

Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure ....

## Langmuir Adsorption Isotherm

In 1916, Irving Langmuir proposed another **Adsorption Isotherm** which explained the variation of **Adsorption** with pressure. 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.

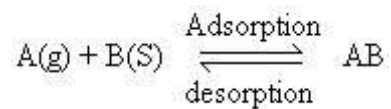
- **Non-Dissociative** adsorption is said to occur when a molecule adsorbs on to the surface from the gas phase without fragmentation.
- When fragmentation does occur, the adsorption process is termed **dissociative**.
- The free gas and the adsorbed gas are in dynamic equilibrium.
- Fractional coverage ( $\theta$ ) or extent of adsorption depends on : T, P (gas) or conc. (solute) and on effective surface area.
- The variation of  $\theta$  with pressure at a chosen temperature is called the adsorption isotherm.

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### Assumptions of Langmuir Isotherm

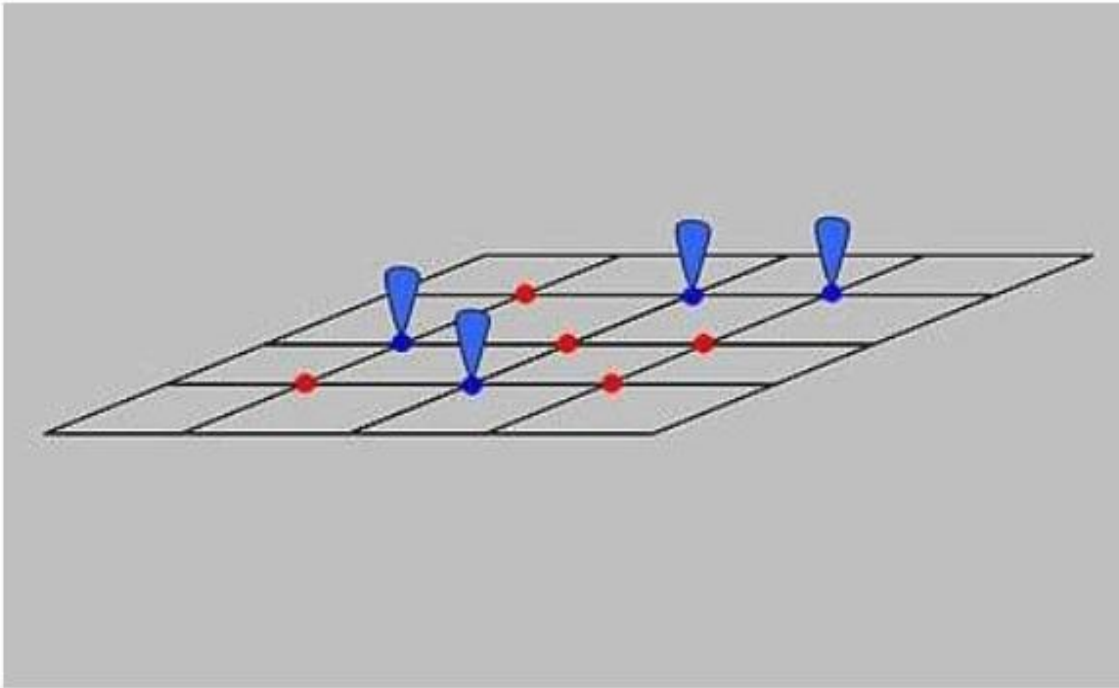
Langmuir proposed his theory by making following assumptions.

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.



Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

5. Adsorption is monolayer or unilayer.

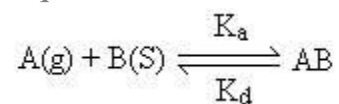


An schematic showing equivalent sites, occupied(blue) and unoccupied(red) clarifying the basic assumptions used in the model. The adsorption sites(heavy dots) are equivalent and can have unit occupancy. Also, the adsorbates are immobile on the surface

## Derivations of the Langmuir Adsorption Equation

### Calculation of Equilibrium Constant

Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.



Where  $K_a$  represents equilibrium constant for forward reaction and  $K_d$  represents equilibrium constant for backward direction.

According to Kinetic theory,

Rate of forward reaction =  $K_a [A] [B]$

Rate of backward reaction =  $K_d [AB]$

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

$$K_a [A] [B] = K_d [AB]$$

$$\text{Or, } \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

$$K = \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

The above equation represents the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

### Derivation

Langmuir Equation which depicts a relationship between the number of active sites of the surface undergoing adsorption (i.e. extent of adsorption) and pressure.

To derive Langmuir Equation and new parameter '  $\theta$  ' is introduced. Let  $\theta$  the number of sites of the surface which are covered with gaseous molecules. Therefore, the fraction of surface which are unoccupied by gaseous molecules will be  $(1 - \theta)$ .

Now, Rate of forward direction depends upon two factors: Number of sites available on the surface of adsorbent,  $(1 - \theta)$  and Pressure, P. Therefore rate of forward reaction is directly proportional to both mentioned factors.

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

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

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

Similarly, Rate of backward reaction or Rate of Desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

$$\text{Rate of desorption} \propto \theta$$

$$\text{Or, Rate of desorption} = K_d \theta$$

At equilibrium, rate of adsorption is equal to rate of desorption.

$$K_a P (1 - \theta) = K_d \theta$$

We can solve the above equation to write it in terms of  $\theta$ .

$$K_a P - K_a P \theta = K_d \theta$$

$$K_a P = K_a P \theta + K_d \theta$$

$$K_a P = (K_d + K_a P) \theta$$

$$\theta = \frac{K_a P}{K_d + K_a P}$$

Divide numerator and denominator on RHS by  $K_d$ , we get

$$\theta = \frac{\frac{K_a P}{K_d}}{\frac{K_d}{K_d} + \frac{K_a P}{K_d}}$$

Now put

$$K = \frac{K_a}{K_d}$$

in above equation we get

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

Langmuir Adsorption Equation

This is known as Langmuir Adsorption Equation.