

Surface Chemistry

[TOPIC 1] Adsorption

The phenomenon of accumulation of higher concentration of any molecular species at the surface than in the bulk of a solid (or liquid) is called **adsorption**. It deals with the chemistry at the boundary which separates two bulk phases. This boundary is also known as surface or interface. ΔH (change in enthalpy) and ΔS (change in entropy) of adsorption are negative. Mostly adsorption processes are exothermic, therefore, adsorption decreases with increasing temperature.

- (i) **Adsorbent** is a substance on the surface of which adsorption takes place.
- (ii) **Adsorbate** is the species which concentrates or accumulates at the surface.
- (iii) In adsorption, the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption, the concentration is uniform throughout the bulk of the solid. Adsorption is a **surface phenomenon** while, absorption is a **bulk phenomenon**, e.g. water vapours are absorbed by anhydrous CaCl_2 but adsorbed by silica gel.
- (iv) The term **sorption** is used when both the processes of adsorption and absorption takes place simultaneously.
- (v) **Desorption** is the process of removing an adsorbed substance from the surface on which it is adsorbed.

1.1 Types of Adsorption

Depending on forces which hold the adsorbate on the surface of adsorbent there are mainly two types of adsorption of gases on solid.

- (i) In **physical adsorption**, forces of attraction between adsorbent and adsorbate is weak **van der Waals'** type with low heat of adsorption. Characteristics of physisorption are:
 - (a) It lacks specificity.
 - (b) The amount of gas adsorbed by solid depends on the nature of gas. Easily liquefiable gases with high critical temperature are readily adsorbed.
 - (c) At a given temperature and pressure with the increase in the surface area of the adsorbent, the extent of adsorption increases too.
 - (d) It is an exothermic process and has low enthalpy of adsorption ($20 - 40 \text{ kJ mol}^{-1}$).
 - (e) It decrease with increase in temperature.

1.2 Factors Affecting Adsorption of Gases on Solids

- (f) No appreciable activation energy is required.
- (g) It results in formation of multimolecular layers on adsorbent surface under high pressure.
- (ii) In **chemical adsorption**, adsorbate is held to adsorbent by strong chemical bond. Enthalpy of adsorption is high. Characteristics of chemisorption are:
- It is highly specific in nature and forms unimolecular layer.
 - With the increase of surface area, rate of chemisorption increases.
 - It has high heat of adsorption (80-240 kJ mol⁻¹).
 - It first increases and then decreases with increase of temperature.
 - Sometimes, high activation energy is required.

NOTE Both types of adsorption increases with increase in surface area of the adsorbent.

Comparison of Physisorption and Chemisorption

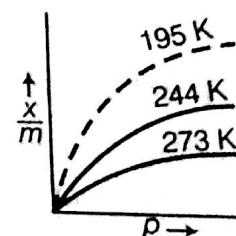
Physisorption	Chemisorption
It arises due to van der Waals' forces.	It is caused by chemical bond formation.
It is non-specific in nature.	It is highly specific in nature.
It is reversible in nature.	It is irreversible.
It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which can react with the adsorbent, show chemisorption.
Enthalpy of adsorption is low (20-40 kJ mol ⁻¹).	Enthalpy of adsorption is high (80-240 kJ mol ⁻¹).
It decreases with increase of temperature. Low temperature is favourable for physisorption.	It increases with the increase of temperature. High temperature is favourable for chemisorption.
No appreciable activation energy is needed.	High activation energy is sometimes needed.
It depends on the surface area. It increases with an increase of surface area.	It also depends on the surface area. It too increases with an increase of surface area.
It results into multimolecular layers on adsorbent surface under high pressure.	It results in formation of unimolecular layer.

- Nature of adsorbent** Greater are the strained forces on the surface, more is the ease with which adsorption takes place on the surface. The activated adsorbents have high adsorbing power.
- Surface area of adsorbent** Greater the surface area, more is the adsorption.
- Nature of gas being adsorbed** Easily liquefiable gases like NH₃, HCl, Cl₂, SO₂, CO₂, etc. (whose critical temperature is high) are adsorbed to greater extent.
- Pressure** Adsorption increases with increase in pressure. The effect of pressure is large at low temperature.
- Temperature** Since, adsorption is an exothermic process so according to Le-Chatelier's principle adsorption decreases with increase in temperature.

1.3 Adsorption Isotherm

When the extent of adsorption

($\frac{x}{m}$; where, x is the amount of adsorbate and m is the mass of adsorbent) is plotted against pressure at constant temperature, curve obtained is known as adsorption isotherm.



Adsorption Isotherm

Freundlich's Adsorption Isotherm

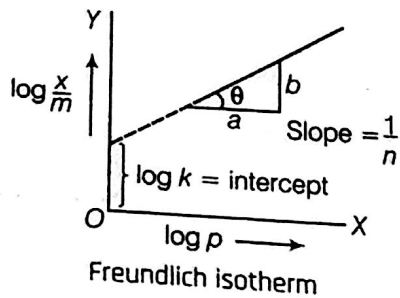
In order to show a relation between the extent of adsorption ($\frac{x}{m}$) and pressure at a particular temperature,

Freundlich proposed the following relation:

$$\left(\frac{x}{m}\right) = k(p)^{1/n};$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

A plot of $\log \frac{x}{m}$ versus $\log p$ gives a straight line with slope = $\frac{1}{n}$ and intercept = $\log k$ as shown below:



In case of solution, the isotherm takes the form,

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

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

where, x is the amount of adsorbate adsorbed on m gram of adsorbent at pressure p or concentration C of the adsorbate, k and n are constants, $n > 1$.

Applications of Adsorption

- (i) Production of high vacuum
- (ii) Gas masks
- (iii) Control of humidity
- (iv) Removal of colouring matter from solutions
- (v) Heterogeneous catalysis
- (vi) Separation of inert gases
- (vii) Froth floatation process
- (viii) Adsorption indicators
- (ix) Chromatographic analysis
- (x) In curing diseases

[TOPIC 2] Catalyst

Substances which alter the rate of a chemical reaction while remaining themselves chemically and quantitatively unchanged, are known as **catalysts** and the phenomenon is known as **catalysis**.

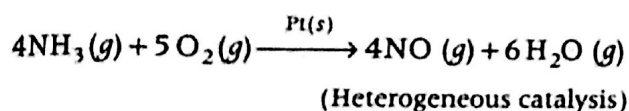
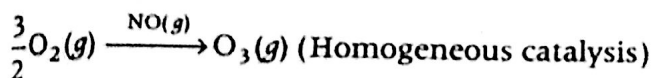
Promoters are the substances which increase the activity of a catalyst while **poisons** are the substances which decrease the activity of a catalyst.

2.1 Catalytic Activity

Catalysis on the basis of phases, is of two types i.e. homogeneous catalysis and heterogeneous catalysis. Types and mechanism of catalysis are discussed further.

Homogeneous and Heterogeneous Catalysis

In **homogeneous catalysis**, the reactants and the catalysts are in the same phase (i.e. liquid or gas) while in **heterogeneous catalysis**, the reactants and the catalysts are in different phases, e.g.

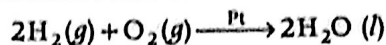


Adsorption Theory of Heterogeneous Catalysis

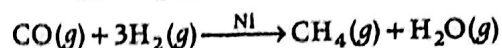
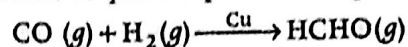
According to **adsorption theory of heterogeneous catalysis**, the reactants in gaseous state or in solutions are adsorbed on the surface of the solid catalyst by physisorption or chemisorption. The increase in concentration of the reactants on the surface increases the rate of reaction. As adsorption is an exothermic process, the heat of adsorption is utilised in enhancing the rate of the reaction.

Features of Solid Catalysts

- (i) **Activity** The activity of a catalyst depends on the strength of chemisorption to a large extent. It is the ability of a catalyst to accelerate chemical reaction. e.g. H_2 and O_2 , in presence of platinum react to form water explosively.



- (ii) **Selectivity** For a particular reaction, the selectivity of a catalyst is its ability to direct a reaction to yield a particular product. e.g.



Shape Selective Catalysis

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 microporous aluminosilicates with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al—O—Si framework. They are good shape-selective catalysts because of their honeycomb like structures. An important zeolite catalyst used in the petroleum industry is ZSM-5 which converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

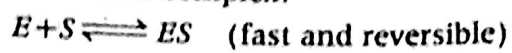
2.2 Enzymes

Enzymes are complex nitrogenous organic compounds. They are usually protein molecules of high molecular mass. These are biochemical catalysts as numerous reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes. They are highly efficient, highly specific in nature and highly active under optimum temperature and optimum pH.

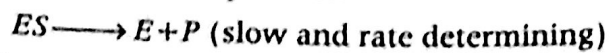
- The enzymatic activity is increased in the presence of certain substances, known as **co-enzymes**.
- Certain substances known as inhibitors or poisons reduce or completely destroy the catalytic activity of the enzymes.

- The enzyme catalysed reactions may be considered to proceed in two steps:

Step I Binding of enzyme to substrate to form an activated complex.



Step II Decomposition of the activated complex to form product.



where, E is enzyme, S is substrate and P is product.

Some industrial catalytic processes are as follows:

Process	Catalyst
Haber's process for the manufacture of ammonia. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	Finely divided iron, molybdenum as promoter. Now-a-days, a mixture of iron oxide, potassium oxide and alumina is used.
Ostwald's process for the manufacture of nitric acid.	Platinised asbestos.

[TOPIC 3] Colloids

Finely divided particles of any substance with diameter lying within 1 to 1000 nm range dispersed in any medium constitute **colloidal system**. They are intermediate between true solutions and suspensions.

On the basis of the size of the dispersed phase, solutions are divided into following three classes.

True Solution

It has dispersed particles with size less than 1 nm (i.e. $< 10^{-9}$ m).

Here, the dispersed particle constitute single molecules or ions. e.g. sugar in water or salt in water.

Colloidal Solution

Here, the size of dispersed particles range between 1nm and 1000 nm (i.e. 10^{-9} m- 10^{-6} m). e.g. Protein globules in blood plasma, fat droplets in milk.

Suspension

It has size of dispersed particles greater than 1000 nm (i.e. $> 10^{-6}$ m) which are aggregates of millions of molecules.

e.g. soil particles in water or soot particles in smoke.

3.1 Types of Colloidal Solutions

Classification Based on Nature of Interaction between Dispersed Phase and Dispersion Medium

Lyophilic Colloids

Lyophilic colloids have strong interaction between dispersed phase and dispersion medium.

These are directly formed by mixing the substance with dispersion medium. These are reversible and more stable.

Lyophobic Colloids

Lyophobic colloids have very less interaction between dispersed phase and dispersion medium.

These cannot be prepared by direct mixing. These are irreversible and less stable. They need stabilising agents for their preservation.

Classification based on Physical State of Dispersed Phase and Dispersion Medium.

Types of colloidal systems

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gemstones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream

Classification based on Type of Particles of the Dispersed Phase

Multimolecular Colloids

It consist of aggregates of atoms or small molecules with diameter of less than 1 nm, e.g. gold sol and sulphur sol.

Macromolecular Colloids

The dispersed particles are themselves large molecules of colloidal dimensions, e.g. cellulose, starch, proteins, synthetic polymers, etc.

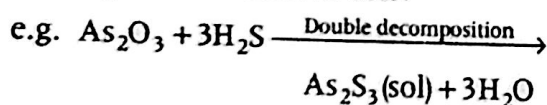
Associated colloids (Micelles).

Surface active agents like soaps and synthetic detergents belong to this class. CMC (Critical Micelle Concentration) is the lowest concentration at which micelle formation appears. Micelles from the ionic surfactant can be formed only above a certain temperature, called the **Kraft temperature**.

NOTE Function of surface active agents (soaps, detergents) is to convert oily and greasy dirt to micelles.

Preparation of Colloids

- (i) **Chemical methods** Colloidal solutions can be prepared by chemical reactions leading to the formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate leading to formation of sols.



- (ii) **Electrical disintegration** (Bredig's Arc method) This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by this method.
- (iii) **Peptisation** The process of conversion of fresh precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte (peptising agent) is known as **peptisation**.

3.3 Purification of Colloidal Solution

Colloidal sols are purified by following methods.

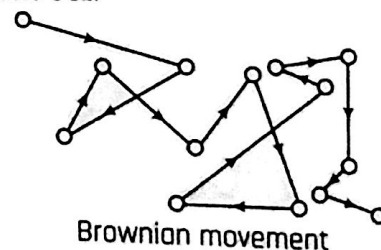
- (i) **Dialysis** is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. In the presence of electric field, it is called **electrodialysis**.
- (ii) **Ultrafiltration** is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution.

3.4 Properties of Colloidal Solutions

Colloids are heterogeneous in nature, have colligative properties, undergo Brownian motion, electro-osmosis and electrophoresis, exhibit Tyndall effect (scattering of light).

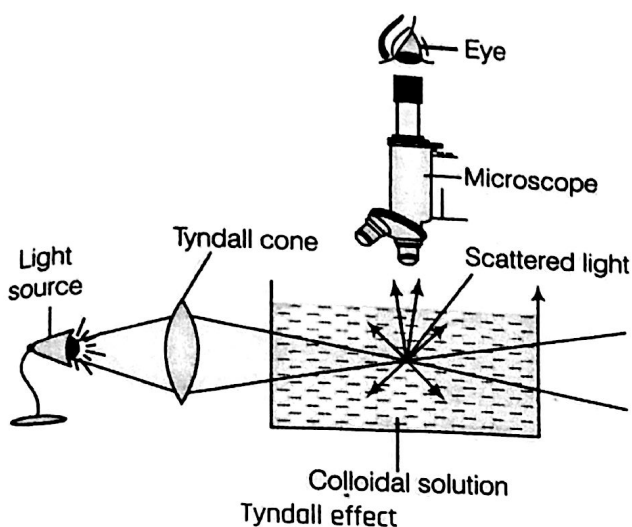
Brownian movement

The continuous rapid *zig-zag* motion of the colloidal particles in the dispersion medium is called Brownian movement. It is due to the unbalanced bombardment of the particles by the molecules of dispersion medium. This stabilises the sol.



Tyndall Effect

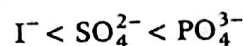
When a beam of light is passed through a colloidal solution and viewed perpendicular to the path of incident light, the path of beam is illuminated by a bluish light. This phenomenon is known as Tyndall effect and the bright cone of the light is called Tyndall cone.



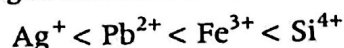
Coagulation

Change of state from colloidal to suspended is called **coagulation** or **flocculation**.

Greater the valency of the coagulating ion, the greater will be the coagulating power (**Hardy Schulze rule**). Coagulating power of anions to coagulate a positively charged colloidal sol is



Coagulating power of cations to coagulate a negatively charged colloidal sol is



Electrophoresis

The movement of colloidal particles towards positive or negative electrode in an electric field is called electrophoresis. It is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is known as **electro-osmosis**.

Charge on the Colloidal Sol

Charge on the colloidal sol is due to the preferential adsorption of either positive ion or negative ion which is common and present in excess.

- (i) AgI will adsorb I^- of KI (I^- being common) to make negatively charged sol $[AgI] I^-$.
- (ii) AgI will adsorb Ag^+ of $AgNO_3$ (Ag^+ being common) to form positively charged sol $[AgI]Ag^+$.

Zeta Potential

There is formation of an **electrical double layer** of opposite charges on the surface of colloidal particles.

The potential difference between these two layers of opposite charges is called the zeta potential or electrokinetic potential.

Flocculation Value

Minimum concentration of an electrolyte required to cause coagulation or flocculation of a sol is its flocculation value ($mmol L^{-1}$).

Protective Colloids

Coagulation can be prevented by the addition of suitable lyophilic colloidal sols. Such sols are called protective colloids.

Gold Number

The minimum number of milligrams of a lyophilic sol needed to protect 10 mL of gold sol by the addition of 1 mL of 10% NaCl is called gold number.

Protective power is the reciprocal of gold number.

3.5 Emulsion

Emulsion is dispersion of one liquid into another liquid which is immiscible.

Types of emulsions

- (i) Oil dispersed in water (O/W)
- (ii) Water dispersed in oil (W/O)

To obtain stable emulsion, emulsifier is added. Proteins, gums, natural and synthetic soaps are emulsifiers for **oil in water** type emulsions. While, heavy metal salts of fatty acids, long chain alcohols and lamp black, etc. are emulsifiers for **water in oil** type emulsions.

Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc. The process of making emulsion is called emulsification.

To stabilise an emulsion, an emulsifying agent or emulsifier is added. Soaps and detergents are most frequently used as emulsifiers.

3.6 Applications of Colloids

- (i) Electrical precipitation of smoke
- (ii) Purification of drinking water
- (iii) Medicines
- (iv) Tanning
- (v) Cleansing action of soaps and detergents
- (vi) Rubber industry, etc