SURFACE CHEMISTRY

The surface of a solid has a tendency to attract and retain molecules of other species with which it is brought into contact. As these molecules remain only at the surface, their concentration is more at the surface than in the bulk of the solid. The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as adsorption. The solid that takes up a gas or vapour or a solute from a solution, is called the adsorbent while the gas or vapour or the solute, which is held to the surface of the solid, is called adsorbate.

Factors affecting adsorption:

① Surface area of the adsorbent:

The extent of adsorption of gases by solids depends upon the exposed surface area of the adsorbent. It is well known that larger the surface area of the adsorbent the larger will be the extent of adsorption under given conditions of temp & pre.

② Nature of the ~~adsorbate~~ and adsorbate:

The amount of the gas adsorbed depends upon the nature of the gas (adsorbate) which is to be adsorbed.

Gases like SO_2, NH_3, HCl and CO_2 which liquefy more readily are adsorbed more easily than the permanent gases like H_2, N_2 & O_2 which do not liquefy easily. Since the easily liquefiable gases have greater vander-Waal's or the molecular forces of attra^n.

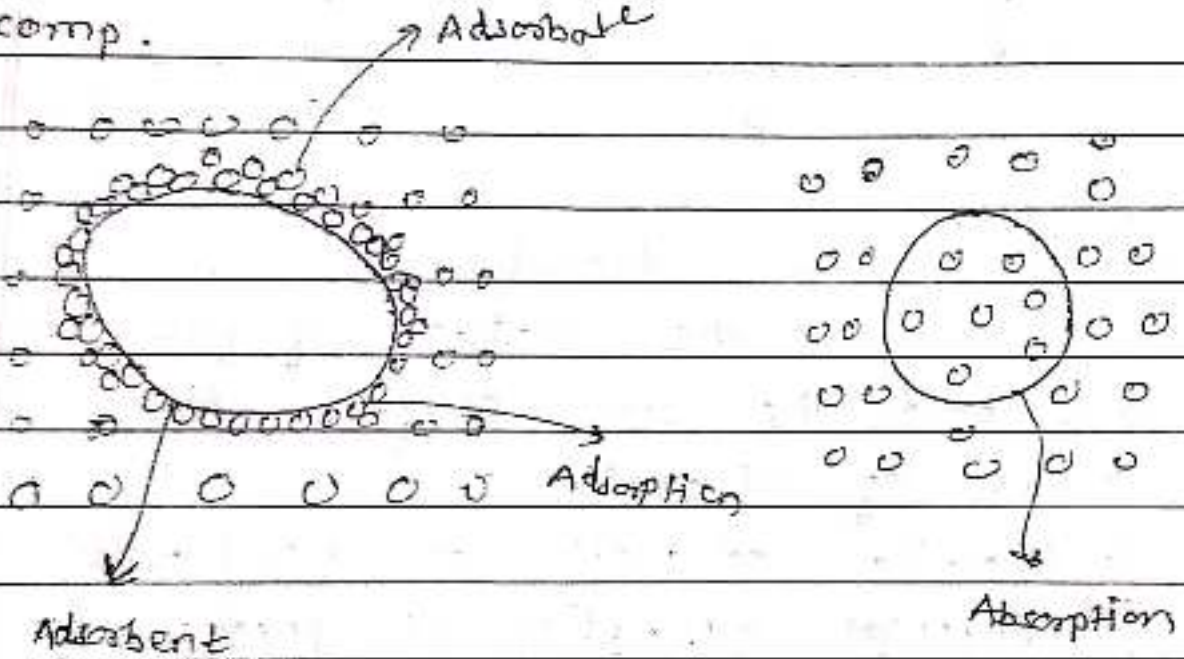
③ Effect of temp:

For a given adsorbate and adsorbent the extent of adsorption depends upon the temp of the expt. According to the Le Chatelier's principle, the decrease in temp will increase the adsorption and vice versa.

④ Effect of pre : For a given gas and a given solid the extent of adsorption depends on the pre of the gas. According to Le Chatelier's principal principle, the magnitude of adsorption decreases with the decrease in pre & vice versa.

Differences bet^n adsorption and absorption :

① Adsorption is a surface phenomenon whereas absorption is a bulk phenomenon in which the sub distributed thr'out the body of a solid or liq to form a sol^n or a comp.

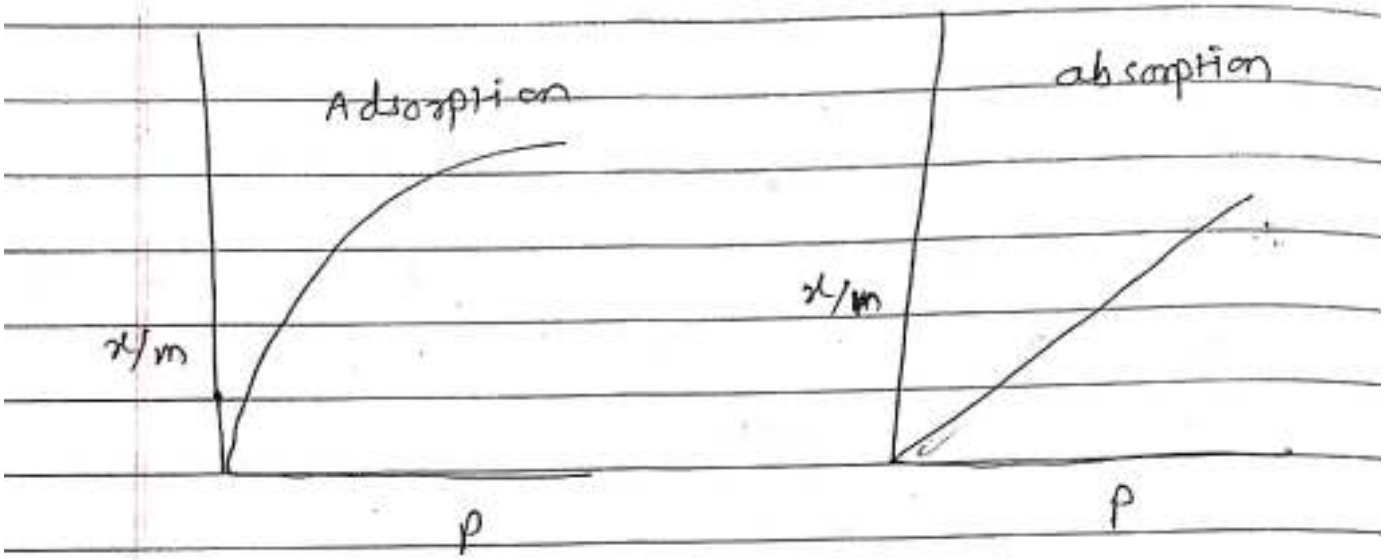


② In case of adsorption, the equillibrium is readily reached in a very short time whereas in absorption the equilibrium takes place slowly.

③ In adsorption, the conc^n of the adsorbed mole, is always found to be greater in vicinity of the surface. On the contrary, absorption involves bulk penetration of the molecules

into the stru of the solid or liq by diffusion process.

④ If x/m is plotted against p or c, the graph must be straight line in absorption and a typical curve for adsorption as shown below



Types of adsorption:

Based on the nature of forces betⁿ the gas and the solid surface, there are two kinds of adsorption:

① Chemical adsorption or chemisorption
② Physical adsorption or physisorption.

chemical adsorption or chemisorption:

If the chemical forces hold the gas moles to the surface of the adsorbent, the adsorption is called chemisorption.

In this case the adsorbate undergoes a strong chemical interaction with the unsaturated surface & produces high

heat of adsorption generally of the order of 400 KJ/mole.

The magnitude of chemisorption increases with rise in temp

Physical adsorption or physisorption:

If the physical forces of attra^n hold the gas molecs to the solid, the adsorption is known as physical adsorption.

In case of physisorption, the forces of attra^n which hold the gas molecs to the solid are very weak so it is characterised by a low heat of adsorption usually of the order of 40 KJ/mole.

The magnitude of physisorption decreases with rise in temp.

Adsorption of gaseous by solids:

Several methods for determining adsorption of gases on solid adsorbents under the given conditions have been devised. In one such method, the gas is contained in a vessel of known vol at a given temp. The pre of the gas is measured on a manometer takesplace attached to the vessel. The adsorbent is then introduced into the vessel by a suitable device. Adsorption takesplace quickly and the pre of the gas falls. This is noted on the

manometer, knowing the fall of pre, the quantity of the gas adsorbed by the solid can be calculated by Boyle's law eqn.

Types of adsorption isotherm:

① Freundlich adsorption isotherm:-

The relnship betn the magnitude of adsorption & pre can be expressed mathematically by an empirical eqn commonly known as Freundlich adsorption isotherm.

$$\frac{x}{m} = kp^{\frac{1}{n}} \quad \text{---} \quad (1)$$

where x is the amount of gas adsorbed per unit mass of the adsorbent at pre p, and k and n are constants depending upon the nature of the gas and the nature of the adsorbent.

or $\frac{x}{m} = kp^{\frac{1}{n}}$ —②

Eqn ① is usable to the adsorption of gases on solids.

In soln, eqn ① takes the form

$$\frac{x}{m} = kc^{1/n} \quad \text{---} \quad (2)$$

where c is the concn of the solute in gm moles per lit.

x = mass of gas adsorbed

m = mass of adsorbent

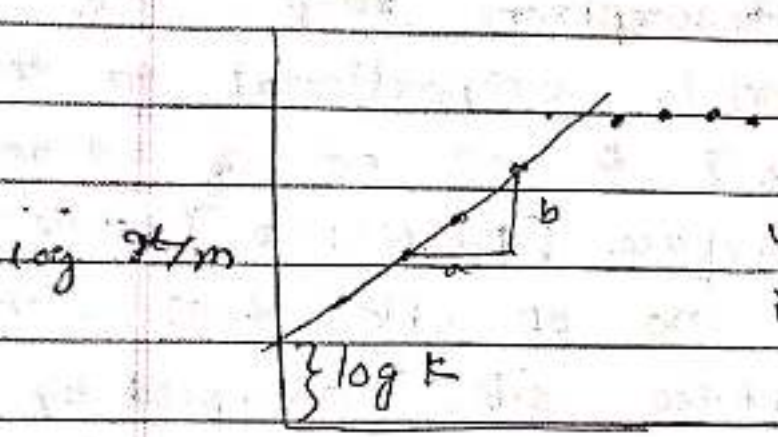
Test of Freundlich's adsorption isotherm:

Taking log of eqn (i) & (ii)

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

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

If log x/m is plotted against log p or log c nature of graph is as follows:



The slope of the line will give the value of 1/n & the intercept on the y-axis gives value of log k.

$$\text{Intercept} = \log k$$

$$\text{slope} = \frac{1}{n} = \frac{b}{a}$$

The value of n is less than 1 and & therefore x/m doesnot increase as rapidly as p.