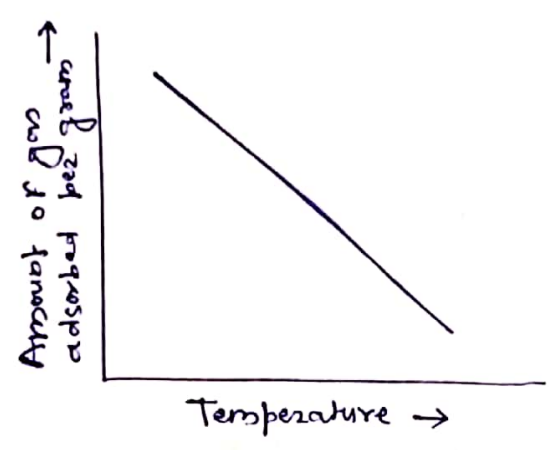


* Adsorption Isobar :-

The effect of temperature on the extent of adsorption, at a given pressure of the adsorbate, is also expressed graphically as:

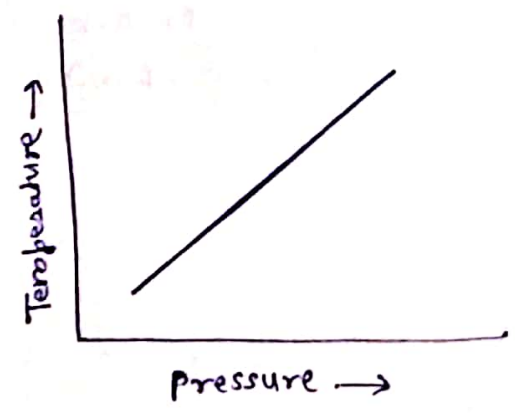


The curve showing the effect of temperature on the extent of adsorption at a given pressure is called an adsorption isobar.

The amount of adsorption evidently, decreases with rise in temperature.

* Adsorption Isotherm :-

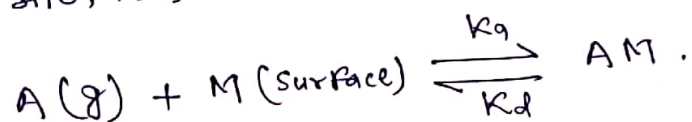
The curve showing the variation of pressure with temperature, for a given amount of adsorption is called an adsorption isotherm.



* Langmuir adsorption isotherm :-

Langmuir proposed his theory of adsorption of a gas on the surface of a solid. He considered the surface of the solid to be made up of elementary site each of which could adsorb one gas molecule. He assumed that a dynamic equilibrium exists between the adsorbed molecules and the free molecules.

Let 'A' is the gas molecule and 'M' is the surface site, then -



Where, k_a = rate constant for adsorption.

k_d = rate constant for desorption.

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

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

Thus, the rate of adsorption = $k_a P_A N(1-\theta)$ ——— (1)

The rate of desorption is proportional to the number of adsorbed molecules $N\theta$

Thus, rate of desorption = $k_d N\theta$ ——— (2)

continued ———

At equilibrium,

The rate of adsorption is equal to the rate of desorption

∴ $k_a P_A N(1-\theta) = k_d N \theta$ ——— (3)

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

$\implies K P_A (1-\theta) = \theta$ ——— (4)

[where, $K = \frac{k_a}{k_d}$]

$\implies \frac{1-\theta}{\theta} = \frac{1}{K P_A}$ ——— (5)

$\implies \frac{1}{\theta} - 1 = \frac{1}{K P_A}$ ——— (6)

$\implies \frac{1}{\theta} = \frac{1}{K P_A} + 1$ ——— (7)

$\implies \frac{1}{\theta} = \frac{1 + K P_A}{K P_A}$ ——— (8)

∴ $\theta = \frac{K P_A}{1 + K P_A}$ ——— (9)

Equation (9) is called the Langmuir adsorption isotherm.

⇒ At low pressure :-

$K P_A \ll 1$

∴ eqⁿ (9) becomes -

$\theta = K P_A$ ——— (10)

i.e. The fraction of the surface covered is directly proportional to the partial pressure of the gas molecules.

⇒ At high pressure :-

$$kP_n \gg 1$$

∴ eqs - (9) becomes -

$$\theta = 1 \quad \text{--- (11)}$$

Thus, at high pressure, the value of θ tends to become unity.
i.e. The entire surface gets covered by a monomolecular layer of the gas.

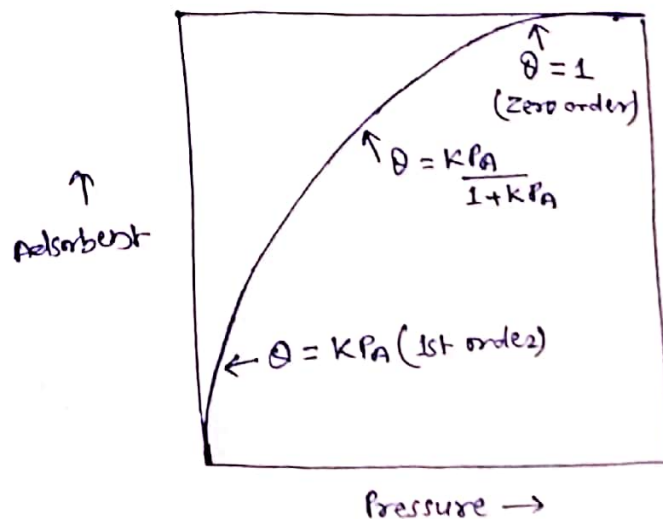
Thus on combining the results of eqs - (10) & eqs - (11) it is evident that from this theory -

The magnitude of adsorption at a given temperature should first increase in proportion to increase of pressure and finally tend to attain a certain limiting value.

⇒ At intermediate pressure :-

$$\theta = k(P_n)^n \quad \text{--- (12)}$$

Where n lies between 0 & 1.



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