

# SURFACE CHEMISTRY

## → 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 known as **Surface/Interface**.
- $\Delta H$  (change in enthalpy) and  $\Delta S$  (change in entropy) of adsorption are Negative.
- **Mostly adsorption are exothermic, therefore, adsorption decreases with increase in temperature.**
- Adsorbent is a substance on the surface of which adsorption takes place.
- Adsorbate is the species which concentrates or accumulates at the surface.
- In adsorption, the concentration of the adsorbate increases only at the surface of the adsorbent while in absorption, the concentration is uniform through out the bulk of the solid.
- **Adsorption is a surface phenomenon while absorption is a bulk phenomenon.** eg) Water vapours are absorbed by anhydrous  $\text{CaCl}_2$ , but adsorbed by silica gel.
- The term sorption ~~animo~~ is used when both the processes of adsorption and absorption takes place simultaneously.
- Desorption is the process of removing an adsorbed substance from the surface on which it is adsorbed.

## → 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.

→ **Physical Adsorption**, Forces of attraction b/w adsorbent and adsorbate is weak Van der Waal's type with low heat of adsorption. Characteristics of physisorption are:

(i) It lacks specificity.

(ii) The amount of gas adsorbed by solid depends on the nature of gas. Easily liquefiable gas with high critical temperature are readily adsorbed.

(iii) At a given temperature and pressure with increase in surface area adsorption also increases.

(iv) It is an exothermic process and has low enthalpy of adsorption ( $20-40 \text{ kJ mol}^{-1}$ )

(v) It decrease with increase in temperature.

(vi) No appreciable activation energy required.

(vii) It results in formation of multimolecular layers on adsorbent surface under high pressure.

→ **Chemical Adsorption**, adsorbate is held to adsorbent by strong chemical bond. Enthalpy of adsorption is high.

Characteristics of chemisorption are:

(i) It is highly specific in nature and forms unimolecular layer

(ii) With increase in surface it increases.

(iii) It has high heat of adsorption.

(iv) It first increases and then decreases with temp.

(v) Sometimes high activation energy is required.

→ Both type of adsorption  $\uparrow$ es with  $\uparrow$  in surface area.

→ Factors affecting adsorption of gases.

(i) **Nature of Adsorbent**, Greater are the stained forces on the surface, more is the ease with which adsorption takes place on the surface. The activated adsorbent have high adsorbing power.

(ii) **Surface area of adsorbent**, Greater the surface area, more is the adsorption.

(iii) **Nature of gases being adsorbed**, Easily liquefiable gases like  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{CO}_2$  etc. (whose critical temperature is high) are adsorbed to greater extent.

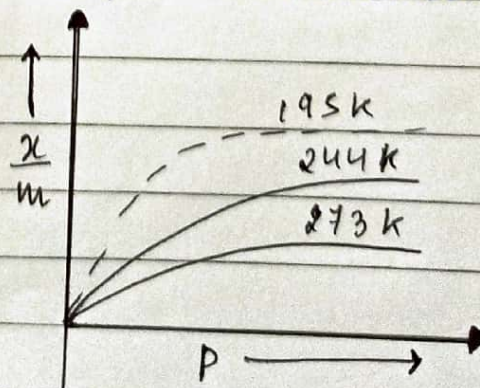
(iv) **Pressure**, Adsorption  $\uparrow$  es with increase in pressure.

(v) **Temperature**. Since adsorption is exothermic process so according to Le-Chatelier's principle adsorption decreases with increase in temperature.

→ 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.

extent of adsorption ( $\frac{x}{m}$ )  
Decreasing with increasing temperature.



eg) Why is a finely divided substance more effective as an adsorbent? Because, it has more surface area so, more adsorption occurs.  
- The No. of active sites (active centres) become more and the extent of adsorption increases.

eg) Physisorption is multilayered, while chemisorption is monolayered.  
Physical adsorption occurs due to molecular forces b/w the adsorbate and adsorbent. If the size of the adsorbent pores is close to the size of adsorbate molecules, multilayer adsorption takes place such that all the pores are filled with adsorbate molecules.  
Whereas in chemisorption, chemical bonds are formed b/w adsorbate and adsorbent molecules. Therefore it is monolayered.

## → CATALYST

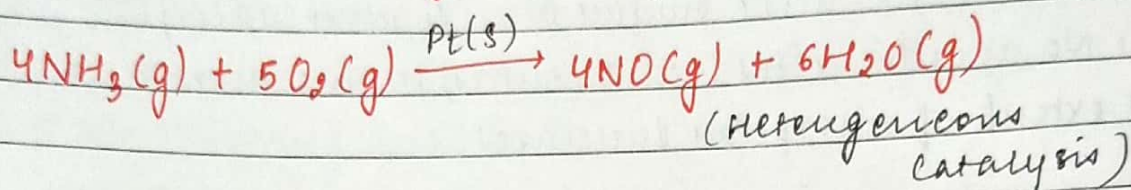
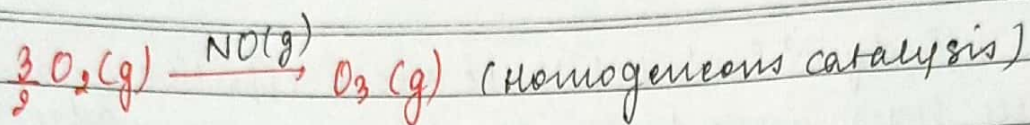
- Substances which alter the rate of a chemical reaction while remaining themselves remain chemically and quantitatively unchanged, are known as catalysts and the phenomenon is known as catalysis.
- Promoters are the substances which increase the activity of a catalyst while poisons are the substances which decrease the activity of a catalyst.

## → CATALYTIC ACTIVITY

On the basis of phase of reactant and product it is of 2 type:

- ① Homogeneous Catalysis
- ② Heterogeneous Catalysis.

→ In homogeneous catalysis, the reactants and the catalyst are in the same phase (solid, liquid/gas) while in heterogeneous catalysis, the reactants and the catalyst are in different phases.



→ Adsorption Theory of Heterogeneous Catalysis.

→ According to adsorption theory of heterogeneous catalysis, the reactants in gaseous state or in solution are adsorbed on the surface of the solid catalyst by physisorption or chemisorption.

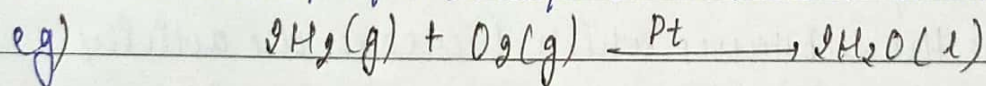
→ The increase in conc. of reactant on the surface ↑ the rate of reaction.

As adsorption is an exothermic process, the heat of adsorption is utilised in enhancing the rate of reaction.

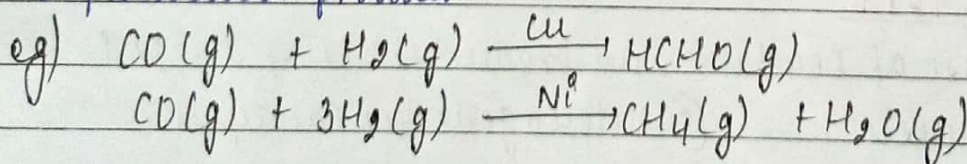
→ Features of Solid Catalyst.

(i) Activity: the activity of a catalyst depends on the strength of the chemisorption to a large extent.

It is the ability of a catalyst to accelerate chemical reaction



(ii) Selectivity: For a particular reaction, the selectivity of a catalyst is its 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 is called shape-selective catalysis.

→ Zeolites are microporous aluminosilicates with 3-D network of silicates in which some silicon atoms are replaced by aluminium atom giving Al-O-Si framework

- They are good shape selective catalyst because of their Honeycomb like structure.

- 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.

## → ENZYMES

Enzymes are complex Nitrogenous Organic compound.

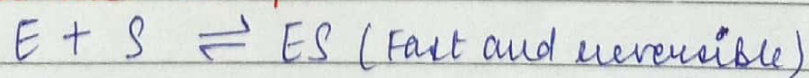
- They are usually protein molecules of high molecular mass these are biochemical catalyst as numerous reactions that occur in the bodies of animal and plant to maintain the life process are catalysed by enzymes.

- They are highly efficient, specific in nature and highly active under optimum temp. and pH.

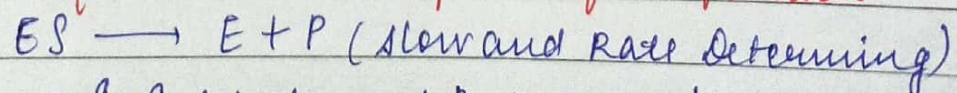
- The enzymatic activity is increased in the presence of certain substances, known as co-enzymes.

- Certain substances known as inhibitors or poison reduce or completely destroy the catalytic activity of enzymes.

→ The enzyme catalysed reactions may be considered to proceed in 2 steps: ① Binding of enzyme to substrate to form an activated complex.



② Decomposition of the activated complex to form product



(where E = enzyme, S = Substrate and P = Product)

- Some industrial catalytic process are follow:

| Process   | Catalyst.   |
|---|---|
| Haber's process for the manufacture of $\text{NH}_3$ .<br>$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ | finely divided iron, Mo as a promoter. Now a days a mixture of iron oxide, $\text{K}_2\text{O}$ and $\text{Al}_2\text{O}_3$ is used |
| Ostwald's process for the manufacture of $\text{HNO}_3$   | Platinised asbestos.  |

## → COLLOIDS

→ Finely divided particles of any substance with diameter lying within 1 to 1000nm range dispersed in any medium constitute colloidal system.

- They are intermediate b/w true sol<sup>n</sup> and suspensions

On the Basis of the size of the dispersed phase, solutions are:

→ True Solutions: It has dispersed particles with size less than 1nm (i.e.,  $<10^{-9}\text{m}$ )

eg) sugar in water or salt in water.

→ Colloidal Solution: Here the size of dispersed particle range between 1nm and 1000nm (i.e.,  $10^{-9} - 10^{-6}\text{m}$ )

eg) Proteins globules in blood plasma etc.

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

eg) soil particles in water etc.

→ Types of colloidal solution

→ Classification based on nature of interaction b/w dispersed phase and Dispersion Medium.

→ Lyophilic colloids - Lyophilic colloids have strong interaction b/w dispersed phase and medium.

- These are directly formed by mixing the substance with Dispersion medium. These are reversible & more stable.

→ Lyophobic colloids - Lyophobic colloids have very less interaction b/w D.P and D.M.

- These can't be prepared by direct mixing. These are irreversible and less.

- They need stabilising agents for their preservation.

→ Classifications based on type of particles of Dispersed phase.

→ Multimolecular colloids

It consist of aggregate of atoms or small molecules with diameter of less than 1nm eg) gold sol and sulphur sol \*

→ Macromolecular colloids: The dispersed particle are themselves large molecule of colloidal dimensions eg) cellulose, starch, proteins, synthetic polymer etc.

→ Associated colloids (micelles): surface active agents like soaps and synthetic detergent belong to this class. CMC (critical micelle concentration) is the lowest conc<sup>n</sup> at which micelle formation appears.

- Micelle from the ionic surfactant can be formed only above a certain temp. called Krafts Temperature.

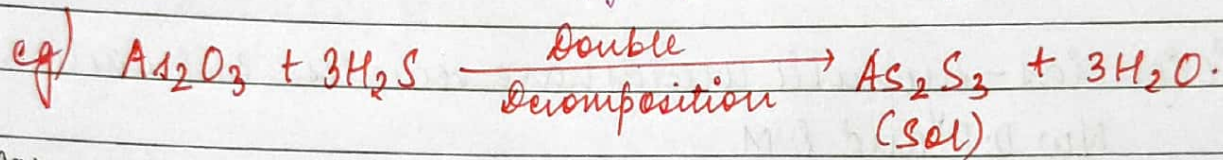


**(NOTE)** Emulsion of surface active agents (soaps, Detergent) is to convert oily and greasy dirt to micelles.

## → Preparation of colloids

(i) Chemical Methods: Colloidal sol<sup>n</sup> can be prepared by chemical reaction leading to the formation of molecules by double decomposition, Oxid<sup>n</sup>, 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 sol of metals such as Gold, silver, platinum etc can be prepared by this method.

(iii) Peptisation: the process of conversion of fresh ppt. into colloidal sol by shaking it with dispersion medium in the presence of small amt. of electrolyte (peptising agent)

## → Purification of colloidal solution

→ Dialysis is a process of removing a dissolved sub<sup>d</sup> from a colloidal sol<sup>n</sup> by means of diffusion through a suitable membrane & the presence of electric field is called electro dialysis.

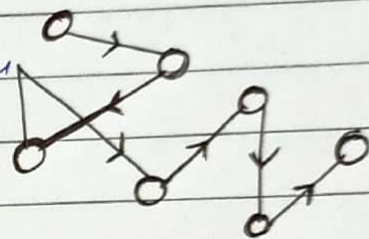
→ Ultrafiltration: is a process of separating the colloidal particle from the solvent and soluble solutes present in the colloidal solution.

## → Properties of Colloidal solutions

- colloids are heterogeneous in nature, have colligative properties, undergo Brownian motion, electro-osmosis and electrophoresis, exhibit Tyndall effect.

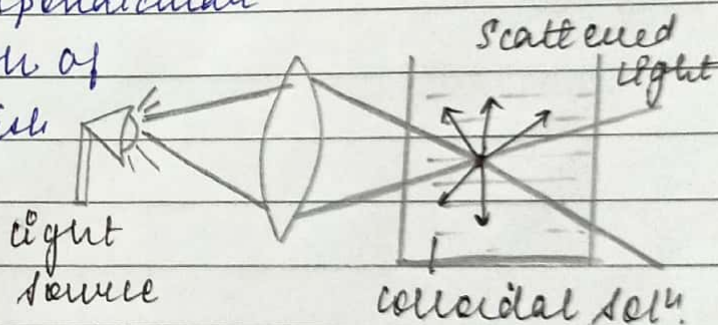
## BROWNIAN Movement.

The continuous rapid zig-zag movement of the colloidal particles in the dispersion medium is Brownian motion



## TYNDALL EFFECT

When a beam of light is passed through a colloidal sol<sup>n</sup> and viewed perpendicular to the path of incident, the path of beam is illuminated by a bluish light.



## ELECTROPHORESIS.

The movement of the colloidal particle toward 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 is called Electro-osmosis.

## → Charge On 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.

eg)  $\text{AgI}$  will absorb  $\text{I}^-$  of  $\text{KI}$

$\text{AgI}$  will absorb  $\text{Ag}^+$  of  $\text{AgNO}_3$

## ZETA POTENTIAL

There is formation of an electric double layer of charges on the surface of colloidal particles.

The potential difference b/w the two layers of opposite charges is zeta potential.

## COAGULATION

→ Change of state from colloidal to suspension is called coagulation or flocculation.

- Greater the Valency of the coagulation ion, the greater is the coagulation power (Hardy Schulze rule)

- Coagulation power of  
Anions  $I^- < SO_4^{2-} < PO_4^{3-}$   
Cations  $Ag^+ < Pb^{2+} < Fe^{3+}$

→ Flocculation Value - % minimum conc. of an electrolyte required to cause coagulation or flocculation of a sol is flocculation value.

→ Protective colloids: Coagulation can be prevented by the addition of suitable lyophilic colloid sol. Such sols are called protective sol.

→ Gold Number: The min. No. of milligram 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.

## EMULSION

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

Types of emulsion:

(i) Oil in water (O/W)

eg) Protein, gums, Natural and Synthetic soaps

(ii) Water in oil (W/O)

eg) Heavy metals, salts of fatty acid, lamp black etc.

→ Application of colloids.

- Electrical precipitation of smoke
- Purification of drinking water.
- medicines
- Tanning.
- Rubber Industry etc.