Absorption Isotherms:-

An equation that relates the amount of substance attached to the surface to its concentration in the gas phase or in, the solution, at a fixed temperature, is known as an adsorption isotherm.

The Langmuir isotherm:-

The simplest isotherm was first observed in 1916.

Let us suppose that, at ~~thermal~~ equilibrium a fraction θ of the surface is covered by adsorbed ~~by~~ molecules.

A fraction that is uncovered = 1 − θ — (1)

Rate of Adsorption ∝ [A] in gas or liquid phase

It is also proportional to the unused fraction of area.

Adsorption can only occur if the molecule strikes the bare surface.

The rate of adsorption v_a is thus

$$v_a = k_a [A] (1-\theta) \quad \text{--- (2)}$$

where k_a is rate constant relating to the adsorption process.

The rate of desorption v_d is proportional only to the number of molecules attached to the surface, which in turn is proportional to the fraction of surface covered.

$$v_d = k_d \theta \quad \text{--- (3)}$$

where k_d is a rate constant of desorption.

At equilibrium

Rate of adsorption = Rate of desorption

$$k_a [A] (1-\theta) = k_d \theta \quad \text{--- (4)}$$

or

$$\frac{\theta}{1-\theta} = \frac{k_a}{k_d} [A] \quad \text{--- (5)}$$

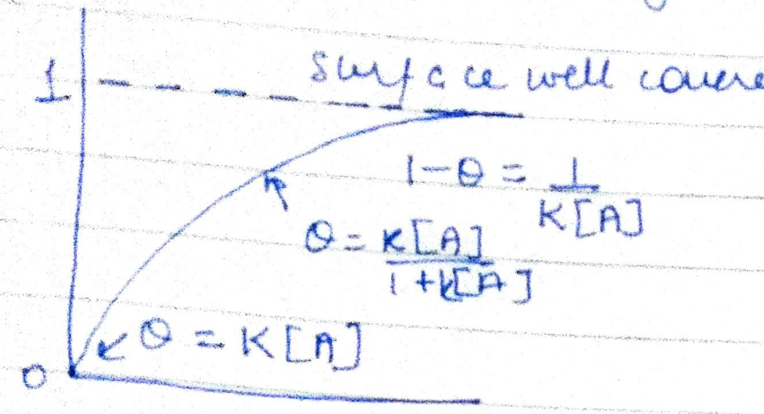
The ratio $\frac{k_a}{k_d}$ is an equilibrium constant and can be written as K, then,

$$\frac{\theta}{1-\theta} = K [A]$$

or $\theta = K [A] (1-\theta)$

or $$\theta = \frac{K [A]}{1 + K [A]} \quad \text{--- (6)}$$

A graph of θ against [A]



At sufficiently low concentration we can neglect K[A] in comparison with unity and θ is proportional to [A].

So at very high pressure / concentration

$$1-\theta = \frac{1}{1+K[A]}$$

$$1-\theta \approx \frac{1}{K[A]}$$