

B.Sc. (Honours) Part-III
Paper-VA

Topic: Langmuir Isotherm

UG

Subject-Chemistry

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Langmuir Isotherm

On the basis of certain theoretical postulates, Langmuir proposed an equation showing variation in the extent of adsorption with pressure. He successfully explained type I adsorption isotherm, in which, at lower pressure, the extent of adsorption increased linearly with pressure and thereafter became saturated at high pressures.

The various assumptions of Langmuir adsorption isotherm are as follows:

- 1) Adsorption of adsorbate molecules takes place only on fixed number of adsorption sites that are available on the surface of (solid) adsorbent.
- 2) Adsorption is a process of 'sticky collision'. This means when a gas molecule hits a vacant site on the adsorbent surface, it will get adsorbed; however, if it hits an occupied site, there occurs an elastic collision and the gas molecule gets rebound. This implies that adsorption takes place only on a vacant site, where each such site can hold only one gas molecule.
- 3) All active sites on the adsorbent surface are energetically equivalent, i.e., they involve constant heat of adsorption.
- 4) The surface of the solid adsorbent is assumed to be completely flat and uniform on microscopic dimensions.
- 5) Under conditions of low pressure and moderately high temperature, a monomolecular layer of adsorbate molecules is formed on the adsorbent surface. This is particularly true as the influence of active site on the adsorbent surface usually extends up to $1.5-2 \text{ \AA}$.
- 6) There are no interactions between the gas molecules that are getting

adsorbent on the adsorbent surface; adsorption of gas molecules takes place independent of the occupation of the neighboring sites. These gaseous molecules are thus assumed to behave ideally.

7) A state of dynamic equilibrium exists as follows:



Where, M = free gas molecule

S = Active site on solid adsorbent

MS = Adsorbed gas

molecule on the solid surface This means that adsorption takes place on vacant sites and desorption takes place from occupied sites, till a state of equilibrium is attained.

As per the law of mass action,

Rate of forward reaction (adsorption) = $K_f [M][S]$

Rate of backward reaction (desorption) = $K_b [MS]$

At equilibrium, Rate of adsorption = rate of desorption

$$\Rightarrow K_f [M][S] = K_b [MS]$$

On the basis of above postulates, Langmuir derived the equation as follows.

Under conditions of constant temperature and pressure, let the number of adsorbate molecules hitting unit area of the adsorbent in unit time t, = N

Let the fraction of surface area of the adsorbent that is

covered = θ Therefore, the uncovered surface area of

the adsorbent = $1 - \theta$ Now,

Rate of desorption $\propto \theta$

Or Rate of desorption = $K_d \theta$

Where K_d is a constant for desorption

The rate of adsorption will be proportional to uncovered surface area of the adsorbent, and the number of adsorbate molecules hitting unit area of adsorbent in unit time. The latter, in turn, will be proportional to the pressure of the gas.

Thus, we have

$$\text{Rate of adsorption} \propto P(1-\theta)$$

$$\text{or Rate of adsorption} = K_a P(1-\theta)$$

Where K_a is a constant for adsorption

At equilibrium,

$$\text{Rate of adsorption} = \text{Rate of desorption}$$

$$\text{Solving for } \theta, \quad = \frac{K_a}{K_d + K_a} P$$

$$K_d + K_a P$$

$$\theta = \frac{K_a/K_d P}{1 + (K_a/K_d) P}$$

Where, $K_1 = (K_a/K_d)$

Characteristics of Langmuir isotherm

- It could explain type I adsorption isotherm only and was associated with certain limitations
- Langmuir adsorption is based on certain theoretical postulates
- The adsorption process is dynamic in nature. Langmuir assumes the formation of monolayer of adsorbate molecules on the surface of solid adsorbent. The gas molecules are also assumed to behave ideally
 - Langmuir adsorption isotherm is valid over a wide range of pressure and successfully explains type I adsorption isotherm

Limitations of Langmuir isotherm

Based on his theory, Langmuir derived an equation which explained the relationship between the number of active sites of the surface undergoing adsorption and pressure. This equation is called Langmuir equation.

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

where, θ - the number of sites of the surface which are covered with gaseous molecule,

P - pressure

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 denominator is nearly equal to KP. So Langmuir equation reduces to

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

$$\theta = KP$$