Surface Chemistry

Adsorption - Mechanism and Types

Adsorption

- Phenomenon of accumulation of molecules at the surface of a solid, which results into a higher concentration at the surface than in the bulk
- The substance adsorbed is called adsorbate.
- The substance on which adsorption takes place is called adsorbent.
- The phenomenon of removing adsorbate from adsorbent is called desorption.

Distinction between Adsorption and Absorption

- **Adsorption**is a surface phenomenon of accumulation of molecules of a substance at the surface rather than in the bulk of a solid or liquid. In adsorption, the substance gets concentrated at the surface only. It does not penetrate through the surface to the bulk of the solid or liquid. For example, when we dip a chalk stick into an ink solution, only its surface becomes coloured. If we break the chalk stick, it will be found to be white from inside.
- On the other hand, the process of **absorption** is a bulk phenomenon. In absorption, the absorbed substance gets uniformly distributed throughout the bulk of the solid or liquid.

Mechanism of Adsorption

- All the forces acting between the particles inside the adsorbent are mutually balanced. However, on the surface, the particles are not surrounded by atoms or molecules of their kind on all sides and hence, they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface.
- The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.
- Adsorption is an exothermic process (ΔH = negative).
- It is accompanied by decrease in entropy of the system (ΔS = negative).
- Reason − When a gas is adsorbed, the freedom of movement of its molecules becomes restricted.
- Adsorption process is spontaneous in nature (ΔG = negative).
- When $\Delta G = 0$, state of equilibrium is attained.

Types of Adsorption

1. **Physical adsorption or physisorption –** When the accumulation of gas on the surface of a solid occurs on account of weak van der Waal's forces

2. **Chemical adsorption or chemisorption –** When the gas molecules or atoms are held to the surface by chemical bonds

- Chemical bonds may be covalent or ionic.

3. Comparisons of physisorption and chemisorption are listed in the given table.

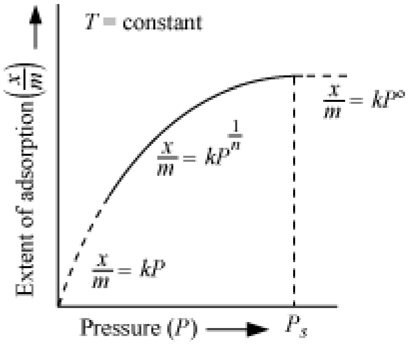
Physisorption	Chemisorption
Arises because of van der Waals forces	Arises because of chemical forces
Not specific in nature	Highly specific in nature
Reversible in nature	Irreversible in nature
Depends on the nature of gas More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which can react with adsorbent show chemisorption.
Enthalpy of adsorption is low.	Enthalpy of adsorption is high.
No appreciable activation energy is required.	Sometimes, high activation energy is required.
Results into multi-molecular layers	Results into uni-molecular layer

Low temperature is favourable for adsorption. It decreases with increase of temperature.	High temperature is favourable for adsorption. It increases with the increase of temperature.
Increases with increase in surface area	Also increases with increase in surface area

Adsorption Isotherms, Adsorption from Solution Phase & Applications of Adsorption

Adsorption Isotherms

- The plots between the extent of adsorption $\left(\frac{x}{m}\right)$ against the pressure (*P)* of the gas at constant temperature (*T*)



- **Freundlich adsorption isotherm**
- Freundlich adsorption isotherm gives an empirical relationship between the quantity of gas adsorbed by a unit mass of solid adsorbent and pressure at a specific temperature.
- From the given plot it is clear that at pressure P_s, $\frac{x}{m}$ reaches the maximum value. P_s is called the saturation pressure. Three cases arise from the graph.
- **Case I: At low pressure**

The plot is straight and sloping, indicating that the pressure is directly proportional to $\frac{x}{m}$

i.e., $\frac{x}{m} \propto P$

$\Rightarrow \frac{x}{m} = k\,P$ $\qquad (k \text{ is a constant})$

- **Case II: At high pressure**

When pressure exceeds the saturated pressure, $\frac{x}{m}$ becomes independent of *P* values.

$\frac{x}{m} \propto P^{\circ}$

$\Rightarrow \frac{x}{m} = k\,P^{\circ}$

- **Case III: At intermediate pressure**

At intermediate pressure, $\frac{x}{m}$ depends on *P* raised to the powers between 0 and 1.

- This relationship is known as the Freundlich adsorption isotherm.

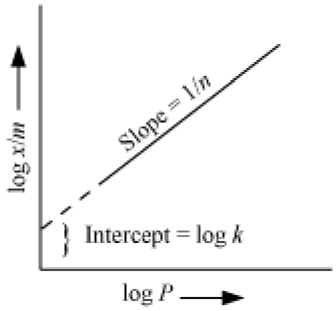
$\frac{x}{m} \propto P^{\frac{1}{n}}$

$\frac{x}{m} = kP^{\frac{1}{n}}$ $\qquad n > 1$

Now, taking log,

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

- On plotting the graph between log $\left(\frac{x}{m}\right)$ and log *P*, a straight line is obtained, with the slope equal to $\frac{1}{n}$ and the intercept equal to log *k*.



Adsorption from Solution Phase

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

- With the increase in temperature, the extent of adsorption decreases.
- With an increase in the surface area of the adsorbent, the extent of adsorption increases.
- The extent of adsorption depends on the concentration of the solute in solution, and on the nature of the adsorbent and the adsorbate.
- Can be approximately described by Freundlich's equation by using the concentration (*C*) of the solution instead of pressure

$$\frac{x}{m} \propto C^{\frac{1}{n}}$$

$$\Rightarrow \frac{x}{m} = kC^{\frac{1}{n}} \qquad n > 1$$

Now, taking log,

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

- On plotting the graph between log $\left(\frac{x}{m}\right)$ and log *C*, a straight line is obtained, with the slope equal to $\frac{1}{n}$ and the intercept equal to log *k*.

Applications of Adsorption

- Production of high vacuum: The traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump, to give a very high vacuum
- Gas mask: Used for breathing in coal mines, to adsorb poisonous gas

- Silica and aluminium gels are used as adsorbents for controlling humidity.
- A number of drugs are used for killing germs; the drugs get adsorbed on the germs.
- Used in heterogeneous catalysis
- Used in chromatographic analysis: It is based on the phenomenon of adsorption; finds a number of applications in analytical and industrial fields

Catalysis

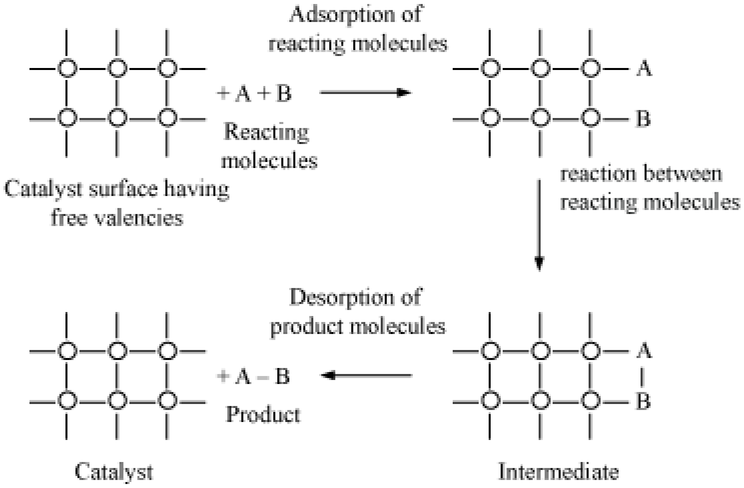
- **Catalysts** alter the rate of a chemical reaction, and remain chemically and quantitatively unchanged after the reaction.
- **Promoters** enhance the activity of a catalyst.
- **Poisons** decrease the activity of a catalyst.
- **Homogeneous catalysis –** When the reactants and the catalyst are in the same phase
- **Heterogeneous catalysis –**When the reactants and the catalyst are in different phases

Adsorption Theory of Heterogeneous Catalysis

This theory explains the mechanism of heterogeneous catalysis. The mechanism involves the following steps:

- Diffusion of reactants to the surface of the catalyst
- Adsorption of the reactant molecules on the surface of the catalyst
- Occurrence of chemical reaction on the catalyst's surface through the formation of an intermediate
- Desorption of reaction products from the catalyst surface (making the surface available for more reactions to occur)
- Diffusion of reaction products away from the surface of the catalyst

The adsorption of reacting molecules, formation of intermediate and desorption of products are shown in the given figure.



Important Features of Solid Catalysts

- **Activity –** Depends upon the strength of chemisorption to a large extent
- **Selectivity –** Ability to direct a reaction to yield a particular product

Shape-Selective Catalysis

- The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules
- Zeolites are good shape-selective catalysts

  Reason: They have honeycomb-like structures.

Enzyme Catalysis

- **Enzymes –**Complex nitrogenous compounds which are produced by living plants and animals
- They catalyse numerous reactions in the bodies of animal and plants to maintain the life processes.
- Example:

  Inversion of cane sugar into glucose and fructose by enzyme invertase

  Conversion of glucose into ethyl alcohol by enzyme zymase

- The given table lists some enzymatic reactions.

Enzyme	**Source**	**Enzymatic reaction**

Invertase	Yeast	Sucrose → Glucose and fructose
Zymase	Yeast	Glucose → Ethyl alcohol and carbon dioxide
Diastase	Malt	Starch → Maltose
Maltase	Yeast	Maltose → Glucose
Urease	Soyabean	Urea → Ammonia and carbon dioxide
Pepsin	Stomach	Proteins → Peptides

- **Characteristics of Enzyme Catalysis**
- Highly efficient
- Highly specific in nature
- Highly active under optimum temperature
- Highly active under optimum pH
- Increase in activity in the presence of activators and co-enzymes
- Influenced by inhibitors and poisons
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- **Mechanism of Enzyme Catalysis**

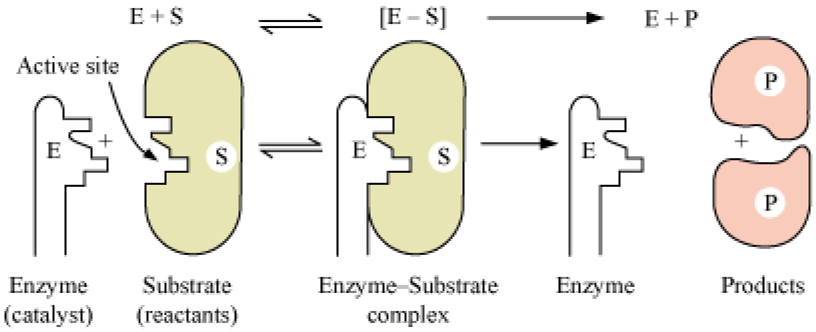
  Steps involved are –
- Binding of enzyme to substrate to form an activated complex

  $E + S \rightarrow ES^{\#}$

- Decomposition of the activated complex to form products

  $ES^{\#} \rightarrow E + P$

  The given figure represents the mechanism of an enzyme-catalysed reaction.



Catalysts in Industry

Some of the important catalytic processes are listed in the given table.

-	Process	Catalyst
1.	Haber's process for the manufacture of ammonia $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$	Finely divided iron, molybdenum as promoter; conditions: 200 bar pressure and 723–773K temperature
2.	Ostwald's process for the manufacture of nitric acid $4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$ $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ $4NO_{2(g)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 4HNO_{3(aq)}$	Platinised asbestos; temperature 573K

3.	Contact process for the manufacture of sulphuric acid $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$ $SO_{3(g)} + H_2SO_{4(aq)} \rightarrow H_2S_2O_{7(l)}$ (oleum) $H_2S_2O_{7(l)} + H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)}$	Platinised asbestos or vanadium pentoxide (V_2O_5); temperature 673−723K

Colloids - Classification and Preparation

Colloid

- Heterogeneous system
- Intermediate between true solutions and suspensions
- The range of diameters of colloidal particles is between 1 and 1000 nm.
- Consists of two phases − dispersed phase and dispersion medium

Classification of Colloids

Colloids are classified depending upon the following three criteria:

- Physical state of dispersed phase and dispersion medium
- Nature of interaction between dispersed phase and dispersion medium
- Type of particles of the dispersed phase

Depending Upon the physical state of Dispersed Phase and Dispersion Medium

Dispersed phase	Dispersion medium	Type of colloid	Example
Solid	Solid	Solid sol	Gem stones, some coloured glasses

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
Gas	Solid	Solid sol	Pumice stone, foam, rubber
Gas	Liquid	Foam	Froth, soap lather

Differences Between True Solution, Colloid and Suspension

S.No.	True solution	Colloid	Suspension
1.	Homogeneous	Heterogeneous	Heterogeneous
2.	Particles are ions or molecules.	Particles are either single macromolecules or aggregates of molecules or atoms.	Particles are aggregates of molecules or atoms.
3.	Particle size varies between 0.1 nm to 1 nm.	Particle size varies between 1 nm to 10^3 nm.	Particle size is larger than 10^3 nm.
4.	The particles do not settle.	The particles do not settle.	The particles settle out.
5.	The particles do not scatter light.	The particles scatter light.	The particles do not scatter light.

6.	It does not exhibit properties like electrophoresis, Brownian movement, etc.	It exhibits properties like Brownian movement, electrophoresis etc.	It does not exhibit properties like electrophoresis, Brownian movement, etc.

Depending Upon the Nature of Interaction between Dispersed Phase and Dispersion Medium

- **Lyophilic colloids** (solvent attracting)
- Also called reversible sols
- Quite stable and cannot be easily coagulated
- **Lyophobic colloids** (solvent repelling)
- Also called irreversible sols
- Unstable and can be easily coagulated

Depending Upon the Type of Particles of the Dispersed Phase

- **Multi-molecular colloids –** Species having size in the colloidal range

  (diameter < 1 nm)

- **Macromolecular colloids –** Macromolecules (such as starch, cellulose, proteins, enzymes, etc.) in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range.
- **Associated colloids (Micelles) –** Some substances at low concentration behave as normal electrolytes, but at higher concentrations exhibit colloidal behaviour due to formation of aggregates. The aggregated particles are called micelles and are also known as associated colloids.
- The temperature above which the formation of micelles takes place is called Kraft temperature (T_k).
- The concentration above which the formation of micelles takes place is called critical micelle concentration (CMC).

Preparation of Colloids

- **Chemical method –** Can be prepared by chemical reactions leading to the formation of molecules, which then aggregate leading to the formation of sols

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decompositon}} As_2S_3(sol) + 3H_2O$$

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

$$2\ AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au(sol) + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3(sol) + 3HCl$$

- **Electrical disintegration or Bredig's Arc method –** It involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc. can be prepared by this method.
- **Peptisation –** Process of converting a precipitate into colloidal sol by shaking it with dispersion medium in presence of small amount of electrolyte (peptising agent)

Purification of Colloidal Solutions & Properties of Colloidal Solutions

Purification of Colloidal Solutions

- Reduction of the amount of impurities to a requisite minimum
- **Dialysis**
- It is the process of removing a dissolved substance by diffusion through a suitable membrane.
- The apparatus used for this purpose is called dialyser.
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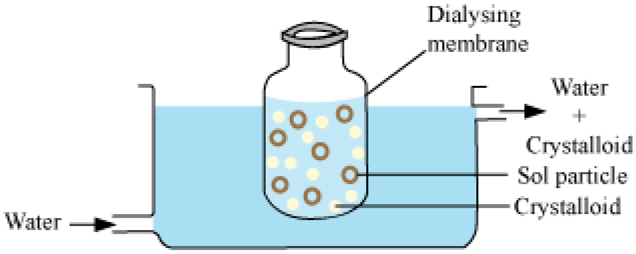
- The colloidal solution is placed in a bag of suitable membrane while pure water is taken outside.



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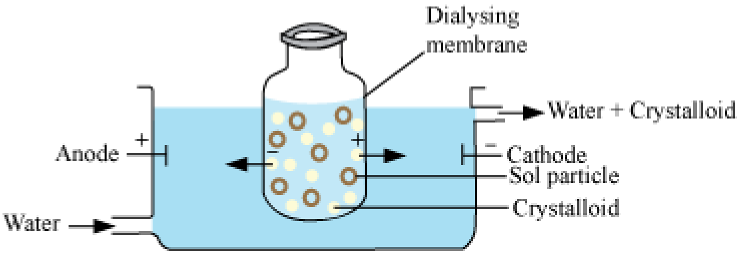
- The molecules and ions diffuse through the membrane into the outer water and pure colloidal solution is left behind.
- **Electro-dialysis**

- The process of dialysis is quite slow and can be made faster by applying an electric field.



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- When the electric field is applied, the ions present in the colloidal solution migrate out to the oppositely charged electrodes.
- **Ultra-filtration**
- It is the process of separating the colloidal particles from the solvent, and the soluble solutes present in the colloidal solution, by specially prepared filters.
- The filters are permeable to all substances, except the colloidal particles.
- It is a slow process and to speed it up, pressure or suction is applied.

Properties of Colloidal Solutions

- **Colligative properties**
- Osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point
- The values of these properties are of a small order as compared to the values shown by true solutions at the same concentrations.
- **Tyndall effect**
- It is due to the fact that colloidal particles scatter light in all directions in space.
- The scattering of light illuminates the path of the beam of light.
- **Colour**
- Depends on the wavelength of the light scattered by the dispersed particles
- Wavelength of light depends on the size and nature of the particles.
- **Brownian movement**

- Zig-zag movement of colloidal particles
- Smaller the size and lesser the viscosity, faster is the motion.
- **Charge on colloidal particles**
- Colloidal particles carry an electric charge.
- May either positive or negative
- The given table lists some common sols with the nature of charge on their particles.

Positively charged sols	Negatively charged sols
Hydrated metallic oxides (e.g., $Al_2O_3.xH_2O$, $CrO_3.xH_2O$, $Fe_2O_3.xH_2O$)	Metals (e.g., copper, silver, gold sols)
Basic dye stuffs (e.g., methylene blue sol)	Metallic sulphides (e.g., As_2S_3, Sb_2S_3, CdS sols)
Haemoglobin (blood)	Acid dye stuffs (e.g., eosin, congo red sols)
Oxides (e.g., TiO_2 sol)	Sols of starch, gum, gelatin, clay, charcoal, etc.

- **Electrophoresis**
- Movement of colloidal particles under applied electric potential
- Electro osmosis: Movement of dispersion medium through the membrane, in an applied electric field
- **Coagulation or precipitation**

Process of settling of colloidal particles

Ways to Carry Out Coagulation of Sol

- By electrophoresis
- By mixing two oppositely charged sols
- By boiling
- By persistent dialysis
- By addition of electrolytes

Hardy–Schulze rule

The greater the valence of the flocculating ion added, the greater is its power to cause precipitation.

Emulsions & Applications of Colloids

Emulsions

- Colloidal systems in which both the dispersed phase and the dispersion medium are liquids
- There are two types –
- Oil dispersed in water (O/W type)
- Water dispersed in oil (W/O type)
- Emulsifying agent: The third component used for stabilising an emulsion
- Emulsification:Process of making an emulsion

Preparation of Emulsion

- It is prepared by shaking vigorously the mixture of two immiscible liquids.
- A small amount of an emulsifying agent or an emulsifier is added to the emulsion during its preparation to prevent its breaking as the two immiscible liquids are unstable and separate out in two layers on standing.
- The emulsifier forms a protective layer around the dispersed phase which prevents the particles from coming closer to one another, thereby undergoing coagulation.

Properties of Emulsion

- The particles of disperse phase in emulsions are globules which are larger in size than the particles of disperse phase in sols.
- The globules migrate under the application of an electric field as they are negatively charged.
- On addition of electrolytes containing divalent or trivalent particles, the globules coagulate.
- The globules show Tyndall effect and Brownian motion.

Breaking of Emulsion

- Heating, freezing and centrifugation can be employed to separate the two liquids in emulsions.
- Addition of electrolytes in large quantities causes coagulation of dispersed phase particles.
- Any chemical species capable of causing chemical destruction of the emulsifier results in separation of the two liquids.

Colloids around Us

- Blue colour of the sky: Dust particles along with water suspended in air scatter blue light.

- Food particles such as milk, butter, fruit juices are all colloids.

- Fog,mist and rain are also colloids.

- Blood:A colloidal solution of an albuminoid substance

- River water: A colloidal solution of clay

- Fertile soils are colloidal in nature, in which humus acts as a protective colloid.

Applications of Colloids

- Purification of drinking water: Water obtained from natural resources often contains suspended impurities. Alum is added to coagulate the suspended impurities.

- Medicines :Most medicines are colloidal in nature. Example: Milk of magnesia(an emulsion)

- In the cleansing action of soaps and detergents

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

- Paints, inks, rubber, graphite lubricants, etc., are all colloidal solutions.

- Rubber industry: Rubber is obtained by the coagulation of latex, which is a colloidal solution of rubber particles.

- Electrical precipitation of smoke:

- Smoke is a colloidal solution of solid particles (carbon, dust, arsenic compounds, etc.).
- Smoke can be electrically precipitated by using the Cottrell precipitator.