

## Surface chemistry

Surface chemistry can be roughly defined as the study of chemical reactions at interfaces. It is closely related to surface engineering which aims at modifying the chemical composition of a surface by incorporation of selected elements or functional groups that produce various desired effects or improvements in the properties of the surface or interface.

### Dispersed phase

The phase in a two-phase system that consists of finely divided particles (as colloidal particles), droplets, or bubbles of one substance distributed through another substance also called discontinuous phase or internal phase. In muddy water, dispersed phase is mud.

### Dispersing Medium

The substance in which the colloidal particles are distributed.  
e.g. Water, air, etc.

### Colloids on the basis of physical state of dispersed phase and dispersion medium

TABLE 13.6 Types of Colloids				
Phase of Colloid	Dispersing (solventlike) Substance	Dispersed (solutelike) Substance	Colloid Type	Example
Gas	Gas	Gas	—	None (all are solutions)
Gas	Gas	Liquid	Aerosol	Fog
Gas	Gas	Solid	Aerosol	Smoke
Liquid	Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Liquid	Emulsion	Milk
Liquid	Liquid	Solid	Sol	Paint
Solid	Solid	Gas	Solid foam	Marshmallow
Solid	Solid	Liquid	Solid emulsion	Butter
Solid	Solid	Solid	Solid sol	Ruby glass

### Colloids on the basis of nature of interaction between dispersed phase and dispersed medium

- Lyophilic
- Lyophobic

If water is the dispersing medium, then the types are hydrophilic and hydrophobic.

### **Colloids on the basis of particles of dispersed phase**

- Multi-molecular solids
- Macromolecular colloids
- Associated colloids

#### **Lyophilic colloids**

Lyophilic colloids are liquid loving colloids (Lyo means solvent and philic means loving). When these colloids are mixed with the suitable liquid, high force of attraction exists between colloidal particles and liquid. This results in formation of very stable solution called lyophilic sol. E.g. Sols of organic substances like gelatin, gum, starch.

#### **Lyophobic colloids**

Lyophobic colloids are liquid hating colloids (Lyo means solvent and phobic means hating). When these colloids are mixed with the suitable liquid, very weak force of attraction exists between colloidal particles and liquid and system does not pass into colloidal state readily.

#### **Multimolecular colloids**

When the dissolution of smaller molecules of substance or large number of atoms takes place, they combine together to form a species whose size is in the range of colloidal size. The species formed is known as the multi-molecular colloids. For example: Sulphur sol contains particles which have thousands of S<sub>8</sub>.

#### **Macromolecular colloids**

In this type of colloids, the macromolecules form a solution with suitable solvent. The size of the particles of this macromolecular solution lies in the range of colloidal particles size. Thus this solution is also known as the macromolecular colloids. The colloids formed here are similar to that of true solution in many respects and are very stable. Example: Starch, proteins, enzymes and cellulose are the naturally occurring macromolecular colloids whereas poly-ethene, synthetic rubber etc. are the synthetic macromolecules.

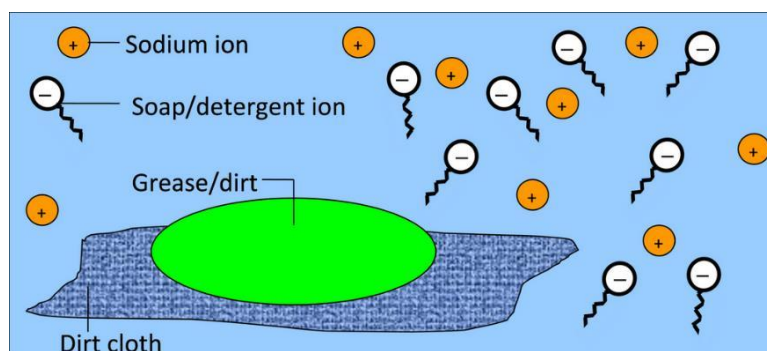
## Micelle

The cleaning action of soap is due to micelle formation and emulsion formation. Inside water a unique orientation forms clusters of molecules in which the hydrophobic tails are in the interior of the cluster and the ionic ends on the surface of cluster. This results in the formation of micelle. Soap in the form of micelle cleans the dirt as the dirt will be collected at the centre of micelle.

## Kraft temperature

The formation of the micelles takes place only above a particular temperature known as the **Kraft temperature** ( $T_k$ ) and also above a particular concentration called the **critical micelle concentration**.

## Cleansing action of soap



As we know that the micelle consist of a hydrophobic hydrocarbon and the soap molecules form micelle around the oil droplets in such a way that hydrophobic part of the stearate ions is in the oil droplets and hydrophilic part projects out of the grease droplet. So the polar group can interact with water and the oil droplets surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus, soap helps in emulsification and washing away of oils and fats.

## Colloidion

A syrupy solution of nitrocellulose in a mixture of alcohol and ether, used for coating things, chiefly in surgery and in a former photographic process.

## Methods of preparing a colloidal sol

**A. Dispersion or disintegration methods:** In this method colloidal size are formed by the breaking of bigger particles.

Example: Mechanical disintegration, Bredig's Arc method and peptization.

**B. Condensation or Aggregation methods:** In this method colloidal size particle are formed by joining together of a large number of smaller particles.

Example: By chemical reaction, by exchange of solvent and by excessive cooling.

### Dispersion methods

- Mechanical disintegration
- Electro-disintegration
- Peptization

#### Mechanical disintegration

Mechanical disintegration: In this method, solid and the liquid dispersion medium are poured into the colloidal mill to form a colloidal sol.

#### Electro-disintegration method

Hydrosols of metals e.g., platinum, silver, gold are prepared by this method. The metal electrodes are kept at the two sides of the arc which is enclosed by deionized water. The excessive heat provided by the spark vaporizes some traces of the metal and water gets condensed by vapour. Some amount of KOH is added to water as a stabilizing agent.

#### Concept of peptization

In peptization method, some amount of electrolyte are added to the precipitate to form a colloidal sol by shaking it with dispersion medium.

Example: Ferric chloride is added to a freshly prepared precipitate of ferric hydroxide which converts it into a colloidal sol of reddish brown in color.

### **Peptizing agents**

Peptization is the process responsible for the formation of stable dispersion of colloidal particles in dispersion medium. In other words it may be defined as a process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of small amount of electrolyte.

### **Purification of colloidal solutions**

The process of reducing the impurities of the electrolytes to the minimum required level is known as purification of the colloidal solution.

#### **Methods for purification of colloidal solutions**

- Dialysis
- Ultra-filtration
- Ultra-centrifugation

### **Preparation of lyophilic sols**

Starch, gum etc. form lyophilic sol with water. Instead of boiling water, warm water is used to for the preparation of sol because gum is quite soluble in warm water. Egg albumin which is obtained from eggs forms lyophilic sol with cold water.

### **Dialysis**

The process in which the ions are removed from the sol by the phenomenon of diffusion through a permeable membrane is known as dialysis. In this process a sol consisting of ions or molecules is filled in a permeable membrane bag, dipped in the water. The ion from the sol diffuses from the permeable membrane. Because of the continuous flow of water the concentration of electrolyte outside the membrane is neutralized. For e.g.: Ferric hydroxide sol is purified by using this method.

### **Ultrafiltration**

Ultrafiltration is defined as the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially designed filters, which are permeable to all substance except the colloidal particles.

### **Ultra-centrifugation**

In this method, the impure sol is taken in a tube placed in ultracentrifuge. The tube is rotated at a high speed. The colloidal particles settle down at the bottom whereas the crystalloids and other soluble impurities remain in the solution. The solution is decanted off and the colloid particles are remixed with the dispersion medium to give the pure colloid sol.

### **Electrolysis**

*Electrolysis* refers to the decomposition of a substance by an electric current. It is used extensively in metallurgical processes.

### **Physical properties of colloidal solution**

- Colloidal solution forms heterogeneous mixtures consisting of particles of dispersed phase and dispersed medium
- Colloidal sols are quite stable
- The particles in colloidal solution are not visible to naked eyes

### **Osmotic pressure**

Osmotic pressure is defined as, the minimum pressure applied on a solvent to stop the flow of water through the semi-permeable membrane.

### **Brownian motion**

It is defined as a continuous zig-zag movement of the colloidal particles in a colloidal solution. Brownian motion does not depend upon the nature of the colloid but depends on the size of the colloidal particles and viscosity of the solution. The reason of the Brownian motion is based on the fact that the molecules of dispersion medium due to their kinetic motion strikes against the colloidal particles, from all sides with different forces. The resultant force cause them to move.

### **Tyndall effects**

It is defined as the scattering of light by the colloidal particles present in a colloidal sol. The illuminated path of beam is called Tyndall cone. e.g., this phenomenon is observed when a beam of light is projected in a cinema hall.

## Tyndall Effect

The scattering of light by the particles in a colloid.

e.g. The blue color sometimes seen in the smoke emitted by motorcycles.

## Electrical properties of colloidal solution

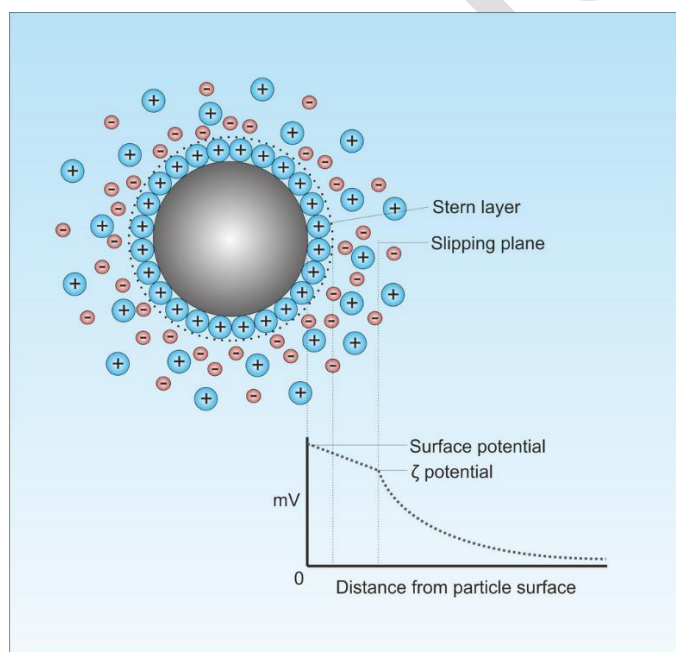
1. The phenomenon of movement of colloidal particles under an applied electric field is called electrophoresis.
2. The electrical properties of colloids can also be explained by electrical double layer theory. According to this theory a double layer of ions appear at the surface of solid.
3. Electro-osmosis : In it the movement of the dispersed particles are prevented from moving by semipermeable membrane.

## Stability of colloidal sols

The particles repel one another and do not coalesce to form large non-colloidal particles.

Colloidal particles carry either positive or negative charge. All the dispersed particles in a colloidal solution carry the same charge while the dispersion medium has an opposite and equal charge.

## Electrokinetic or zeta potential



The potential difference existing between the surface of a solid particle immersed in a conducting liquid (e.g., water) and the bulk of the liquid.

### **Electrophoresis**

The movement of colloidal particles under the influence of an electric field is called electrophoresis.

### **Isoelectric point**

The isoelectronic point or iso ionic point is the pH at which the amino acid does not migrate in an electric field. This means it is the pH at which the amino acid is neutral, i.e. the zwitter ion form is dominant.

### **Electro-osmosis**

It is defined as a phenomenon in which the molecules of the dispersion medium are allowed to move under the influence of electric field whereas colloidal particles are not allowed to move.

### **Coagulation and coagulation value**

Coagulation is a process of aggregating together the colloidal particles so as to change them into large sized particles which ultimately settle as a precipitate.

The minimum amount of an electrolyte that must be added to one litre of a colloidal solution so as to bring complete coagulation is called coagulation value

### **Hardy-Schulze law**

Greater is the valency of the oppositely charged ion of the electrolyte being added, the faster is the coagulation. The idea behind this is the attractive electrostatic forces between ions of opposite charges.

### **Methods which can cause coagulation**

- electrophoresis
- mutual precipitation
- prolonged dialysis
- heating or cooling



## **Flocculation**

The process by which individual particles of clay aggregate into clot like masses or precipitate into small lumps. Flocculation occurs as a result of a chemical reaction between the clay particles and another substance, usually salt water.

## **Cogulation of lyophobic sol**

The coagulation of the lyophobic sols can be carried out by following methods:  
By electrophoresis, By mixing two oppositely charged sols, By boiling etc.

## **Coagulation of lyophobic and lyophilic colloids**

Stability of lyophilic sol depends on the following two factors i.e. charge and solvation. When the above two factors are removed then lyophilic sols can be coagulated. This can be done by either adding an electrolyte or a suitable solvent. Lyophobic sols are less stable and hence more easily coagulated than lyophilic colloids. The stability of lyophobic sol is only due to charge.

## **Gold sol and its method of preparation**

Gold Sol is Colloidal Gold. Gold Sol can be produced by boiling a solution of tetrachloroauric acid with a reducing agent. At the beginning of the reduction process the gold atoms are liberated from the chloroauric sol.

The formation of uniform gold sols produced by the citrate reduction of auric acid is explored as a function of temperature and reagent concentration. As aurate ions are reduced, the reaction medium changes from black to purple to blue before turning deep red. These color changes are shown to result from a decrease in particle size over the course of the reaction.

## **Gold number**

Gold number of a protective colloid is the minimum weight of it in milligrams which must be added to 10ml of a substance red gold sol so that no coagulation of the gold sol takes place when 1 ml of 10% sodium chloride solution is rapidly added to it. Evidently smaller the gold number of a protective colloid, the greater is its protective action.

## **Protective action of lyophilic colloids**

Lyophilic sols are more stable than lyophobic sols. Lyophilic colloids are extensively solvated. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around

the lyophobic particles and protects the latter from electrolytes. Hence they also act as protective colloid.

### **Application of colloids**

- Medicines
- Sewage disposal
- Purification of water
- Photography
- Artificial rain

### **Emulsions**

The colloidal dispersions of two immiscible liquids in which one liquid acts as the dispersion medium and the other as dispersed phase is called an emulsion.

E.g. Oil in water is an emulsion

### **Methods of preparation of emulsion**

They are usually prepared by vigorously mixing the two liquids by using either a high speed mixing machine or by using ultrasonic vibrators. The process is known as emulsification. Since the two liquids used for the preparation of an emulsion are completely immiscible, a stabilising substance, known as emulsifying agent or emulsifier is required to stabilise the resulting emulsion. The emulsifier is added along with the liquid components. In the absence of emulsifying agent, the dispersed phase particles of colloidal size combine together resulting in the breaking up of emulsion into two separate layers.

### **Role of emulsifiers**

Emulsifiers are molecules with one water-loving (hydrophilic) and one oil-loving (hydrophobic) end. They make it possible for water and oil to become finely dispersed in each other, creating a stable, homogenous, smooth emulsion.

### **Demulsification**

Demulsification is the breaking of a crude oil emulsion into oil and water phases.

### **Applications of emulsion**

- a) In the metallurgical processes, the concentration of ore by froth floatation process is based upon the treatment of the powdered ore with oil emulsion. The valuable particles of the ore form foam which comes to the surface and is skimmed off.
- b) Asphalt emulsified in water is used for building roads without the necessity of melting the asphalt.
- c) Milk which is an important constituent of our diet is an emulsion of liquid fats in water.
- d) Several oily drugs are prepared in the form of emulsions.
- e) The cleansing action of ordinary soap for washing clothes, crockery etc. is based upon the formation of oil-in-water emulsion.

### **Harmful effects of emulsion**

The formation of emulsions is sometimes harmful. For example: petroleum forms emulsion with water. Thus, in the petroleum wells, we get the emulsion sometimes instead of petroleum alone. Likewise, the areas where small amounts of petroleum are present, the well water becomes unfit for use.

### **Gel**

A gel is a sol in which the solid particles are meshed such that a rigid or semi-rigid mixture results. Fruit jelly is an example of a gel. Cooked and cooled gelatin is another example of a gel. The protein molecules of gelatin cross-link to form a solid mesh which contains pockets of liquid.

Gels are classified into elastic and non elastic gels.

- **Elastic gels:**

These are those gels which possess the property of elasticity i.e. they change to solid mass on dehydration which can again be converted into gel by addition of water followed by heating and cooling. When they are placed in contact with water they absorb water and swell. This property is known as imbibition. Examples of elastic gels are gelatin, agar, starch etc.

- **Non-elastic gels:**

These are those gels which do not possess the property of elasticity i.e. they change to solid mass on dehydration which becomes rigid and cannot be converted into the original form by heating with water. They do not show the phenomenon of imbibition. Best example of these gels is silicic acid.

## Catalyst

A substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. Hydrogen peroxide will decompose into water and oxygen gas. Two molecules of hydrogen peroxide will produce two molecules of water and one molecule of oxygen. A catalyst of potassium permanganate can be used to speed up this process.

### Properties of catalyst and mechanism of catalyst action

1. A catalyst increases the speed of a reaction, and it also improves the yield of the intended product.
2. A catalyst actually takes part in the reaction even though it itself is not consumed or used up in the course of the reaction.
3. A catalyst makes the reaction faster by providing an alternative pathway with a lower activation energy.
4. A catalyst is reaction-specific. It may not be effective in another reaction even if the two reactions are of similar type.
5. In a reversible reaction, a catalyst accelerates both the forward and the reverse reactions. So, the inclusion of a catalyst does not alter the equilibrium constant of a reversible reaction.

Mechanism of catalyst action : Catalysts work by changing the activation energy for a reaction, i.e., the minimum energy needed for the reaction to occur. This is accomplished by providing a new mechanism or reaction path through which the reaction can proceed. When the new reaction path has a lower activation energy, the reaction rate is increased and the reaction is said to be catalyzed.

## Catalysis

Catalysis is the increase in the rate of a chemical reaction due to the participation of an additional substance called a catalyst . With a catalyst, reactions occur faster and require less activation energy. Because catalysts are not consumed in the catalyzed reaction, they can continue to catalyze the reaction of further quantities of reactant. Often only tiny amounts are required. Adding potassium permanganate to the hydrogen peroxide will cause a reaction that produces a lot of heat, and water vapor will shoot out. The catalytic converter in a car contains platinum, which serves as a catalyst to change carbon monoxide, which is toxic, into carbon dioxide.

## Types of catalysis

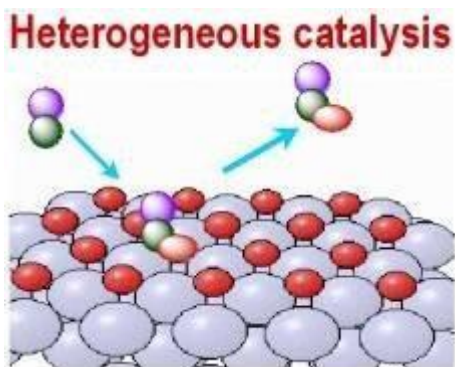
Two types of catalysis:

- 1) **Homogeneous catalysis:** When the reactant and catalyst are in the same phase.
- 2) **Heterogeneous catalysis:** When the reactant and the catalyst are in different phase.

## Types of catalysis

Homogeneous catalysis are catalytic reactions where the catalyst is in the same phase as the reactants, so homogeneous catalysis applies to reactions in the gas phase and even in a solid. Heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Phase here refers not only to solid, liquid or gas, but also immiscible liquids, e.g. oil and water.

## Heterogeneous and surface catalysis



This involves the use of a catalyst in a different phase from the reactants. Typical examples involve a solid catalyst with the reactants as either liquids or gases.

## Catalytic promoters and Catalytic poisons

Substances which themselves are not catalysts, but when mixed in small quantities with the catalysts increase their efficiency are called as promoters or activators. For example, in Haber's process for the synthesis of ammonia, traces of molybdenum increases the activity of finely divided iron which acts as a catalyst. Catalytic poisons : Substances which destroy the activity of the catalyst by their presence are known as catalytic poisons. For example, the presence of traces of arsenious oxide in the reacting gases reduces the activity of platinized asbestos which is used as catalyst in contact process for the manufacture of sulphuric acid.

## **Catalytic converter**

A catalytic converter is a device used to reduce the emissions from an internal combustion engine (used in most modern day automobiles and vehicles). Not enough oxygen is available to oxidize the carbon fuel in these engines completely into carbon dioxide and water; thus toxic by-products are produced. Catalytic converters are used in exhaust systems to provide a site for the oxidation and reduction of toxic by-products (like nitrogen oxides, carbon monoxide, and hydrocarbons) of fuel into less hazardous substances such as carbon dioxide, water vapor, and nitrogen gas.

### **Active centres**

On a molecular level, most catalysts (or most substances really) are not just flat surfaces, they have complex three-dimensional shapes. The substrate often has to bind to the catalyst in a very specific way in order for the catalysed reaction to take place - this is the active centre.

### **Intermediate compound formation theory**

According to this theory, the desired reaction is brought about by a path involving the formation of an unstable intermediate compound, followed by its decomposition into the desired end products with the regeneration of the catalyst. (a) When the intermediate compound is reactive and reacts with the other reactants.

### **Modern adsorption theory**

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:

- (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 catalysts surface through formation of an intermediate.
- (iv) Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur.

### **Advantages of modern adsorption theory**

- Small quantity of the catalyst is sufficient because the catalyst is regenerated again and again

- The catalyst takes part in the reaction but is produced back unchanged in mass and chemical composition at the end of the reaction

#### **Activity, selectivity and specificity of a catalyst**

**Activity:** It means the capacity to increase the speed of the chemical reaction.

**Selectivity:** By selectivity of a catalyst we mean its ability to direct the reaction to form particular products excluding others.

**Specificity:** Action of a catalyst is highly specific in nature, i.e a given substance can act as a catalyst only in a particular reaction and not for all the reactions.

#### **Functions of zeolites**

Important use for zeolites is as catalysts in drug (pharmaceutical) production and in the petrochemical industry, where they're used in catalytic crackers to break large hydrocarbon molecules into gasoline, diesel, kerosene, waxes and all kinds of other byproducts of petroleum. Again, it's the porous structure of zeolites that proves important. The many pores in a zeolite's open structure are like millions of tiny test tubes where atoms and molecules become trapped and chemical reactions readily take place. Since the pores in a particular zeolite are of a fixed size and shape, zeolite catalysts can work selectively on certain molecules, which is why they're sometimes referred to as shape-selective catalysts (they can select the molecules they work on in other ways beside shape and size, however). Like all catalysts, zeolites are reusable over and over again.

#### **Enzymes**

Enzymes are biological catalysts. Catalysts are substances that increase the rate of chemical reactions without being used up. Enzymes are also proteins that are folded into complex shapes that allow smaller molecules to fit into them. The place where these substrate molecules fit is called the active site. Examples are lactase, alcohol dehydrogenase and DNA polymerase.

#### **Characteristics of enzyme**

- Enzymes possess great catalytic power.
- Enzymes are highly specific.
- Enzymes show varying degree of specificities.
- Absolute specificity where the enzymes react specifically with only one substrate.

- Stereo specificity is where the enzymes can detect the different optical isomers and react to only one type of isomer.
- Reaction specific enzymes, these enzymes as the name suggests reacts to specific reactions only.

### **High efficiency of a small quantity of enzymes**

The reason is that enzymes are also generated after their catalytic activity but their rate of regeneration is very fast, of the order of 1 million times per minute.

### **Action of enzyme as a catalyst**

Enzyme catalysis follows the Lock and key mechanism and a particular substrate can combine with a particular enzyme to form an activated complex which further decompose to form the product and regenerate the enzyme.

Example of enzyme-catalyst reaction:

Conversion of milk to curd : Reaction carried out by lacto bacilli enzyme present in curd.

### **Enzyme activators**

The activity of certain enzymes is increased in the presence of certain substances called co-enzymes. It has been observed that if a protein contains a small amount of vitamin as the non-protein part, its activity is enhanced considerably.

### **Enzyme inhibitors and poisons**

The activity of enzyme is slowed down in the presence of certain substances. They are called inhibitors or poisons. They act by combining with the active functional group thereby reducing or completely destroying the catalytic enzymes.

### **Characteristics of enzyme inhibitors and poisons**

Both acts by combining with the active functional group thereby reducing or completely destroying the catalytic activity of the enzymes. The use of many drugs is on the account of their action as enzyme inhibitors in the body.



### Describe auto catalysis and its example.

A single chemical reaction is said to have undergone autocatalysis, or be autocatalytic, if one of the reaction products is also a reactant and therefore a catalyst in the same or a coupled reaction. The reaction is called an autocatalytic reaction.

### Different catalysts used in industries

Process	Catalyst	Equation
Making <u>ammonia</u>	Iron	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
Making <u>synthesis gas</u> (carbon monoxide and hydrogen)	Nickel	$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
<u>Catalytic cracking</u> of gas oil	Zeolite	Produces: a gas (e.g. ethene, propene) a liquid (e.g. petrol) a residue (e.g. fuel oil)
<u>Reforming</u> of naphtha	Platinum and rhenium on alumina	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{g}) \rightarrow \text{C}_6\text{H}_{12}(\text{g}) + \text{H}_2(\text{g})$
Making <u>epoxyethane</u>	Silver on alumina	$\text{C}_2\text{H}_4(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{C}-\text{CH}_2(\text{g})$
Making <u>sulfuric acid</u>	Vanadium(V) oxide on silica	$\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$
Making <u>nitric acid</u>	Platinum and rhodium	$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

### Adsorption

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. They are of two types: Physiosorption and Chemisorption, e.g., oxygen molecules (red) adsorbed on a bimetallic surface of platinum (purple) and cobalt (green).

### Absorbate

A material that has been or is capable of being adsorbed is known as adsorbate.  
e.g Oxygen molecule adsorbed on cobalt. Here oxygen is adsorbate.

### Adsorbent

The substance on which adsorbate is adsorbed is called adsorbent. Major types of adsorbents in use are: activated alumina, silica gel, activated carbon, molecular sieve carbon, molecular sieve zeolites and polymeric adsorbents. Most adsorbents are manufactured (such as activated carbons), but a few, such as some zeolites, occur naturally.

## Desorption

Removal of the adsorbed substance from the surface is known as desorption. Imagine a tank of water in equilibrium with its surroundings. The amount of oxygen entering and leaving the water from the air will be the same and the oxygen concentration in the water will be constant. If the water temperature increases, the equilibrium and solubility are changed, and the oxygen will desorb from the water lowering the oxygen content.

## Sorption

When both adsorption and absorption take place simultaneously. The term sorption is used. e.g: Dyes get adsorbed as well as absorbed in the cotton fibres.

## Difference between adsorption and absorption

Adsorption	Absorption
It is a surface phenomenon	It is a bulk phenomenon
The concentration on the surface of adsorbent is different from that in the bulk	The concentration is same throughout
Its rate is high in the beginning and then decreases	It remains same throughout the process

## Occlusion

The adsorption of gases on the surface of metals is known as occlusion. e.g Hydrogen is adsorbed on the surface of nickel or palladium.

## Experiment which show that adsorption occurs

- If silica gel is placed in a closed vessel containing moist air, the air becomes dry after sometime. This is because the water molecules are adsorbed on the surface of silica gel
- Add finely divided solid into a closed vessel containing a gas at low pressure. The pressure of the gas decreased showing the gas has been adsorbed

### Heat of adsorption

The amount of heat evolved when 1 mole of the gas is adsorbed on the adsorbent is called heat of adsorption.

### Exothermic nature of adsorption and the entropy change

When adsorption takes place, surface energy decreases. This appears in the form of heat of adsorption. Hence, adsorption is invariably an exothermic process, i.e.  $\Delta H_{\text{adsorption}}$  is always negative.

### Positive and negative sorption

In case of adsorption by solids from the solutions, mostly the solute is adsorbed on the surface of the solid adsorbent so that the concentration of solute on the surface of the adsorbent is greater than in the bulk. This is known as positive adsorption.

In some cases, the solvent from the solution may be adsorbed by the adsorbent so that the concentration of the solution increases than the initial concentration. This is called negative adsorption.

### Physical adsorption

When a gas is adsorbed on the surface of a solid by the weak intermolecular forces of attraction (van der Waals forces) without the formation of any chemical bond between the adsorbate and the adsorbent, it is called physical adsorption.

### Chemical adsorption

When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemical adsorption or chemisorption.

Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption. It can take place at all temperature. With the increases in temperature, Chemisorption first increases and then decreases.

### Characteristics of physical adsorption

- Physical change
- Reversible nature

- Low enthalpy of adsorption
- Low activation energy
- Multimolecular layers of adsorption
- Non-specific in nature

#### Characteristics of chemical adsorption

- Formation of chemical bond between molecules
- High activation energy
- High heat of adsorption
- Unimolecular layer of adsorption

#### Difference between physical and chemical adsorption

Physical adsorption	Chemical adsorption
1. The forces operating in this case are weak Vander wall's forces.	1. The Forces operating are chemical bonds (ionic or covalent bond).
2. The heat of adsorption is low about 20-40 KJ mol <sup>-1</sup>	2. The heat of absorption are high about 40-400 KJ mol <sup>-1</sup>
3. The process is reversible, desorption can be occur by increasing tem. Or decreasing pressure.	3. The process is irreversible. Efforts to free the adsorbed gas give different Compounds.
4. It does not require any activation energy.	4. It requires activation chergy.
5. It takes place at the low temperature and decreases with increase in the temperature.	5. This type of adsorption first increases with increase in temperature
6. It is not specific in nature all gases adsorbes on all solids to same extent.	6. It is highly specific in nature occurs only by the possibility of formation of chemical bond.
7. It increases with the increase insurface area of the adsorbent.	7. It also increases with the increases with the increase in surface area of adsorbent.
8. It forms multimolecular layer.	8. It forms unimolecular layer.

#### Adsorption isotherm

A graph between the amount of the gas adsorbed per gram of the adsorbent and the equilibrium pressure of the adsorbate at constant temperature.

#### Langmuir adsorption isotherm

Langmuir proposed his theory by making following assumptions.

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.

3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

#### **Limitation of Fredundlich adsorption isotherm**

There is a deviation between the experimental and theoretical values specially at high pressures. This isotherm is valid over a limited range of pressure.

#### **Factors affecting adsorption from solutions**

- Nature of the adsorbate and the adsorbent
- Temperature
- Surface area of the adsorbent
- Concentration of the solute in the solution

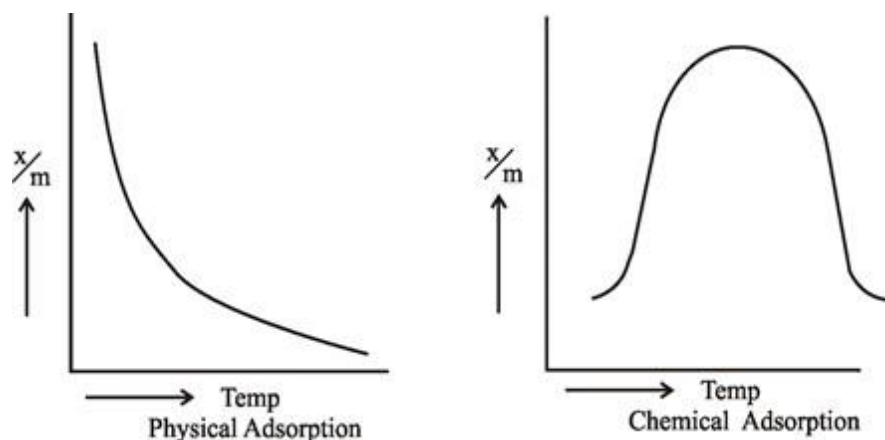
#### **Factors affecting adsorption of gases by solids**

- Nature and surface area of the absorbent
- Nature of the gas being adsorbed
- Temperature
- Pressure
- Activation of the solid adsorbent

#### **Methods of activating a solid adsorbent**

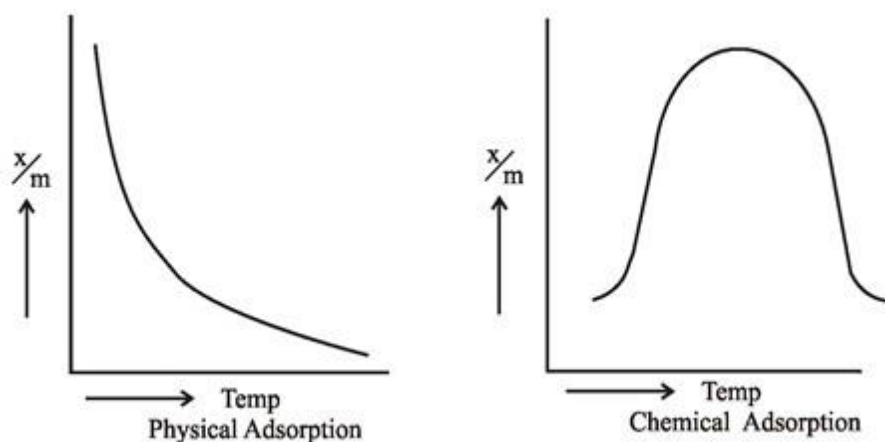
- By making the surface of the adsorbent rough
- By subdividing the adsorbent into smaller pieces or grains
- By removing the gases already adsorbed

### Adsorption isobars



A graph drawn between the amount of gas adsorbed per gram of adsorbent and the temperature at constant pressure.

### Graph of adsorption isobar



The physical adsorption isobar shows a decrease in  $x/m$  throughout the temperature. The chemical adsorption isobar shows an initial increase and then decrease with the rise in temperature.

### Applications of adsorption

- In preserving vacuum
- In softening hard water
- In froth floatation process
- In paint industry

- In dyeing
- In the separation of inert gases

### Crystalloids

A substance that, when dissolved, forms a true solution rather than a colloid and is able to pass through a semipermeable membrane. E.g sugar, salt.

### Colloids

They are homogeneous, noncrystalline substance consisting of large molecules or ultra-microscopic particles of one substance dispersed through a second substance. Colloids include gels, sols, and emulsions; the particles do not settle and cannot be separated out by ordinary filtering or centrifuging like those in a suspension. E.g gelatin.

### Examples of Colloids

Dispersed Material	Dispersed in Gas	Dispersed in Liquid	Dispersed in Solid
Gas(bubbles)	Not possible	Foams: soda pop, whipped cream	Solid foams: plaster, pumice
Liquid(droplets)	Fogs: mist, clouds	Emulsions: milk, blood	Butter, cheese
Solid(grains)	Smokes: Dust, Industrial Smoke	Sols and gels: gelatin, starch solution	Solid Sol: pearl, colored glass

### True Solution

A true solution is a mixture of two or more than two substances. The solute can't be seen even with a microscope. The particles are smaller than 1 nanometer.  
e.g. sugar or salt solution in water

### Colloidal Solution

The substance like starch, gum, gelatin etc are non crystalline in nature and in the dissolved state they do not diffuse through the parchment membrane were given the name **colloid** and the solution formed by the colloids knows as **colloidal solution**.  
e.g. Milk, Smoke, etc.

## **Suspension**

A suspension is a heterogeneous mixture containing solid particles that are sufficiently large for sedimentation.

e.g. mud in water

## **Separation by filtration**

Filtration is used to separate the two substances which can exist in any of three phases (solid, liquid and gas). Particles of larger size in a suspension can be separated from the liquid or air by the filtration, because their size ( $>10^{-6}\text{m}$ ) is visible to naked eye or under the microscope.

## **Particle Size**

In a suspension, the size of the particles is of the order of 0.1 micrometer or larger.

## **Visibility**

The particles in a suspension can be seen with naked eyes or under a simple microscope.

## **Electrophoresis**

**Electrophoresis** is defined as the movement of colloidal particles towards one or the other electrode when placed under the influence of electric field.

## **Electro-osmosis**

The phenomenon of osmosis in which the molecules of the dispersion medium are allowed to move under the influence of an electric field whereas colloidal particles are not allowed, this process is known as **electro-osmosis**.

## **Brownian Motion**

The zig zag motion of the colloidal particles.



## Tyndall Effect

The scattering of light by the particles in a colloid.

e.g. The blue color sometimes seen in the smoke emitted by motorcycles.

## True solutions, Colloidal solutions and Suspension

S.No.	Property	True Solution	Colloids Solution	Suspension
1.	Size	Size of particles is less than 1 nm.	Size of particles is between 1 nm and 100 nm.	Size of particles is greater than 100 nm.
2.	Filterability	Pass through ordinary filter paper and also through animal membrane.	Pass through ordinary filter paper but not through animal membrane.	Do not pass through filter paper or animal membrane.
3.	Settling	Particles do not settle down on keeping	Particles do not settle down on their own but can be made to settle down by centrifugation.	Particles settle down on their own under gravity.
4.	Visibility	Particles are invisible to the naked eye as well as under a microscope.	Particles are invisible to the naked eye but their scattering effect can be observed with the help of a microscope.	Particles are visible to the naked eye.
5.	Separation	The solute and solvent cannot be separated by ordinary filtration or by ultra filtration.	The solute and solvent cannot be separated by ordinary filtration but can be separated by ultra-filtration.	The solute and solvent can be separated by ordinary filtration.
6.	Diffusion	Diffuse quickly	Diffuse slowly	Do not diffuse