

**Adsorption:**

Unbalanced or residual forces act along the surface of a liquid giving rise to surface tension. Such forces also exist on the surface of a solid. As a result of these residual forces, the surface of a solid has a tendency to attract and retain molecules of other Species with which it is brought into contact. As these molecules remain only at the surface and do not go deeper into the bulk, their concentration is more at the surface than in the bulk of the solid.

“The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as adsorption.

The forces involved are intermolecular forces (Van der Waals forces).

Solids when finely divided, have a large surface area and therefore, show this property to a large extent.

The solid that takes up a gas or vapour or a solute from a solution, is called the adsorbent while the gas or vapour or the solute, which is held to the surface of the solid, is; -called the adsorbate.

Adsorption is to be carefully distinguished from absorption. The latter term implies that a substance is uniformly distributed throughout "the body of a solid or a liquid.

**Chemisorption:**

Adsorption is not necessarily a physical phenomenon always. It may as well be a chemical process involving chemical interaction-between the surface atoms of the adsorbent and the atoms of the adsorbate. This type of adsorption is known as chemisorption.

**Applications of Adsorption:**

1. A very good method of creating a high vacuum is to connect a bulb of charcoal cooled in liquid air to a vessel which has already been exhausted as far as possible by a vacuum pump. Since the magnitude of adsorption at such low temperatures is quite high, the remaining traces of air, in spite of the low pressure, are adsorbed by the charcoal almost completely.

2. Activated charcoal is used in gas masks in which all toxic gases and vapours are adsorbed by the charcoal while pure air passes through its pores practically unchanged.
3. Silica and alumina gels are used as adsorbents for removing moisture for controlling humidities of rooms.

**Adsorption of Gases by Solids:**

The gas is contained in a vessel of known volume at a given temperature. The pressure of the gas is measured on a manometer, attached to the vessel. The adsorbent is then introduced into the vessel by a suitable device.

Adsorption takes place fairly quickly and the pressure of the gas falls. This is noted on the manometer knowing the fall of pressure, the quantity of the gas adsorbed by the solid can be calculated, assuming Boyle's law holds good. It is necessary to apply correction due to the volume of the adsorbent added.

Factors influencing Adsorption:

- i) Temperature
- ii) Pressure
- iii) Nature of the gas and
- iv) Nature of the adsorbent

Decrease of temperature and increase of pressure both tend to cause increase in the magnitude of adsorption of a gas on a solid.

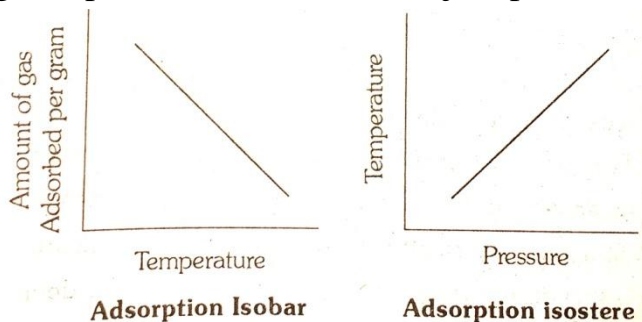
The relationship between the magnitude of adsorption and pressure can be expressed mathematically by an empirical equation commonly known as Freundlich adsorption,

$$a = kP^n$$

where  $a$  is the amount of gas adsorbed per unit mass of the adsorbent at pressure  $p$ , and  $k$  and  $n$  are constants depending upon the nature of the gas and the nature of the adsorbent.

**Adsorption Isotherm:**

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



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

### Sticking probability:

The proportion of collisions that successfully lead to adsorption is known as sticking probability,  $S$

$$S = \frac{\text{Rate of adsorption of adsorbate molecules}}{\text{Rate of collisions of adsorbate molecules with adsorbent } 1 \text{ (- surface)}}$$

### Desorption Activation Energy:

Since an adsorbed molecule has a low binding energy, it will remain bound on the surface for a very short time only called the life time ( $\tau$ ) of the adsorbate molecule. It is related to the desorption activation energy,  $E_a$ , by the expression

$$\tau = \tau_0 e^{E_a/RT}$$

Integration of this equation yields the integrated van't Hoff-type or Arrhenius - type equation,

$$\ln\left(\frac{\tau_2}{\tau_1}\right) = \frac{E_a}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

This equation enables the evaluation of  $E_a$ .

### Langmuir Adsorption Isotherm:

Langmuir visualised the adsorption process to consist of two opposing tendencies of gaseous molecules.

i) the tendency of molecules to condense from gaseous phase on to the surface of a solid and

ii) the tendency of these molecules to evaporate back into the gaseous state.

He assumed further that the adsorbed layer is unimolecular in thickness. Based on these assumption, he derived the following expression for the adsorption isotherm.

$$a = \frac{k_1 k_2 p}{1 + k_1 p}$$

At low pressures, the above expression takes the form  $a = kp^1$  and at high pressures, it takes the form  $a = kp^0$ . Hence at intermediate pressures,  $a = kp^n$  where  $n$  lies between 0 and 1. This equation is exactly the same as the Empirical Freundlich adsorption isotherm.

### BET equation for Multilayer Adsorption:

The Langmuir theory of adsorption is restricted to the formation of a unimolecular layer of adsorbate molecules. However, the true picture of adsorption, as proposed by Brunauer, Emmett and Teller, is the formation of multilayers. This is known as the BET theory.

Assuming that adsorption on one site on the adsorbent does not affect adsorption at neighbouring sites and that molecules can be adsorbed in second, third, ..... and  $n^{\text{th}}$  layers, Braunauer, Emmett and Teller derived the following equation, known as the BET equation.

$$\frac{p}{v_{\text{total}} (p_0 - p)} = \frac{1}{v_{\text{mono}} c} + \frac{c-1}{v_{\text{mono}} c} \left[ \frac{p}{p_0} \right]$$

The plot of  $\frac{p}{v_{\text{total}} (p_0 - p)}$  versus  $\frac{p}{p_0}$  gives a straight line whose slope =  $\frac{c-1}{v_{\text{mono}} c}$  and intercept  $\frac{1}{v_{\text{mono}} c}$

Thus from the slope and the intercept, both  $v_{\text{mono}}$  and  $c$  can be evaluated. Knowing  $v_{\text{mono}}$  and crosssectional area of the adsorbate gas molecule, the surface area of the adsorbent can be calculated.

### Adsorption chromatography:

It has been found that closely related substances With almost similar physical and chemical properties which cannot be separated from one another by ordinary means, are adsorbed to different extends on the surface of adsorbents. This facilitates their separation and purification. If a solution containing different solutes is poured down a column filled with a finely divided adsorbent, the solute most readily absorbed is retained on the top layer along with smaller amounts of the other constituents, while the less readily adsorbed constituents are held on lower portions of the column. A partial separation of the constituents of the mixture is thus easily achieved. A fuller separation is possible by repeating, and modifying the process.

This process of separation, also known as column chromatography, was first developed in 1900 by Day, an American petroleum chemist. However a more extensive study was made in 1906 by Tswett, a polish botanist. He observed that when a solution of plant pigments in petroleum ether is passed slowly through a, column packed with alumina, a number of horizontal bands of different colours are produced-in the column. This is evidently, due to the fact that different constituents of the mixture are adsorbed to different extents. The most readily adsorbed constituent is held at the top. The others with decreasing order of adsorbabilities are held up in different zones down the column in the same order. This, of course gives only a partial separation of the various constituents as some of the less readily adsorbed constituents are still present mixed up with the more readily adsorbed constituents and so on.

The initial separation of the various coloured constituents can be improved by passing either the original or some other suitable Solvent slowly through the column. The solvent used is called eluent. The various coloured zones then become more sharply defined. Therefore, the name chromatography, which implies, colour, was given to this technique.

The banded column of the adsorbed constituents is called a chromatogram.

The process of improving the separation by passing the original solvent or some other suitable solvent, is known as development the chromatogram.

5

The solvents' used in chromatography have three functions to perform:

1. They dissolve the mixture of various constituents and introduce them into the column. The solvents used for this purpose are generally non polar (such as benzene and petroleum ether) since adsorption takes place more readily from such solvents.

2. They are introduced into the column for the development of the chromatogram. In this process, the various Zones of the chromatogram get separated sharply from one another. The solvents when used for this purpose are termed as, developers. The developer is generally a solvent in "which the components of a mixture are not highly soluble.-It is usually a liquid of low molar mass. Attempt is often made, to use the same-solvent which is used for introducing the mixture, as a developer. But it is not always possible. Hence, other suitable solvents are used quite often.

3. They are also used for removing the various constituents of a mixture from the chromatogram after it is properly developed. The solvents used for this purpose are called eluents. A good eluent must be .a liquid which can dissolve readily the various components. It must also get itself to some extent. This helps in displacing components from the column. Further, the eluent should be a low boiling liquid so that it can easily be removed from the recovered component. Sometimes it is desirable to use two eluents one after the other. If one eluent can desorb only a portion of an adsorbate, the second, a more powerful eluent, maybe used to desorb the remaining portion of the adsorbate. Thus, benzene is used as the first eluent, ether may be used as the second eluent.

Join Us on FB :

For English – [Examsdaily](#)

For Tamil – [Examsdaily Tamil](#)

Join US on Whatsapp



For English - [Click Here](#)



For Tamil – [Click Here](#)