The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate.
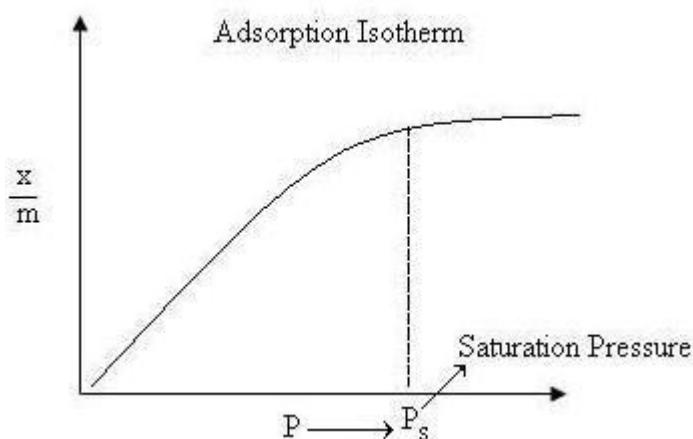
What is Adsorption Isotherm?

The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature. Different adsorption isotherms have been Freundlich, Langmuir and BET theory.

Basic Adsorption Isotherm

In the process of adsorption, adsorbate gets adsorbed on adsorbent.
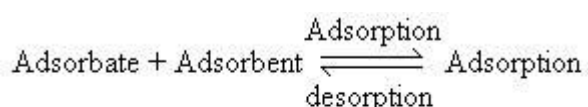
According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favoured.

Basic Adsorption Isotherm

From the graph, we can predict that after saturation pressure Ps, adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, Adsorption is independent of pressure.

Freundlich Adsorption Isotherm

In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm.

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature. Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure.

Langmuir Adsorption Isotherm

In 1916 Langmuir proposed another Adsorption Isotherm known as Langmuir Adsorption isotherm. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A(g) + B(S) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB$$
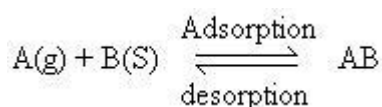
Where A(g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

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

Where θ the number of sites of the surface which are covered with gaseous molecule, P represents pressure and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase. The basic limitation of Langmuir adsorption equation is that it is valid at low pressure only.

At lower pressure, KP is so small, that factor (1+KP) in denominator can almost be ignored. So Langmuir equation reduces to

$\theta = KP$

At high pressure KP is so large, that factor (1+KP) in denominator is nearly equal to KP. So Langmuir equation reduces to

$$\theta = \frac{KP}{KP} = 1$$

BET adsorption Isotherm

BET Theory put forward by Brunauer, Emmett and Teller explained that multilayer formation is the true picture of physical Adsorption.

One of the basic assumptions of Langmuir Adsorption Isotherm was that adsorption is monolayer in nature. Langmuir adsorption equation is applicable under the conditions of low pressure. Under these conditions, gaseous molecules would possess high thermal energy and high escape velocity. As a result of this less number of gaseous molecules would be available near the surface of adsorbent.

Under the condition of high pressure and low temperature, thermal energy of gaseous molecules decreases and more and more gaseous molecules would be available per unit surface area. Due to this multilayer adsorption would occur. The multilayer formation was explained by BET Theory. The BET equation is given as

$$V_{total} = \frac{V_{mono} C \left(\dfrac{P}{P_0} \right)}{\left(1 - \dfrac{P}{P_0} \right) \left(1 + C \left(\dfrac{P}{P_0} \right) - \dfrac{P}{P_0} \right)}$$

The another form of BET equation is

$$\frac{P}{V_{total}(P - P_0)} = \frac{1}{V_{mono} C} + \frac{c - 1}{V_{mono} C} \left(\frac{P}{P_0} \right)$$

Where V_{mono} be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecules,
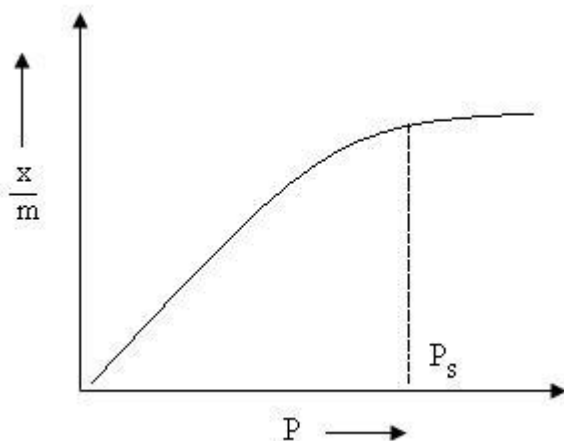
$$\frac{K_1}{K_L}$$

the ratio is designated C. K_1 is the equilibrium constant when single molecule adsorbed per vacant site and K_L is the equilibrium constant to the saturated vapour liquid equilibrium.

Type of Adsorption Isotherm

Five different types of adsorption isotherm and their characteristics are explained below.
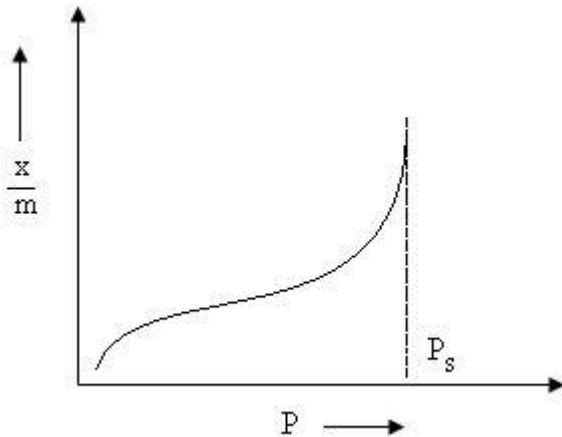
Type I Adsorption Isotherm

Type I Adsorption Isotherm

- The above graph depicts Monolayer adsorption.

- This graph can be easily explained using Langmuir Adsorption Isotherm.

- If BET equation, when $P/P_0 \ll 1$ and $c \gg 1$, then it leads to monolayer formation and Type I Adsorption Isotherm is obtained.

- Examples of Type-I adsorption are Adsorption of Nitrogen (N_2) or Hydrogen (H) on charcoal at temperature near to -1800 °C.
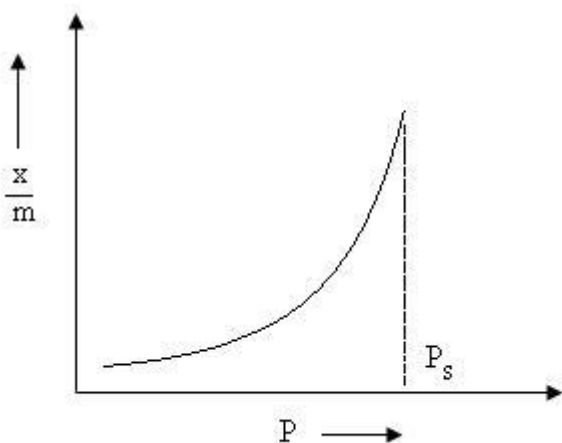
Type II Adsorption Isotherm

Type II Adsorption Isotherm

- Type II Adsorption Isotherm shows large deviation from Langmuir model of adsorption.
- The intermediate flat region in the isotherm corresponds to monolayer formation.
- In BET equation, value of C has to be very large in comparison to 1.
- $\Delta H^0_{des1} > \Delta H^0_{vap\,1}$
- Examples of Type-II adsorption are Nitrogen (N_2 (g)) adsorbed at -1950 °C on Iron (Fe) catalyst and Nitrogen (N_2 (g)) adsorbed at -1950 °C on silica gel.
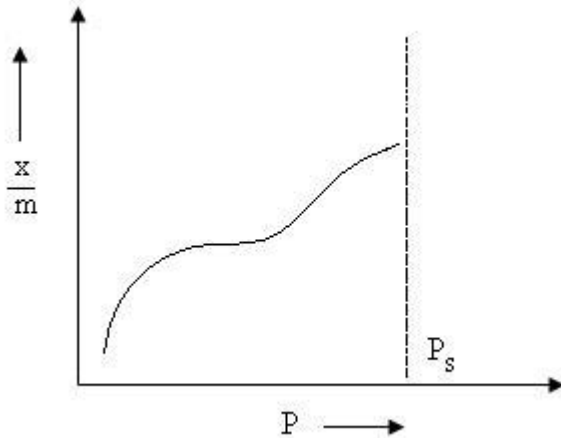
Type III Adsorption Isotherm

Type III Adsorption Isotherm

- Type III Adsorption Isotherm also shows large deviation from Langmuir model.
- In BET equation value if C <<< 1 Type III Adsorption Isotherm obtained.

- This isotherm explains the formation of multilayer.

- There is no flattish portion in the curve which indicates that monolayer formation is missing.

- Examples of Type III Adsorption Isotherm are Bromine (Br_2) at 790 °C on silica gel or Iodine (I_2) at 790 °C on silica gel.
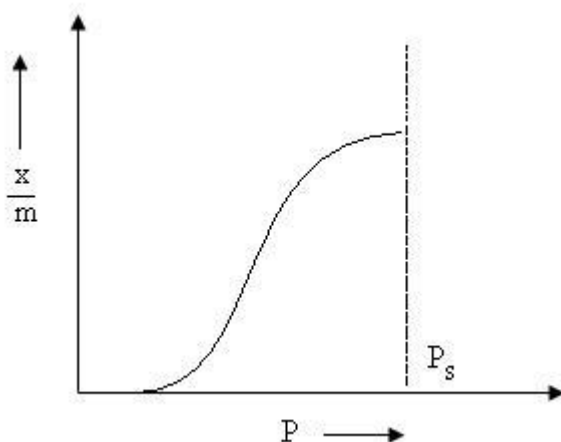
Type IV Adsorption Isotherm

Type IV Adsorption Isotherm

- At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer.

- The saturation level reaches at a pressure below the saturation vapour pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure (PS) of the gas.

- Examples of Type IV Adsorption Isotherm are of adsorption of Benzene on Iron Oxide (Fe_2O_3) at 500 °C and adsorption of Benzene on silica gel at 500 °C.

Type V Adsorption Isotherm

Type V Adsorption Isotherm

- Explanation of Type V graph is similar to Type IV.

- Example of Type V Adsorption Isotherm is adsorption of Water (vapours) at 1000 °C on charcoal.

- Type IV and V shows phenomenon of capillary condensation of gas.