B.Sc. (Honours) Part-III

Paper-VA

Topic: Types of Adsorption

UG

Subject-Chemistry

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Types of Adsorption

Adsorption: Adsorption is essentially a surface phenomenon. There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption. The molecular species or substance, which concentrates or accumulates at the surface is termed adsorbate and the material on the surface of which the adsorption takes place is called adsorbent.

The adsorbed molecular species can be removed from the surface of the adsorbent and the process of removing an adsorbed substance from a surface on which it is adsorbed is called **desorption**.

Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.

Adsorbate: The substance that concentrates at the surface is called adsorbate.

Adsorbent: The material upon whose surface the adsorption takes place is called an adsorbent. Mostly activated carbon is used as an adsorbent

(i) Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm.

(ii) They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption.

(iii) The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapors.

Factors influencing adsorption: Adsorption on a solid is influenced by a number of factors such as,

- Surface area
- Nature of the adsorbate
- Hydrogen ion concentration (pH) of the solution
- Temperature
- Mixed solutes and
- Nature of adsorbate

Types of Adsorption – Physisorption and chemisorption

Depending on the type of attractions between adsorbate and adsorbent, the adsorption can be divided into two types. Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Vanderwaal forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types: Physical Adsorption or Chemical Adsorption. If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces, the adsorption is termed as **physical adsorption** or **physisorption**. When

the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed **chemical adsorption** or **chemisorption**. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption. Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, dihydrogen is first adsorbed on nickel by van der Waals' forces. Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface by chemisorption.

Physical Adsorption or Physisorption: When the force of attraction existing between adsorbate and adsorbent are weak Vanderwaal forces of attraction, the process is called Physical Adsorption or Physisorption. Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e. ΔH adsorption is 20-40KJ/mol. takes place at low temperature below boiling point of adsorbate. As the temperature increases in, process of Physisorption decreases.

Characteristics of Physisorption

Energetics and kinetics: Physisorption is an exothermic process. However it is characterized by low enthalpy values (20– 40 kJ mol-1), due to

weak van der Waals forces of attraction. The activation energy for physisorption is also very low and hence it is practically a reversible process.

Effect of temperature: Since physical adsorption is an exothermic process, it occurs more readily at lower temperatures and decreases with increase in temperature (Le-Chatelier's Principle).

Effect of pressure: In case of physisorption of gases over solids, the extent of adsorption increases with increase in pressure as the volume of the gases decrease during adsorption (Le-Chatelier's Principle).

Specificity: Since the van der Waals' forces are universal, a given surface of an adsorbent does not show any preference for an adsorbate in physisorption i.e. it is not specific with respect to adsorbent.

Nature of adsorbate: However, the extent of adsorption depends on the nature of gas (adsorbate). In general, easily liquefiable gases with higher critical temperatures) are readily adsorbed as the van der Waals' forces are stronger, especially, near the critical temperatures.

Surface area of adsorbent: The extent of adsorption increases with the increase of surface area of the adsorbent. Hence finely powdered metals and porous substances having large surface areas perform well as adsorbents.

Chemical Adsorption or Chemisorption: When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemical Adsorption or Chemisorption. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption. It can take place at

all temperature. With the increases in temperature, Chemisorption first increases and then decreases.

Characteristics of Chemisorption

Energetics and kinetics: Chemisorption is also an exothermic process and the enthalpy values are higher (80-240 kJ mol^{-1}) as it involves formation of chemical bonds. However, the activation energy for chemisorption is high and occurs slowly. Hence it is also called activated adsorption. It is practically irreversible.

Effect of temperature: Even though chemical adsorption is an exothermic process, it does not occur slowly at lower temperature due to high kinetic energy barrier. Hence, like most chemical changes, the extent of chemisorption increases with increase in temperature up to certain limit and then after that it starts decreasing. It is also observed that, in some cases, physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperatures.

Effect of pressure: The chemisorption is not appreciably affected by small changes in pressure. However, very high pressures are favourable for chemisorption.

High specificity: Chemisorption is highly specific and occurs only if there is some possibility of chemical bonding between adsorbent and adsorbate.

Surface area: Like physisorption, chemisorption also increases with increase of surface area of the adsorbent.

Comparison of Physisorption and Chemisorption

Physisorption	Chemisorption
1. It arises because of van der Waal's forces.	1. It is caused by chemical bond formation.
2. It is not specific in nature.	2. It is highly specific in nature.
3. It is reversible in nature.	3. It is irreversible.
4. It depends on the nature of gas. More liquefiable gases are adsorbed readily.	4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
5. Enthalpy of adsorption is low (20-40 kJ $mol^{-1)}$ in this case.	5. Enthalpy of adsorption high (80-240 kJ mol^{-1}) in this case.
6. Low temperature is favourable for adsorption. It decreases with increase of temperature.	6. High temperature is favourable for adsorption. It increases with the increase of temperature.
7. No appreciable activation energy is needed.	7. High activation energy is sometimes needed.
8. It depends on the surface area. It increases with an increase of surface area.	8. It also depends on the surface area. It too increases with an increase of surface area.
9. It results into multimolecular layers on adsorbent surface under high pressure.	9. It results into unimolecular layer.