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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.

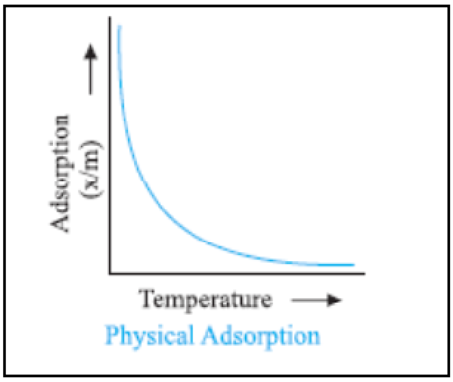
Sr. No.	Physical adsorption	Chemical adsorption
1.	It is caused by intermolecular van der Waal's forces.	It is caused by chemical bond formation.
2.	It is not specific and is reversible.	It is highly specific and is irreversible.
3.	It depends on the nature of gas. More easily liquefiable gases are adsorbed 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:

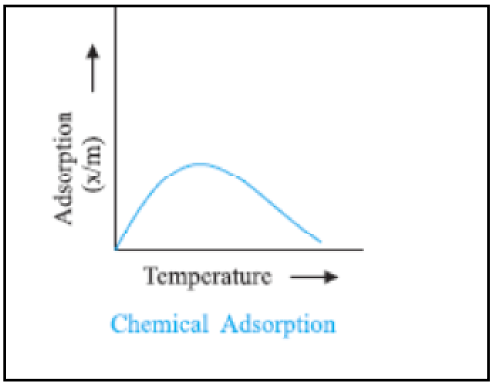
The extent of adsorption of a gas on the surface of a solid depends on the following factors:

- **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,

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

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

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.

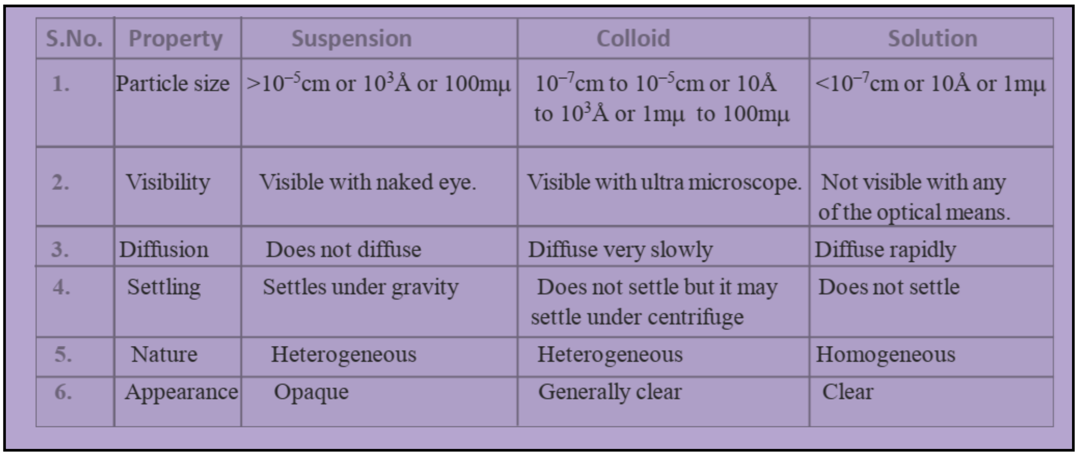
The former type of substances on account of their crystalline nature like common salt, sugar, urea, etc., were named crystalloids while the second type of substances were termed as colloids (Greek word, kola, meaning glue-like).

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^{3}Å or 100mμ	10^{-7}cm to 10^{-5}cm or 10Å to 10^{3}Å 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.

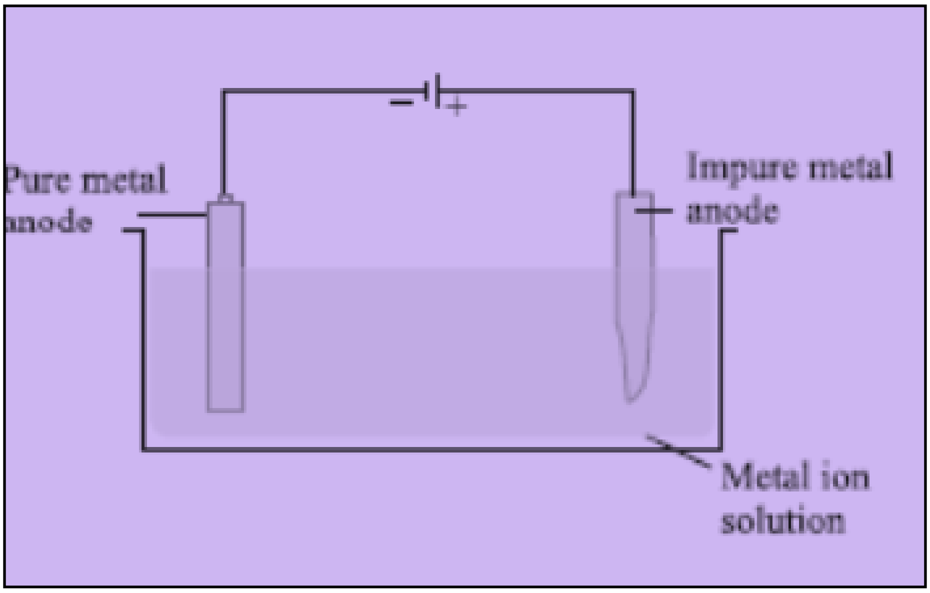
Sr. No	Dispersion Methods	Condensation Methods
1.	Mechanical dispersion	Exchange of solvents
2.	Electro-dispersion	Change of physical state

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 Fe^{3+}. Similarly, a precipitate of AgCl on shaking with dilute solution of $AgNO_3$ 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.

$$As_2O_3 + 3H_2O \longrightarrow As_2S_3\text{(yellow sol)} + 3H_2O$$

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

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

- **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.

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

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

- **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.

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

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

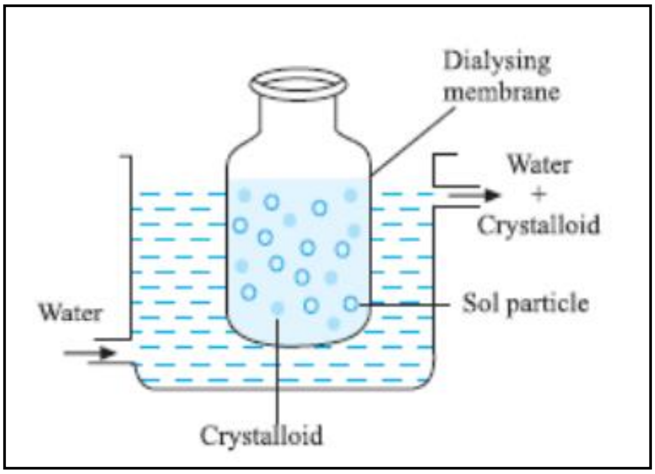
- **Hydrolysis:** By this method hydroxide sols of less electropositive metals like Fe, Al or Sn are prepared. A red sol of ferric hydroxide is obtained by the hydrolysis of ferric chloride with boiling water.

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

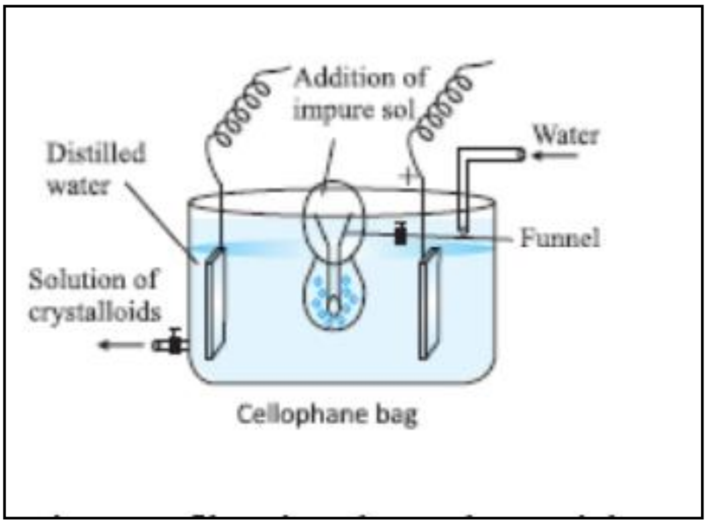
1.2.3 Purification of Colloidal Solutions:

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

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)

$C_2H_4 + H_2 \xrightarrow[\Delta]{\text{Ni}} C_2H_6$ (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) $2H_2O_2(\ell) \xrightarrow{\text{Pt}} 2H_2O(\ell) + O_2(g)$

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

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

(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.