Chapter 10

Surface Chemistry

ADSORPTION

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into higher concentration of the molecules on the surface is called adsorption.

There are two types of adsorption

(i) Physical adsorption

(ii) Chemical adsorption

Physical adsorption or Physisorption	Chemical adsorption or Chemisorption
1. Enthalpy of adsorption usually is of the order of –20 kJ mol^{-1} *i.e*. exothermic.	1. Enthalpy of adsorption is of the order of –200 kJ mol^{-1}.
2. Molecule of adsorbate and adsorbent are held by weak van der Waal's interaction.	2. Molecules of adsorbate and adsorbent are held by chemical bonds.
3. It usually takes place at low temperature and decreases with increasing temperature.	3. It takes place at relatively high temperature.
4. It is not very specific *i.e*. all gases are adsorbed on all solids to some extent.	4. It is highly specific and take place when there is some possibility of compound formation between adsorbate and adsorbent molecule.
5. Multimolecular layers may be formed on adsorbent.	5. Usually monomolecular layer is formed on the adsorbent.
6. It is reversible in nature.	6. It is usually irreversible in nature.
7. It does not require activation energy.	7. It requires activation energy.

ADSORPTION ISOTHERM

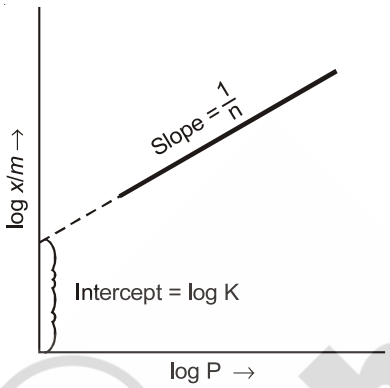
A relation or graph between x/m (x are number of moles of adsorbate and m is the mass of adsorbent) and the pressure (P) of the gas at a constant temperature is called adsorption isotherm.

A. Freundlich Adsorption Isotherm

Freundlich gave an equation $x/m = KP^{1/n}$ $(n > 1)$ to explain the effect of pressure on amount of gas adsorbed where K and n are parameters of the equations depending upon the nature of the gas and solid.

$\frac{x}{m}$ increases with increase in pressure. Since n > 1, so x/m does not increase, as rapidly as 'P'

$\log\frac{x}{m} = \log K + \frac{1}{n}\log P$ (Taking log on both sides)



From this graph it is possible to find out value of K and n

B. Langmuir Adsorption Isotherm

Langmuir considered that adsorption consist of the two opposing processes *i.e.*, adsorption and desorption both take place and dynamic equilibrium established between the above two processes. He also assumed that the layer of the adsorbed gas was only one molecule thick *i.e.*, unimolecular as in chemisorption.

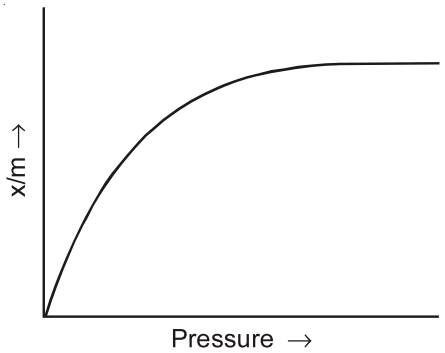
The Langmuir adsorption isotherm is represented by the relation.

$\frac{x}{m} = \frac{aP}{1+bP}$ where a and b are two Langmuir parameters.

$\frac{x}{m} = \frac{a}{b}$ (At very high pressure $1 + bP \simeq bP$)

and $\frac{x}{m} = aP$ (At very low pressure $1 + bP \simeq 1$)

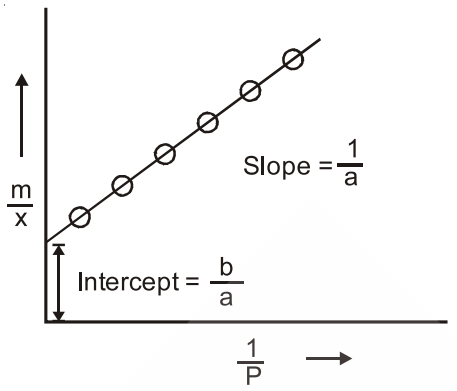
So at high pressure of the gas $\frac{x}{m}$ remains constant and nature of graph is linear at very high pressure



In order to determine the parameters a and b, we may write

$$\frac{m}{x}=\frac{1+bP}{aP}=\frac{b}{a}+\frac{1}{aP}$$

A plot of $\frac{m}{x}$ against $\frac{1}{P}$ gives a straight line with slope and intercept equal to $\frac{1}{a}$ and $\frac{b}{a}$ respectively



COLLOIDS

Colloidal state of matter is a state in which the size of particles is such (10Å – 10000Å) that they can pass through filter paper but not through animal or vegetable membrane.

CLASSIFICATION OF COLLOIDS

(i) **Based on physical state of dispersed phase and dispersion medium**–The physical state of dispersed phase and dispersion medium may be solids, liquids or gases, eight types of colloidal system are possible.

Dispersed Phase	Dispersion Medium	Name	Examples
Solid	Solid	Solid Sol	Some coloured glasses, gem stones
Solid	Liquid	Sol	Some paints, cell fluids, muddy water
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 foam	Pumice stone, foam rubber
Gas	Liquid	Foam	Whipped cream, soap lather

Note : *A gas mixed with another gas form a homogeneous mixture and not a colloidal system.*

(ii) Based on nature of interaction between dispersed phase and dispersion medium–

Divided into two types namely Lyophilic and Lyophobic Colloids

	Lyophilic Sols	Lyophobic Sols
1. Nature	Reversible	Irreversible
2. Preparation	Prepared by direct mixing with liquid dispersion medium i.e. solvent loving (greater affinity for solvent)	Cannot be prepared directly but by special method i.e. solvent hating (no affinity for solvent)

3. Stability	Quite stable and not easily precipitated or coagulated	Precipitated by adding small amount of suitable electrolyte
4. Hydration	Highly hydrated	Not much hydrated
5. Nature & substances	These sols are usually formed by the organic substances like starch, gum, proteins etc.	These are usually formed by the inorganic materials like metals, their sulphides etc.
6. Viscosity	Much higher than that of medium	Almost same as that of medium
7. Surface tension	Lower than that of dispersion medium	Nearly same as that of dispersion medium

EMULSIONS AND ITS TYPE

Emulsions are colloids in which both dispersed phase and dispersion medium are liquids and broadly classified into two types

(i) Oil in water emulsion – In this type of emulsion, oil acts as dispersed phase and water acts as dispersion medium. **Ex.**– Milk, vanishing cream etc.

(ii) Water in oil emulsion – In this type of emulsion, water acts as dispersed phase and oil acts as dispersion medium.

Ex.– Cold cream, butter, cod liver oil etc.

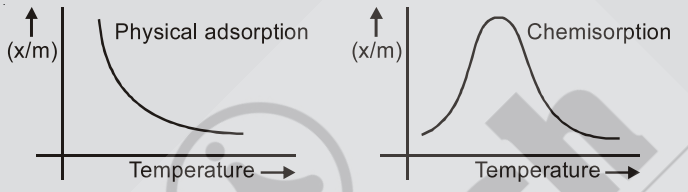
KEY POINTS

1. Colloid is not a substance, it is a state of a substance, which depends upon particle size.
2. **Emulsifier :** Long-chain hydrocarbons terminating in polar end groups are added to stabilise emulsion.
3. In **true solutions**, particle size is less than 1 nm and in **suspensions**, the particle size is more than 1000 nm.
4. The **coagulating power** of an electrolyte is inversely related to its coagulating value.
5. A phenomenon in which the molecules of dispersion medium are allowed to move under influence of electric current, whereas colloidal particles are not allowed to move, is called **electro-osmosis**.
6. The presence of electrical charge (either positive or negative) on colloidal particle is responsible for **stability of colloidal solutions**.
7. **Gold number** of a protective colloid is minimum weight of it in milligrams which must be added to 10 ml of a standard red gold sol so that no coagulation of gold sol (*i.e.*, change of colour from red to blue) take place when 1 ml of 10% NaCl solution is rapidly added to it. Obviously, smaller the gold number of a protective colloid, greater is the protective action *e.g.*, gelatin has very small value of gold number.
8. Gold number is assigend to lyophilic colloids only.
9. **Multimolecular colloids** consist of aggregated atoms or molecule *e.g.*, gold, sulphur sol.
10. **Macromolecular colloids** have dispersed phase particles as macromolecule or polymers *e.g.* protein sol.
11. Substances which possess surface activity *i.e.*, property to lower surface tensions of liquids or the tendency to increase surface area, are called **surfactants**.
12. The substances which at low concentration in a medium behave as normal strong electrolyte but at higher concentration exhibit colloidal properties due to formation of aggregated particles are called **associated colloids** or **micelles**. Their formation take place above a particular temperature called kraft temperature (T_k) and above a particular concentration (CMC – Critical Micelle Concentration), *e.g.*, soaps and detergents.

ADDITIONAL POINTS

1. SnO_2 forms a positively charged colloidal sol in acidic medium and negatively charged sol in basic medium.
2. Delta is generally formed as result of coagulation when river meets the ocean.
3. A solid metal in a finely divided state is a better catalyst.
4. H_2O is absorbed by anhydrous $CaCl_2$ whereas, it is adsorbed on **silica gel**.
5. Gases are adsorbed on solid surface (Ni, Co, Pt, Pd etc.) but absorbed in solvent phase.
6. During adsorption, ΔH = –ve, ΔS = –ve hence adsorption is spontaneous at low temperature, when ΔG = – ve.

   At adsorption equilibrium $\Delta G = 0$ and rate of adsorption becomes equal to rate of desorption.
7. Easily liquefiable gases (*e.g.*, HCl, NH_3, CO_2) are adsorbed to greater extent than others (H_2, N_2, O_2 etc.)
8. The adsorption of gases on finely divided metal surface is also called **occlusion**.
9. As temperature increases, rate of chemisorption first increases and then decreases.



10. Freundlich adsorption isotherm is only a special case of Langmuir adsorption isotherm for intermediate pressures (Freundlich isotherm fails at high pressure of the gas).
11. Catalytic promoters increase the activity of catalyst e.g. Mo acts as promoter for Fe. (catalyst) in Haber process of formation of NH_3.
12. The potential difference set up across the surface of separation of two oppositely charged layers just in contact with each other on the surface of colloid is known as **electrokinetic** or **zeta potential**.

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