

SURFACE CHEMISTRY

It is the branch of chemistry that deals with the study of nature of surfaces and the different processes taking place at the surface. The important surface phenomena are adsorption, corrosion, electrode process, heterogeneous catalysis, dissolution etc.

ADSORPTION

It is the process of concentration or accumulation of a substance on the surface of another substance. The substance which is adsorbed is called adsorbate and the substance whose surface on which adsorption takes place is called adsorbent. The commonly used adsorbents are charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state etc.

Adsorption is a surface phenomenon. Some examples of adsorption are:

1. Powdered charcoal adsorbs gases like H_2 , O_2 , CO , Cl_2 , NH_3 , SO_2 etc.
2. Silica gel adsorbs moisture
3. Animal charcoal adsorbs colouring material from sugar solutions

Desorption: The process of removal of an adsorbed substance from the surface of adsorbent is called desorption. i.e. it is the reverse of adsorption.

Distinction between adsorption and absorption

In adsorption, the substance is concentrated only at the surface while in absorption, the substance is uniformly distributed throughout the bulk of the solid. So adsorption is a surface phenomenon while absorption is a bulk phenomenon.

Sorption: If adsorption and absorption occur simultaneously, the process is called sorption.

Mechanism of Adsorption

The surface particles of the adsorbent are not in the same environment as the particles inside the bulk (inner part). Inside the adsorbent, all the forces are mutually balanced. But at the surface, there is always some unbalanced or residual forces. These forces of the adsorbent are responsible for adsorption.

Heat of adsorption (Enthalpy of Adsorption)

Adsorption is an exothermic process. i.e. some heat is always evolved during adsorption. The amount of heat evolved when 1 mole of an adsorbate is adsorbed on the surface of an adsorbent is called heat of adsorption.

Thermodynamic aspects of adsorption

Adsorption is an exothermic process. When a gas is adsorbed, the degree of freedom (randomness) of its molecules decreases and hence the entropy decreases. i.e., ΔS becomes negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, ΔG must be negative. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if $\Delta H > T\Delta S$. As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state equilibrium is attained.

Types of adsorption

Depending on the force of attraction between adsorbent and adsorbate, adsorption is of two types – physical adsorption or physisorption and chemical adsorption or chemisorption.

If the force of attraction between adsorbent and adsorbate is weak van der Waals force, it is called physical adsorption or physisorption. For physisorption, the heat of adsorption is low and it is not specific since the van der Waals forces are universal. That is any substance can form van der Waals force with any surface.

In chemisorptions, the force of attraction between adsorbent and adsorbate is chemical bond. It is also called activated adsorption since it involves some activation energy. For chemisorption, the enthalpy of adsorption is high and it takes place at high temperature. It is highly specific in nature and it will occur only if there is some possibility of chemical bonding between adsorbent and adsorbate.

A physisorption at low temperature may pass into chemisorption at high temperature. For e.g. Hydrogen gas is first adsorbed on nickel by van der Waals force. But at high temperature, the molecules of H_2 dissociate to form H atoms and they are adsorbed on the surface of Ni by chemical bond.

Both physisorption and chemisorption increases with increase in surface area of the adsorbent. Surface area can be increased by powdering the adsorbent.

Distinction between physisorption and chemisorption

	Properties	Physisorption	Chemisorption
1	Force of attraction	Weak van der Waals force	Strong chemical bond
2	Specificity	Not specific in nature	Highly specific
3	Reversibility	Reversible	Irreversible
4	Extent of adsorption and nature of gas	Easily liquefiable gases (e.g. CO ₂ , HCl, NH ₃ etc) are easily adsorbed than permanent gases (e.g. H ₂ , N ₂ , O ₂ etc)	Gases which can react with the adsorbent show chemisorption
5	Heat of adsorption	Low (20-40 kJ/mol)	High (80-240 kJ/mol)
6	Temperature	Low temperature is favourable. It decreases with increase in temperature	High temperature is favourable. It increases with increase in temperature
7	Activation energy	No appreciable activation energy is needed	High activation energy is required
8	Nature of layer	Multimolecular layer of adsorption occurs	Only unimolecular layer of adsorption occurs

Adsorption Isotherms

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a graph called adsorption isotherm.

Freundlich adsorption isotherm:

Freundlich gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure, at a particular temperature. The relationship can be expressed by the following equation:

$$x/m = k \cdot P^{1/n} \text{ (where } n > 1 \text{)}$$

where x is the mass of the gas adsorbed, m is the mass of the adsorbent, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

The above relationship can be represented in the form of a graph as follows:

From the graph it is clear that x/m (extent of adsorption) increases with pressure up to a certain pressure called *saturation pressure* (P_s) and after that it becomes constant.

If we take logarithm of the above equation, we get

$$\log x/m = \log k + 1/n \log P$$

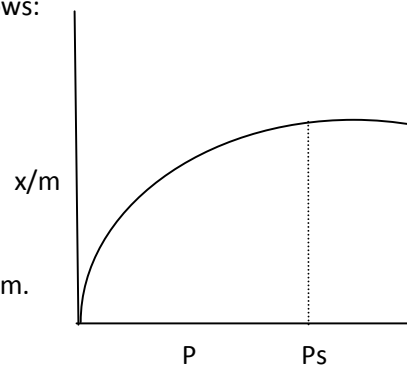
This equation is of the form $y = mx + c$, equation for a straight line. So if we plot $\log x/m$ against $\log P$, we get a straight line, which verifies Freundlich isotherm.

The value of $1/n$ in Freundlich isotherm ranges from 0 to 1

When $1/n = 0$, $x/m = a \text{ constant}$. i.e. the adsorption is independent of pressure.

When $1/n = 1$, $x/m = k \cdot P$, the adsorption varies linearly with pressure.

Freundlich adsorption isotherm failed to explain adsorption at very high pressures.



Adsorption from solution

Certain solid adsorbents can adsorb solute particles from solution. This is known as adsorption from solution. E.g.:

1. 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.
2. Animal charcoal adsorbs colouring materials from sugar solution. So it is used for the purification of sugar.

The important characteristics of adsorption from solution are:

- (i) The extent of adsorption decreases with an increase in temperature.
- (ii) The extent of adsorption increases with an increase of surface area of the adsorbent.
- (iii) The extent of adsorption depends on the concentration of the solute and the nature of the adsorbent and the adsorbate.

Freundlich adsorption isotherm is applicable to adsorption from solution also. Here instead of pressure, concentration of the solution is used.

i.e., $x/m = kC^{1/n}$ (where C is the equilibrium concentration).

On taking logarithm of the above equation, we have

$$\log x/m = \log k + 1/n \log C$$

On plotting $\log x/m$ against $\log C$, a straight line is obtained which verifies Freundlich isotherm.

Applications of adsorption

The important applications of adsorption are:

1. Production of high vacuum: For the complete evacuation of a vessel, activated charcoal is used.
2. Gas masks: The poisonous gases in coal mines can be removed by using gas masks containing activated charcoal.
3. Control of humidity: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.
4. Animal charcoal is used for the purification of cane sugar solution.
5. Adsorption finds application in heterogeneous catalysis.
6. A mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.
7. In curing diseases: A number of drugs are used to kill germs by getting adsorbed on them.
8. In froth floatation process for the purification of sulphide ores in metallurgy.
9. Adsorption indicators like eosin, fluorescein etc. are used in volumetric analysis.
10. Chromatographic analysis for the separation of a mixture is based on adsorption.

CATALYSIS

A catalyst is a substance that changes the rate of a chemical reaction without undergoing any permanent chemical change by itself. The process of changing the rate of a chemical reaction by a catalyst is known as Catalysis.

Eg: MnO_2 (Manganese dioxide) acts as a catalyst in the decomposition of KClO_3 (Potassium chlorate)



Promoters and poisons

Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst. For example, in Haber's process for the manufacture of ammonia, molybdenum (Mo) acts as a promoter for the catalyst iron.



Types of Catalysis

Positive and Negative Catalysis

A catalyst that increases the rate of a chemical reaction is called Positive catalyst and that decreases the rate of a chemical reaction is called negative catalyst (inhibitors).

E.g. In the Haber's process for the manufacture of ammonia, Fe acts as a positive catalyst



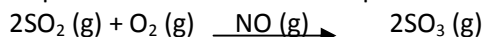
For decreasing the rate of dissociation of H_2O_2 , Phosphoric acid is used as a negative catalyst.

Homogenous and Heterogeneous Catalysis

Homogeneous Catalysis

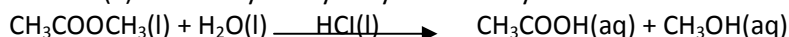
A catalytic process in which the reactants and the catalyst are in the same phase (i.e., liquid or gas), is said to be homogeneous catalysis.

e.g.: (i) In the *lead chamber process* for the manufacture of Sulphuric acid, oxidation of sulphur dioxide into sulphur trioxide is done in the presence of Nitric Oxide as catalyst

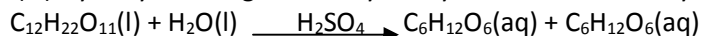


Here the reactants (sulphur dioxide and oxygen) and the catalyst (nitric oxide) are all in the same phase.

(ii) Acid catalysed hydrolysis of methyl acetate



(iii) Hydrolysis of sugar is catalysed by H^+ ions furnished by sulphuric acid.

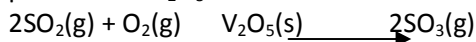


Heterogeneous catalysis

The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis.

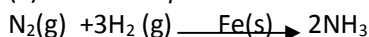
Some of the examples of heterogeneous catalysis are:

(i) In *contact process* for the manufacture of H_2SO_4 , Oxidation of sulphur dioxide into sulphur trioxide is done in presence of V_2O_5 .



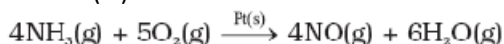
Here the reactants are in gaseous state while the catalyst is in the solid state.

(ii) In *Haber's process* for the manufacture of ammonia finely divided iron is used as catalyst.



Here the reactants are in gaseous state while the catalyst is in the solid state.

(iii) Oxidation of ammonia into nitric oxide in the presence of platinum gauze in Ostwald's process.



Here also the reactants are in gaseous state while the catalyst is in the solid state.

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

Adsorption Theory of Heterogeneous Catalysis

This theory explains the mechanism of heterogeneous catalysis. According to this theory the catalytic activity takes place on the surface of the catalyst. The mechanism involves five steps:

- (i) Diffusion of reactants to the surface of the catalyst.
- (ii) Adsorption of reactant molecules on the surface of the catalyst.
- (iii) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate.
- (iv) Desorption of reaction products from the catalyst surface.
- (v) Diffusion of reaction products away from the catalyst's surface.

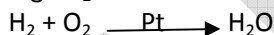
This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective even in small quantities. But it does not explain the action of catalytic promoters and catalytic poisons.

Important features of solid catalysts

1. Activity

The activity is the ability of a catalyst to increase the rate of a chemical reaction. It depends upon the strength of chemisorption.

e.g.: H_2 combines with O_2 to form H_2O in presence of Platinum (Pt) catalyst

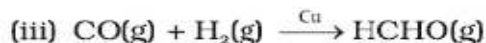
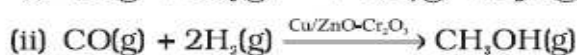
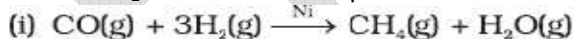


In absence of Pt, the reaction does not take place.

2. Selectivity

It is the ability of a catalyst to direct a chemical reaction to a particular product.

e.g.: CO reacts with H_2 to form different products based on the nature of the catalyst.



Shape-Selective Catalysis by Zeolites

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis.

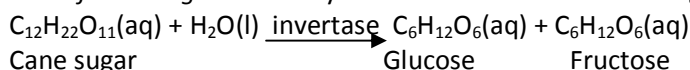
Zeolites are good shape-selective catalysts because of their honey comb-like structures. They are microporous aluminosilicates with three dimensional networks of silicates in which some silicon atoms are replaced by aluminium atoms. They contain Al–O–Si framework. The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites. They are found in nature as well as prepared artificially.

Zeolites are used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

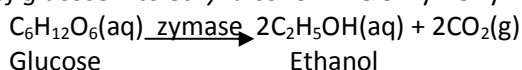
Enzyme Catalysis

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass. They are very effective catalysts and catalyse numerous reactions taking place in plants and animals. So enzymes are also called **biochemical catalysts** and the phenomenon is known as **biochemical catalysis**.

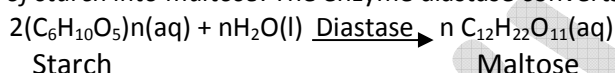
e.g.: (i) *Inversion of cane sugar*: The enzyme invertase converts cane sugar into glucose and fructose.



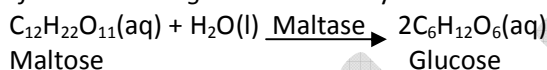
(ii) *Conversion of glucose into ethyl alcohol*: The enzyme zymase converts glucose into ethyl alcohol and carbon dioxide.



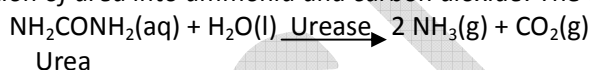
(iii) *Conversion of starch into maltose*: The enzyme diastase converts starch into maltose.



(iv) *Conversion of maltose into glucose*: The enzyme maltase converts maltose into glucose.



(v) *Decomposition of urea into ammonia and carbon dioxide*: The enzyme urease catalyses this decomposition.



Characteristics of enzyme catalysis

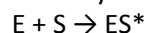
The important characteristics of enzyme catalysis are:

1. Enzyme catalysis is highly specific in nature. I.e., Each enzyme is specific for a given reaction or an enzyme that catalyses a particular reaction does not catalyse another reaction.
2. Enzyme activity is highly efficient. i.e., one molecule of an enzyme may transform one million molecules of the reactant per minute.
3. The rate of an enzyme reaction becomes maximum at a definite temperature, called the optimum temperature. The optimum temperature range for enzymatic activity is 298-310K.
4. The rate of an enzyme-catalysed reaction is maximum at a particular pH called optimum pH, which is between pH values 5-7.
5. The enzymatic activity is increased in the presence of certain substances, known as co-enzymes.
6. Enzymes activity is inhibited or poisoned by the presence of certain substances.

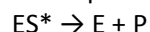
Mechanism of enzyme catalysis

There are a number of cavities present on the surface of colloidal particles of enzymes. These cavities have characteristic shape and possess active groups such as $-\text{NH}_2$, $-\text{COOH}$, $-\text{SH}$, $-\text{OH}$, etc. These are the active centers on the surface of enzyme particles. The molecules of the reactant (substrate) fit into these cavities just like a key fits into a lock. So an activated complex is formed, which then decomposes to yield the products. This theory is known as **lock and key theory**. Thus, the enzyme-catalysed reactions may be considered to proceed in two steps.

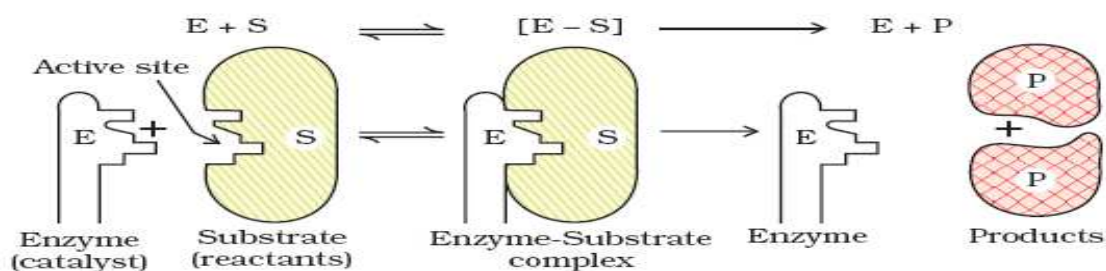
Step 1: The enzyme combines with the substrate to form an activated complex.



Step 2: Decomposition of the activated complex to form product.



The schematic representation of the mechanism of enzyme catalysis is as follows:



THE COLLOIDAL STATE

Colloid is an intermediate state between true solution and suspension. In a true solution, the size of the particles is $< 1\text{nm}$. The particles do not settle down under the influence of gravity or by any method and they cannot be filtered by a filter paper. A true solution is homogeneous and transparent.

In a suspension the size of the particles is $> 1000\text{nm}$. The particles settle down under the influence of gravity. They can be filtered by an ordinary filter paper. It is heterogeneous and opaque.

In colloids, the particle size is in between **1 nm and 1000nm**. The particles do not settle down under the influence of gravity. They cannot be filtered by ordinary filter paper, but can be filtered by ultra filters. They are heterogeneous and translucent.

Colloids are heterogeneous systems containing two phases – *dispersed phase* and *dispersion medium*. The substance which is dispersed (distributed) is called *dispersed phase* and the medium in which the particles are dispersed is called *dispersion medium*.

e.g.: In starch solution, starch is the dispersed phase and water is the dispersion medium.

Classification colloids

1. Based on the physical state of dispersed phase and the dispersion medium

Depending upon physical state of the dispersed phase and the dispersion medium, there are eight types of colloidal systems. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The different types colloidal dispersion are:

Dispersed Phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid Sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, Cell fluids
Solid	Gas	Aerosol of solid	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream, cod liver oil
Liquid	Gas	Aerosol of liquid	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid foam	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

2. Based on the dispersion medium, colloids are classified as follows:

Dispersion medium	Name of colloid
Air	Aerosol
Water	Hydrosol
Alcohol	Alco sol
Benzene	benzosol

3. Based on the attraction between the dispersed phase and the dispersion medium, colloids are of two types: **lyophilic** (solvent loving) and **lyophobic** (solvent hating). If the force of attraction between dispersed phase and dispersion medium is strong, it is called **lyophilic sol**

e.g. gum, gelatin, starch, rubber etc in suitable dispersion medium.

If the force of attraction between dispersed phase and dispersion medium is weak, it is called **lyophobic sol**. e.g. Arsenic sulphide (As_2S_3) sol, sulphur sol and metal sols like gold sol, silver sol etc.

Differences between lyophilic and lyophobic sols

Properties	Lyophilic sol	Lyophobic sol
Force of attraction	Strong	Weak
Preparation	Can be easily prepared by mixing the dispersed phase with the dispersion medium	Some special methods are used for the preparation
Reversibility	Reversible (i.e. they can be easily separated and remixed)	irreversible
Stability	Self stabilized	Less stable and requires some stabilizing agent
Coagulation	large amount of electrolyte is required for coagulation	Only small amount of electrolyte is required.

4. Based on the nature of particles:

Based on this, colloids are of three types – Multimolecular colloids, Macro molecular colloids and Associated colloids.

1. Multimolecular colloids: They contain an aggregate of atoms or molecules having dimension $< 1\text{nm}$. These particles are bind together by weak van der Waal's force of attraction and form particles of colloidal dimension. e.g. Arsenic sulphide (As_2S_3) sol, sulphur sol and metal sols like gold sol, silver sol etc.

2. Macromolecular colloids: Macromolecules (Polymers) in suitable solvents form solutions in which the size of the particle is in the colloidal range. Such systems are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many properties.

Example: solutions of starch, cellulose, proteins, enzymes, polythene, nylon, polystyrene, synthetic rubber, etc. in suitable dispersion medium.

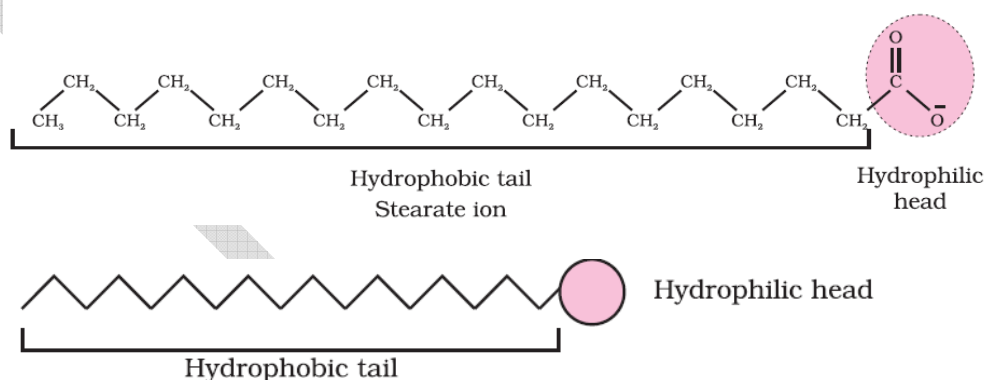
3. Associated colloids: These are substances which behave as normal strong electrolytes at low concentrations, but as colloids at higher concentrations. The colloidal behavior is because of the formation of aggregates. They are also called **micelles**.

The formation of micelles takes place only above a particular temperature called **Kraft temperature (T_k)** and above a particular concentration called **critical micelle concentration (CMC)**.

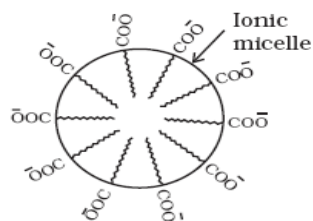
Surface active agents such as soaps and synthetic detergents are examples for micelles. These colloids have both lyophobic and lyophilic parts.

Mechanism of micelle formation

An example for micelle is soap solution. Soap is sodium or potassium salt of a higher fatty acid and may be represented as RCOO^-Na^+ . When dissolved in water, it dissociates into RCOO^- and Na^+ ions. The RCOO^- ions consist of two parts — a long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water repelling), and a polar group COO^- (also called polar-ionic 'head'), which is hydrophilic (water loving).



The RCOO^- ions are present on the surface with their COO^- groups in water and the hydrocarbon chains (R) at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape. Thus a micelle is formed.



Cleansing action of soaps

The cleansing action of soap is due to micelle formation. The soap molecules form micelle around the oil droplet in such a way that hydrophobic part is in the oil droplet and hydrophilic part projects out. Since the polar groups (hydrophilic end) can interact with water, the oil droplets are pulled in water and removed from the dirty surface. Thus soap helps in emulsification and washing away of oils and fats.

Preparation of colloids

Some of the methods used for the preparation of colloids are:

a) Chemical methods:

Colloidal solutions can be prepared by chemical reactions like oxidation, reduction, double decomposition, hydrolysis etc.

1. **Oxidation:** Sulphur sol can be prepared by passing H_2S gas through an aqueous solution of sulphur dioxide.

$$\text{SO}_2 + 2\text{H}_2\text{S} \xrightarrow{\text{Oxidation}} 3\text{S}(\text{sol}) + 2\text{H}_2\text{O}$$
2. **Reduction:** Sols of metals like silver, gold and platinum are obtained by the reduction of their salts with reducing agents like formaldehyde, stannous chloride etc.

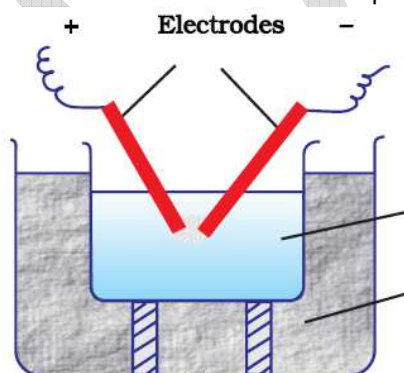
$$2\text{AuCl}_3 + 3\text{HCHO} + 3\text{H}_2\text{O} \xrightarrow{\text{Reduction}} 2\text{Au}(\text{sol}) + 3\text{HCOOH} + 6\text{HCl}$$
3. **Hydrolysis:** Ferric hydroxide sol is obtained when concentrated solution of ferric chloride is added drop-wise to hot water.

$$\text{FeCl}_3 + 3\text{H}_2\text{O} \xrightarrow{\text{Hydrolysis}} \text{Fe}(\text{OH})_3(\text{sol}) + 3\text{HCl}$$
4. **Double decomposition:** A colloidal solution of arsenic sulphide is formed by passing H_2S through a dilute solution of arsenious oxide in water.

$$\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} \xrightarrow{\text{Double decomposition}} \text{As}_2\text{S}_3(\text{sol}) + 3\text{H}_2\text{O}$$

b) Electrical disintegration (Bredig's arc method):

This method is used for the preparation of metal sols like Ag, Au, Pt etc. The metal whose sol is to be prepared is taken in the form of two rods and it is kept in suitable dispersion medium containing small amount of electrolyte. The whole arrangement is kept in an ice bath. When high voltage is passed through the metal, the intense heat produced vapourises the metal, which then condensed to form particles of colloidal dimension.



c) Peptization:

The process of conversion of a freshly prepared precipitate into a colloidal sol by shaking it with suitable dispersion medium in the presence of small amount of electrolyte is called *peptization*. The electrolyte added is called *peptizing agent*.

During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface and forms a positive or negative charge on it. Thus the particles of the precipitate break up into smaller particles of the colloidal size.

Purification of colloids

The colloidal solution prepared contains excess amount of electrolyte and some other soluble impurities. Even though small amount of electrolyte is required for the stability of colloid, large amount may cause precipitation. The process of reducing the concentration of electrolyte and other impurities is known as purification of colloids. Some methods used for purification are:

1. Dialysis: It is the process of removing dissolved substances from a colloidal solution by means of diffusion through a semi-permeable membrane. Here the sol particles are taken in a parchment or cellophane bag and it is suspended in a running stream of water. The impurities are diffused through the membrane and the sol particles are left behind. These particles are then suspended in suitable dispersion medium so as to get a colloidal dispersion.

The speed of dialysis can be increased by using hot water instead of cold water. Then the process is known as *hot water dialysis*.

The speed of dialysis can also be increased by dipping two electrodes and passing electricity. Then the process is known as *electrodialysis*.

2. Ultrafiltration: It is the process of separating the colloidal particles from the impurities by using a special type of filter paper called ultrafilters or ultra filter paper. It is prepared by dipping ordinary filter paper in *collodion solution* (a 4% solution of nitrocellulose in a mixture of alcohol and ether).

When colloidal particles are filtered using ultrafilters, the sol particles are retained on the filter paper while the impurities and the electrolyte are passed through it. When these sol particles are suspended in suitable dispersion medium, we get a colloidal solution.

Properties of colloids

1. Colligative properties:

In colloids, the number of particles are very small compared to that of true solution. So the values of colligative properties such as relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure are small compared to that of true solution.

2. Tyndall effect:

When a light beam is passed through a colloidal solution, we can see the path of the light beam. This phenomenon is known as Tyndall effect. It is due to the scattering of light beam by the colloidal particles. The visible path is called *tyndall cone*.

Tyndall effect is observed only when the following conditions are satisfied:

- (i) The diameter of the dispersed particles is much larger than the wavelength of the light used.
- (ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

True solutions do not show tyndall effect since the size of particles are very small so that they cannot scatter the light beam. Thus tyndall effect is used to distinguish a colloidal solution from a true solution.

Ultramicroscope used to see the colloidal particles works on the principle of tyndall effect.

3. Brownian movement

In colloids, the particles of dispersion medium are in a state of continuous zig-zag motion. This motion was first observed by Robert Brown and it is known as Brownian movement. It is independent of the nature of the colloidal particles but depends on the size of the particles and viscosity of the solution. Smaller the size and lesser the viscosity of the medium, faster is the motion.

Brownian movement is due to the unbalanced bombardment of particles of the dispersed phase by the particles of dispersion medium. It is responsible for the stability of colloids.

4. Charge on colloidal particles:

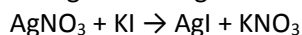
Colloidal particles always carry an electric charge. For a given colloidal solution, the nature of the charge is the same on all the particles.

<i>Positively charged sol</i>	<i>Negatively charged sol</i>
Hydrated metallic oxides like $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{CrO}_3 \cdot x\text{H}_2\text{O}$ etc.	Metal sols (e.g. Cu sol, Ag sol, Au sol)
Basic dyes (e.g. methylene blue)	Metallic sulphides (e.g. As_2S_3 , CdS etc)

Haemoglobin in blood	Acid dyes (e.g. eosin, congo red etc.)
Metal oxides (TiO ₂)	Sols of starch, gum, gelatin, clay, charcoal etc.

The charge on the sol particles is mainly due to *preferential adsorption of ions* from solution. When 2 or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle takes place.

e.g. when AgNO₃ is added to KI, AgI is precipitated, which adsorbs iodide ions from the dispersion medium and thus get a negative charge.



But when KI is added to AgNO₃, the precipitated AgI adsorbs Ag⁺ ions from the solution and thus get a positive charge.

Due to the positive or negative charge in the sol particles, they attract the counter ions (opposite ions) from the medium. Thus a double layer of opposite charges is formed. This is known as **Helmholtz electrical double layer**. The layer in which the ions are directly adsorbed to the sol particles is termed as *fixed layer*. The second layer is mobile and is termed as *diffused layer*.

Due to the opposite charges on the fixed and diffused layers, there arises a potential difference between these layers. This *potential difference between the fixed layer and the diffused layer of opposite charges is called the electrokinetic potential or zeta potential*.

The presence of similar charges on colloidal particles leads to repulsion between the particles and prevent them from coagulation when they come closer. So the charge on the sol particles is mainly responsible for the stability of colloidal solution.

5. Electrophoresis:

Since colloidal particles carry charge, they move under the influence of an electric field. This movement of colloidal particles is called *electrophoresis*. The positively charged sol particles move towards cathode (*cataphoresis*) and the negatively charged particles move towards the anode (*anaphoresis*).

If the movement of the sol particles is prevented by some suitable method, the particles of dispersion medium itself move under the presence of electric field. This migration is termed as **electro-osmosis**.

6. Coagulation (precipitation or flocculation)

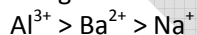
The process of settling of colloidal particles is called coagulation or precipitation of the sol. This can be done by different ways:

- i) By electrophoresis
- ii) By mixing two oppositely charged sols
- iii) By continuous dialysis
- iv) By boiling
- v) By the addition of electrolyte

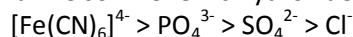
When an electrolyte is added to the sol, the ions carrying opposite charge to that of the sol neutralize the charge and causes precipitation. *The ion of the electrolyte which causes the precipitation is called the coagulating ion or the flocculating ion*. A negatively charged ion causes the precipitation of positively charged sol and vice versa.

Generally, **the greater the valency of the coagulating ion, the greater will be the coagulating power. This is known as Hardy – Schulze rule.**

Thus for the coagulation of a negative sol like As₂S₃, the flocculating power of the +ve ions is of the order:



Similarly for a +ve sol like ferric hydroxide, the flocculating power of the counter ion is of the order:



Coagulating value: The minimum concentration of an electrolyte in millimoles per litre required for the coagulation of a sol within 2 hours is called coagulating value. The smaller the coagulating value, the higher will be the coagulation power.

Protection of colloids

Lyophilic sols are self stabilized, while lyophobic sols require some stabilizing agents. For this purpose, some lyophilic sols are added to lyophobic sols. These lyophilic sols are called protective colloids.

When a lyophilic sol is added to a lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect them from electrolytes.

EMULSIONS

These are colloidal solutions in which a liquid is dispersed in another liquid. Generally one of the two liquids is water. There are two types of emulsions: 1. Oil in water (O/W) type and 2. Water in oil (W/O) type

In oil in water type emulsion, oil is the dispersed phase and water is the dispersion medium.

E.g. milk. In milk, the liquid fat is dispersed in water

In water in oil type emulsion, water is the dispersed phase and oil is the dispersion medium.

E.g. butter and cream

An emulsion obtained by mixing oil with water or water with oil is not stable. In order to prepare a stable emulsion, a third substance called *emulsifying agent* is added. The emulsifying agent forms an interfacial film between dispersed phase and the dispersion medium.

The common emulsifying agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc., and for W/O, heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.

The two types of emulsions can be distinguished by *dilution with dispersion medium*.

The droplets in emulsions carry negative charge and they can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect.

Applications of Colloids

1. Formation of Delta:

Deltas are formed at the river mouth. This is because river water is a negatively charged colloid of sand particles. When this water enters into sea, the positive ions present in sea water coagulate the colloidal solution of sand and so the particles settle down. This will result in the formation of delta.

2. Electrical precipitation of smoke (Cottrell precipitation):

Smoke is a colloidal solution of carbon, arsenic compounds, dust particles etc. in air. The smoke before coming out of the chimney is passed through a chamber (Cottrell precipitator) containing plates having a charge opposite to that of smoke particles. Thus neutralization of charges occurs and the particles settle down and pure air flows out of the chimney.

3. Purification of drinking water:

The water obtained from natural sources often contains suspended impurities. In order to coagulate these impurities, alum is added to water. The positive ions present in alum neutralize the suspended impurities and hence get purified.

4. Medicines:

Most of the medicines are colloidal in nature. This is because they have large surface area and are therefore easily assimilated. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. Colloidal gold is used for intramuscular injection.

5. Tanning:

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

6. Photographic plates and films:

Photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

7. Rubber industry:

Rubber latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of the latex.

8. Food articles:

Milk, butter, halwa, ice creams, fruit juices, etc., are all colloids in nature.

9. Blood:

Blood is a colloidal solution of an albuminoid substance. When alum and ferric chloride (FeCl_3) solution are added to blood, then coagulation of particles take place which results in clotting of blood.

10. Industrial products:

Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal in nature.

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