SURFACE CHEMISTRY

1. ADSORPTION

If we consider a liquid or a solid substance then we find that a molecule which is present in the bulk or interior of the substance is being attracted uniformly from all sides by the neighbouring molecules and hence there is no net force acting on the molecule.

On the other hand , if we consider a molecule that is present near the surface , we find that such a molecule is not bonded to other molecules from all sides but has some unutilized valencies because there are no neighbouring molecules above the surface to which it can be bonded.

As a result of these unbalanced forces the molecules present at the solid or liquid surface tend to satisfy their residual forces by attracting or retaining on their surface the molecule of other species when brought in contact with them. This result in increase in concentration of the substance near the surface compared with the bulk phases.

Adsorbed : A substance which has different concentration at the surface than in the bulk or interior phase is said to be adsorbed and the existence of a substance at a surface in a different concentration than in the adjoining bulk phases is called adsorption.

Adsorbent : The material upon whose surface the adsorption takes place is called adsorbent while the molecular species used to get adsorbed are called adsorbate.

Desorption : The process of removal of an adsorbed substance from the surface on which it is adsorbed is called desorption. It is reverse of adsorption and can be brought about by heating or by reducing the pressure

Difference between adsorption and absorption

ADSORPTION	ABSORPTION
1. It is a surface phenomenon.	1. It concerns with the whole mass of the absorbent
2. In it, the substance is only retained on the surface and does not go into the bulk or interior of the solid or liquid.	2. It implies that a is substance is uniformly distributed, through the body of the solid or liquid.
3. In it the concentration of the adsorbed molecules is always greater in the free phase.	3. In it the concentration is low.
4. It is rapid in the beginning and slows down near the equilibrium.	4. It occurs at the uniform rate.
5. Examples	5. Examples
(a) Water vapours adsorbed by silica gel	(a) Water vapours absorbed by anhydrous. $CaCl_2$.
(b) NH_3 is adsorbed by charcoal.	(b) NH_3 is absorbed in water forming NH_4OH.
(c) N_2 is adsorbed on mica.	
(d) O_2 is adsorbed on tungsten surface	
(e) Declourisation of sugar solution by activated or animal charcoal.	
(f) Ink is adsorbed by bloting paper.	

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Common adsorbents :

(a) Charcoals (Both vegetable and Animal)

(b) Silica gel (prepared by heating a mixture of sodium silicate and 10% HCl at 50°C).

REVERSIBLE AND IRREVERSIBLE ADSORPTION

The adsorption is reversible , if the adsorbate can be easily removed from the surface of the adsorbent by physical methods . It is called irreversible adsorption , if the adsorbate cannot be easily removed from the surface of the adsorbent.

Example :

Reversible : A gas adsorbed on a solid surface can be completely removed in vacuum.

Irreversible : Adsorption of O_2 on tungusten adsorbent

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Note :

(i) Freundlich equation is valid for physical adsorption only.

(ii) Freundlich's equation is valid only in the lower pressure range

(ii) Langmuir Adsorption isotherm :

Freundlich adsorption isotherm fails at high pressure and hence langmuir adsorption isotherm is of importance which is based on kinetic consideration.

According to Langmuir —

(a) There is adsorption of gas molecules on the surface of the solid.

(b) There is desorption of the adsorbed molecules from the surface of the solid.

(c) There is formation of unimolecular layer and thus it is chemisorption

(e) A dynamic equilibrium is attained when rate of adsorption = rate of desorption.

(f) Based on the above facts, langmuir adsorption isotherm is represented as

$$\boxed{\frac{x}{m} = \frac{ap}{1+bp}}$$

Where a & b Langmuir parameters.

Case-I At very high pressure

$bp >>> 1$, hence $1 + bp \approx bp$

$$\therefore \frac{x}{m} = \frac{ap}{bp} = \frac{a}{b} = \text{constant}$$

This shows saturation point as shown along BC.

Case-II At very low pressure

$bp <<< 1 \therefore 1 + bp \approx 1$

$$\therefore \frac{x}{m} = ap$$

$$\Rightarrow \frac{x}{m} \propto p$$

This is shown along OA

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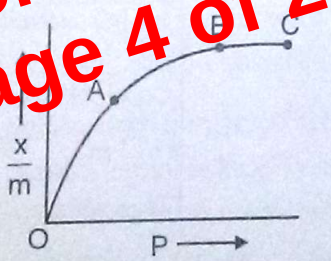
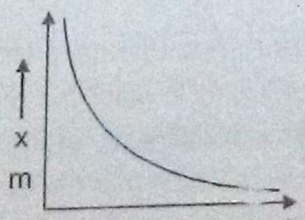
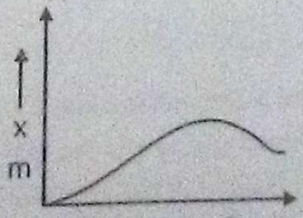


(iv) Effect of temperature :

As adsorption is accompanied by evolution of heat , so in accordance with the Le-chatelier's principle, the magnitude of adsorption should decrease with rise in temperature.



(a) Physical adsorption T →



(b) Chemisorption T →

[adsorption isobar]

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Common Colloidal System

Dispersed Phase	Dispersion medium	Colloidal system	Examples
Gas	Liquid	Foam or froth	Soap sols, lemonade froth, whipped cream.
Gas	Solid	Solid foam/Sol	Pumice stone, styrene, foam, foam rubber.
Liquid	Gas	Aerosols of Liquids	Fog, clouds, fine insecticide sprays.
Liquid	Liquid	Emulsions	Milk
Liquid	Solid	Gels	Cheese, butter, boot polish, table jellies.
Solid	Gas	Aerosols of Solid	Smoke, dust
Solid	Liquid	Sols	Most paint, starch dispersed in water, gold sol, muddy water, inks.
Solid	Solid	Solid sols	Ruby glass, some gem stones.

- A colloidal system in which the dispersion medium is a liquid or gas are called sols. They are called hydrosols or aqua sols, if the dispersion medium is water. When the dispersion medium is alcohol or benzene, they are accordingly called alcosols or benzosol.
- Colloidal systems in which the dispersion medium is a gas are called aerosols.
- Colloids in which the dispersion medium is a solid are called gels, e.g. cheese etc. They have a more rigid structure. Some colloids, such as gelatin, can behave both as a sol and a gel. At high temperature and low concentration of gelatin, the colloid is a hydrosol but at low temperature and high gelatin concentration, the hydrosol can change into a gel.

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(2) **Based on interaction or affinity of phases :** On the basis of the affinity or interaction between the dispersed phase and the dispersion medium, the colloids may be classified into two types :

(i) **Lyophilic Colloids :** The colloidal system in which the particle of dispersed phase have great affinity for the dispersion medium, are called lyophilic (solvent-loving) colloids. In such colloids, the dispersed phase does not get easily precipitated and the sols are more stable. Such colloidal systems, even if precipitated, may be reconverted to the colloidal state by simply agitating them with the dispersion medium. Hence lyophilic colloids are reversible. When the dispersion medium is water, these are called hydrophilic colloids. Some common examples of lyophilic colloids are gum, gelatin, starch, rubber, proteins, etc.

(ii) **Lyophobic colloids :** The colloidal system in which the dispersed phase have no affinity for the dispersion medium are called lyophobic (solvent hating) colloids. They are easily precipitated (or coagulated) on the addition of small amounts of the electrolyte, by heating or by shaking. They are less stable and irreversible. When the dispersion medium is water, these are known as hydrophobic colloids. Examples of lyophobic colloids include sols of metals and their insoluble compounds like sulphides and oxides.

The essential differences between the lyophilic and lyophobic colloids are summarized in table.

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