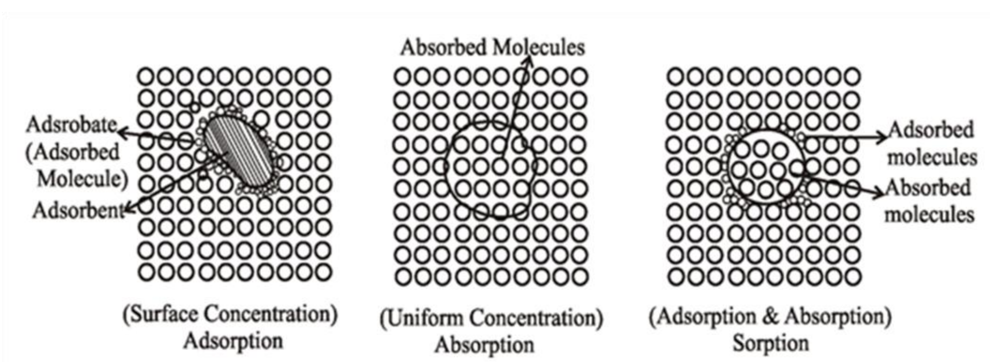
Chapter 12

Surface chemistry

Day - 1

1. Adsorption: The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid.
2. Adsorbate: The molecular species or substance, which Concentrates at the surface.
3. Adsorbent: The material on the surface of which the adsorption takes place.
4. Absorption: It is the phenomenon in which a substance is uniformly distributed all over the surface
5. Desorption: The process of removing an adsorbed substance from a surface on which it is adsorbed
6. Sorption: When adsorption and absorption take place simultaneously, it is called sorption.

Absorption	**Adsorption**
it's a bulk phenomenon	it's a surface phenomenon
The substance is uniformly distributed throughout the bulk of the solid.	the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent
Water vapours are absorbed by anhydrous calcium chloride	Water vapours are adsorbed by silica gel.
Absorption proceeds at a steady state	Adsorption is fast in the beginning, decreases gradually until equilibrium is reached
Both adsorption and absorption can take place simultaneously also.	The term sorption is used to describe both the processes.



Enthalpy or heat of adsorption: Adsorption generally occurs with release in energy, i.e., it is exothermic in nature. The enthalpy change for the adsorption of one mole of an adsorbate on the surface of adsorbent is called enthalpy or heat of adsorption.

Types of adsorption:

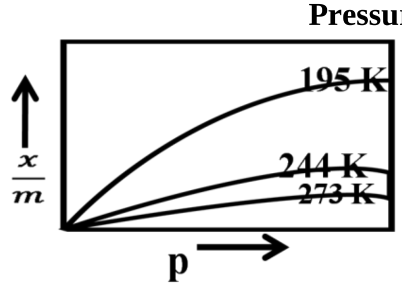
a. Physical adsorption or Physisorption: If the adsorbate is held on a surface of adsorbent by weak Vander Waals' forces, the adsorption is called physical adsorption or physisorption.

b. Chemical adsorption or chemisorption: If the forces holding the adsorbate are as strong as in chemical bonds, the adsorption process is known as chemical adsorption of chemisorption.

	Physical Adsorption (Physisorption)		**Chemical Adsorption (Chemisorption)**
1.	It arises because of Vander Waals' 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 easily 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}).	5.	Enthalpy of adsorption is high(180-240 KJ/mole)
6.	Low temperature is favourable for adsorption. It decreases with increase of temperature	6.	High temperature is favourable for adsorption. It first increases with the increase of temperature, then decreases
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 multi-molecular layers on adsorbent surface under high pressure	9.	It results into Unimolecular layer.
10.	The variation in pressure is as follows	10.	This is independent of pressure

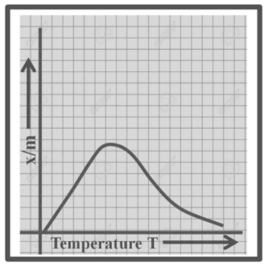
Change in Physisorption with **Pressure**.

Chemisorption does not change with **Pressure**

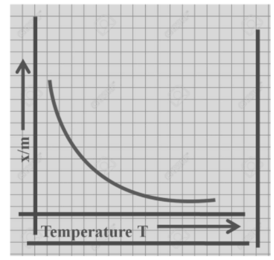


Change in Physisorption with **Temperature** Chemisorption does not change with **Temperature**.

Physical Adsorption (Physisorption)



Chemical Adsorption (Chemisorption)



FACTORS AFFECTING ADSORPTION OF GASES ON SOLIDS

a. **Nature of adsorbate**: Physical adsorption is non-specific in nature and therefore every gas gets adsorbed on the surface of any solid to a lesser or greater extent. However, easily liquefiable gases like NH_3. HCl, CO_2, etc. which have higher critical temperatures are absorbed to greater extent whereas H_2, O_2, N_2 etc. are adsorbed to lesser extent. The chemical adsorption being highly specific, therefore, a gas gets adsorbed on specific solid only if it enters into chemical combination with it.

b. **Nature of adsorbent**: Activated carbon, metal oxides like aluminium oxide, silica gel and clay are commonly used adsorbents. They have their specific adsorption properties depending upon pores.

c. **Specific area of the adsorbent**: The greater the specific area more will be the extent of adsorption. That is why porous or finely divided forms of adsorbents adsorb larger quantities of adsorbate. The pores should be large enough to allow the gas molecules to enter.

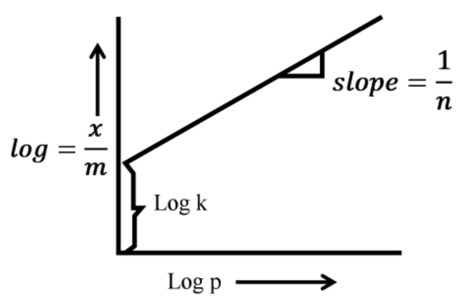
d. **Pressure of the gas**: Physical adsorption increases with increase in pressure.

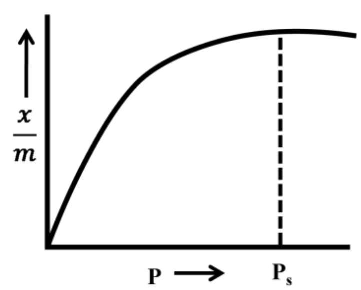
Adsorption isotherm: The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve is termed as adsorption isotherm

Freundlich adsorption isotherm: Empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

$x/m = k.P^{1/n}$ ($n > 1$) where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure P, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

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





The phenomenon of adsorption finds a number of **applications.**

Important ones are listed here:

(i) Production of high vacuum: The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.

(ii) *Gas masks*: Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

(iii) *Control of humidity*: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.

(iv) *Removal of colouring matter from solutions*: Animal charcoal removes colours of solutions by adsorbing coloured impurities

(v) Heterogeneous catalysis: Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H2SO4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

(vi) *Separation of inert gases*: Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.

(vii)*In curing diseases*: A number of drugs are used to kill germs by getting adsorbed on them.

(viii)*Froth floatation process*: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent

(ix)*Adsorption indicators*: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.

(x)*Chromatographic analysis*: Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields