Adsorption → Accumulation of a material only at the surface of a solid or liquid.

⇒ Accumulating material is known as adsorbate

⇒ the solid or liquid surface on which accumulation of material occurs is known as adsorbent.

⇒ Adsorbate is adsorbed on the surface of the adsorbent.

⇒ Adsorption is a surface phenomenon

⇒ Adsorption is different from absorption

⇒ In absorption, accumulating material is uniformly distributed throughout the body of the solid or liquid.

⇒ Two types of adsorption occurs
1) Physisorption or physical adsorption
2) Chemisorption or chemical adsorption

⇒ Physisorption differs from chemisorption as follows:

1- Physisorption occurs due to weak electrostatic force of attraction between adsorbent and adsorbate molecules where as chemisorption occurs due to donor-acceptor chemical bonds.

2. Physisorption exist only at lower temperature whereas chemisorption exist at all temperatures.
3. Magnitude of physisorption decreases on increasing temperature and ~~at~~ magnitude of chemisorption increases on increasing temperature.
4. The heat evolve in physisorption is low (4-40 $kJmol^{-1}$) whereas in chemisorption it is very high (40-400 $kJmol^{-1}$).
5. Chemisorption is irreversible whereas physisorption is reversible.
6. Chemisorption operate within short distance (only in monolayer) whereas physisorption may operate even at large distance (~~multilayer~~) (beyond monolayer).

Aplication of adsorption

⇒ Activated charcoal is used in gas masks in which all toxic gases and vapours are adsorbed by the charcoal while pure air passes through its pores.

⇒ Silica and alumina gels are used as adsorbent for removing moisture and for controlling humidity of rooms.

⇒ Animal charcoal is used as a decoloriser in the manufacture of cane-sugar.

⇒ Adsorption play an important role in heterogeneous catalysis

⇒ Adsorption is accompanied by decrease in enthalpy i.e. ΔH is always negative

⇒ Adsorption is accompanied by decrease in entropy.

For a spontaneous process

$$\Delta G = \Delta H - T\Delta S \text{ should be negative.}$$

by experiment it was established the ΔH becomes lesser and lesser negative and ultimately ΔH becoms equal to $T\Delta S$ at equilibrium.

Factors affecting Adsorption

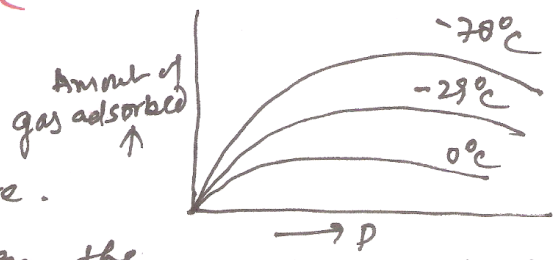
The magnitude of gaseous adsorption depends upon the following factors.

(I) Temperature, (II) Pressure (III) Nature of gas (IV) Nature of adsorbent. (V) Surface area

(I) Effect of temperature — Magnitude of adsorption ~~ttt~~ increases on decreasing temp.

(II) Effect of pressure

Each curve is known as adsorption isotherm at a particular temperature.



Adsorption isotherms

Fig. 1

The relationship between the magnitude of adsorption and

pressure is expressed mathematically by an empirical equation known as Freundlich's adsorption isotherm viz

$$a = kp^n \quad \text{—— (1)}$$

where a = Amount of gas adsorbed per unit mass of the adsorbent at pressure (p)

k, and n are constants. The value of n is always less than 1. Therefore a does not increase as rapidly as p, as is evident from the fig. 1.

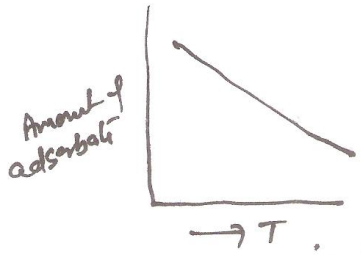
② Nature of the gas and adsorbent –

More readily soluble and easily liquefiable gases (NH_3, HCl, Cl_2, SO_2 etc) are easily adsorbed as compared to permanent gases (H_2, N_2 and O_2). ~~dee~~

③ Surface area —— Greater the surface area of adsorbent greater is the adsorption.

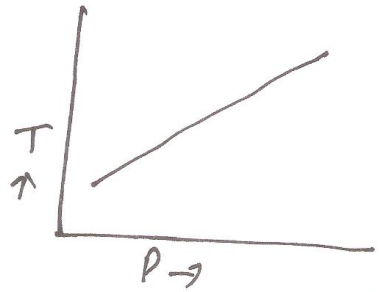
Adsorption Isobar and Adsorption Isostere

The effect of temperature on the extent of adsorption, at a given pressure of the adsorbate, is also expressed as shown in fig. 2 and 3



adsorption isobar

Fig 2



Adsorption Isostere

Fig 3

The curve showing the effect of T on extent of adsorption at a given pressure is called an adsorption isobar. The amount of adsorption, evidently decreases with rise in temperature.

The curve showing the variation of pressure with temperature for a given amount of adsorption is called Isostere (Fig 3).

FREUNDLICH ADSORPTION EQUATION.

$$\left(\frac{x}{m}\right) = kp^{1/n} \quad \text{——} \quad (2)$$

x is the mass of gas adsorbed
m is the mass of adsorbent at pressure p

k and n are constants for a given pair of adsorbent and adsorbate

n is normally > 1

This accounts the fact that the increase of adsorption is not as fast as the increase of pressure.

$$\log\left(\frac{x}{m}\right) = \log k + \left(\frac{1}{n}\right)\log p \quad \text{——} \quad (3)$$

A plot of $\log\left(\frac{x}{m}\right)$ vs ~~log k~~ $\log p$ would give a straight line with slope equal to $(1/n)$ and intercept $\log k$.
From these the value of k and n can be determined.

LANGMUIR ADSORPTION EQUATION.

Approximations :

(i) The surface of solid consists of a fixed number of adsorption sites where only adsorption of gaseous molecules take place

(ii) Each site can hold only one gaseous molecule and involve a constant heat of adsorption.

(iii) The adsorption is monolayer i.e only one layer of adsorption of gaseous molecules is formed.

(iv) The gaseous molecules adsorbed at different sites do not interact with each other.

(v) The phenomenon of adsorption involves a dynamic equilibrium

$$A(g) + M(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} AM \quad -(1)$$

k_a and k_d are rate constant for adsorption and desorption, respectively.

The rate of adsorption is proportional to the pressure of A (P_A) and number of vacant sites on the surface. viz $N(1-\theta)$ where N is the total number of sites and θ is the fraction of surface sites occupied by the gas molecules.

$$\theta = \frac{\text{No. of adsorption sites occupied}}{\text{No. of adsorption sites available}}$$

Thus rate of adsorption $= k_a P_A N(1-\theta)$ (2)

The rate of desorption is proportional to the number of adsorbed molecules ~~$\propto k_d$~~ $N\theta$.

Thus rate of desorption $= k_d N\theta$ — (3)

At equilibrium

$$k_a P_A N(1-\theta) = k_d N\theta$$

or

$$\frac{k_a}{k_d} P_A (1-\theta) = \theta$$

$$K P_A (1-\theta) = \theta \quad \text{where } \frac{k_a}{k_d} = K$$

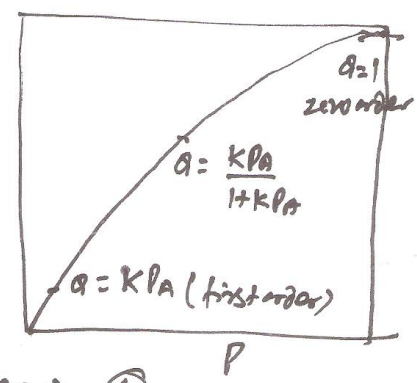
$$\frac{(1-\theta)}{\theta} = \frac{1}{K P_A}$$

$$\frac{1}{\theta} - 1 = \frac{1}{KP_A}$$

$$\frac{1}{\theta} = \frac{1}{KP_A} + 1 = \frac{1 + KP_A}{KP_A}$$

$$\boxed{\theta = \frac{KP_A}{1 + KP_A}} \quad \text{—— (4)}$$

This equation is called Langmuir adsorption isotherm.



At low pressure eq. (4) becomes

$KP_A << 1$ so

$$\boxed{\theta = KP_A} \text{ (first order) (5)}$$

At high pressure $KP_A >> 1$

$$\theta = \frac{KP_A}{KP_A} = 1 \text{ (zero order) (6)}$$

From (5) and (6) it is evident that According to this theory magnitude of adsorption at a given temperature first increases and attain a limiting value.

at intermediate pressure

$\theta = K(P_A)^n$ where n lies between 0 and 1

Since according to Langmuir Theory, single layer of molecule is adsorbed on the surface of the adsorbent, the fraction θ gives the amount of the gas adsorbed per unit mass of the adsorbent

ie

$$a \propto \theta$$

$$a = k_1 \theta \quad \text{where } k_1 \text{ is constant}$$

Thus

$$a = k_1 \theta$$

$$= k_1 K (p_A)^n$$

$$a = k (p_A)^n \quad \text{— (7)}$$

Eq. (7) is same as Freundlich equation

BET Theory of Multilayer Adsorption

As per BET theory multilayer adsorption is possible.

In BET theory, it is assumed that the solid surface possesses uniform, localised sites and that adsorption at one site does not affect adsorption at neighboring sites as assumed by Langmuir theory. It is also assumed that molecules can adsorbed in second, third, .. nth layers. The energy of adsorption. The energy of adsorption in the first layer E_1, is assumed to be constant and energy of adsorption in succeeding layers is assumed to be the same as E_L the energy of liquification of the gas. Based on the above assumptions Brunauer, Emmett and Teller derived the following equation known as BET equation

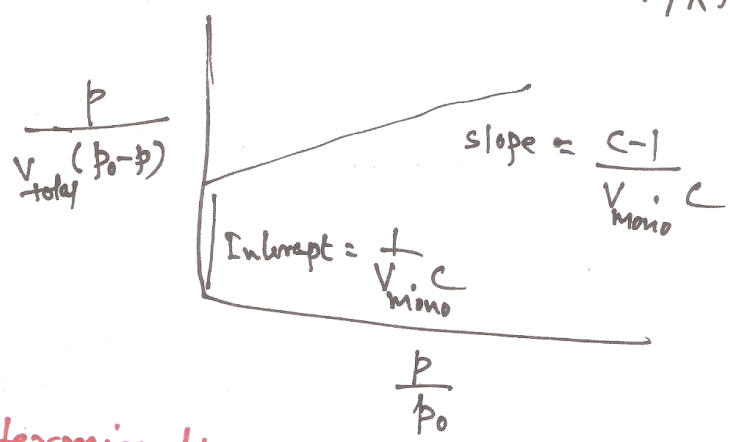
$$\frac{p}{V_{total}(p_0 - p)} = \frac{1}{V_{mono} C} + \frac{C-1}{V_{mono} C}\left(\frac{p}{p_0}\right)$$

where

V_{total} = volume of the gas adsorbed at pressure p

V_{mono} = volume adsorbed gas when the surface is completely covered by mono layer.

C = constant and its numerical value is given by $C = \exp(E_1 - E_L)/RT$



Determination of Surface Area

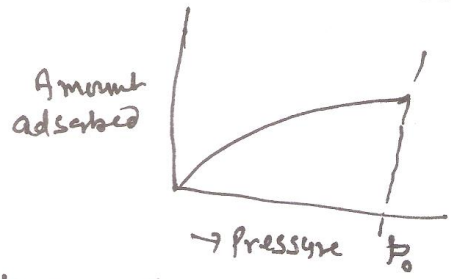
Knowing V_{mono}, the surface area of the adsorbent can be easily calculated.

$$\frac{p}{V(p^0-p)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C}\left(\frac{p}{p_0}\right)$$

The left side of this equation is experimently measured

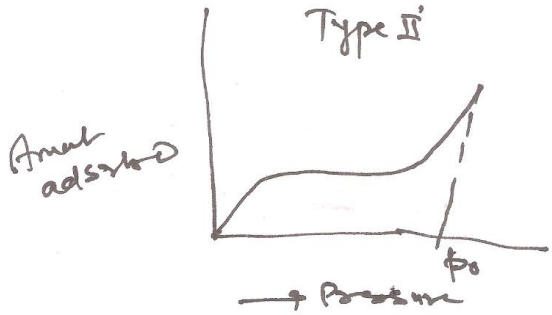
Type of adsorption Isotherms

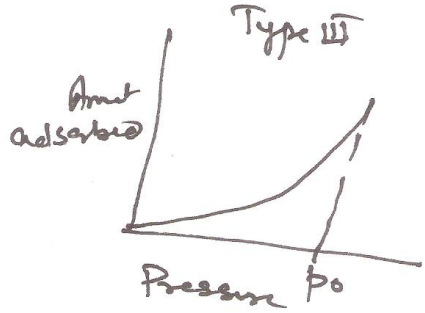
1- Type I



Corresponds to monolayer adsorption as suggested by Langmuir adsorption. The amount of the gas adsorbed approaches a limiting value.

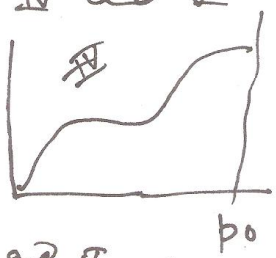
Type II and III

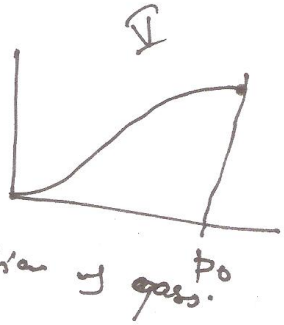




Type II and III show large deviation from Langmuir adsorption. Type II and III show multi-layer adsorption.

Type IV and V





Type IV and V condensation of gases.