T.D.C 4th Semester (General)

(I) Surface Chemistry.

Adsorption

The process by which a solid holds molecules of a gas or liquid or solute as a thin film is called adsorption. Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. It is a surface phenomenon.

The solid substance which adsorps the liquid or gas molecules, ions etc are called adsorbent. and the liquid or gaseous substance which are adsorbed are called adsorbate.

There are two types of adsorption (a) Physical adsorption and (b) Chemical adsorption.

Physical adsorption :— If the physical forces of attraction hold the gas molecules to the solid, the adsorption is known as Physical adsorption.

The forces of attraction bringing about physical adsorption ~~are~~ are vander waals forces. The vander waals forces ~~(1) Per vander Waals force~~, are very weak and characterised by a low heat of adsorption (nearly 1 Kcal/mole). Physical adsorption is reversible and the adsorbed material may be removed either by raising the temperature or lowering the pressure.

Chemical adsorption :— If the chemical forces hold the gas molecules to the surface of the adsorbent the adsorption is known as chemical adsorption or chemisorption. Here chemical bond is formed between the adsorbent and adsorbate. In Chemisorption the adsorption first rapidly increases and gradually approaches a limiting value. The rapid rise in the beginning is due to the strong tendency of the surface to hold the gas molecules, when these forces are satisfied, the limiting value is reached. The heat of adsorption here are very much higher than Physical adsorption.

Why adsorption takes place ?

Atoms or molecules of a solid surface behave like the surface of a liquid. These are not surrounded on all sides by atoms or molecules of their kind and hence possess unbalanced attractive (residual force) similar to valency force. These forces attract the molecules of the adsorbate A that come in contact with the solid (let metal M). Due to adsorption, the residual forces decrease, and therefore the surface energy get decreased considerably. This energy is lost as heat energy. Thus adsorption is always accompanied by evolution of heat and energy liberated when 1 gm mole of a gas is adsorbed on the surface of the solid, is called heat of adsorption.

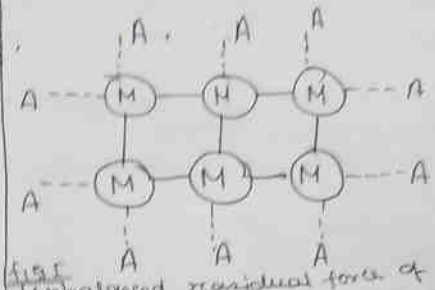


fig: Unbalanced residual force of M attracts A.

Difference between physisorption and chemisorption.

Physical adsorption	Chemical adsorption
(1) In physical adsorption vander waals forces hold the adsorbate molecules to the adsorbent	(1) Here chemical bond is formed between adsorbent and adsorbate
(2) The heat of adsorption is low, It is between 20 – 40 KJ mol^{-1}	(2) The heat of adsorption is high. It is of the range 80 – 200 KJ mol^{-1}.
(3) It is reversible.	(3) It is irreversible.
(4) It involves the formation of a multilayer of adsorbed molecules.	(4) It involves the formation of a monolayer of adsorbed particles.
(5) It is not specific in nature. i.e any gas can be adsorbed by any solid.	(5) It is specific in nature. Here adsorption occur when a chemical bond can be formed between adsorbate and adsorbent
(6) It occurs at low temperature. With rise of temp^{r} physical adsorption decreases.	(6) It occurs at high temperature.

Adsorption Isotherm :— The extent of adsorption on a surface generally depends on the nature of the adsorbent and adsorbate. It is also a function of its pressure or Concentration and temperature. The relationship between the amount of substance adsorbed and the pressure or Concentration of the adsorbate at constant temperature is called adsorption ~~isotherm~~ isotherm.

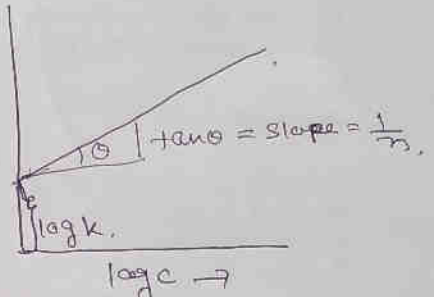
Freundlich Adsorption Isotherm :— It is an empirical equation which was proposed by Freundlich to connect the quantity of a substance adsorbed and the concentration of the adsorbent solution at a fixed temperature.

If "x" gms of the substance are adsorbed on "m" gms of adsorbent and "C" is the equilibrium concentration of the adsorbate solution. Then the adsorption isotherm is mathematically expressed as $\frac{x}{m} = KC^{1/n}$.

where K and n are constants. Taking logs on both sides,

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

This equation is comparable to the general equation of a straight line. It is therefore, clear that a plot of $\log x/m$ vs $\log C$ would be straight line. The slope of the straight line is $1/n$ and the intercept is $\log K$.



Langmuir Adsorption Isotherm :— Langmuir worked out an adsorption isotherm known as Langmuir adsorption isotherm. To derive the isotherm Langmuir gave some assumptions.

(i) The adsorbed layer is assumed to be unimolecular thick.

(ii) Adsorption takes place on the fixed site and there is no interaction between the adsorbed molecules on the surface.

③ The process of adsorption is a dynamic process. Both adsorption and desorption takes place. When equilibrium is reached the rate of condensation becomes equal to rate of evaporation

④ gas ~~be~~ adsorbed are supposed to be ideal.

⑤ The energy of the whole surface is uniform.

Derivation of Langmuir adsorption Isotherm:-

If A is the gas molecule and M is the surface site

Then $A(g) + M(\text{surface}) \underset{K_d}{\overset{K_a}{\rightleftharpoons}} AM$.

Where K_a and K_d are the rate constants for adsorption and desorption, respectively. The rate of adsorption is proportional to the pressure of A (let P_A), and the number of vacant sites on the surface, i.e $N(1-\theta)$, where N is the total number of site and θ is the site of the surface occupied by the gas molecules, i.e $\theta = \frac{\text{Number of adsorption site occupied}}{\text{Total No of adsorption site}}$.

Thus the rate of adsorption $= K_a P_A N(1-\theta) \rightarrow ①$

The rate of desorption is proportional to the number of adsorbed molecule. $N\theta$, or equal to $K_d N\theta \Rightarrow ②$

At equilibrium $K_a P_A N(1-\theta) = K_d N\theta$ (3),

or $\theta = \frac{K_a P_A N(1-\theta)}{K_d N} = K P_A (1-\theta)$ where $K = K_a/K_d$. $\rightarrow ④$

Eqn ④ may be written as $\frac{1-\theta}{\theta} = \frac{1}{K P_A}$.

or $\frac{1}{\theta} - 1 = \frac{1}{K P_A}$ or $1/\theta = \frac{1}{K P_A} + 1 \rightarrow ⑤$.

$= \frac{1 + K P_A}{K P_A}$.

$$\boxed{\theta = \frac{K P_A}{1 + K P_A}} \rightarrow ⑥$$

Eqn ⑥ is called ~~the~~ Langmuir adsorption isotherm.