COLLOIDS

Colloids: Mixtures in which microscopically dispersed insoluble particles of one substance are suspended in another substance.

Colloidal particles is 10^{-4} to 10^{-7} cm, which is intermediate between the true solution and suspension.

Ex: Fog, Whipped cream, Milk, Cheese, Blood plasma, Pearls etc.

They considered as a heterogeneous system consisting of two components:

1. A dispersed phase: It is also known as discontinuous or inner phase.
   It consists of discrete particles significantly larger than ordinary molecules and in this small particle of solute is diffused in solvent.
2. A dispersion medium or continuous phase or the outer phase:
   It is the medium in which dispersed phase is present. This consists of continuously interlinked molecules.

Classification of Colloids

a) On the basis of Nature of Interaction between Dispersed phase and Dispersion Medium

i) Lyophilic colloids:

When dispersed phase has a greater affinity for the dispersion medium, the colloids are termed as lyophilic colloids.

They are prepared by simply dissolving the material in the solvent. Because of attraction between the dispersed phase and dispersion medium, salvation of the particles occurs.

Ex: proteins, starch, albumin etc.

They are reversible sols due to their ability to reconstitute on adding dispersion medium after separation.

They are quite stable and do not coagulate easily.

ii) Lyophobic colloids:

When the dispersed phase has less affinity for the dispersion medium, the colloids are termed as lyophobic colloids.

Ex: Gold sol, As_2S_3 sol etc

They are usually inorganic in nature. They are irreversible sols as they cannot be reconstituted by simply adding dispersion medium after precipitation. They are unstable and can coagulate easily on adding electrolyte, shaking or heating. Lyophobic colloids can be prepared by special methods and require a stabilising agent.

b) On the basis of Physical State of Dispersed Phase and Dispersion Medium

Dispersed Phase	**Dispersion medium**	**Type**	**Examples**
Solid	Solid	Solid Sol	Coloured gem
Solid	Liquid	Sol	Milk of magnesia
Solid	Gas	Aerosol	smoke

Liquid	Solid	Gel	Jelly
Liquid	Liquid	Emulsion	Milk, face cream
Liquid	Gas	Aerosol	Fog, clouds
Gas	Solid	Solid sol	Foam, sponge
Gas	Liquid	Foam	Shaving cream

c) Depending on the structure of colloid particles:

a. Multimolecular colloids:

The multimolecular colloidal particles consists of aggregate of atoms of small molecules with diameter less than 10^{-9} m or 1 nm. Ex: A sol. of Sulphur consists of particles containing a thousand or so S_2 molecules. These particles are hold together by vandal Waal's forces. These are usually lyophobic sols.

b. Macromolecular colloids:

The macromolecular colloidal particles themselves are large molecules. They have very high molecular weights varying from thousand to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polystyrene, Dacron, synthetic rubber, plastics, etc.

c. The associated colloids:

These colloids behave as normal electrolytes at low concentrations but colloids at higher concentrations. This is because at higher concentrations, they form aggregated (associated) particles called miscellas.
Ex: Soap and synthetic detergents.

Coagulation (or **precipitation**)**:** The phenomenon of aggregation or accumulation of colloidal particles to settle down as a precipitate.

Due to the existence of charge on colloidal particles, lyophobic sols are stable. The same type of charge on colloidal particles repels one another and keeps them in a suspended state. The particles will move closer to one another to form aggregates (or coagulate) and settle down under the influence of gravity if the charge is somehow eliminated. This process is called coagulation.

Process of Coagulation of lyophobic sols

The methods of coagulation of lyophobic sols are:

1. **Electrophoresis**: Moving towards electrodes with opposing charges, the colloidal particles discharge, and then get precipitated.

2. **Mixing two oppositely charged sols**: When oppositely charged sols are mixed in almost equal amounts, they neutralize their charges and get precipitated. Ex: Arsenic sulfide (-ve sol) and hydrated ferric oxide (+ve sol) are combined to generate precipitated forms.
3. **Addition of electrolyte**: The colloidal particles precipitate when an excess of an electrolyte is introduced. The interaction of colloids with ions having charges opposite to their own causes neutralization, and hence lead to their coagulation.
4. **Boiling**: Boiling a sol causes more collisions with the molecules of the dispersion medium, which disturbs the adsorbed layer. This lowers the charge on the particles, which eventually causes them to settle as a precipitate.
5. **Dialysis**: Continuous dialysis is one of the methods to coagulate lyophobic sols. Persistent dialysis causes the sol to lose its stability and eventually coagulate as parts of the electrolytes are fully removed.

Hardy-Schulze Rule :

Hardy-Schulze's rule states that the greater the valency of the flocculating ion added, the greater will be its power to cause precipitation.

In other words, the coagulation power depends on the valency of the coagulation ion.

The coagulating power in the coagulation of a negative sol is

$Al^{3+} > Ba^{2+} > Na^{+}$

Similarly, coagulating power in the coagulation of a positively charged sol is

$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$

Coagulation of lyophilic sols

The stability of lyophilic sols is primarily attributed to two factors. Colloidal particles' charge and solvation. This is accomplished by adding an electrolyte and a suitable solvent, respectively. The dispersion phase of hydrophilic sols dehydrates when solvents like alcohol and acetone are introduced. A minimal amount of electrolyte can cause coagulation in this condition.

Protection of Colloids:

Process of addition of lyophilic sols by which the lyophobic sols are protected from precipitation on adding an electrolyte is known as protection of colloids.

The lyophilic colloid is added as the protective colloid and lyophobic sols achieve extra stability. This is due to lyophilic colloid that adsorbs onto the lyophobic particles, forming a protective layer that prevents the precipitating ions from reaching the sol particles.

For eg. Hydrophilic colloids such as gelatin, starch etc. act as protective colloids for the gold sol and prevents their precipitation by addition of limited amount of NaCl.

Gold number: The minimum weight in milligrams of a protective colloid needed to prevent the coagulation of 10 mL of a standard gold sol when 1 mL of a 10% NaCl solution is added is known as gold number.

It was first used by R.A.Zsigmondy

A lower gold number indicates a more effective protective colloid. It means meaning it provides greater protection against coagulation at a smaller mass.

The gold number of colloids are

I) Gelatin - 0.005–0.01
II) Gum - 0.15
III) Haemoglobin - 0.03
IV) Starch - 25

Adsorption

Adsorption is a phenomenon of an increase in the concentration of any substance or molecules on the surface of a solid or liquid.

or

The phenomenon of attracting and retaining the molecules of a gas or a dissolved substance by the surface of a solid or a liquid, resulting in their higher concentration on the surface is called **adsorption.**

The substance which gets adsorbed or deposited is called adsorbate, while the substance on which adsorption/deposition takes place is called adsorbent.

Examples: adsorption of dyes by charcoal, adsorption of gases by charcoal, adsorption of water on silica gel, and so on.

The phenomenon of an increase in the concentration of any substance or molecules in the bulk of another substance is called absorption.

Occlusion: When adsorption of gases occurs on the surface of metals it is called occlusion.

Sorption is a process that involves both adsorption and absorption phenomena simultaneously.

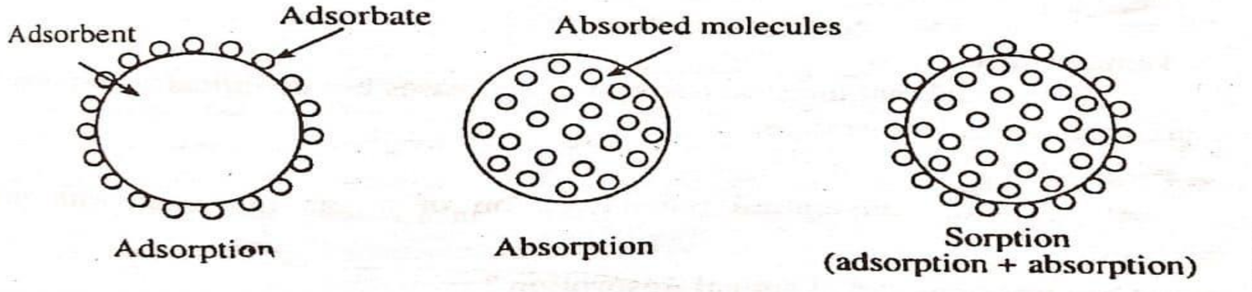


Fig. The process of adsorption, absorption and sorption

Mechanism of Adsorption

The molecules or atoms that make up the majority of the adsorbent are symmetrically surrounded by other atoms or molecules. As a result, it will have no net attractive force. However, since the surface molecules are not symmetrically surrounded, they have some residual force due to the valence force. Adsorption occurs at the surface of the adsorbent due to the residual force remaining at the surface.

Types of Adsorption

- **Physical Adsorption**: Physical adsorption occurs when an adsorbate is held on the adsorbent's surface by a weak van der Waal's force of attraction.

  Ex: Adsorption of oxygen on charcoal is an example of physical adsorption.

- **Chemical Adsorption**: Chemical adsorption occurs when an adsorbate is held on the adsorbent's surface by forces similar to a chemical bond.

  Ex: Adsorption of hydrogen on nickel is one of the examples of it.

Physical adsorption and Chemical adsorption

Physical adsorption (Physiosorption)	**Chemical adsorption (Chemisorption)**

Adsorbate is kept on the adsorbent's surface by a weak van der Waal's force of attraction.	Adsorbate is kept on the adsorbent's surface by a strong chemical bond.
No new compounds are formed in this phenomenon.	Surface compounds are formed in chemisorption.
Decreases with a decrease in temperature.	Increases with an increase in temperature.
It is a reversible process.	It is an irreversible process.
It doesn't require activation energy.	Activation energy is required.
Heat of adsorption is low (20-40 KJ mol^{-1})	Heat of adsorption is high (40-400 KJ mol^{-1})
Involves the formation of the multilayer.	Only a monolayer is formed.
The adsorption is effective at low temperatures and high pressure.	The adsorption is effective at high temperatures.
It is not specific in nature.	It is specific in nature.

Factors affecting adsorption of gases by solids

The Factors affecting adsorption of gases by solids are

1. **Nature and Surface Area of the Adsorbent:**

   Different solids would adsorb different amounts of the same gas even under similar conditions. Substances like charcoal and silica gel are excellent adsorbents. The substances that are porous in nature and have rough surfaces are better adsorbents.

   The extent of adsorption also depends upon the surface area of the solid. Greater the surface area, more is the surface available for adsorption and greater is the adsorption. The surface area depends upon the particle size of the substance.

2. **The Nature of the Adsorbed Gas** : The extent of adsorption also depends upon the nature of the gas. The gases which are more easily liquifiable or are more soluble in water are more readily adsorbed than others. For example, under similar conditions, the amount of SO2 or NH3 adsorbed by charcoal is much more than that of H2 or O2 gases. It is because the intermolecular forces are stronger in more easily liquifiable gases, therefore, they get adsorbed more

3. **Temperature**: Physical adsorption decreases with an increase in temperature, while chemisorption increases with an increase in temperature.

4. **Pressure**: The adsorption of gas increases with increasing pressure at a constant temperature.

Freundlich Adsorption Isotherm:

Freundlich gave an empirical mathematical relationship between the extent of adsorption x/m and the equilibrium pressure (p) of the gas as

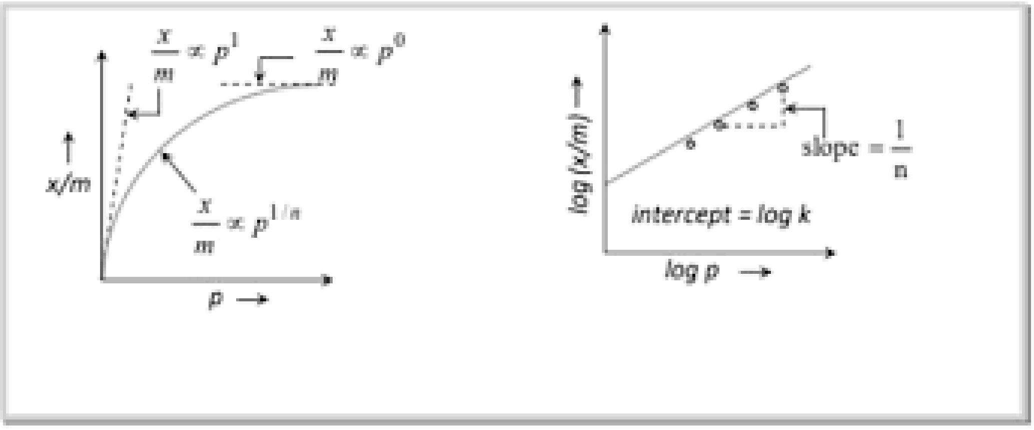
$$x/m = k\,p^{1/n} \quad \text{where } n > 1$$

In this relation k is a constant at a given temperature and depends upon the nature of the adsorbate and adsorbent. The value of n changes with pressure. It is 1 at low pressures and increases with pressure. The relationship is valid at a constant temperature. Therefore, it is called Freundlich Adsorption Isotherm.

On taking logarithm of the above equation, we get

$$\log x/m = \log k + 1/n \log p$$

This is an equation of a straight line and a plot of log x /m against log p should be a straight line with slope 1/ n as depicted in Fig.



The extent of adsorption from solution,(depends upon the concentration of the solute in the solution) is expressed as

$$x/m = kc^{1/n}$$

$$\log (x/m) = \log k + 1/n \log c$$

One of the drawbacks of the Freundlich adsorption isotherm is that it fails at high pressure of the gas.

Langmuir Adsorption Isotherm:

Langmuir derived an adsorption isotherm on theoretical considerations based on kinetic theory of gases known as the Langmuir adsorption isotherm.

This isotherm is based on the assumption that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not nearby sites are occupied.

Langmuir considered adsorption to consist of two opposing processes:

1) Adsorption of the gas molecules on the surface of the solid.

2) Desorption of the adsorbed molecules from the surface of the solid.

Eventually a dynamic equilibrium is established between the above two opposing processes.

He also assumed that the layer of the adsorbed gas is only one molecule thick i.e., unimolecular. Since such type of adsorption is obtained in the case of chemisorption. Langmuir adsorption isotherm works particularly well for chemisorption.

Let θ be the fraction of surface covered by a gas molecule, P the pressure, and “1-θ” be the fraction of surface uncovered by a gas molecule.

Since the rate of adsorption depends on the fraction uncovered and the pressure

i.e. rate of adsorption α (1-θ)P

$R_1 = K_1 (1-\theta)P$…………………(i)

Since the rate of desorption depends on the fraction covered

$R_2 = K_2 \theta$…………………….(ii)

where K_1 and K_2 are adsorptions and desorption constant.

At equilibrium, the rate of desorption is equal to the rate of adsorption. So,

$K_1 (1-\theta)P = K_2 \theta$

$K_1P - K_1\theta P = K_2 \theta$

$K_1P = \theta (K_2 + K_1P)$

$$\theta = \frac{K_1P}{K_2 + K_1P}$$

$$\theta = \frac{(K_1P)K_2}{(K_2 + K_1P)K_2}$$

$$\theta = \frac{bp}{1+bp}, \text{ where } b = \frac{K_1}{K_2}$$

The amount of the gas adsorbed on the surface of adsorbent is proportional to θ.

$$\frac{x}{m} \alpha \theta$$

$$\frac{x}{m} = K_3\theta \text{………………(iv)}$$

Substituting the value of equation (iii), we get

$$\frac{x}{m} = K_3 \frac{bp}{1+bp}$$

$$\frac{x}{m} = \frac{ap}{1+bp} \text{ …………(v), where } a = K_3b \text{ is constant.}$$

Thus, Equation (v) is the required Langmuir equation, and a & b are Langmuir constant

On rearranging the above Langmuir equation, a straight line equation should be obtained.

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

$$\frac{x/m}{P} = \frac{a}{1+bP}$$

$$\frac{P}{x/m} = \frac{1}{a} + \frac{b}{a}\,\mathrm{P}$$

On plotting P/x/m against P, we should get a straight line with a slope equal to b/a and the intercept 1/a.

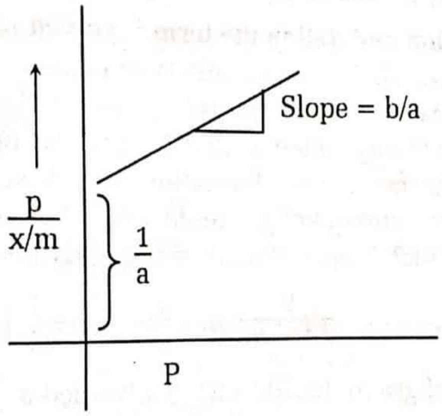


Fig. p/x/m Vs P plot

Limitations:

Langmuir Isotherm is applicable at low pressures but fails at high pressures.

Applications of Adsorption

1. Activated charcoal is used in gas masks in which toxic gases are adsorbed and air passes through it.
2. Silica gel packed in small cloth bags is used for adsorbing moisture in bottles of medicine and in small electronic instruments.
3. Animal charcoal is used for decolourizing many compounds during their manufacture.
4. In chromatography, the selective adsorption of different solutes on the surface of solid adsorbent helps in their separation.
5. Mordants are used during dyeing process with certain dyes. In such cases, the mordants fix the dye on the fabric by adsorption.
6. Cleansing of sugars
7. Purification of water
8. In adsorption indicator
9. Used in preserving vacuum
10. Separation of inert gases
11. Applicable in Froth Flotation process