Physical chemistry -Surface chemistry and Photo Chemistry

ADSORPTION

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Surface Chemistry and Photo Chemistry

Class :II-M.Sc
Semester :VI

Unit-I Adsorption

Aim:

- To make the students to understand about the basic study of surface chemistry

Objectives:

- Elucidate the concepts Adsorption and absorption in surface chemistry.
- Explain the different types of adsorption .

Expected Out Come

- After studying this unit students will be able to be
  - Derive the various equation.
  - Learn about different types of adsorption, isotherm..

Pre-requesities

- Basic study of adsorption and absorption.
- Various examples of adsorption and absorption
- Adsorbate , adsorbent, sorption, desorption

Unit-I

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Adsorption

The surface of a solid has a tendency to attract and to retain molecules of gas or liquids with which such surfaces come in contact. This phenomenon of surfaces is termed as adsorption.

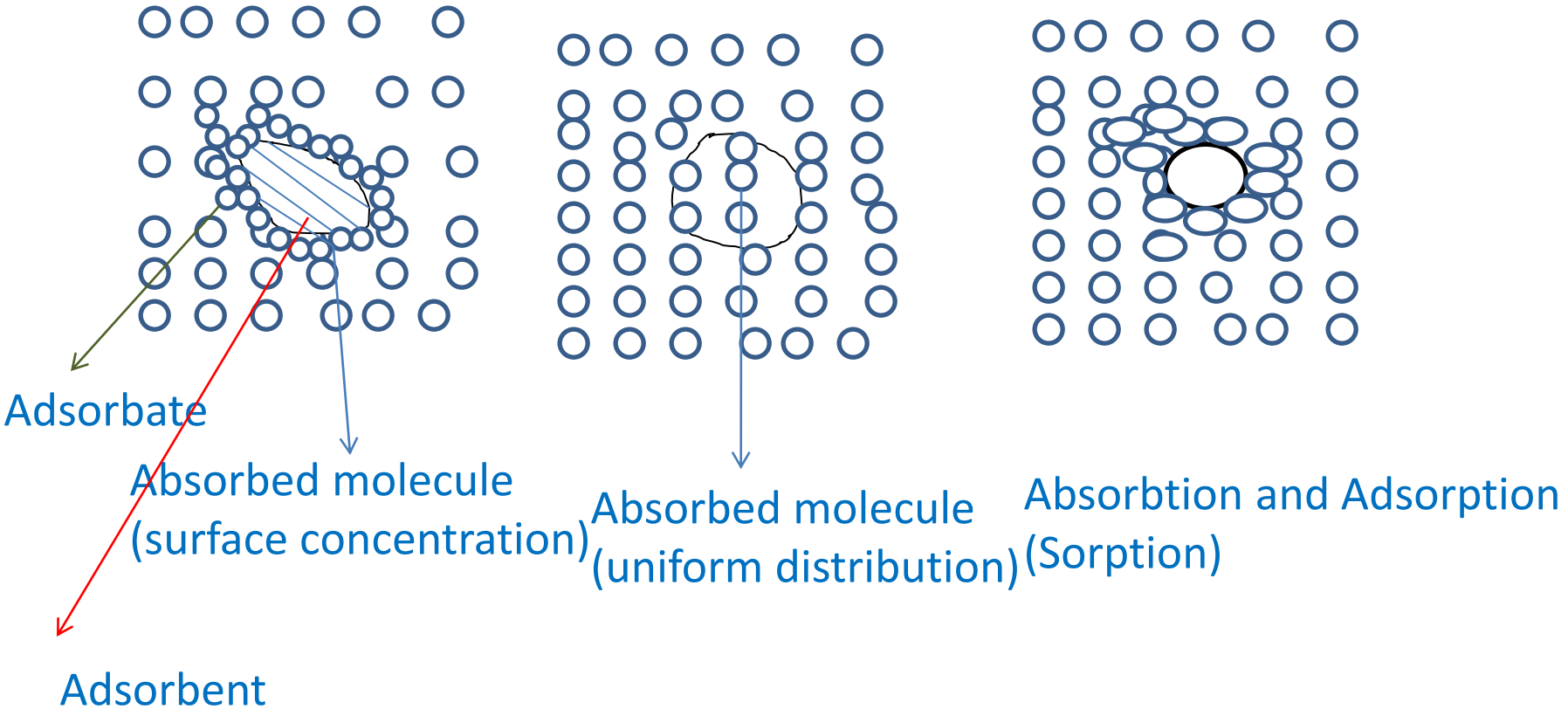
“Adsorption is a tendency technical term coined to denote the talking of gas, vapor, liquid by a surface or interface”.

Adsorption

- Adsorption : is a surface phenomenon where

absorption is a bulk phenomenon in which the substance assimilated is a uniformly distributed throughout the body of a solid or liquid to form a solution or a compound.

Difference between adsorption , absorption and sorption



Difference beween adsorption and absorption

- i) In Adsorption the substanc is distributed throughout the body of a solid or a liquid to form a solution or a compound.
- On the other hand , adsorption only takes place on the surface and not in the body of adsorbent.
- Thus adsorption is a surface phenomenon and adsorption is a bulk phenomenon.

Difference between adsorption and absorption

- ii)In absorption the concentration of the adsorbed molecules is always found to be greater in the immediate vicinity of the surface (Adsorbent)then in the free phase(Adsorbate).
- iii)In case of adsorption the equilibrium is easily attained in a very short time whereas in absorption the equilibrium takes place slowly.

Difference between adsorption and absorption

- iv)Typical isotherm for adsorption and absorption are shown in fig.
- V) If x/m is plotted against p or c, the graph should be a straight line in adsorption fig.a and typical curve for absorption as shown in the fig.b

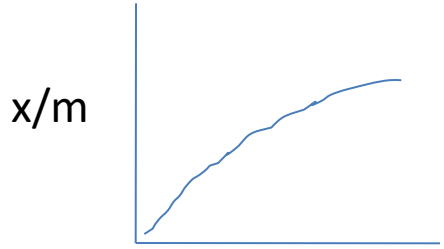


Fig.a. Adsorption

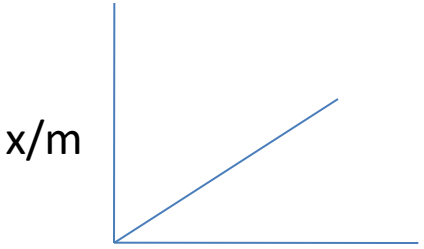


Fig.b.Absorption

Examples for Adsorption and absorption

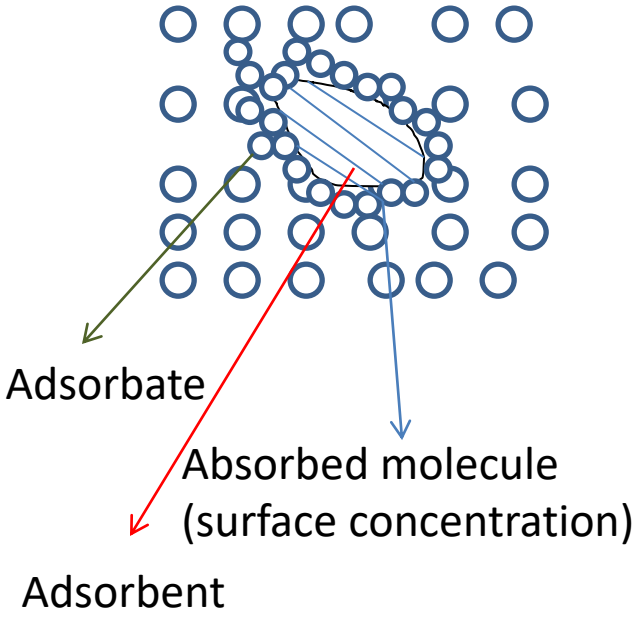
- Water vapor is absorbed by anhydrous calcium chloride while it is adsorbed by silica gel.
- Ammonia is adsorbed by charcoal while it is absorbed by water to form ammonium hydroxide
- Decolourisation of sugar solution by activated charcoal is another example of adsorption. In this example charcoal adsorbs the colouring material and thus decolorises th solution.

Examples for Adsorption and absorption

- The color of the lake test for aluminium ions is due to adsorption of dye (litmus) on the freshly precipitated aluminium hydroxide.
- When a hot crucible is allowed to cool in air, a film of moisture is formed at the surface.
- This is the case of adsorption of water vapor on the surface of a crucible
- When sponge is put into water, it takes up water . It is an example of absorption.

Adsorbent and Adsorbate

- Adsorbent : The material on the surface of which adsorption takes place is called adsorbent.
- Adsorbate: The substance adsorbed by a material is called adsorbate.



Examples of adsorbents & adsorbates

Examples of adsorbents

- Silica-gel
- Metal
- Colloids

Examples of adsorbates:

- Various gases(He,Ne, N_2,SO_2,NH_3 etc)
- Substance in solution (NaCl,KCl)

Solid- Interface

- The common surface separating two phases where the adsorbed molecule concentrates is referred to as the interface.
- The larger surface area of the adsorbentthe more the adsorption .
- Due to this reason colloids are good adsorbents , due to their high surface area per unit mass although they have very small dimensions

Solid- Interface

- If the concentration is more at an interface, the adsorption is said to be positive.If the concentration is less at an interface ,the adsorption is said to be negative.
- The reverse process of removal of an adsorbed substance from the surface of a solid is known as desorption

Characterisation of Adsorption

- Adsorption is a spontaneous process and takes place in so time.
- The phenomenon of adsorption can occur at all surfaces and five types of interfaces can exist:
- Gas-solid, Liquid –solid, liquid-liquid, solid-solid.
- The gas-solid interface has probably received the most attention in the literature and is the best understood.

Characterisation of Adsorption

- The liquid –solid interface is now receiving much attention because of its importance in many electrochemical and biological systems.
- It is accompanied by a decrease in the free energy of the systems.ie.,ΔG.
- The adsorption will continue to such an extent that ΔG continues to be negative .

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Characterisation of Adsorption

- Eventually magnetitude of ΔG decreases to zero.
- When ΔG for further adsorption reaches a value for zero, a adsorption equilibrium is said to be established.
- As the process of adsorption involves loss of degree of freedom of the gas in passing from free gas to the adsorbed film there is a decrease in the entropy of the system.

Characterisation of Adsorption

- It follows from the Gibbs-Helmoltz equation
  - $\Delta G = \Delta H - T\Delta S$
  - $\Delta H = \Delta G + T\Delta S$
- ΔG is the change in free energy, ΔH is the change in heat content, ΔS is the change in entropy and T is the temperature of the system.
- As the entropy and free energy decrease in adsorption , the value of ΔH decreases.
- This decrease in heat content(ΔH) appears as heat.
- Hence the adsorption process must always be exothermic.

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 H_2, O_2, N_2 adsorbs on the surface of activated charcoal.

Adsorption of gases on solids

- The study of the gas-solid adsorption process has excited the interest of both academic and industrial scientists for many years and the reactions are not hard to find.
- Industrially , it is known that this phenomenon plays an essential role in the catalytic process.

Adsorption of gases on solids

- The study of surface to selectively accelerate the rates of many chemical reactions is the basis of much of the heavy chemical production in the world.
- In generally belived that all gases or vapours are adsorbed on the surface of all solids with which they are in contact.

Factors of the adsorbent and adsorbate

- The phenomenon of adsorption of gases by solids depends upon the following factors:
- i) Nature of adsorbent and adsorbate
- ii)Surface area of the adsorbent
- iii)The partial pressure of the gas in the phase
- iv)Effect of temperature

i) Nature of adsorbent and adsorbate

- The amount of gas adsorbed depends upon the nature of the adsorbent and gas (adsorbate)which is to be adsorbed.

- Gases like SO_2,NH_3,HCl,and CO_2 which liquify more easilyare adsorbed more readily than thepermanent gases like H_2,N_2 and O_2 which do not liquify easily.

i) Nature of adsorbent and adsorbate

- This is because the easily liquifiable gases have greater vander walls are the molecular forces of attraction are the chohisive force.
- As the critical temperature of the easily liquifiable gases are more than permanent gases, it flows that higher the critical temperature of the gases, the greater the extent of adsorption.

ii)Surface area of the adsorbent

- The extent of adsorption gases by solids depends upon the exposed surface area of the adsorbent.
- It is well known that larger the surface area of the adsorbent, the larger will be the extent of adsorption under given conditions of temperature and pressure.
- It is for this reasons silica gel and charcoal obtained from the different animal and vegetable sources become activated because they posses a porous structure and there by render a larger surface.

iii)The partial pressure of the gas in the phase

- For a given gas and a given adsorbent the extent of adsorption depends on the pressure of the gas.
- Adsorption of gas is followed by a decrease of pressure .
- Therefore in accordance with Le-chatelier Principle, the magnetitude of adsorption decreases with the decrease in pressure and vice-versa.
- The variation of adsorption with pressure at constant temperature is expressed graphically by a curve known as adsorption isotherm

iv)Effect of temperature

- For a given adsorbate and a adsorbent, the extent of adsorption depends upon the temperature of the experiment.
- As discussed earlier, adsorption usually takesplace with the evolution of heat.
- Therefore, according to the Le-chatlier principle the decrease in temperature will increase the adsorption and vice-versa.
- An example is that if the temperature of the coconut charcoal is lowered from -29^0 to -78^0c. The amount of nitrogen gas adsorbd increases from 20-45 ml under the same pressure.

Types of Adsorption of the Gases on Solids.

- Based on the nature of forces between the gas and the solid surface, there are two types of adsorption :
- 1. Physisorption or Physical Adsorption.
  - If the physical forces of attraction hold the gas molecules to the solid, the adsorption is known as physical adsorption or physisorption.

Types of Adsorption of the Gases on Solids.

1. Physisorption or Physical Adsorption.

The forces of attraction bringing about physiical adsorption are :

- (i) Permanent dipole moment in the adsorbed molecule.
- (ii)Polarisation.
- (iii) Dispersion effects.
- (iv) Short range repulsive effect.

Types of Adsorption of the Gases on Solids.

- 1. Physisorption or Physical Adsorption.
- In case of physisorption, the forces of attraction which hold the gas molecules to the solid are very weak.
- Therefore it is characterised by a low heat of adsorption, usually of the order of 40 kJ per mole.
- This value is of the same order of magnitude as the heat of vaporisation of the adsorbate and lends credence to the concept of a weak 'physical' bonding.

Types of Adsorption of the Gases on Solids.

- . 1. Physisorption or Physical Adsorption.
- Physical adsorption is usually observed at low temperatures or on relatively inert' surfaces.
- Examples of physisorption are as follows :
  (i) Adsorption of various gases on charcoal.
  (ii) Adsorption of nitrogen on mica.

Types of Adsorption of the Gases on Solids.

- 2. Chemisorption or Chemical adsorption.
  - If the chemical forces hold the gas molecules to the surface of the adsorbednt, the adsorption is known as chemisorption.
  - In this case the adsorbate undergoes a strong chemical interaction with the unsaturated surface and gives rise to a high heat of adsorption, usually of the order of 400 kJ per mole.

Types of Adsorption of the Gases on Solids.

- Chemisorption is often characterised by taking place at elevated temperatures and is often an activated process.
- It may be dissociative, non-dissociative or reactive in nature.

- Some examples of chemisorption are :
- (a) Ethyl alcohol vapours condensed on the divided nickel.
  (b) Adsorption of oxygen on tungsten.
  (c) Adsorption of hydrogen on nickel.

Difference between physisorption and chemisorption

Physisorption	chemisorption
1.It involves physical forces	It involves transfer of electrons between gas and solid
2.It is reversible	It is not reversible
3.Heat adsorption is generally less than 40kJ/mole	Heat adsorption is almost 40-400kJ/mole
4.It is a general phenomenon which will occur forming With any gas-solid system provided only that the condition of temp and press are suitable.	It will only takes place if the gas is capable of chemical bond with the surface atoms.
5.Multilayer are possible .	Only monolayer is formed.
6.It is appreciable low-temperature chemisorption and high –pressure. pressure	It can occur at hightemperatures. The rate of decreases with the increase of
7.No appreciable activation energy Is involved	It involves activation energy
8.It is an instantaneous process	It may be rapid of slow.
9.It is a function of coverage of surface	It is adsorbed at fixed sites on the surface . These sites known as active centres.
10.Not very specific	Often very specific.

Text Books

- Gurdeep Raj, Advanced Physical Chemistry, 22nd edition, Goel Publications, 1998.
- Keith J. Laidler, Chemical Kinetics, Third Edition, Pearson Education, 2004.
- J. Rajaram, J.C. Kuriacose, Kinetics and Mechanisms of Chemical Transformations, First edition, Macmillan, 1993, reprint 2011.
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- Thank you