Chapter:3 Adsorption

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1. Introduction

The term 'adsorption' was proposed by du Bois-Raymond but used by Heinrich Kayser in order to explain the condensation of gases by on the surfaces of solids. McBain introduced the term 'absorption' in 1909. He proposed the term 'sorption' for adsorption and absorption.

Innumerable physical, chemical and biological processes take place at the boundary between two phases, while others are initiated at that interface. The change in concentration of a given substance at the interface as compared with the neighboring phases is referred to as adsorption.

Adsorption is often described as a surface phenomenon where particles are attached to the top layer of material. It normally involves the molecules, atoms or even ions of a gas, liquid or a solid in a dissolved state that are attached to the surface. This process, known as adsorption, involves nothing more than the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. From the early days of using bone char for decolorization of sugar solutions and other foods, to the later implementation of activated carbon for removing nerve gases from the battlefield, to today's thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation.

Adsorption phenomena are operative in most natural physical, biological, and chemical systems, and adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters.

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption, a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a "solution". The term sorption is a general expression encompassing both processes. Adsorption is essentially a surface phenomenon.

It is the study of the chemical phenomena that occur at the interface of two surfaces which can be solid-liquid, solid-gas, solid-vacuum, liquid- gas, etc. Some applications of surface chemistry are known as surface engineering. There are various phenomena taking place on the surface of a substance and out of them some are: Dissolution, crystallization, electrode reactions, heterogenous catalysis, colloid formation, chromatography. Surface Chemistry has a major role in various chemical processes such as: Enzymatic reactions at the biological interfaces found in the cell walls and membranes.

A surface separating two phases of matter, each of which may be solid, liquid, or gaseous. An interface is not a geometric surface but a thin layer that has properties differing from those of the bulk material on either side of the interface. OR the common surface between adsorbent and adsorbate is called an interface.

2. Adsorption

The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as adsorption. Adsorption is mainly a consequence of surface energy. Generally, the surface particles which can be exposed partially tend to attract other particles to their site.

3. Adsorbent

The component at the surface of which adsorption occurs is called adsorbent. The component which is being, adsorbed is called adsorbate. The more or less uniformly concentration of a particular component throughout the bulk of another component is called absorption.

4. Desorption

The reverse of adsorption is called desorption. This occurs due to decrease in the pressure or on supplying heat that the molecules adsorbed on the surface get separated or convert into gas.

5. Sorption

When the process of adsorption and absorption takes place simultaneously then the combined process is called sorption.

6. Occlusion

Occlusion means the absorption of a substance from a gaseous medium by solids or melts. During occlusion, gases are absorbed by the entire volume of the absorbent rather than by the surface layer. In this way, occlusion is similar to absorption, which is the dissolution of gases in liquids.

The most common type of occlusion is the absorption of gases by metals.

Adsorption Isotherm is a curve that expresses the variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature.

7. Differences between Adsorption and Absorption

Absorption	Adsorption
Complete deposition of a substance in another substance is absorption	Deposition of a substance on the surface is known as adsorption.
It is not a surface Phenomena	It is a surface process.
It is not spontaneous.	Adsorption of gas on solid is spontaneous.
It takes place uniformly throughout.	It does not take place uniformly.
Greater molecular interaction.	Less molecular interaction.

8. Types of adsorption

Due to the force of interaction between adsorbate and adsorbent, adsorption in surface chemistry is classified into two types.

Physical Adsorption or Physisorption There exists a weak van der Waals force between adsorbate and adsorbent. is also known as Vander Waal's Adsorption. This type of adsorption can be easily reversed by heating or by decreasing the pressure. For example, H_2 and N_2 gases adsorb on coconut charcoal.

9. Characteristics of Physical Adsorption

- **Nature of forces:** weak van der Waals forces
- **Specificity:** It is not specific in nature
- **Reversibility:** The process is reversible
- **Layer:** It is a multi-layered process
- **Enthalpy of adsorption:** Low enthalpy of adsorption [20 – 40 KJ/mole]
- **The energy of activation:** Very low
- **Desorption:** Very easy
- **Factors affecting:** Surface area of adsorbent nature of adsorbate, pressure, temperature.

10. Chemical Adsorption or Chemisorption

It is due to strong chemical forces between adsorbate and adsorbent. It is also known as Langmuir adsorption. The force of attraction being very strong, adsorption cannot be reversed. Example: the formation of iron nitride on the surface when iron is heated in N_2 gas at 623 K.

11. Characteristics of Chemical Adsorption

- **Nature of forces:** Strong chemical forces
- **Specificity:** Highly specific nature
- **Reversibility:** It is irreversible
- **Layer:** It is a single layered process
- **Enthalpy of adsorption:** High enthalpy of adsorption [40 – 400 KJ/mole]
- **The energy of activation:** Very high
- **Desorption:** Very difficult
- **Factors affecting:** Surface area of adsorbent, nature of adsorbate Temperature.

12. Characteristics of adsorption

[1] Accumulation of species on higher concentration on the surface of a substance due to intermolecular force is known as adsorption.

[2] Adsorption is accompanied by decrease in the free energy ΔG. When ΔG=0, adsorption equilibrium is said to be established.

[3] Adsorption is accompanied generally by the evolution of heat, i.e. it is an exothermic process. ΔH is always negative.

[4] When a gas is adsorbed, the freedom of the molecules is restricted. Hence the entropy decreases, i.e. ΔS is negative.

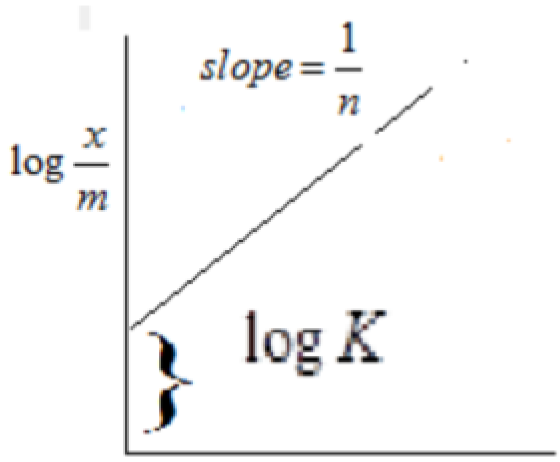
[5] For a process to be spontaneous, the thermodynamic requirement is that ΔG must be negative, i.e. decrease in the free energy. On the basis of Gibb's Helmholtz equation, ΔG= ΔH –TΔS, ΔG can be negative if ΔH has sufficiently high negative value and TΔS has positive value.

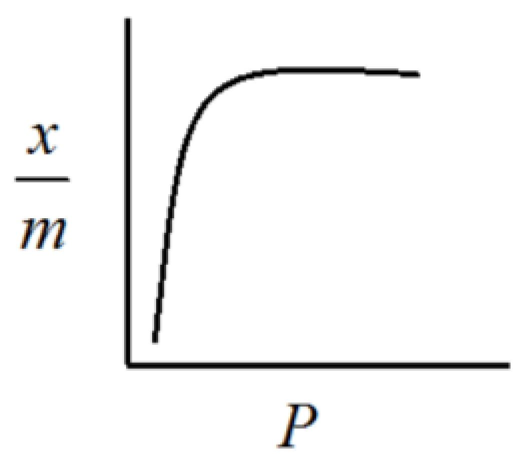
13. Factors affecting the adsorption of gases by solids

Nature of the adsorbate: It has been observed that more readily soluble and easily liquifiable gases which as ammonia, hydrochloric acid, chlorine and sulphur dioxide are adsorbed more than permanent gases such as hydrogen and nitrogen.

Nature of the adsorbent surface: Greater the surface area of the adsorbent surface, the greater will be adsorption. Surface area of the solid adsorbent: A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces.

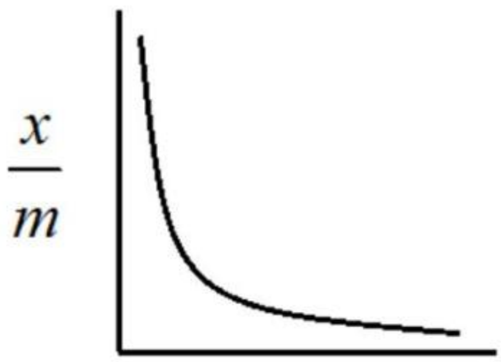
Effect of pressure on the adsorption of a gas on a solid: The fraction of gas adsorbed is proportional to the pressure of the gas. Adsorption increase with pressure reaches the maximum and becomes constant.



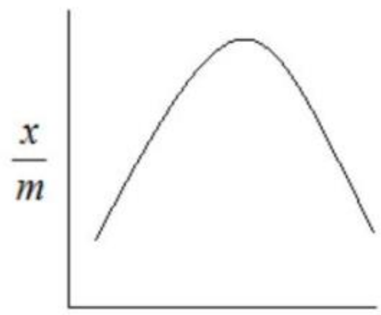


Effect of temperature on adsorption of gases on solid:

Adsorption of gases on solid is always exothermic. Physical adsorption follows Le Chatlier Principle, the amount of gas adsorbed decrease with the increase of temperature. Chemisorption increases with increase in the temperature. It reaches the maximum and then decreases. The curve obtained by plotting fraction of gas adsorbed and temperature at constant pressure is adsorption isobars.



temperature
Physisorption



temperature
chemisorption

14. Activation of the solid adsorbent:

a. By making the surface of the adsorbent rough
b. By substituting the adsorbent into smaller pieces or grains
c. By removing the gases already adsorbed.

15. Adsorption isotherm

Adsorption is usually described by isotherms. It is due to the fact that temperature plays an important role or that it has a great effect on the whole process. Moreover, there are several isotherm models that are used to describe the adsorption technique. These include Freundlich, Langmuir and BET theory BET theory (after Brunauer, Emmett, and Teller)

The BET theory was proposed by Brunauer, Emmett and Teller in the year 1938. This theory explains the formation of multilayer adsorption during physisorption. This theory also talks about the uniformity in the sites of adsorption of solid surfaces. It assumes that when adsorption occurs at one site it will not affect adsorption at neighboring sites.

16. Freundlich Adsorption Isotherm

Freundlich adsorption isotherm is obeyed by the adsorption where the adsorbate forms a monomolecular layer on the surface of the adsorbent.

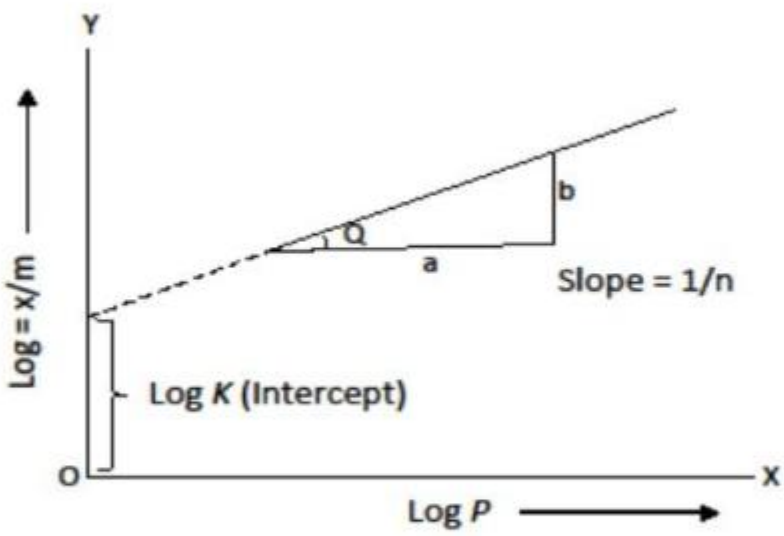
$x/m = k.P\ 1/n\ (n > 1)$

where ‘x’ is the mass of the gas adsorbed on mass ‘m’ of the adsorbent at pressure ‘P’. ‘k’ and ‘n’ are constants that depend on the nature of the adsorbent and the gas at a particular temperature.

The mass of the gas adsorbed per gram of the adsorbent is plotted against pressure in the form of a curve to show the relationship. Here, at a fixed pressure, physical adsorption decreases with increase in temperature. The curves reach saturation at high pressure. Now, if you take the log of the above equation –

$\log x/m = \log k + 1/n \log P$

To test the validity of Freundlich isotherm, we can plot log x/m on the y-axis and log P on the x-axis. If the plot shows a straight line, then the Freundlich isotherm is valid, otherwise, it is not. The slope of the straight line gives the value of 1/n, while the intercept on the y-axis gives the value of log k.



17. Limitations of Freundlich Adsorption Isotherm

Freundlich isotherm only approximately explains the behavior of adsorption. The value of 1/n can be between 0 and 1, therefore the equation holds good only over a limited range of pressure.

- When 1/n = 0, x/m is constant, the adsorption is independent of pressure.
- When 1/n =1, x/m = k P, i.e. x/m ∝ P, adsorption is directly proportional to pressure.

Experimental results support both of the above-mentioned conditions. At high pressure, the experimental isotherms always seem to approach saturation. Freundlich isotherm does not explain this observation and therefore, fails at high pressure.

The Freundlich isotherm was followed by two other isotherms – Langmuir adsorption isotherm and BET adsorption isotherm. Langmuir isotherm assumed that adsorption is monolayer in nature whereas BET isotherm assumed that it is multi-layer.

18. Langmuir adsorption isotherm

In 1916 Langmuir proposed theory of adsorption of a gas on the surface of the solid to be made up of elementary sites each of which would adsorb one gas. It is assumed that all adsorption sites are equivalent and the ability of a gas molecule to get bound to any one site is independent whether or not the neighboring sites are occupied. Additionally, it is also assumed that dynamic equilibrium exists between adsorbed and non-adsorbed gas molecule.

Following principles can be obtained from Langmuir adsorption isotherm

- The gas adsorbed behaves ideally in a vapor phase.
- Only monolayer adsorption takes place.
- The surface of the solid is homogeneous.
- There is no lateral interactive force between the adsorbate molecule.
- The adsorbed gas molecules are localized.

The adsorbate binding is treated as a chemical reaction between the adsorbate molecule Ag empty site, S. This reaction yields an adsorbed complex A_{ad} with an associated equilibrium constant, Keq.

$$Ag + S = AS$$

Where Ag is the gas molecule and S is an adsorption site. If θ is the fraction of the total available surface covered with gas molecules them (1- θ) is the fraction of the surface of the solid which is empty. The rate of the adsorption depends on the b pressure of the gas and the fraction of surface available for adsorption.

Hence,

Rate of Adsorption = Ka (1- θ)P …….(1)
Rate of Desorption = Kd. θ …….(2)

At equilibrium, the rate of adsorption is equal to the rate of desorption, i.e.

Ka (1- θ)P = Kd. θ

So, $\theta = Ka\,P / Kd+KaP$ or $\theta = K\,P / 1+K\,P$ …….(3) (where ,$K = Ka / Kd$)

Now, the extent of adsorption(x/m) is proportional to the fraction of the surface covered.

Therefore, x / m = k

θ = k . $(K\,P / 1+K\,P)$

= $a\,P / 1+K\,P$ …….(4) (where, k.K=a)

OR Mathematically, $x / m = a\,P / 1+bP$

Where a and b are constants and their values depend upon the nature of the gas, nature of the solid adsorbent and the temperature.

The above equations can be expressed in two situations:

at low pressure

In the above equation if the pressure is considered to be very low, the equation will take the following form:

x/m = ap (bp can be neglected in comparison to 1)

at high pressure

At high pressure, equation (1) will assume the following form:

x / m = , a / b (1 can be neglected in comparison to bp)

$x / \text{m} = ap / 1+bp$

= ap

= a / b

If the graph is plotted for m/x against 1/p on the basis of Langmuir adsorption isotherm, the value of slope will be equal to 1/a and the intercept will be equal to b.

Limitation of Langmuir Isotherm

1) It is valid at low pressures and high temperatures.
2) When the pressure is increased or temperature is lowered, additional layers are formed. This led to the modern concept of multilayer adsorption.

19. Applications of adsorption

[1] Manufacture Of Gas Masks

Activated charcoal used in gas masks removes all undesirable toxic and poisonous gases while purified air passes through its pores.

[2] Removing Of Coloring Matter From Sugar Juice & Vegetable Oils

Activated animal charcoal is used as decolorize in removing coloring matter of sugar solution and other vegetable materials.

[3] Dehydration & Purification Of Gases

Silica gel and Alumina are used as good adsorbents for removing moisture and for controlling humidity's in rooms which store delicate articles.

[4] Dyeing of Clothes

Mordent dyes used in dyeing adsorb the coloring matter which does not attach to fabric otherwise.

[5] Creation of High Vacuum In Laboratory

Finely divided coconut charcoal adsorbs all gases creating a vacuum as low as 10-4 mm.

[5] Heterogeneous Catalysis

The action of heterogeneous catalysts like finely divided nickel, finely divided platinum, finely divided iron in hydrogenation of oils, conversion of SO_2 to SO_3 and manufacture of ammonia respectively is based on the phenomenon of adsorption.

[7] Ion-Exchange Resins

The organic high polymers containing groups such as —COOH, —SO_3H or — NH_2 possess the property of selective adsorption of ions from solution. These resins are largely used in Industrial softening of water and separation of rare earths from their mixture.

[8} Chromatography

There are a number of chromatographic techniques like adsorption chromatography, paper chromatography and vapor phase chromatography which are based on selective adsorption of different substances of the adsorbent.

[9] Qualitative Inorganic Analysis

The confirmatory lake test for Al^{+3} ions is based on the adsorption of color of litmus by $Al(OH)_3$.

[l0]Drugs

Various drugs get adsorbed on the tissues which then are heated. The germicidal action of medicines is also based on the property of adsorption.

18. Questions:

1) What are the factors effective adsorption of gases on solids?
2) What is adsorption?
3) What is absorption?
4) What is physisorption?
5) What is chemisorption?
6) Explain Freundlish Adsorption Isotherm
7) Explain Langmuir Adsorption Isotherm
8) Write the differences between adsorption and absorption.