Unit II SURFACE CHEMISTRY & CATALYSIS

SURFACE CHEMISTRY

2.1 INTRODUCTION

Important terms in surface chemistry

Differences between adsorption and absorption

Types (or) Classification of adsorption

Physical adsorption (or) Physisorption

Chemical adsorption (or) Chemisorption

Differences between Physisorption and chemisorption

Characteristics of adsorption

SURFACE CHEMISTRY

2.1 INTRODUCTION

Surface chemistry is referred to as the study of the phenomenon occurring on the surfaces of substances. This is very applicable in industries and day to day lives. In other words, surface chemistry deals with all types of surface phenomenon.

What is Surface Chemistry?

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 substances and some of them are:

- Adsorption
- Heterogeneous Catalysis
- Corrosion
- Crystallization

Applications of Surface Chemistry

In a wider perspective, surface chemistry deals with the interaction of surfaces of one system with that of the other system. Some phenomena work on this principle such as:

- Catalysis
- Colloid Formation
- Electrode Reactions
- 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.
- In the electronics industry, they are used in the surface and interface of microchips found in computers.

- In automobile exhausts, the heterogeneous catalysts found in the catalytic converter for cleaning emissions.

Role of Adsorption in Surface Chemistry

Accumulation of species on higher concentration on the surface of a substance due to intermolecular force is known as adsorption. For Example, gases such as H2, O2, N2 adsorbs on the surface of activated charcoal.

IMPORTANT TERMS IN SURFACE CHEMISTRY

ADSORPTION

It is a surface phenomenon. It is defined as the accumulation of a substance on the surface of a solid or liquid".

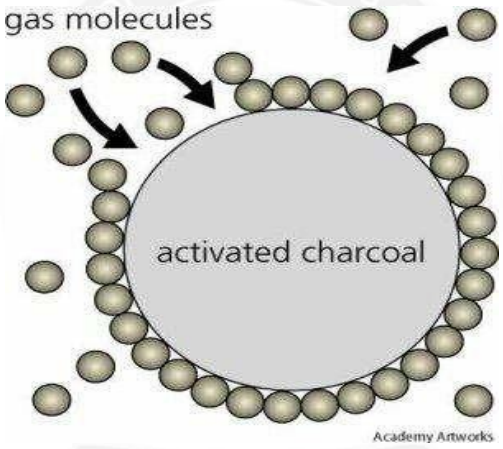

Figure 2.1.1 Illustration of adsorption

[Source: https://www.emedicalprep.com/study-material/chemistry/surface-chemistry/adsorption/]

Examples

- Activated charcoal adsorbs gases like CO_2, SO_2, Cl_2etc.
- Pt or Ni metal kept in contact with a gas adsorbs the gas - Hydrogenation of oils.
- Animal charcoal, when added to acetic acid solution and shaken vigorously, adsorbs aceticacid.
- Molasses is decolorized by activated charcoal.

ADSORBATE

The substance held on the surface of the solid is called adsorbate.

Example: Various gases (NH_3, water vapour, CO_2, etc)

Substances in solution (NaCl, dye, etc.)

ADSORBENT

The substance on which adsorption occurs. (OR) The solid that takes up a gas or a solute fromthe solution is called adsorbent.

Example: Silica gel, charcoal, Pd, Pt, Ni, alumina gel, etc.

EXAMPLES OF ADSORPTION

- In the adsorption of acetic acid by charcoal, "acetic acid is adsorbate and the charcoal is adsorbent".
- In the adsorption of H_2 gas on platinum or nickel, "H_2 gas is adsorbate and Pt or Ni is adsorbent".

ABSORPTION

It is a bulk phenomenon. It is defined as "process in which a substance is uniformly distributed throughout the body of the solid or liquid".

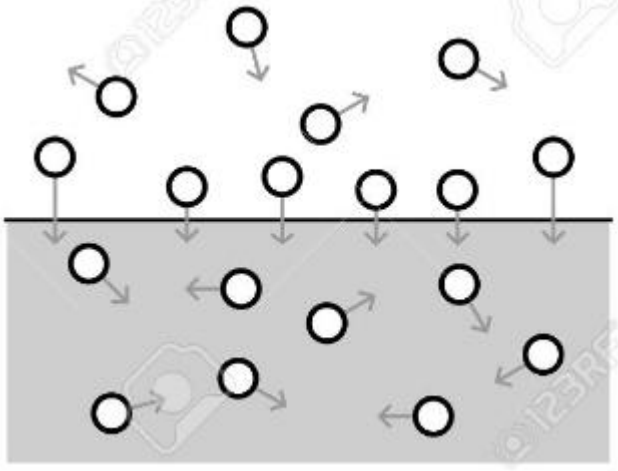

Figure 2.1.2 Illustration of absorption

[Source: https://www.123rf.com/photo_93069281_stock-vector-scheme-of-absorption-and-adsorption.html]

Examples:

- If a chalk piece is dipped into a solution of coloured ink and kept for some time, the chalkpiece absorbs the coloured substance.
- A sponge placed in water absorbs water into it.
- H_2 gas kept in contact with finely divided palladium metal is absorbed by Pd metal.

Thisabsorption of H_2 gas by Pd is known as occlusion.

OCCLUSION

The adsorption of gas on a solid surface is called occlusion.

SORPTION

It is a process in which both adsorption and absorption takes place simultaneously.

DESORPTION

The removal of adsorbed substance from the surface is called desorption.

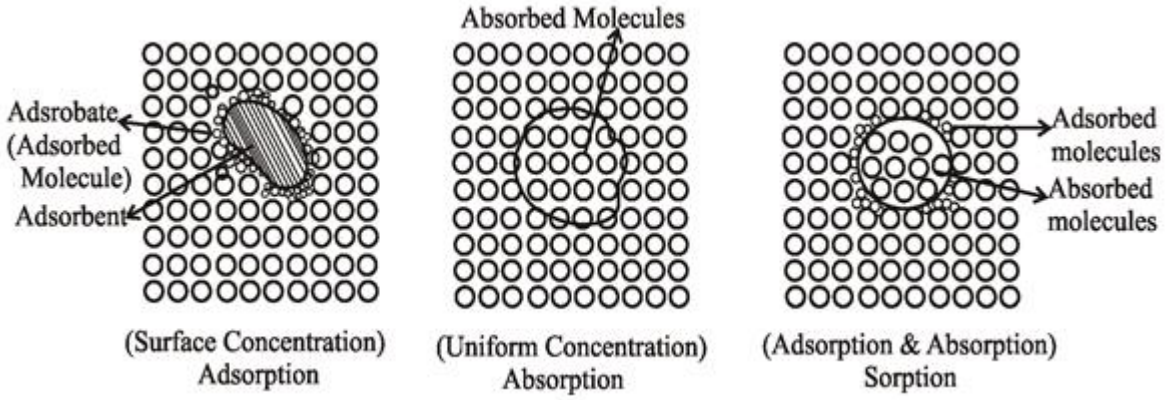

Figure 2.1.3 Illustration of adsorption, absorption and sorption

[Source: https://chemistry-desk.blogspot.com/2012/10/adsorption.html]

Examples of Adsorption and Absorption

- When a sponge is put into water, the water enters into the whole body of sponge – it is anexample of absorption.
- When a solution of methylene blue (dye-coloured substances) in water is stirred with solid carbon, the dye gets adsorbed by charcoal and thus decolourises the water – it is an exampleof adsorption.
- Ammonia is adsorbed on charcoal while it is absorbed by water.
- Water vapours are adsorbed on silica gel while they are adsorbed by anhydrous $CaCl_2$.
- NH_3 can undergo adsorption and absorption. When ammonia is passed through water in contact with charcoal. Water dissolves NH_3 (absorption) which is then adsorbed by charcoalcrystals.

Exothermic nature of adsorption

The amount of heat evolved when 1 mole of any gas is adsorbed on a solid adsorbent surface iscalled enthalpy or molar heat of adsorption".

DIFFERENCES BETWEEN ADSORPTION AND ABSORPTION

S.No.	Adsorption	Absorption
1.	It is a surface phenomenon i.e. higherconcentration of a liquid or gas molecules over the surface of a solid.	It is a bulk phenomenon i.e. accumulation of substrate on the surface of the solid, in which the substrate is uniformly distributed throughout the body of the solid substance.
2.	It is a fast process.	It is a slow process.
3.	Equilibrium is attained easily.	Equilibrium is attained slowly.
4.	It depends upon the surface area of the adsorbent. Adsorption is more rapid when the surface of adsorbent is more.	No such effect is observed.
5.	Example: Ammonia is adsorbed oncharcoal.	Example: When a sponge is put into water,the liquid enters into the whole body of the sponge.

Table 2.1.1 Differences between adsorption and absorption

TYPES (OR) CLASSIFICATION OF ADSORPTION

Adsorption is classified into two types:

- Physical adsorption (or) Physisorption (or) Vander Vaal's Adsorption
- Chemical adsorption (or) Chemisorption (or) Activated Adsorption

PHYSICAL ADSORPTION (OR) PHYSISORPTION

It is a process in which the adsorbed molecules are held to the surface of the adsorbent by weak physical or Vander Vaal's forces.

(e.g.) Adsorption of H_2 on charcoal

CHEMICAL ADSORPTION (OR) CHEMISORPTION

It is a process in which the adsorbed molecules are held to the surface of the adsorbent by strong chemical bonds.

(e.g) Adsorption of H_2 on Ni, adsorption of O_2 on tungsten

Example: Adsorption of H_2 on Ni

H_2 molecule is first adsorbed by Vander Vaal's forces and then undergoes dissociation to hydrogen atoms. Then the H-atoms are chemisorbed on Ni.

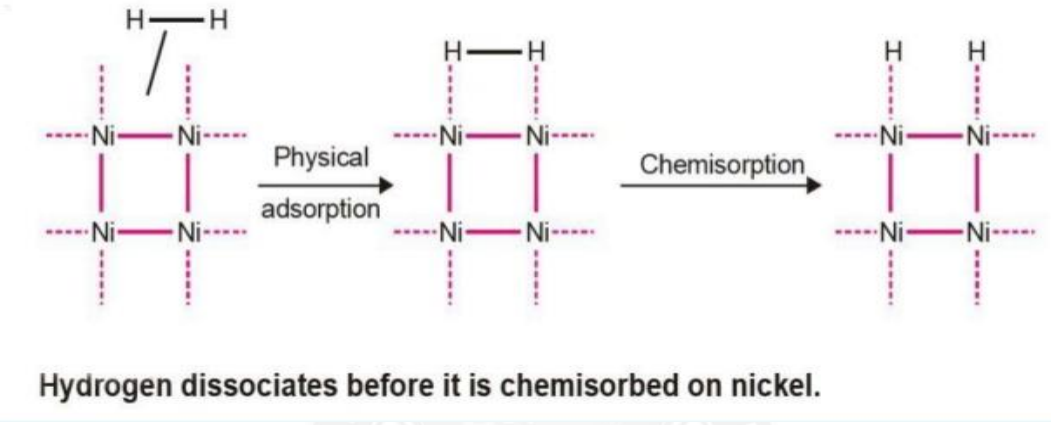

Figure 2.1.4 Adsorption of H_2 on Ni

[Source: https://www.slideshare.net/aminul308/adsorption-83054943]

DIFFERENCES BETWEEN PHYSISORPTION AND CHEMISORPTION

S.No.	Property	Physical adsorption	Chemical adsorption
1.	Nature of adsorption	Weak	Strong
2.	Enthalpy of adsorption	Low. (20-40 Kcal/mol)	High. (40 – 400 Kcal/mole)
3.	Reversibility of adsorption process	Reversible and occurs rapidly.	Irreversible and occurs slowly.
4.	Temperature at which adsorption is more pronounced	Low temperatures (below the B.pt of the adsorbate gas)	High temperatures (generally above the B.pt. of the adsorbate gas)
5.	Effect of change in temperature	Decreases with rise in temperature.	Increases with rise in temperature.
6.	Specificity of adsorption	Not specific. Generally takes place on all surfaces.	Highly specific. Takes place on specified surfaces only.
7.	Nature of adsorbate layers formed	Multilayered	Unilayered

8.	Effect of pressure on adsorption	Increases with rise in pressure of adsorbate gas and finally attains a limiting value.	Pressure of the adsorbate has a negligible effect.
9.	Energy of activation	Insignificant i.e. very low.	Significant i.e. relatively high.
10.	Dependence on the nature of the adsorbate & adsorbent	Depends on the adsorbate (gas) only. Easily liquefiable gases are more readily adsorbed.	Depends on the adsorbate as well as adsorbent. No correlation can be given.
11.	Ease of desorption	Easy since Vander Waals forces are involved.	Not easy since chemical forces are involved.

Table 2.1.2 Differences between Physisorption and chemisorption

CHARACTERISTICS OF ADSORPTION

- Adsorption is a highly selective process.
- It is a physical phenomenon accompanied by a chemical change.
- It depends on the nature of the adsorbent and adsorbate.
- It is always spontaneous.
- It is always accompanied by evolution of heat.
- The rate of adsorption depends on temperature, pressure and concentration.