Surface Chemistry

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Adsorption

The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid (or liquid) is known as **adsorption**.

The solid that takes up a gas or vapour or a solute from solution, is called **adsorbent.**

While the gas or the solute, which is held to the surface of the solid is called **adsorbate.**

→ Rate of adsorption = rate of desorption

The removal of the adsorbed substance from a surface is called desorption .

bulk of the adjoining phase , it is called **positive adsorption.**

If t When equilibrium is reached at the surface of another substance is less than in the bulk of the adjoining phase , it is called **negative adsorption.**

Difference Between Adsorption and Absorption

S.No.	Adsorption	Absorption
1.	It is surface phenomenon	It is bulk phenomenon.
2.	Adsorbate is accumulated at the surface.	The substance getting absorbed is uniformly distributed throughout the bulk of the substance.
3.	The rate of adsorption is very rapid in the beginning. The rate however decreases gradually until equilibrium is reached.	Absorption proceeds at a steady rate.

Types of Adsorption

Depending upon the nature of forces between the adsorbate (solute) and the adsorbent (solvent) molecules, adsorption can be classified into two groups:

Physical Adsorption

Chemical Adsorption

Difference Between Physical and Chemical Adsorption

S.No	Physical Adsorption	Chemical Adsorption
1.	It is caused by intermolecular van der Waal’s forces	It is caused by chemical bond formation.
2.	It is not specific and is reversable.	It is highly specific and is irreversible.
3.	It depends on the nature of the gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which form compounds with the adsorbent exhibit chemi-sorption.
4.	Heat of adsorption is low and is negative.	Heat of adsorption is high and is negative.
5.	Low temperature is favourable. Decrease of pressure causes desorption.	High temperature is favourable. It increases with the increase of temperature.
6.	It depends on the surface area. It increases with the increase of surface area.	High activation energy is involved.
7.	High pressure is favourable. Decrease of pressure causes desorption.	High pressure is favourable. Decrease of pressure does not cause desorption
8.	It depends on the surface area. It increases with the increase of surface area.	It also depends on the surface area. It increases with increase of surface area.
9.	It forms multi-layers on adsorbent surface under high pressure.	It form uni-molecular layer.

Factors Affecting Adsorption : Nature of Gas

physical adsorption is **non-specific** in nature

any gas will be adsorbed on the surface of a solid to some extent or other.

under any given conditions of temperature and pressure, easily liquefiable gases such as NH_3, CH_4, HCl, CO etc. are adsorbed more than permanent gases like O_2, N_2 etc.

Chemisorption is specific in nature → only those gases will be adsorbed which form chemical bonds with it.

Factors Affecting Adsorption: Nature & Area of Solids

Nature of solid :

Activated charcoal is the most common adsorbent for easily liquefiable gases Poisonous gases such as CH_4 and CO fall in this group. Therefore, it is used in gas masks.

Other gases such as O_2, H_2 and N_2 adsorb more on metals such as Ni, Pt and Pd.

Specific area of solid :

Specific area of an adsorbent is the surface area available for adsorption, greater will be the adsorption.

The specific area of an adsorbent can be increased by making the surface rough.

The pores must be large enough to allow penetrations of gas molecules.

Factors Affecting Adsorption : Pressure of Gas

As physical adsorption is reversible, it is accompanied by decrease in pressure.

it is expected that at a given temperature the extent of adsorption will increase with the increase of pressure of the gas.

The extent of adsorption is measured as x/m where m is the mass of adsorbent and x that of adsorbate

$$x/m = kp^{(1/n)}$$

At low pressure , x/m varies linearly with p

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

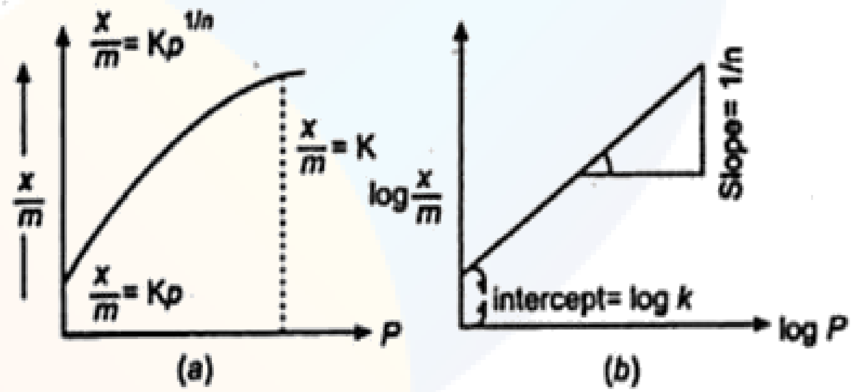
This is called **Freundlich adsorption isotherm**

The factor 1/n can have value between 0 and 1

When n=0 , x/m= constant ,the adsorption is independent of pressure

When 1/n =1 , x/m=kp

x/m ∝ p the adsorption react varies directly with pressure.



Limitations of Freundlich adsorption Isotherm

Concept of **Freundlich adsorption isotherm** is purely empirical.

It considers adsorption to be multimolecular.

Hence it is applicable only to physical adsorption.

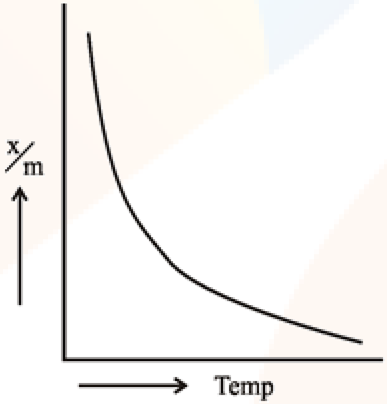
Factors Affecting Adsorption : Temperature

As adsorption is accompanied by release of heat energy, so in accordance with Le-Chatelier’s principle, the increase of temperature should decrease the extent of adsorption.

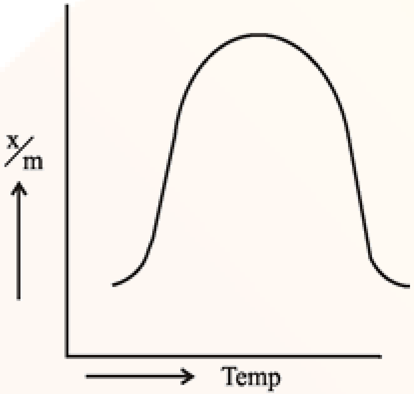
A plot of x/m vs temperature at constant pressure is called **adsorption isobar.**

Physical adsorption x/m decreases with increase of temperature whereas in the case of chemisorption, x/m initially increases with temperature and then decreases.

The initial increase is due to the fact that chemisorption requires activation energy.



Physical Adsorption



Chemical Adsorption

Factors Affecting Adsorption: Activation of Solids-1

Activation of adsorbent means increasing its absorbing power

This is increased by increasing specific area either by making the surface rough or by breaking the solid into smaller particles

But care must be taken so that particles do not become very small then inter-particle spaces will be too small to allow penetration of gas molecules.

Adsorbing power of an adsorbent x can be increased by:

- By making the surface of the adsorbent rough.
- By subdividing the adsorbent into smaller pieces or grains
- By removing gases already adsorbed

Applications of Adsorption

- **Gas mask**

  Activated charcoal is used in gas masks to remove poisonous gases such as carbon monoxide, methane etc. Animated charcoal is used to remove coloring matter from cane-sugar juice in the manufacture of juice.

- **catalysis**

  The catalytic effect of a number of catalysts, like spongy iron in the manufacture of ammonia and nickel, platinum or palladium in the reduction of unsaturated hydrocarbons, is based on the principle of adsorption.

- **In softening of water**

  Ion exchange resin is used to remove hardness of water.

- **In removing of moisture from air in the storage of delicate instruments**

  Silica gel is used for removing and controlling humidity used as **dehumidizer.**

- Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

Types of Colloidal Solutions

Classification on the basis of the size of the particle of the solute:

S.No.	Property	Suspension	Colloid	Solution
1.	Particle size	$> 10^{-5}$ or 10^{3}Å or $100\text{m}\mu$	10^{-7}cm to 10^{-5}cm or 10 Å to 10^{3}Å or $1\text{m}\mu$ to $100\text{m}\mu$	$< 10^{-7}$cm or 10Å or $1\text{m}\mu$
2.	Visibility	Visible with naked eye	Visible with ultra microscope	Not visible with any of the optical means
3.	Diffusion	Does not diffuse	Diffuse very slowly	Diffuse rapidly
4.	Settling	Settles under gravity	Does not settle but it may settle under centrifuge	Does not settle
5.	Nature	Heterogeneous	Heterogeneous	Homogeneous
6.	Appearance	Opaque	Generally clear	Clear

Classification on the Basis of the Physical State

Classification on the basis of the physical state of dispersed phase and dispersion medium:

Colloidal solution is heterogeneous in nature and always consists of at least two phase namely disperse phase and dispersion medium

The component present in small proportion and consisting of particles of colloidal dimensions is called **disperse phase.**

The medium in which colloidal particles are dispersed is called **dispersion medium.**

Disperse Phase	Dispersion medium	Common name	Example
Solid	Solid	Solid Solution	Alloys
Solid	Liquid	Solution	Au Solution
Solid	Gas	Aerosol	Smoke
Liquid	Solid	Gels	Cheese
Liquid	Liquid	Emulsion	Milk
Liquid	Gas	Liquid Aerosol	Mist, Cloud
Gas	Solid	Solid Foam	Pumice stone
Gas	Liquid	Foam	Soap Lather

Sol

If colloidal solution has fluid like appearance it is called **sol.**

Dispersion medium	Name of the sol
Water	Hydrosol
Alcohol	Alcosol
Benzene	Benzosol
Gases	Aerosol

Colloidal solutions of solids in liquids are abbreviated as sols.

Types of Colloidal Solutions

Types of Colloidal Solutions:

Depending upon the nature of interaction between dispersed phase and dispersion medium

Lyophilic Colloids:

The disperse phase has great affinity for dispersion medium. In such cases the disperse phase does not easily get precipitated and the colloids are quite stable

e.g., gum, gelatin, starch, proteins and certain polymers in organic solvents.

If water is used as the dispersion medium the colloid is called hydrophilic colloid.

Lyophobic Colloids:

The disperse phase has little affinity for the dispersion medium. These sols are relatively less stable. e.g., gold sol and Sulphur sol

If water is used as the dispersion medium. The sol is called **hydro lyophobic colloid.**

Lyophilic and Lyophobic Solutions

S.No.	Property	Lyophilic Sols	Lyophobic Sols
1.	Surface tension	Lower than that of the medium.	Same as that of the medium
2.	Viscosity	Much higher than that of the medium	Same as that of the medium
3.	Reversibility	Reversible	Irreversible
4.	Stability	More stable	Less stable
5.	Visibility	Particles can’t be detected even under ultra microscope	Particles can be detected under ultra microscope
6.	Migration	Particles may migrate in either direction or do not migrate in an electric field.	Particles migrate either towards cathode or anode in an electric field.
7.	Action of Electrolyte	Addition of smaller quantity of electrolyte has little effect.	Coagulation takes place.
8.	Hydration	Extensive hydration takes place.	No hydration takes place.

Preparation of Lyophilic Solutions

The colloidal solutions of lyophilic colloids like starch, glue, gelatin, etc., can be readily prepared by

Substance + water (cold or warm)

Solutions of colloidal electrolytes such as soaps and dye stuffs can also be prepared similarly.

Peptization Causes of Peptization and e.g.

This is a process of converting a precipitate into colloidal solution by shaking it with dispersion medium in the presence of small amount of electrolyte

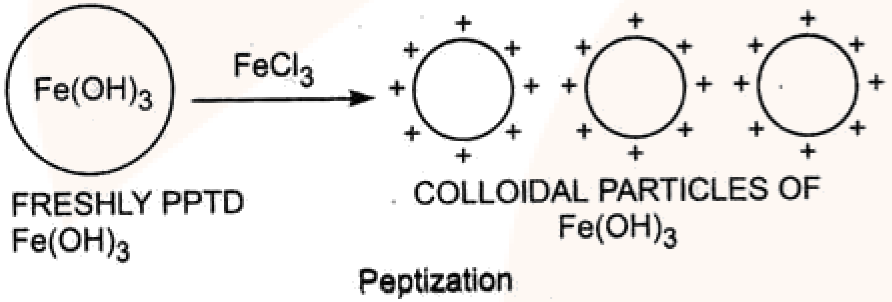
The electrolyte used for this purpose is called **peptizing agent**

This method is generally applied to convert fresh precipitate into colloidal solutions because such precipitates are simply aggregates of colloidal particles held by weak forces.

Causes of Peptization

- During peptization, the precipitate adsorbs one of the ion of the electrolyte on its surface
- the development of positive or negative charge on the precipitates, which ultimately breaks into particles of colloidal dimensions.
- The adsorbed ion is generally common with those of precipitate

Example :



Peptization

when freshly precipitated ferric hydroxide is shaken with aqueous solution of ferric chloride (peptizing agent) it adsorbs Fe^{+3}

Dialysis-1

The process of separating the particles of colloids from those of crystalloids by diffusion of the mixture through a parchment or an animal membrane is known as **dialysis.**

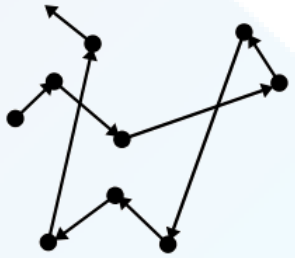
The apparatus used for this purpose is called **dialyser**.

Application of dialysis is in the purification of blood in the artificial kidney machine

The dialysis membrane permits small particles of the excess ions and waste products to pass through whereas colloid sized particles such as hemoglobin do not pass through the membrane.

Brownian Motion

Brownian movement may be defined as continuous zig-zag movement of the colloidal particles in a colloidal sol.



Importance of Brownian moment

- It helped in determination of Avogadro nos.
- Brownian movement opposes the forces of gravity and does not allow the colloidal particles to settle down .it is responsible for stability of colloidal solution.

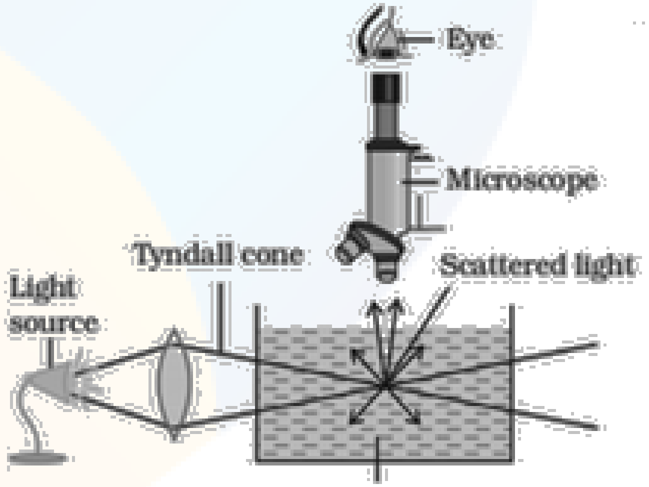
Tyndall Effect

Scattering of light by the colloidal particles present in a colloidal solution is known as **Tyndall effect** and is caused by the scattering of blue part of light by the colloidal particles.

If a strong beam of light is passed through a colloidal solution placed in a dark place, the path of the beam gets illuminated.

The illuminated path of beam is called **Tyndall Cone**

- The scattering is caused if the size of particles is of the order of wavelength of light
- The same effect is not observed when the light is passed through a true solution as the size of solution particles is too small to cause any scattering.
- Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there.



Tyndall effect

Electrophoresis Positive and Negative Charged Colloids

Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form aggregates.

This makes a colloidal solution stable and colloidal particles do not settle down.

common positively and negatively charged colloids

Positively charged :

$Fe(OH)_3$ sol, $Cr(OH)_3$ sol, $Al(OH)_3$ sol, $Ca(OH)_2$ sol, dyes like methylene blue and hemoglobin.

Negatively charged :

As_2S_3 sol, Sb_2S_3 sol, CdS sol, Au sol, Cu sol, Ag sol, and acid dyes like Congo red.

Gold no. of a Few Protective Colloids

S.No.	Protective Colloid	Gold Number
1.	Gelatin	0.005-0.01
2.	Hemoglobin	0.03
3.	Gum Arabic	0.15
4.	Egg Albumin	0.08-0.10
5.	Potato Starch	25
6.	Sodium Oleate	0.4
7.	Gum Tragacanth	2
8.	Starch	25-50

The lyophilic colloids differ in their protective power

Gold number of a protective colloid is the minimum mass of it in milligrams which must be added to mL of a standard red gold sol(0.0053-0.0058% gold) so that no coagulation of the gold sol (i.e., the change of colour from red to blue) takes place when 1mL of 10% NaCl solution is rapidly added to it.

Gold no.

The protective power is measured in terms of **Gold Number** and is defined as the number of milligrams of a lyophilic colloid that will just prevent the precipitation of 10 ml of a gold sol on the addition of 1 ml of 10% sodium chloride solution.

Higher is the gold number, lower will be the protective power.

Emulsions

Emulsions are colloidal solutions in which both the disperse phase and the dispersion medium are liquids. It can be defined as the dispersion of finely divided droplets in another liquid.

Types of Emulsions

Oil in water type emulsions (O/W type):

In this type of emulsion, oil is the dispersed phase and water is the dispersion medium. Foe example milk, vanishing cream etc.

Water in oil type emulsions (W/O type):

In this type of emulsions water is the dispersed phase and oil is the dispersion medium. For example: butter, cod liver oil, cold cream etc.