SURFACE CHEMISTRY

ADSORPTION

ADSORPTION: -

Adsorption is the adherence of atoms, ions, or molecules from a gas, liquid, and dissolving solid to a surface. This process generates an adsorbate layer on the surface of the adsorbent.

Adsorption is the ability of all tangible things to adsorb molecules from the liquids or gasses they come in contact with on their surfaces. In this post, we learn about the meaning of adsorption and its many forms, such as chemical, physical, and isothermal adsorption. We'll also go over different types of adsorbates and adsorbent. So, before we get started, let's define adsorbate and adsorbent. Adsorbents are solids used to adsorb dissolved chemicals or gasses, and adsorbate is a term that refers to the molecules that are adsorbed by solids.

Define Adsorption

Adsorption is the collection of molecules on a solid's internal or external surface or even on a liquid's surface. The collection of molecules by the internal or external cover (walls of capillaries or fissures) of solids or even surfaces of liquids is referred to as adsorption. The method of permeating the substance of blocks of amorphous liquids or solids, or even the genuine inner crystals, is known as absorption. When a solid absorbs a liquid or gas without defining a specific absorption or absorption method, it is called sorption.

Difference between Adsorption vs Absorption

Most people are confused by these two names since they sound similar, but the procedures are different. The surface phenomena of adsorption is an exothermic process. It is temperature-dependent, and also the methods will expand and reduce slowly at first. Absorption, on either hand, is an endothermic reaction. The temperature has little effect on absorption, so it happens consistently. Substances permeate the material's surface. Adsorption does not occur spontaneously, but absorption does. Adsorption isn't unique just on the surface area, but it is distinctive all through the surface area. Absorption has a relatively higher molecule interaction than adsorption.

Types of Adsorptions

Physical adsorption and chemical adsorption are the two types of adsorptions that exist. Adsorption is an exothermic reaction in which heat is generated when an attractive force exists between the adsorbent and the adsorbate. Furthermore, the forces between the adsorbent and adsorbate have a role in physical and chemical adsorption. Gasses condense to liquids during physical adsorption due to Van der Waals forces or forces among adsorbates with solid absorbents.

Solids can adsorb any gas regardless of chemical characteristics if the temperature drops and the gas pressure increases. Chemical adsorption, on the other hand, is dependent on chemical forces acting on solid surfaces plus gas adsorbates. When opposed to physical adsorption, chemical adsorption requires a more significant temperature. Chemical adsorption requires energy activation, so it is a long but slow procedure.

Adsorption Isotherm

The adsorption isotherm is used in environmental studies, including adsorption methods because it assists in calculating the solid material's adsorption capability. Moreover, an adsorption isotherm is a chart that depicts the amount of adsorbed adsorbate just on an adsorbent surface when the pressure and temperature are maintained fixed.

Application of Adsorption

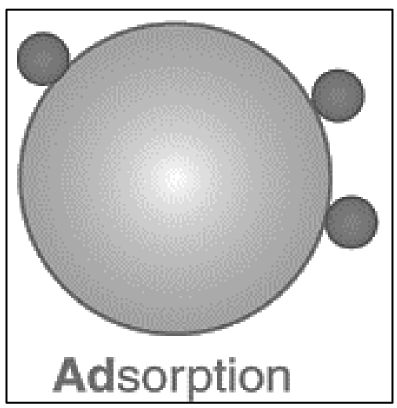
Charcoal decolorizes the coloured sugar solution by adsorbing the colouring molecules. The desiccators use silica gel to absorb moisture. Since they operate as adsorbents, alumina and silica gels remove the moisture, thus managing humidity in workplaces or rooms. Activated charcoal is utilized in gas masks because it adsorbs vapours and harmful fumes, purifying the air. The adsorption technique is used to do heterogeneous catalysis. Charcoal can be utilized as an absorbent to split noble gases. The adsorption phenomenon is used in chromatographic analysis. It produced stable emulsions via adsorption for syrups or cosmetics. Adsorption of drugs destroys bacteria.

Conclusion

The absorption and adsorption processes are fundamentally unique and should not be confused. A liquid or gas collects on a liquid or solid surface and forms an atomic or molecular film during adsorption. In the absorption process, though, a material diffuses into a liquid or solid to generate a solution (i.e., molecules undergoing resorption are taken up by the volume, not by the surface).

Mechanism of adsorption :-

1. Adsorption is the surface phenomenon that means the molecules are accumulated on the surface.
2. The surface on which the phenomenon takes place is called adsorbate and the molecular species are called adsorbents.
3. The process is exothermic because of the release of energy.
4. Enthalpy of adsorption is defined as the amount of energy released during adsorption when one mole of adsorbate is adsorbed on the adsorbent.
5. The enthalpy of adsorption is negative because the entropy decreases.
6. Enthalpy of adsorption is negative because the randomness of the molecules will be restricted.
7. Adsorption is a spontaneous process, which occurs at constant temperature and pressure.
8. Clay, silica gel, and colloids are common examples of adsorbents.
9. Below showing you the picture of adsorption:



Mechanism-

- Adsorption occurs when the particle on the surface and the particle in the adsorbent's bulk are not in the same environment.
- Unbalanced forces, also known as residual attractive forces, act on the particle on the surface.
- Due to these forces, the adsorbent's surface particles attract the adsorbate particles.
- Adsorption always results in a decrease in the surface's residual attractive forces.
- That is, the surface's energy decreases, and this is expressed as heat, which is known as the heat of adsorption.
- The enthalpy change is denoted as negative because when adsorbate molecules are adsorbed on the surface, their freedom of movement is restricted, resulting in a decrease in entropy.

Types of adsorption and factors affecting extent of adsorption: -

Types of Adsorptions

On the basis of interaction forces between adsorbate and adsorbent, adsorption is of two types.

1. **Physical adsorption:**

   This type of adsorption is also known as physisorption. It is due to weak Van der Waals forces between adsorbate and adsorbent.

   For example, H_2 and N_2 gases adsorb on coconut charcoal.

2. **Chemical adsorption:**

   This type of adsorption is also known as chemisorption. It is due to strong chemical forces of bonding type between adsorbate and adsorbent. We can take the example involving the formation of iron nitride on the surface when the iron is heated in N_2 gas at 623 K.

   Adsorption of gas on a solid is a spontaneous exothermic reaction. The amount of heat liberated when a unit mass of a gas is adsorbed on the surface is called heat of adsorption.

Factors affecting the extent of adsorption

The extent to which adsorption will happen on a solid surface depends on the following factors:

Nature of adsorbent

The adsorption of the gas depends on the nature of the adsorbent. A gas can be adsorbed on different absorbent surfaces in different amounts. For example, Hydrogen is weakly adsorbed on the alumina surface whereas it is strongly adsorbed on the nickel surface under certain conditions.

Surface area

When we increase the surface area of the adsorbent there is an increase in the adsorption of gases. This is because when we increase the surface area there is more number of adsorbing sites. So finely divided solids and some porous substances are good adsorbents.

Nature of the gas

In general, if a gas is more liquefiable it will be more easily absorbed. For example, gases like NH_3, HCl, Cl_2, CO_2, which can be liquefied easily are more readily adsorbed on the solids surface rather than permanent gases like O_2, H_2, etc.

Exothermic nature

The heat of adsorption can be defined as the energy liberated when 1 g mol of a gas is adsorbed on a solid surface. When the temperature is increased the kinetic energy of the gas molecules also increases which results in a greater number of collisions between the molecules and the surface.

Pressure

On the solid surface, there is a fixed number of adsorption sites where gas molecules can be adsorbed. Initially when the pressure has increased the rate of adsorption increases due to an increase in the gas molecules striking on the surface. Thus, an increase in the pressure increases the rate of adsorption linearly. But after sometime, it will reach a point when the pressure has no effect on the rate of adsorption as the number of adsorption sites is fixed and no more adsorption can happen in those sites. Hence, at that point, the extent of adsorption will be independent of the pressure.

Types of adsorption isotherm: -

Various adsorption isotherms

The various types of adsorption isotherms are:

I Classical Freundlich adsorption isotherm

in 1909, Freundlich proposed an empirical equation and was known as Freundlich adsorption isotherm. This equation is as follows:

$x/m = kp^{1/n}$ ... (i)

where x is amount of adsorbate, m is the amount of adsorbent, p is the pressure, k and n are two constants depending upon the nature of the adsorbent and adsorbate, and n being less than unity.

Equation (i) is applicable to the adsorption of gases on solids.

In case of solution, equation (i) takes the form

$x/m = kc^{1/n}$ ...(ii)

where c is the concentration of the solute in gm moles per liter.

Equations (i) and (ii) predict the effect of pressure (or concentration) on the adsorption of gases (or solution) at constant temperature in a quantitative manner.

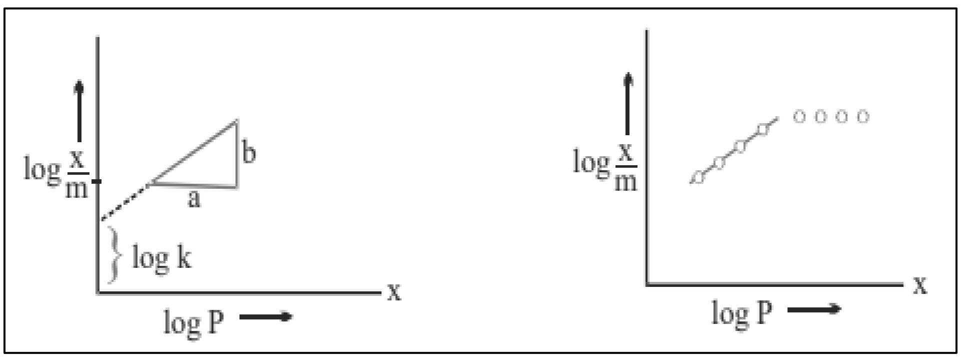
Test of Freundlich's Adsorption Isotherm.

Taking logarithms of equations (i) and (ii), we get

Log $\frac{x}{m} = \log k + \frac{1}{n} \log p$ ... (iii)

and log $\frac{x}{m} = \log k + \frac{1}{n} \log c$ ... (iv)

f log $\frac{x}{m}$ is plotted against log p or log c, a straight line should be obtained as shown in fig. The slope of the line will give the value of and the $\frac{1}{n}$ intercept on the Y-axis gives the value of log k, i.e.



Intercept = log k

and slope = $\frac{b}{a} = \frac{l}{n}$

Thus, by using equations (iii) and (iv), the values of k and n can be calculated from the graph (fig). Analysis of the graph shows that as p increases, $\frac{x}{m}$ also increase and, thus, the

Freundlich's equation indicates no limit to this increase. But experimental values, when plotted, show some deviations from linearity especially at low pressures. This is seen in fig. If we compare theoretical and experimental curves (fig), the two agree over a certain range of pressure only. Thus, Freundlich's equation has a limitation that it is valid over a certain range of pressure only.

Limitations of Freundlich's equation

1. It is valid over a certain range of pressure only.
2. The constant k and n vary with the temperature.
3. Freundlich adsorption equation is a purely empirical formula without theoretical foundation.

II Langmuir Adsorption Isotherm:

It has already been stated that Freundlich adsorption isotherm holds good for a certain range of pressure only. To solve this difficulty, Langmuir (1916) worked out an adsorption isotherm known as Langmuir's adsorption isotherm

The various assumptions are :

a. The adsorbed layer on the solid adsorbent is assumed to be unimolecular in thickness. This view is widely accepted for adsorption at low pressure or at moderately high temperature. However, the adsorbed molecules can hold other gas molecules by van der Waal's forces, so that multimolecular layers are possible. Such behaviour is apparent only at relatively low temperatures and at pressure approaching the saturation value. But Langmuir only considered the formation of unimolecular layer while deriving this relation.

b. The adsorption is taking place on the fixed sites and there is no interaction between the adsorbed molecules on the surface. One site adsorbs one molecule. When the whole surface is completely covered by a unimolecular layer of the gas, further adsorption is not possible and indicates a maximum of saturation of adsorption.

c. The process of adsorption is a dynamic process which consists of two opposing processes:

(i) Condensation Process:

It involves the condensation of the molecules of the gas on the surface of their solid.

(ii) Evaporation Process:

It involves evaporation of the molecules of adsorbate from the surface of the adsorbent. When adsorption starts, the whole adsorbent surface remains bare and so the initial rate of condensation is maximum. As the surface becomes gradually covered, the rate of condensation becomes smaller and smaller. On the contrary, the initial rate of evaporation (desorption) of the condensed molecules is smallest at the beginning of adsorption, but increases as the surface becomes more and more covered. Ultimately, when the equilibrium is reached, the rate of condensation becomes equal to the rate of evaporation. It means that the number of gas molecules condensing on the given surface is equal to the number of molecules evaporating away per unit time from the same surface, i.e. the arrangement of the adsorbed molecule on the surface in unidirectional.

d. Gas behaves ideally.

e. Surface is uniform energetically.

Application of adsorption: -

1. **Air pollution masks:**

   These consist of silica gel or activated charcoal powder, when dust or smoke are paused through them, those particles get adsorbed on the surface of these materials.

2. **Separation of noble gases by Dewar's flask process:**

   A mixture of noble gases of Ne, Ar, Kr is passed through Dewar's flask in presence of heated coconut charcoal. Argon and Krypton gels adsorbed leaving Neon.

3. **Purification of water:**

   By the addition of alum stone to the water, impurities get adsorbed on the alum and water gets purified.

4. **Removal of moisture and humidity:**

   Moisture in the air is removed by placing silica gel on which water molecular gets adsorbed.

5. **Adsorption chromatography:**

   It is used to separate pigments and hormones.

6. **Ion exchange method:**

   In this method of removing the hardness of water, calcium and magnesium ions get adsorbed on the surface of ion exchange resin

7. **In metallurgy:**

   In the froth floatation process of concentration of ore, the particle gets adsorbed on the froth.