

Revision Notes on Surface Chemistry:

Adsorption

Reversible and irreversible adsorption

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

A gas adsorbed on a solid surface can be completely removed in vacuum. It is, therefore, reversible adsorption. Examples of irreversible adsorption are adsorption of oxygen on tungsten adsorbate and adsorption of CO on tungsten surface

Adsorbent, Adsorbate and Interface

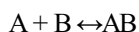
- The substances upon whose surface the change of concentration occurs, is called **adsorbent**.
- The substance taken up on the surface is called **adsorbate**.
- The common surface between the two phases where the adsorbed molecules concentrate is called the **interface**.

Physisorption and Chemisorption:

Physisorption	Chemisorption
Only van der Waals force are present between adsorbate and surface of adsorbent	Chemical bonds are formed between adsorbate and surface of adsorbent
Low enthalpy of adsorption i.e., in the order of 20 kJmol ⁻¹ .	High enthalpy of adsorption i.e., order of 200 kJmol ⁻¹ .
Reversible	Irreversible
It usually takes place at low temperature and does not require any activation energy.	It takes place at high temperature and requires activation energy.
Multi molecular layer of adsorbate are formed on the surface	Only monomolecular layers are formed.
Not specific.	Highly specific.

Langmuir Isotherm:

If A, B & AB represents the adsorbed, adsorbent and the adsorbed – adsorbent complex then, Langmuir Equation



$$K_a = \text{Equilibrium constant for adsorption} = \frac{[AB]}{[A][B]}$$

$$K_d = \text{Equilibrium constant for desorption} = \frac{[A][B]}{[AB]}$$

$$K = \text{Distribution coefficient} = K_a/K_d$$

θ = Fraction of the surface of adsorbent available for adsorption.

P = pressure

So,

$$\theta = \frac{KP}{1+KP} \quad (\text{Langmuir Equation})$$

Freundlich Isotherm:

x = Mass of the gas adsorbed

m = Mass of adsorbent

p = Pressure

K and n = constants

$$x/m = k \cdot p^{(1/n)} \quad [n > 1]$$

or

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

Freundlich Isotherm

Factors Affecting Adsorption:

- **Temperature:** An increase of temperature leads to a decrease in amount adsorbed and vice – versa.
- **Pressure or concentration:** It has been found that in most cases, the adsorption is reversible and an increased pressure of a gases vapour or an increase in concentration of a solute causes increased adsorption.
- **Nature of Adsorbate and Adsorbent:** The amount of the gas adsorbed depends upon the nature of adsorbent and the gas (adsorbate), which is to be adsorbed. It has been found that easily liquifiable gases such as NH_3 , HCl , Cl_2 , SO_2 , CO_2 etc. are more readily adsorbed than so the called permanent gases such as O_2 , N_2 , H_2 etc. This is because that molecules of the former type of gases have greater Vander waal's or molecular force of attraction.

Colloids

Dispersed Phase:

The phase which is dispersed or scattered through the dispersion medium is called Dispersed phase or discontinuous phase.

Dispersion Medium:

The phase in which the scattering is done is called the dispersion medium or continuous medium.

Dispersed Phase	Dispersion Medium	Name	Typical example
Solid	Liquid	Sol	Gold sol, Mud, $\text{Fe}(\text{OH})_3$ sol,
Solid	Solid	Solid sol	Gems, Ruby glass, Minerals
Solid	Gas	Aero sols	Smoke (Carbon in air) Volcanic dust
Liquid	Solid	Gel	Curd, Cheese, Jellies
Liquid	Liquid	Emulsion	Milk, water in benzene, cream
Liquid	Gas	Liquid aero sol	Clouds, fog (water in air) mist
Gas	Solid	Solid foam	Lava, Pumica
Gas	Liquid	Foam	Froth on beer , whipped cream

Lyophobic and Lyophilic Colloids:

Those substance whose colloidal solution cannot be prepared by bringing them in contact with a solvent are called *Lyophobic* (disliking, fearing or hating a liquid). On the other hand those substances whose colloidal solutions can be prepared by bringing them in contact with a liquid solvent are called *lyophilic colloids* (loving a solvent).

Emulsions:

- **Emulsion of oil in water:** Those emulsions in which the dispersed phase is oil and water is the dispersion medium. These

emulsion are generally represented as O in W emulsions. Examples are milk, vanishing cream etc.

- **Emulsions of water in oil:** Those emulsion in which the dispersed phase is water while oil is the dispersion medium. These emulsion are generally represented as W in O emulsions. Examples are butter, ice cream etc.

Difference between True Solutions, Suspension & Colloids

True solution	Suspension	Colloid
Homogenous	Heterogeneous	Heterogeneous
Particle size less than 1nm	Particle size more than 1000nm	Particle size between 1-1000nm
Don't settle down	Settle down under the influence of gravity	Don't settle down
Complements cannot be separated out by filtration	Can be filtered	Can be filtered using special filter papers
Don't show tyndrall effect	Show tyndrall effect	Show tyndrall effect

Methods of preparation of colloids

Chemical Methods:

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Bredig's method:

An electric arc is struck between two metallic electrodes immersed in dispersion medium. The arc produced vapourises the metal which on further condensation produces particles of colloidal size.

Bredig's method

Peptization:

Process of converting a precipitate into colloidal sol by shaking it with electrolyte in dispersion medium.

Hardy Schulze Rule:

- Ion carrying charge opposite to the colloidal particle has capacity to coagulate the colloid.
- Greater the valency of ion, greater will be the coagulating power.
- Gold Number: The minimum amount of lyophilic colloid in milligrams which can prevent the coagulation of 10 ml gold sol against 1 ml of 10% NaCl solution.

Surfactants

substances which gets preferentially adsorbed at the air – water and solid – water interfaces forming an oriented monolayer where the hydrophilic groups point towards the aqueous phase and the hydrocarbon chain point towards the air or towards the oil phase.

- **Anionic surfactants :** Sodium salts of higher fatty acids such as sodium palmitate ($C_{15}H_{31}COONa$), sodium stearate ($C_{17}H_{35}COONa$) and sodium Oleate ($C_{17}H_{33}COONa$).
- **Catiuonic Surfactants:** Those which dissociates in water to yield positively charged ions *examples:* $C_{18}H_{37}$, $C_{16}H_{33}(CH_3)_3$ etc.
- **Non ionogenic:** Those whose molecules cannot undergo dissociation when an alcohol having a higher molecular weight reacts with several molecules of ethylene oxide, a non – ionogenic surfactant is produced.

Miscelles:

Aggregates formed when the surfactant molecules in the water air interface become so packed in the monolayer that no more molecules can be accumulated with ease they accumulate in the bulk of the solution.

At a given temperature and concentration, a miscelle of a surfactant of monodispersed i.e., they contain same number of molecules usually between 25 to 100.

Critical concentration for micelle formation decreases as the molecular weight of hydrocarbon chain of surfactant grows because in this case true solubility diminishes and the tendency of surfactant molecules to associate increases.

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