of certain macromolecular materials may appear to be clear, but in fact they are slightly turbid because of weak light scattering. Only a perfectly homogeneous system would not scatter light; therefore, even pure liquids and dust-free gases are very slightly turbid. The turbidity of a material is defined by the expression,

$$I_t \,/\, I_0 = exp(-\tau l) \qquad 29$$

where I_0 is the intensity of the incident light beam, I_t is the intensity of the transmitted light beam, l is the length of the sample and τ is the turbidity.

4.8.2 Measurement of Scattered Light:

As we shall see, the intensity, polarisation and angular distribution of the light scattered from a colloidal system depend on the size and shape of the scattering particles, the interactions between them, and the difference between the refractive indices of the particles and the dispersion medium. Light-scattering measurements are, therefore, of great value for estimating particle size, shape, and interactions, and have found wide application in the study of colloidal dispersions, association colloids, and solutions of natural and synthetic macro-molecules.

Light scattering offers the following advantages over some of the alternative techniques of particle-size analysis:

- Instantaneous measurements which makes it suitable for rate studies.
- No calibration is required as it is absolute.
- The number of particles involved is exceptionally large, which permits representative sampling of polydispersed samples.
- There is no significant perturbation of the system.

The intensity of the light scattered by colloidal solutions or dispersions of low turbidity is measured directly. To measure the light scattering at several angles a detecting photocell is mounted on a rotating arm and fitted with a polaroid for observing the polarisation of the scattered light (see Figure 4.17). Weakening of the scattered beam itself as it passes through the slightly turbid sample can be neglected, and its intensity can be compared with that of the transmitted beam.

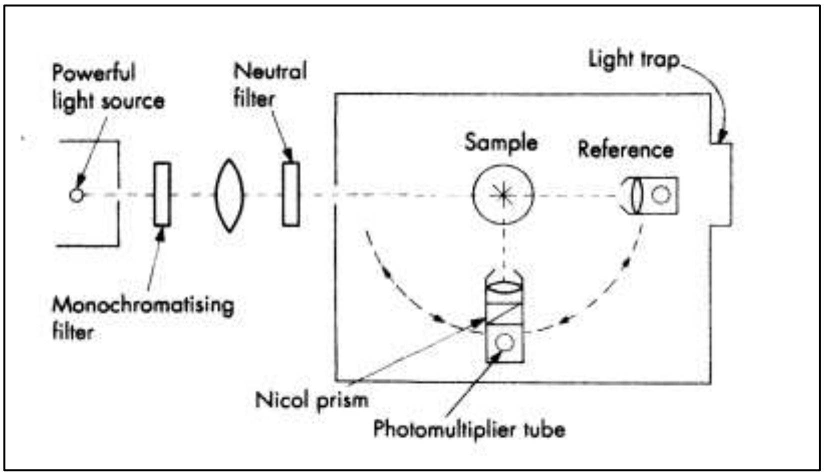


Figure 4.17: Measurement of scattered light

Although simple in principle, light-scattering measurements present several experimental difficulties, the most notable being the necessity to free the sample from impurities such as dust, the relatively large particles of which would scatter light strongly and introduce serious errors.

4.9 Viscosity and Surface Tension:

Lyophilic sols have a higher viscosity and lower surface tension than dispersion medium while lyophobic sols have a nearly same viscosity and surface tension as dispersion medium. This can be understood as lyophilic sols possess higher affinity towards dispersion medium and can be heavily solvated which results in increased viscosity and decreased surface tension than the dispersion medium. On the other hand, lyophobic sols do not possess such affinity for the dispersion medium, and they do not readily solvated. They have much less interaction with dispersion medium due to which their viscosity and surface tension are same as that of dispersion medium.

4.10 Colligative Properties:

Colloidal particles are bigger aggregates. The colligative properties depend on the number of particles. Due to a smaller number of particles compared to true solution, colligative properties are of lower order. Hence the magnitudes of colligative properties, like osmotic pressure, depression in freezing point, and elevation in boiling points are small as compared to the values shown by the true solutions at the same concentration.

4.11 Colour:

Many sols are coloured as they can scatter light rays. Colour of the sol depends upon the wavelength of scattered light by the sol particles, and which again depends upon their size. For example, the colour of silver sol changes from violet to orange red to finally orange yellow as particle size increases (Table 4.3).

Table 4.3: Change in colour of silver sol with increasing particle size.

Colour of Silver sol	Diameter of Colloidal Particles
Violet	15 X 10^{-8} m
Purple	13 X 10^{-8} m
Orange Red	9 X 10^{-8} m
Orange Yellow	6 X 10^{-8} m

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5. Colloidal Solutions

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5.1 Introduction:

Colloids are mixes in which insoluble particles of one substance are suspended in another substance at a microscopic level. In a colloid, the size of the suspended particles can range from 1 to 1000 nanometers. Colloids are defined as a mixture in which one of the components is broken down into very small particles that are spread throughout a second material. Colloidal particles are the tiniest particles.

As a result, the particles in a colloidal solution are bigger and known as colloidal particles. Even though colloidal particles are larger, they are too small to be seen with the human eye. They can, however, be spotted with the use of an ultra-microscope.

Colloidal solutions can flow through standard filter paper but not through an animal membrane. When dispersed in water, gum Arabic, gelatin, glue, and other substances produce colloidal solutions.

5.1.1 Definition:

The colloidal state is the state of subdivision in which molecules or polymolecular particles with at least one dimension in the range of 1 nanometer and 1 micrometer are scattered in some medium," according to the IUPAC definition.

Colloids are made up of chemicals that are uniformly distributed in one another. The dispersed phase is the substance that is dispersed in these combinations, while the continuous phase is the substance through which it is disseminated.

A typical solution consists of a solvent and a solute. In a normal solution, the particles of solute are usually either normal molecules or ions, and their size ranges from 1 to 10 or 0.1 to 1mm. There are systems in which the particles are much larger, ranging from the highest limit for ordinary solutions to several microns in size.

Colloids are media that contain dissolved or scattered particles ranging in size from a few microns to several millimeters. Smaller than coarse, filterable particles, colloidal particles are larger than atoms and tiny molecules.

Thomas Graham (1861) discovered that certain chemicals in the dissolved state, such as sugar, urea, sodium chloride, and others, may diffuse across a mammalian membrane. Certain dissolved substances, such as sugar, urea, sodium chloride, and others, went through the membrane, but solutions of glue, gelatin, gum Arabic, and other substances did not. However, it was quickly apparent that Graham's classification of dissolved substances was untenable since some chemicals may operate as crystalloids and colloids at the same time.

The infusibility of crystalloids and the non-infusibility of colloids via a mammalian membrane were later discovered to be attributable to particle size differences. Crystalloids in solution break down into smaller particles, which pass through the membrane. Colloids, on the other hand, produced bigger particles in solutions and were unable to pass through the membrane.

5.2 Colloids Examples:

a) **Blood:** A water-soluble respiration pigment-containing albumin protein. The dispersed phase in the pigment component is albumin, and the dispersion medium is water. It's a type of hydrosol.
b) **The Cloud:** It has air as the dispersion medium and water droplets as the dispersed phase. These are aerosol canisters.
c) **Gold Sol:** It's a metallic sol made up of gold particles suspended in water.

5.2.1 Classification of Particles:

The systems containing scattered particles can be classified into the three categories below based on particle size.

a. **True solutions:** True solutions are homogenous systems with scattered particles that are less than 1 nm in size, i.e. 10-9. In a genuine solution, the solute particles are either single molecules or ions that are uniformly dispersed throughout the solution.
b. Even a microscope cannot see these particles since they are invisible. True solutions pass through standard filter paper as well as animal membranes due to the tiny size of dispersed particles. In water, sodium chloride, sugar, urea, and other compounds form real solutions.
c. **Colloidal solutions:** Colloidal solutions are heterogeneous systems with scattered particle sizes ranging from 1 nanometer to 1000 nanometers. Colloidal solutions are transitional between genuine solutions and suspensions, as evidenced by the preceding explanation. Colloidal solutions can be made from any substance by subdividing or aggregating its particles in the size range of 1 nm-1000 nm, as indicated above. In theory, any substance can be produced to exist as a colloidal particle.
d. **Suspensions:** Suspensions, are heterogeneous systems with bigger particles. The particles in a suspension have a diameter of greater than 1000 nm. These particles can either be observed with the naked eye or using a microscope. Neither an animal membrane nor conventional filter paper can pass through the suspensions. A suspension is a murky water that has been stirred. The suspended particles in a combination must not settle to be categorized as a colloid. The Tyndall Effect is a phenomenon in which light beams incident on colloids are scattered due to interactions between the light and the colloidal particles.

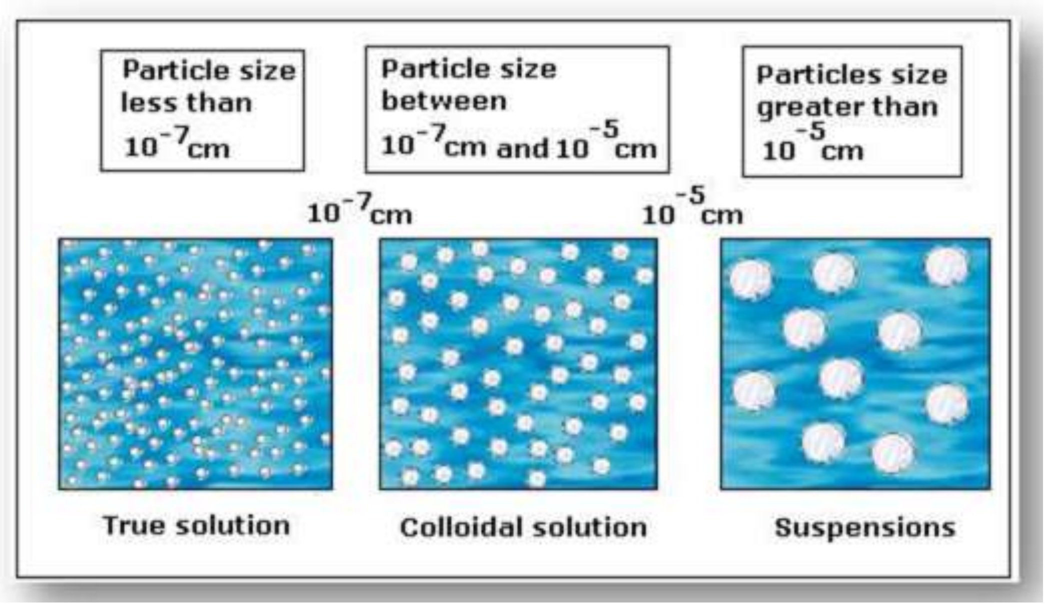


Figure 5.1: Particle Size Distribution and Their Classification

Table 5.1: Comparative Study of Properties of Particles

Property	**True solution**	**Colloidal solution**	**Suspension**
Particle size	Less than 1 nm	Between 1 nm-1000nm	Greater than 100nm
Nature	Homogeneous	Heterogeneous	Heterogeneous
Visibility of particles	Invisible	Visible under ultra-microscope	Visible to the naked eye or under a microscope
Appearance	Transparent	Generally transparent	Opaque
Filterability	It easily passes through both regular filter paper and animal membranes	Passes through regular filter paper without difficulty, but not through mammalian membranes.	Neither conventional filter paper nor mammalian membranes allow it to pass
The setting of particles under gravity	Particles do not settle	Colloidal particles do not settle due to gravity. High-speed centrifugation, on the other hand, can be used to compel them to settle.	Particles settle on standing

Property	**True solution**	**Colloidal solution**	**Suspension**
Diffusion of particles	Diffuses rapidly	Diffuses slowly	Does not diffuse
Scattering of light by particles (Tyndall Effect)	Light is not scattered	Light is scattered and the Tyndall effect is seen.	It's possible to see the Tyndall effect.

A colloidal system is made up of two phases: a dispersed phase and a dispersion medium. The dispersed phase, also known as the discontinuous phase, is the phase that is distributed or scattered through the dispersion medium. The dispersion media, also known as the continuous medium, is the phase in which scattering takes place.

(OR)

A colloidal solution is the dispersion of a solid (dispersed phase) in a liquid (dispersion medium). Solid aerosol is the dispersion of a solid (dispersed phase) in a gas (dispersion medium).

5.3 There Are Numerous Different Types of Colloids:

Colloids are characterized as lyophilic or lyophobic depending on the nature of the interaction between the dispersion medium and the dispersed phase.

5.3.1 Lyophilic:

A lyophilic colloid is one in which the dispersed phase has an affinity for the dispersion medium. The words lyo and philic, respectively, signify "liquid" and "loving." Even if the dispersed phase and the dispersion medium are separated, they can easily be reconstituted by simply mixing them. Furthermore, because of their sturdy nature, they are difficult to coagulate.

Lyophilic colloids or intrinsic colloids are substances that readily form colloidal solutions when mixed with a suitable liquid (dispersion medium), and lyophilic sols are the resulting sols.

Such colloids are known as hydrophilic colloids when water is utilized as the dispersion medium, and their colloidal dispersion in water is known as hydrophilic sols. Lyophilic colloids include things like Arabic gum, gelatin, starch, rubber, protein, and other materials are examples. Intrinsic colloids are another name for them.

Lyophilic sols are very stable and do not readily precipitate. They are self-stabilized, which means they don't need any stabilizing agents to stay in good shape. The fact that if the dispersed phase is isolated from the dispersion medium, the dispersed phase may be brought back into the sol form simply by mixing it with the dispersion media is a key feature of these sols. Lyophilic sols include gum sol, starch sol, protein sols in water, polymer sols in organic solvents, and so on.

5.3.2 Lyophobic:

A lyophobic colloid is one in which the dispersed phase has little or no affinity for the dispersion medium. The words lyo and phobic, respectively, denote "liquid" and "fear." As a result, they despise liquids. Because the dispersed phase does not readily form a colloid with the dispersion medium, they are difficult to manufacture and necessitate the employment of special techniques. They are brittle and require stabilizing substances to stay alive. Extrinsic colloids are another name for them. Sols of metals such as silver and gold, as well as sols of metallic hydroxides, are examples.

Sols are a colloidal system with a liquid or gas as the dispersion medium. Hydrosols or equal sols are the terms used to describe them. If water is used as the dispersion medium. They are called alcohols or benzo sols when the dispersion medium is alcohol or benzene. Aerosols are colloidal systems with air as the dispersion medium.

Gels are colloids in which the dispersion medium is a solid, such as cheese. Their structure is more rigid. Some colloids, such as gelatin, have can the ability to act as both sol and gel. The colloids are hydrosol at high temperatures and low gelatin content. The hydrosol, however, can gel at low temperatures and high gelatin concentrations.

5.4 Classification Based on Physical State:

The solid and the dispersion medium are both present in this dispersed phase. Example, gemstones

- **Aerosol:** The dispersion medium for these colloids is air. Cloud is an example. The dispersion medium is air, and the dispersed phase is water drops. Dust is example number two. The dispersion medium is air, and the dispersed phase is a dent particle. Smoke is an example of the third type of example. Carbon particles are present in the air.
- **Gels:** There is a solid dispersion medium and a liquid dispersed phase in these. Cheese and butter, for example.
- **Emulsion:** These are liquid-liquid solutions with a liquid dispersed medium and a liquid dispersed phase. The emulsion is primarily made up of two components.
- **Type of oil in water:** The dispersed phase is oil, while the dispersion medium is water. Milk is an example.
- **Type of water in oil:** The dispersed phase is water, while the dispersion medium is oil/fat. Vanishing cream is a good example. Sols and gels are interconvertible and reversible. This is referred to as thixotropic.
- **Dispersion Medium-Based Classification:** Sols are classed as follows based on their dispersion medium:
- **Hydrosol:** Water acts as a dispersion medium in these colloids. Starch is a good example.
- **Alcoholic beverages:** Alcohol is used as a dispersion medium in this case.
- **Aerosol:** In the air, these comprise distributed phase particles. Smoke is an example. Colloids can also be classed according to how the dispersed phase interacts with the medium:

Dispersed Phase	Dispersion Medium	Name
Solid	Liquid	Sol
Solid	Solid	Solid sol
Solid	Gas	Aero sols
Liquid	Solid	Gel
Liquid	Liquid	Emulsion
Liquid	Gas	Liquid aerosol
Gas	Solid	Solid foam
Gas	Liquid	Foam

We've already established that the colloidal particles in a colloidal system range in size from 1nm to 100nm. Colloidal solutions can be categorized into three categories based on how different chemicals creating colloidal solutions acquire particle sizes in this range.

5.4.1 Multimolecular Colloids:

Multimolecular colloids are colloidal solutions created when a large number of atoms or tiny molecules (with diameters less than 1nm) of a substance interact in a dispersion medium to form aggregates with sizes in the colloidal range. Vander Waals forces hold the species (atoms or molecules) that make up the scattered particles of Multimolecular colloids together.

Multimolecular colloids include gold sol, sulfur sol, and others. A gold sol may have particles of varying sizes made up of several gold atoms. Sulfur sol, on the other hand, is made up of particles containing thousands of S8 molecules.

5.4.2 Macromolecular Colloids:

Certain compounds generate macromolecular colloids, which are huge molecules with diameters similar to colloidal particles. The resulting colloidal solutions are known as macromolecular colloids when such compounds are dispersed in a suitable dispersion medium. The scattered particles in macromolecular colloids are thus big molecules with extremely high molecular masses.

Macromolecular colloids make up the majority of lyophilic sols. Macromolecular colloids, for example, are colloidal dispersion of naturally occurring macromolecules such as starch, proteins, gelatin, cellulose, nucleic acids, and so on. When dispersed in suitable solvents, synthetic polymers such as polyethylene, polypropylene, and synthetic rubber create macromolecular colloids.

Example: Starch, proteins, cellulose, enzymes, polystyrene, etc.

5.4.3 Associated Colloids (Micelles):

Associated colloids are strong electrolytes that act normally at low concentrations but exhibit colloidal features at greater concentrations due to the production of aggregated particles termed micelles. Micelles are created by the association of scattered particles over a specific concentration, and the process of aggregation requires a particular minimum concentration. Micelle production requires a minimum concentration called critical micellization concentration (CMC), which varies depending on the composition of the dispersed phase. CMC is 10^{-3} mol L^{-1} for soaps. Surfactants (surface active agents) such as soaps and synthetic detergents frequently form the related colloids. When these agents are present in solution at a concentration higher than the critical micellization concentration, they produce micelles (CMC).

Example: Soap, synthetic detergents.

5.4.4 Colloidal Solution Preparation:

Because of their strong affinity for the dispersion medium, lyophilic colloids rapidly form a sol when brought into contact or warmed with it. For example, simply heating with water is sufficient for making starch, gelatin, and gum Arabic sols. However, because lyophobic colloids have no affinity for the dispersion medium, it is difficult to create these sols in practice. The manufacture of lyophobic sols necessitates the use of certain techniques.

There are several different methods for making lyophobic sols, which can be grouped into two categories.

- Dispersion methods and
- Condensation or aggregation methods

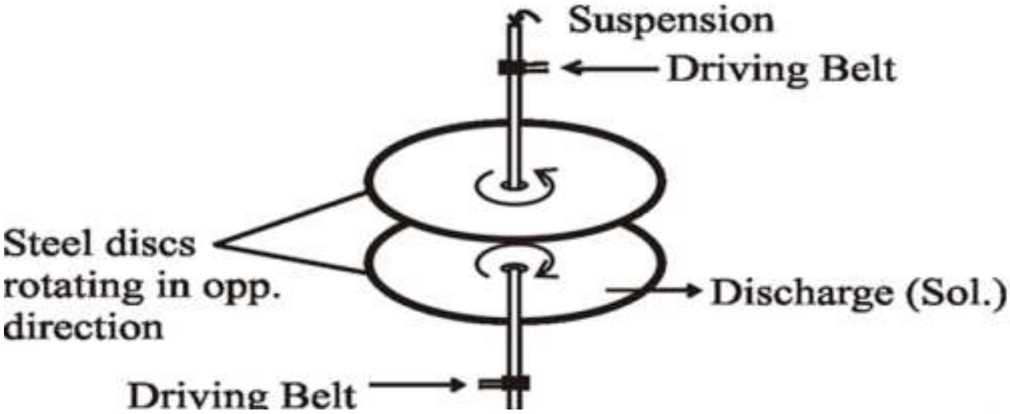
5.5 Methods of Dispersion:

The larger particles of any substance are broken down into minute colloidal particles via dispersion processes. The resulting tiny particles are stabilized by the addition of stabilizing agents.

The following are some of the dispersion methods:

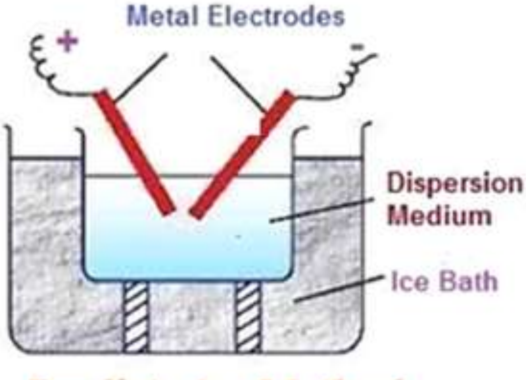
5.5.1 Mechanical Dispersion Method:

The big particles of the material whose sol is to be created are broken down in a machine called a colloid mill in the mechanical dispersion procedure. Two hefty steel discs are separated by a small space in a colloid mill. The particle size can be modified to suit your needs. The two discs spin in opposite directions at a fast rate. The material is suspended in water and added to the mill. The particles in the suspension are ground to form colloidal particles, which are then dispersed in water to form a sol.



5.5.2 Bredig's Arc Method or by Electrical Dispersion:

The electrical dispersion method (Bredig's arc method) is used to prepare sols metals such as gold, silver, platinum, and other precious metals. Two electrodes of the metals whose sol is to be made are immersed in the dispersion medium and a high voltage current is sent through them to create an electric arc. By enclosing the dispersion medium in a freezing liquid, it is kept chilly. The metal begins to vaporize due to the heat created by the electric arc, and the vapor condenses into the cold dispersion media to form colloidal particles upon cooling.



Bredig's Arc Method

5.5.3 Ultrasonic Dispersion:

High-frequency sound waves are commonly referred to as ultrasonic waves. When quartz crystal discs are coupled to a high-frequency generator, these waves can be generated. In 1927, Wood and Loomis were the first to use ultrasonic waves to prepare colloidal solutions. With the use of ultrasonic waves, many compounds such as oils, mercury, sulfides, and metal oxides can be easily dispersed into a colloidal condition.

5.5.4 Peptization:

Peptization is the process of breaking down freshly formed precipitate particles into colloidal-sized particles. This is accomplished by incorporating appropriate electrolytes. A peptizing agent is an electrolyte that is added.

The addition of ferric chloride solution to newly precipitated ferric hydroxide produces a brown-colored colloidal solution. The adsorption of ferric ions on the surface of the precipitate caused this. The formation of positively chafed ferric ions on the surface generates repulsion between them, resulting in the breakdown of large precipitate particles into small colloidal particles.

5.5.5 Method of Condensation/Aggregation:

Some chemical reactions can be utilized to clump together with smaller atomic or ionic particles to generate giant colloidal particles. In these reactions, the scattered phase forms as an insoluble reaction product. Here are a few key processes involved in the creation of hydrophobic soils.

a) By Exchange of Solvents: Due to the limited solubility of sulfur or phosphorus in water, a colloidal solution of sulfur or phosphorus is formed when a solution of sulfur or phosphorus is made in alcohol is put into water. As a result, colloidal solutions of various compounds can be made by taking a solution of the substance in one solvent and pouring it into a solvent in which the substance is less soluble.

b) By change of physical state: Colloidal solutions of some elements, such as mercury and sulfur, are produced by passing their vapors through cold water containing a stabilizer.

c) Oxidation: Sol sulfur is made by oxidizing an aqueous solution of hydrogen sulfide (H_2S) with bromine water, nitric acid, SO_2, or any other suitable oxidizing agent.

$$H_2S + Br_2 \rightarrow \frac{S}{\text{Colloidal sulphur}} + 2HBr$$

$$2H_2S + SO_2 \rightarrow \frac{3S}{\text{Colloidal sulphur}} + 2H_2O$$

a) **Reduction:** Sols of gold, silver, platinum, and other metals are made by reducing dilute salt solutions with an appropriate reducing agent. Gold sol, for example, can be made by reducing a dilute aqueous gold solution with stannous chloride.

$$2AuCl_3 + 3SnCl_2 \rightarrow \frac{2Au}{\text{Colloidal sulphur}} + 3SnCl_4$$

The gold sol thus obtained is called purple of Cassius.

b) Hydrolysis: Ferric and aluminum hydroxide sols are made by boiling the aqueous solution of the appropriate chlorides.

$$FeCI_3 \quad + \quad 3H_2S \qquad \rightarrow \qquad Fe\,(OH)_3 \quad + \quad 3HCI$$

c) Double decomposition: A double decomposition reaction can be used to make sols of inorganic insoluble salts such as arsenous sulfide, silver halides, and other insoluble salts. Arsenous sulfide sol, for example, can be made by passing hydrogen sulfide gas through a dilute aqueous solution of arsenous oxide.

$$\mathbf{As_2O_3 + 3H_2S \rightarrow As_2S_3\,(sol) + 3H_2O}$$

5.6 Colloidal Solutions and Their Physical Properties:

Below are some of the most important features of colloidal solutions.

- **Heterogeneous nature:** There are two phases to the colloidal system: (a) Dispersed phase and (b) dispersion phase. Each particle in a colloidal solution is contained by boundary surfaces that separate it from the dispersion medium.
- **Colligative properties:** Colloidal particles have relatively low mole fractions in colloidal solution due to their high average molecular masses. As a result, colligative qualities such as relative lowering of vapor pressures, the elevation of boiling point, depression of freezing point, and osmotic pressure have very low values.
- **Visibility:** Colloidal solutions are heterogeneous, and they are made up of two phases: dispersed phases and the dispersion medium. Although colloidal solutions are heterogeneous, the dispersed particles present in them are not visible to the naked eye, giving the impression that they are homogeneous. Because colloidal particles are too minute to be seen with the human eye, this is the case.
- **Filterability:** Colloidal particles pass through regular filter paper due to their small size. Animal membranes, cellophane membranes, and ultrafilters, on the other hand, can retain them.
- **Stability:** Lyophilic sols in general, and lyophobic sols in the absence of significant electrolyte concentrations, are quite stable, and the dispersed particles contained in them do not settle down even after keeping. However, after a long period of standing, a few colloidal particles of comparably greater size may progressively sediment.

5.7 Optical properties:

1. Tyndall effect: Tyndall discovered in 1869 that when a powerful beam of light is sent through a colloidal solution in a dark room, the path of the beam is illuminated by a bluish light. This process, known as the Tyndall effect, was first detected by Faraday and later investigated in depth by Tyndall. Tyndall cone refers to the lighted path of a beam. The phenomenon occurs as a result of colloidal particles dispersing light in all directions.

2. Color: The wavelength of the light scattered by the dispersed particles determines the color of the colloidal sol. The wavelength is also affected by the size and composition of colloidal particles. Larger particles absorb longer wavelength light and so transmit shorter wavelength light. A silver with particles of size 150nm, for example, appears violet, whereas one with particles of size 60nm appears orange-yellow. The hue of colloidal sol is also determined by how the dispersed light is received by the viewer. When viewed by reflected light, a mixture of milk and water appears blue, but when viewed by transmitted light, it appears red.

3. Mechanical properties: (a) Brownian movement: A botanist named Robert Brown observed in 1827 that pollen grains placed in water do not stay still but move around randomly. This behavior was later noticed when colloidal particles were examined under an ultra-microscope. The particles were observed to be moving in a zig-zag pattern in all directions. Brownian movement refers to the zig-zag motion of colloidal particles.

Because the repulsive forces between similarly charged particles prevent them from aggregating when they get closer to one another, the presence of equal and similar charges on colloidal particles is also primarily responsible for providing stability to the colloidal solution.

5.8 Applications of Colloids:

Colloids have a wide range of applications in our daily lives, from food to medicine to industries such as rubber. Colloids have a wide range of applications in the food and pharmaceutical industries. Many of the foodstuffs we consume are colloidal. Many milk products, such as cheese, cream butter, and so on, are colloids. Milk is an emulsion, to be precise (liquid in a liquid colloidal system). Butter and fat are diffused in water in milk. Air is disseminated in the cooked dough, making bread a colloidal system. Colloids are widely used in industries, medicine, and everyday life. Syrup, Halwa, and Soup are examples of colloidal systems in cuisine. Colloidal silver, also known as Argosols, is used as an antimicrobial for eye infections Colloids can also be used in the form of medications. Colloidal drugs are more effective than traditional medicines because they are easily absorbed by the body. Some important antibiotics, such as penicillin and streptomycin, are injected into the body as colloidal sol to ensure that they are quickly absorbed.

5.9 The following are some of the applications of colloids.

- **Water Purification:** We all know that adding electrolytes such as potash alum to water is one of the most common techniques of water purification. The addition of these electrolytes is predicated on the fact that colloidal systems are common in dirty water. It frequently comprises scattered colloidal particles that filtration cannot remove. The addition of these electrolytes causes the impurity to coagulate, allowing it to be removed by filtration.
- **Sewage disposal:** As previously stated, sewage water contains colloidal pollutants such as mud and dirt, which are disseminated in the water. Sewage colloidal particles are charged particles, just like any other colloidal system. Electrophoresis can be used to remove the charged particles of pollutants found in sewage.
- The sewage water is routed via a tunnel equipped with metallic electrodes and kept at a high potential difference for this purpose. The charged impurity particles in the sewage water travel to the electrodes with opposing charges, causing them to coagulate.

- **Smoke precipitation:** Smoke is a colloidal system made primarily of charged carbon particles that are depressed in the air. Smoke is a significant environmental issue since it is a major source of air pollution. The problem will be solved by removing the dispersed colloidal particles from the air. Electrophoresis is used once more for this purpose.
- This is accomplished using the Cottrell precipitator. Smoke is forced through a chamber containing numerous metal plates connected by a metal wire to a high-potential source. When electrically charged colloidal carbon particles in the air come into touch with oppositely charged plates, they are discharged and fall to the bottom. A near-top exit lets clean hot air out of the precipitator.
- **Artificial Rain:** Clouds, like artificial rain, are colloidal systems. Water vapors are present in clouds, along with dust particles. In a cloud, the water molecules contain an electric charge and are colloidal in size. As a result, if the charge on the molecules is neutralized in any way, the rain will begin to fall. It is sometimes done by spraying electrolytes over the clouds, and the rain that results is referred to as manufactured rain.
- **Rubber industry:** You should be aware that rubber is made from latex collected from rubber trees. This latex is an emulsion of rubber particles that are negatively charged and distributed in the water. This latex is cooked to obtain rubber, which causes the rubber particles to coagulate. Vulcanization is used to solidify the coagulated substance into natural rubber.
- **Tannery:** Tanning refers to the practice of processing animal skins to obtain leather. When animal skins are immersed in a solution of tannin, which has the opposite charge as the animal skin, particles coagulate and the skin becomes hard. This process is known as tanning. The charged particles of the skin are coagulated using negatively charged materials such as tannin and some aluminum and chromium compounds.
- **Soap cleansing action:** As previously stated, the soap solution is a colloidal system that eliminates oil and filth by generating water-soluble emulsions.
- **Smokescreen:** A smoke screen is a device that uses a layer of smoke to conceal something. In general, it is employed to conceal army movements. Smokescreens are a colloidal system in which titanium oxide particles are spread in the air.
- **Delta formation:** A delta is a large deposit of sand and clay generated at the mouth of any river in the sea at the point where the river meets the sea. The formation of the delta is a fascinating natural process in which the presence of negatively charged colloidal sand and clay particles in river water is unsurprising. Salty seawater, on the other hand, includes several positive ions. When river water meets seawater, the negative charge on colloidal clay particles in river water is neutralized by the positively charged ions in the sea, causing them to congeal and deposit at the spot.
- **Blue Sky:** The blue tint of the sky is caused by the dispersion of the blue color of sunlight by colloidal dust particles scattered in the air existing in the atmosphere. (This is known as the Tyndall effect.)

Nanomaterial preparation: Reverse micelles are utilized to make nanomaterials that are used as catalysts.

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