## Adsorption isotherms.

- A mathematical equation which describes the relationship between pressure (p) of the gaseous adsorbate and the extent of adsorption at any fixed temperature is called **adsorption isotherms**.
- The extent of adsorption is expressed as mass of the adsorbate adsorbed on one unit mass of the adsorbent.
- Thus, if x g of an adsorbate is adsorbed on m g of the adsorbent, then

Extent of adsorption  $=\frac{x}{m}$ 

Various adsorption isotherms are commonly employed in describing the adsorption data.

## (1) Freundlich adsorption isotherm

(i) Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorbate forms a **monomolecular** layer on the surface of the adsorbent.

 $\frac{x}{m} = kp^{\frac{1}{n}}$  (Freundlich adsorption isotherm) or  $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$  where, x is the

weight of the gas adsorbed by m gm of the adsorbent at a pressure p, thus x/m represents the amount of gas adsorbed by the adsorbents per gm (unit mass), k and n are constant at a particular temperature and for a particular adsorbent and adsorbate (gas), n is always greater than one, indicating **that the amount of the gas adsorbed does not increase as rapidly as the pressure.** 

(ii) At low pressure, the extent of adsorption varies linearly with pressure.  $\left|\frac{x}{m} \propto p'\right|$ 

(iii) At high pressure, it becomes independent of pressure.  $\left|\frac{x}{m} \propto p^{0}\right|$ 



Note:Equation  $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$  is similar to the equation of a straight line y = c + mx. Therefore, the plot of log (x/m) against log p should be a straight line with an intercept equal to log k and slope  $\frac{1}{n}$ .

## (2) The Langmuir - adsorption isotherms

(i) One of the drawbacks of Freundlich adsorption isotherm is that it fails at high pressure of the gas. Irving Langmuir in 1916 derived a simple adsorption isotherm, on theoretical considerations based on kinetic theory of gases. This is named as Langmuir adsorption isotherm.

(ii) The main points of Langmuir's theory of adsorption are as follows,

(a) Adsorption takes place on the surface of the solid only till the whole of the surface is completely covered with a unimolecular layer of the adsorbed gas.

(b) Adsorption consists of two opposing processes, namely **Condensation** of the gas molecules on the solid surface and Evaporation(desorption)of the gas molecules from the surface back into the gaseous phase. (c) The rate of condensation depends upon the uncovered (bare) surface of the adsorbent available for condensation. Naturally, at start when whole of the surface is uncovered the rate of condensation is very high and as the surface is covered more and more, the rate of condensation progressively decreases. On the contrary, the rate of evaporation depends upon the covered surface and hence increases as more and more of the surface is covered ultimately an equilibrium will be set up at a stage when the rate of condensation becomes equal to the rate of evaporation (adsorption equilibrium).

(d) The rate of condensation also depends upon the pressure of the gas since according the kinetic theory of gases, **the number of molecules striking per unit area is proportional to the pressure.** 

Mathematically,  $\frac{x}{m} = \frac{ap}{1+bp}$ , where a and b are constants and their value depends upon

the nature of gas (adsorbate), nature of the solid adsorbent and the temperature. Their values can be determined from the experimental data.

## (iii) Limitation of Langmuir theory

(a) Langmuir's theory of unimolecular adsorption is valid only at **low pressures and high temperatures.** 

(b) When the pressure is increased or temperature is lowered, additional layers are formed. This has led to the modern concept of **multilayer adsorption**.

Note:The Langmuir adsorption isotherm is restricted to the formation of unimolecular layer of gas molecules on the surface of solids. However, it was suggested that there is possibility of **multimolecularlayer** of gas molecules on the surface of the solids rather than single layer. On this basis, **Brunauer, Emmett and Teller** proposed a new theory known as **B.E.T theory**.