Surface Chemistry

- Surface Chemistry is closely related to interface and colloidal science.

- Surface chemistry is important in many critical chemical processes, such as enzymatic reactions at biological interfaces found in cell walls and membranes

- in electronics at the surfaces and interfaces of microchips used in computers,

- and the heterogeneous catalysts found in the catalytic converter used for cleaning emissions in automobile exhausts.

Surface Chemistry

- Surface science is the study of chemical phenomena that occur at the interface of two phases (solid–liquid interfaces, solid–gas interfaces, solid–vacuum interfaces, and liquid-gas interfaces).

- It is defined as the study of chemical reactions at interfaces.

Terminologies

- **Adsorbate:** The substance which gets adsorbed on any surface is called ***adsorbate.***
- **Adsorbent:** The substance on the surface of which adsorption takes place is called **adsorbent**.
- **Adsorption**: The process whereby molecules of gases or liquids adhere chemically to the surface of a solid.

(Eg.) Occlusion of Hydrogen gas on Palladium where palladium is adsorbent and hydrogen gas is adsorbate.

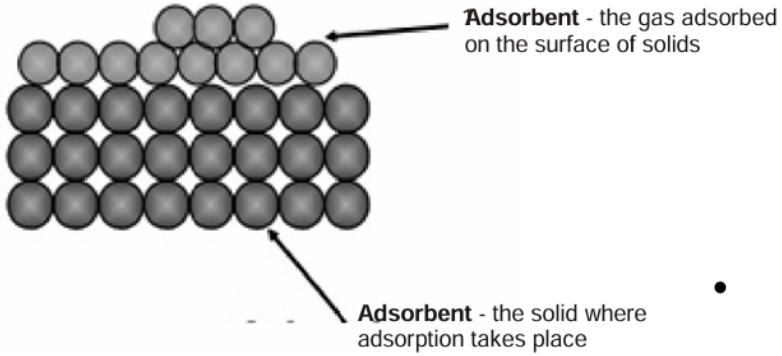


Figure 2.1 : Adsorption Process

- **Desorption:** The removal of the adsorbed substance from a surface is called ***desorption***.
- **Interface:** The plane which separates any two phase is generally called an ***interface.***
- **Absorption:** When the molecules of a substance are uniformly distributed throughout the body of a solid or liquid. This phenomenon is called ***absorption***.
- **Sorption:** The phenomenon in which adsorption and absorption occur simultaneously is called ***sorption.***
- **Occlusion:** When adsorption of gases occurs on the surface of metals it is called ***occlusion.***

Terminologies

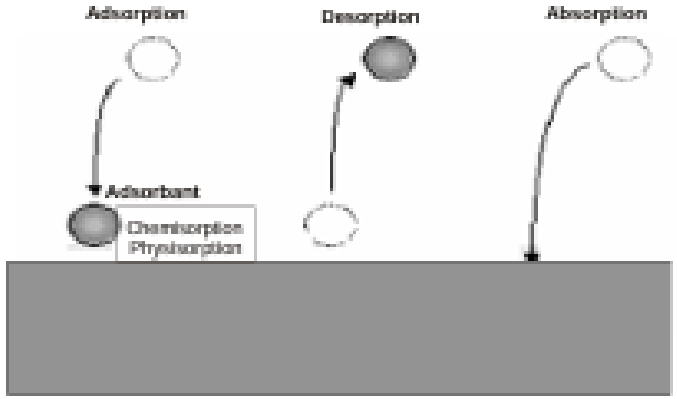


Figure 2.2 : Occlusion Process

- **Positive adsorption:** When the concentration of solute adsorbed on the solid adsorbent surface is greater than in the bulk it is called *positive adsorption.*

  (Eg.) Concentrated solution of KCl is shaken with blood charcoal, it shows positive adsorption

- **Negative adsorption:** When the solvent from the solution may be absorbed by the adsorbent so that the concentration of the solute decreases and the concentration of solution increases than the initial concentration and it is called *negative adsorption.*

  (Eg.) Dilute solution of KCl is shaken with blood charcoal it shows negative adsorption.

Enthalpy or heat of adsorption

Amount of heat evolved when 1 mole of an adsorbate gets adsorbed on the surface of an adsorbent is called ***Molar Heat*** **or** ***Molar Enthalpy of Adsorption.***

S.No.	ABSORPTION	ADSORPTION
1.	It is a bulk phenomenon	It is a surface phenomenon
2.	It is a slow process	It is a fast process
3.	Substance uniformly distributed throughout the surface	Higher concentration of molecular species in the surface than in the bulk
4.	Attainment of equilibrium takes time	Equilibrium attained easily

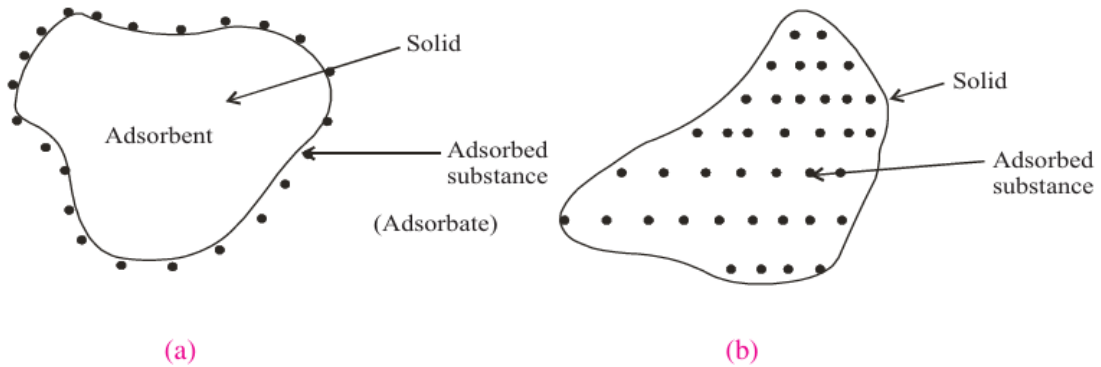


Fig. 15.2 : *(a) Adsorption (b) Absorption*

- Adsorption occurs on the surface of almost all solids. However, the extent of adsorption of a gas on the surface of a solid depends upon the following factors:
- (i) Nature and surface area of the adsorbent
- (ii) Nature of the adsorbed gas
- (iii) Temperature
- (iv) Pressure of the gas

- (i) Nature and surface area of the adsorbent

- Different solids would adsorb different amounts of the same gas even under similar conditions. Substances like charcoal and silica gel are excellent adsorbents.
- The substances that are porous in nature and have rough surfaces are better adsorbents.
- The extent of adsorption also depends upon the surface area of the solid. Greater the surface area, more is the surface available for adsorption and greater is the adsorption.
- The surface area depends upon the particle size of the substance.

- (ii) Nature of the adsorbed gas

- The extent of adsorption also depends upon the nature of the gas. The gases which are more easily liquifiable or are more soluble in water are more readily adsorbed than others.
- For example, under similar conditions, the amount of SO2 or NH3 adsorbed by charcoal is much more than that of H2 or O2 gases.
- It is because the intermolecular forces are stronger in more easily liquifiable gases, therefore, they get adsorbed more strongly.

- (iii) Temperature

- The extent of adsorption decreases with rise in temperature. For example, under one atmosphere pressure, one gram of charcoal adsorbs about 10 cm3 of N2 gas at 272 K, 20 cm3 at 248 K and 45 cm3 at 195 K.
- Adsorption is an exothermic process. The change in enthalpy when one mole of a substance is adsorbed, is called enthalpy of adsorption.

$$\underset{\text{adsorbate}}{\text{gas}} + \underset{\text{adsorbent}}{\text{solid}} \rightleftharpoons \text{gas adsorbed on the solid} + \textit{heat}$$

- (iii) Temperature

- Since the forward process (adsorption) is exothermic in nature, according to the Le Chatelier's principle, it would be favoured at low temperature. Therefore, the extent of adsorption would increase on decreasing the temperature and would decrease on increasing the temperature

- (iv) Pressure of the gas

- At a constant temperature the extent of adsorption increases with increase in the pressure of the gas (adsorbate).

- Adsorption can be divided into two main categories – physical and chemical adsorption.
- (i) Physical Adsorption
- It is the common type of adsorption. The basic feature of physical adsorption is that the adsorbate molecules are held at the surface of the adsorbent by weak van der Waals forces. These are the forces that exist between particles of all matter.
- Because of their universal nature, these forces would operate between any adsorbent and adsorbate pair. Therefore, the physical adsorption is observed on surface of any solid. Physical adsorption is characterized by low enthalpy of adsorption, that is about 10 – 40 kJ/mol

- Adsorption can be divided into two main categories – physical and chemical adsorption.
- (i) Physical Adsorption
- Another feature of the physical adsorption of a gas by a solid is that it is reversible in nature and an equilibrium is established between the adsorbent and the adsorbate as discussed earlier.
- Increase of pressure increases the adsorption and the release of pressure desorbs the gas. When temperature is increased, the physical adsorption decreases and when it is lowered, the adsorption increases.
- In physical adsorption, several layers of adsorbate are adsorbed one over the other.

- Adsorption can be divided into two main categories – physical and chemical adsorption.
- (i) Chemical Adsorption
- This type of adsorption caused by forces similar to chemical bonds between the adsorbent and the adsorbate is called chemisorption or chemical adsorption.
- The enthalpy of chemisorption is as high as that of chemical bonds (bond enthalpies) and is in the range of 40 – 400 kJ/mol. Chemisorption is highly specific and is possible between a specific adsorbent – adsorbate pair.
- Like most of the chemical changes it is irreversible. Attempts to release the adsorbed gas gives the gas and some amount of a definite compound. For example, oxygen gas is chemisorbed on tungsten.

- Adsorption can be divided into two main categories – physical and chemical adsorption.

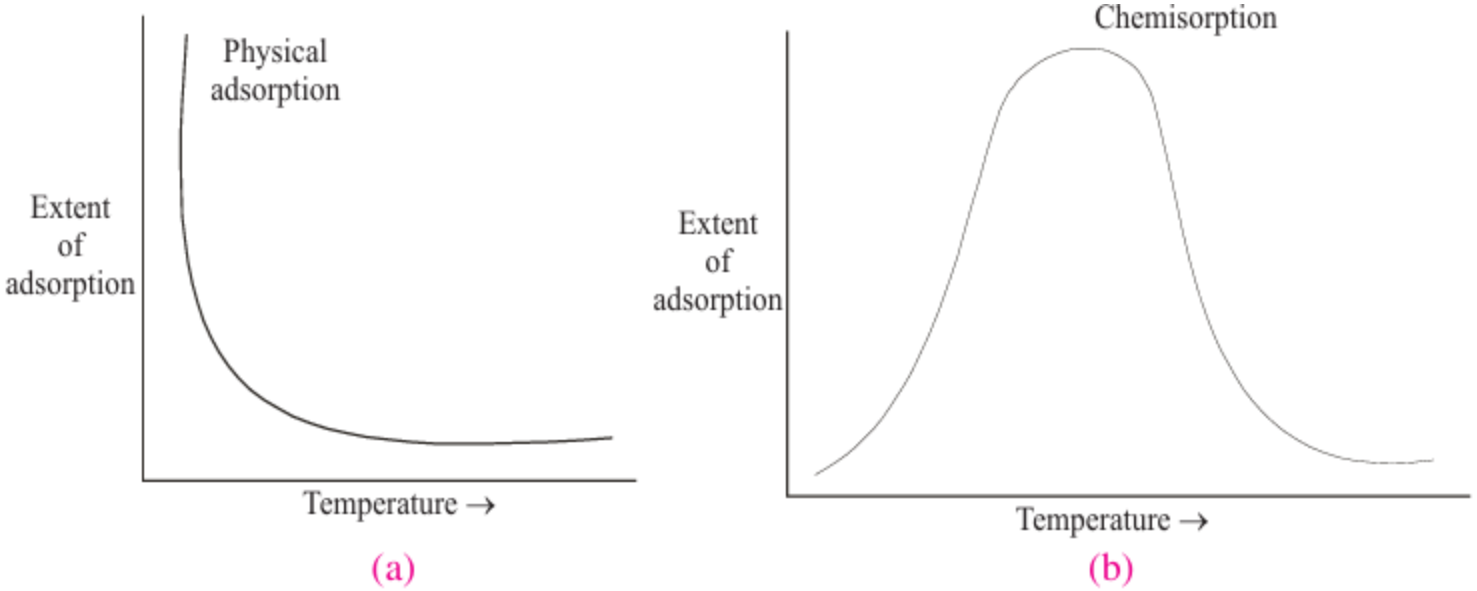


Fig. 15.4 : *Effect of temperature on (a) physical adsorption and (b) chemisorption.*

- Adsorption can be divided into two main categories – physical and chemical adsorption.

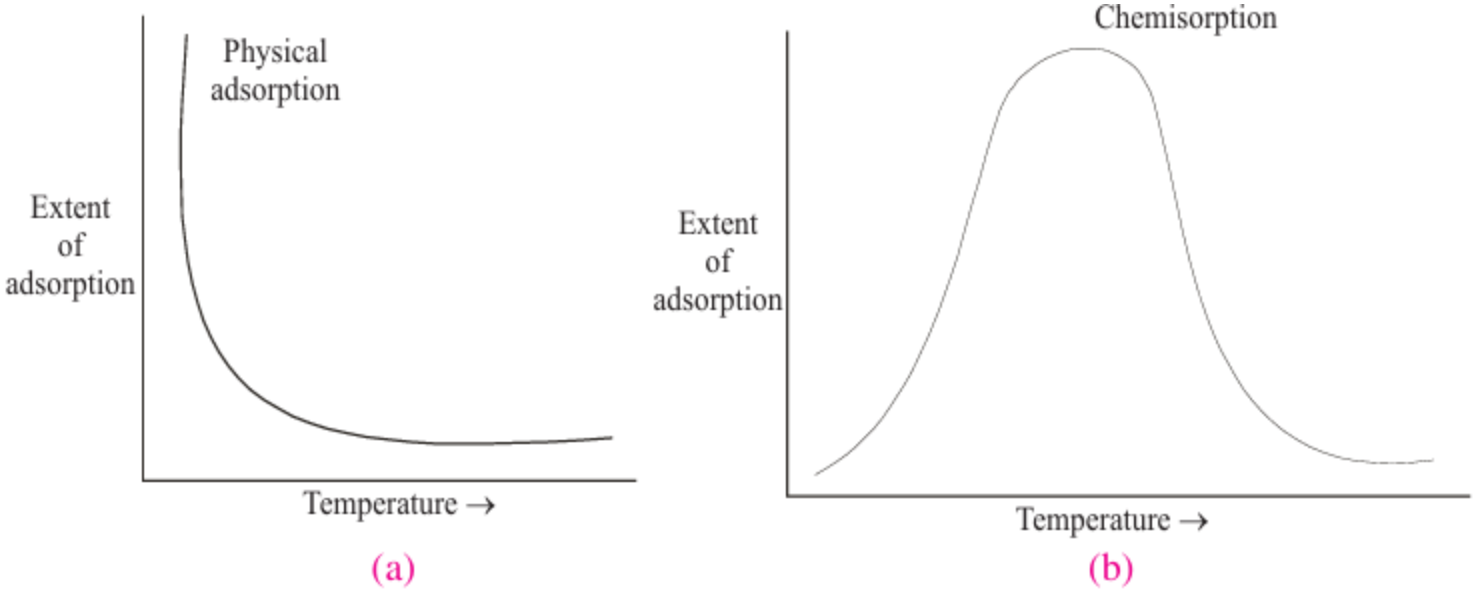


Fig. 15.4 : *Effect of temperature on (a) physical adsorption and (b) chemisorption.*

Physical Adsorption	Chemisorption
1. The forces operating between adsorbate and adsorbent are the weak van der Waals forces.	1. The forces operating between adsorbate and adsorbent are strong and similar to chemical bonds.
2. The enthalpy of adsorption is low and ranges from 10 to 40 kJ mol^{-1}.	2. The enthalpy of adsorption is high and ranges from 40 to 400 kJ mol^{-1}.
3. No activation energy is involved.	3. Significant activation energy is involved.
4. Adsorption occurs more readily at low temperature and high pressure.	4. Chemisorption occurs at relatively high temperature and high pressure.
5. It is not specific in nature. All gases are adsorbed on all solids and no compounds are formed.	5. It is highly specific in nature and occurs between those adsorbents and adsorbates which have a possibility of compound formation between them.
6. It is reversible in nature. The gas is desorbed on increasing the temperature or decreasing the pressure.	6. It is irreversible in nature. Desorption also separates some amount of the compound formed.
7. Multilayer formation is common.	7. Monolayer formation occurs.

Adsorption Isotherms

- An Adsorption Isotherm is obtained by measuring the amount of gas adsorbed across a wide range of relative pressures at a constant temperature (typically liquid N2, 77K). Conversely desorption Isotherms are achieved by measuring gas removed as pressure is reduced

- 5 Classical Iostherm types described by Brunauer, Deming, Deming and Teller.

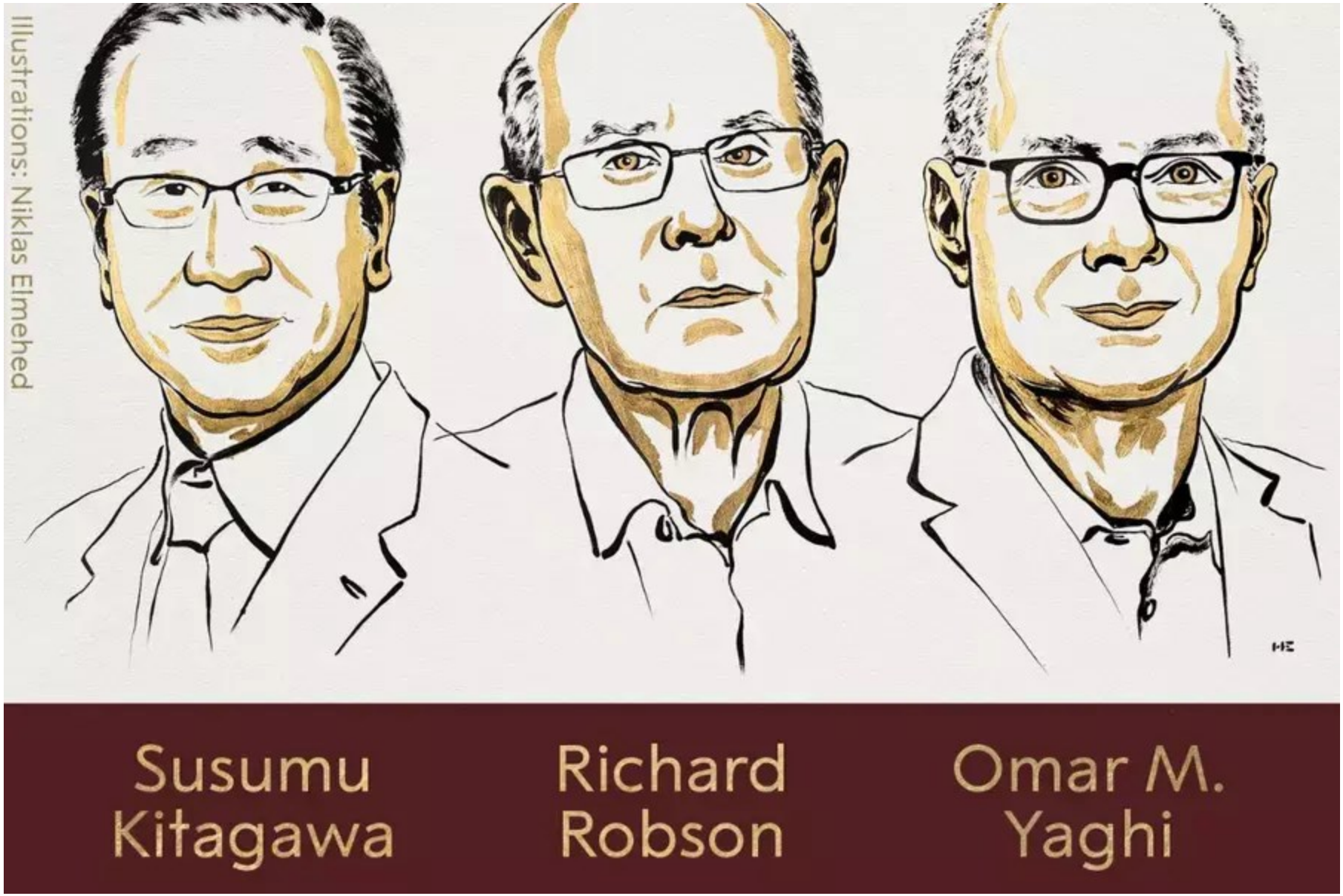
IUPAC classification on pores

- Macroporous (>50nm)

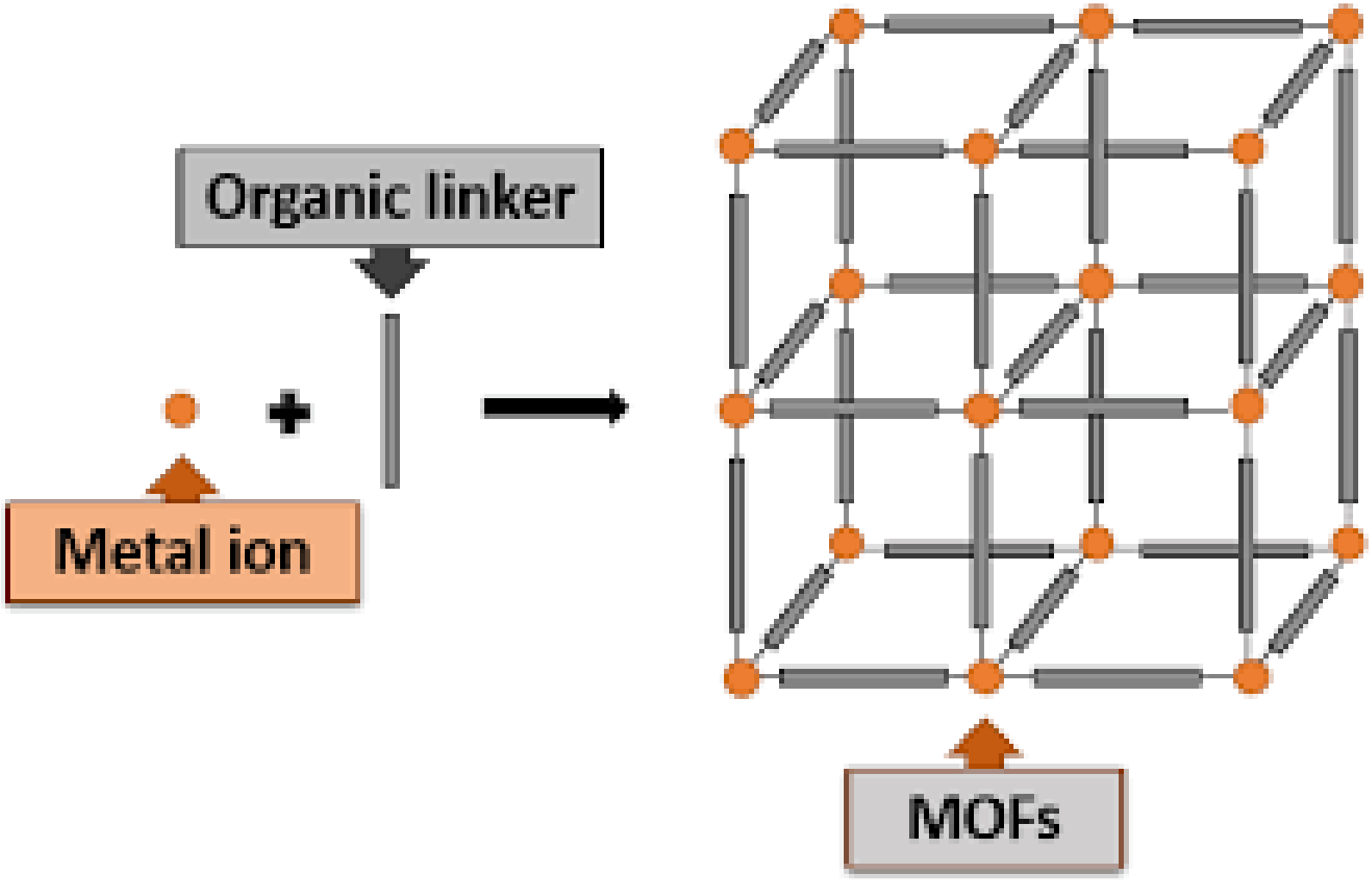
- Mesoporus (2-50nm)

- Microporus (<2nm)

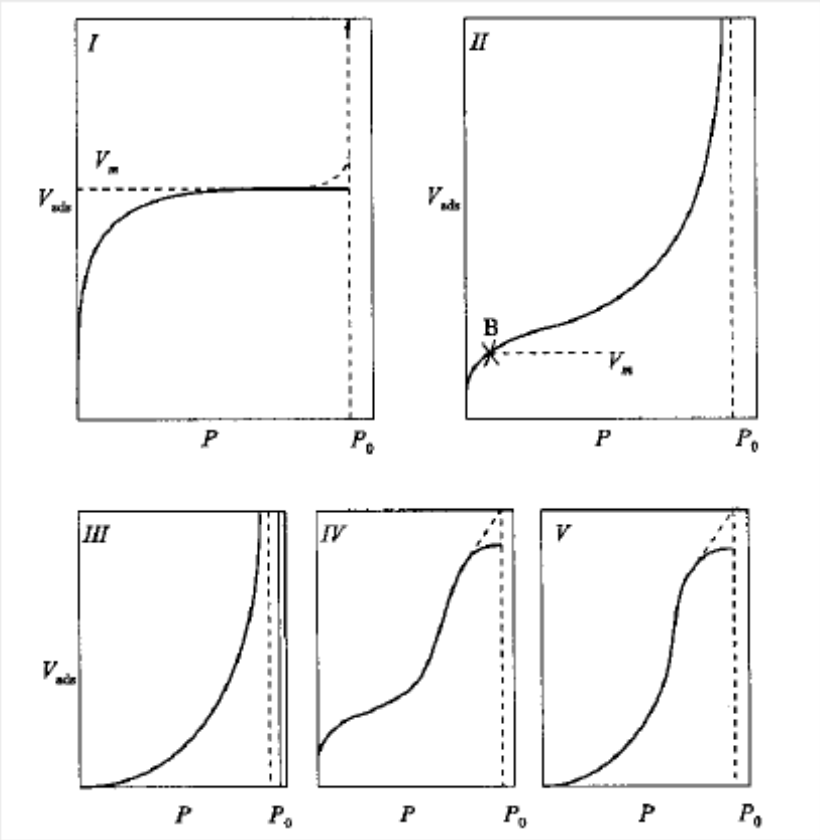
Discovery of Metal Organic Framework

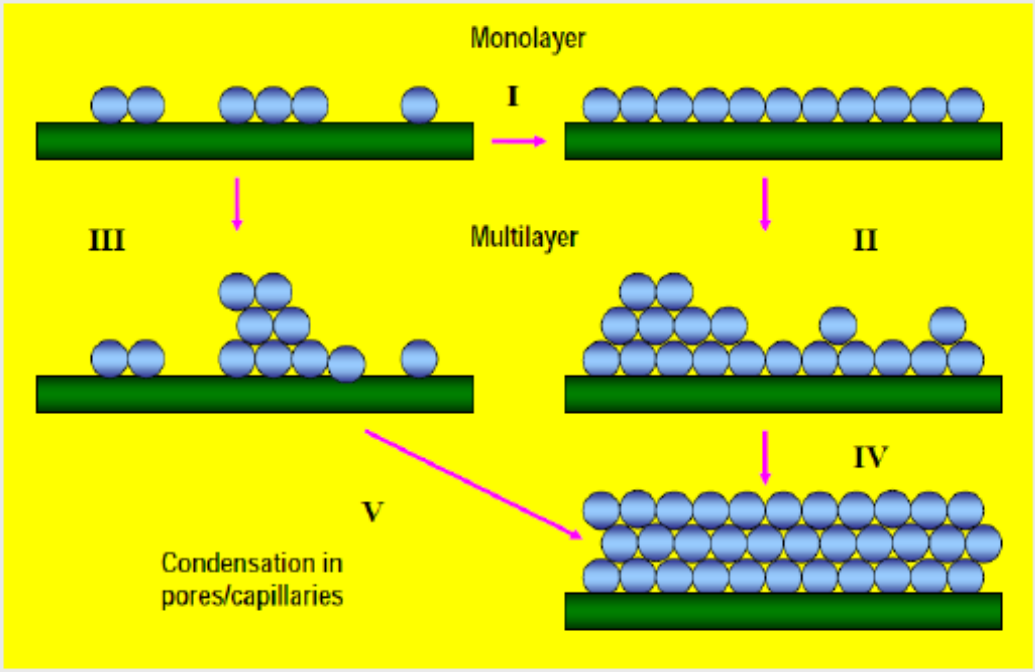


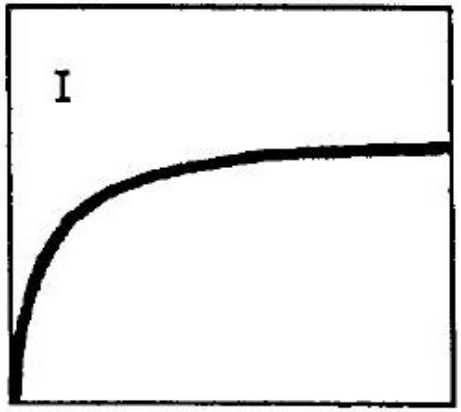
Mesopores Metal Organic Framework



Adsorption Isotherms

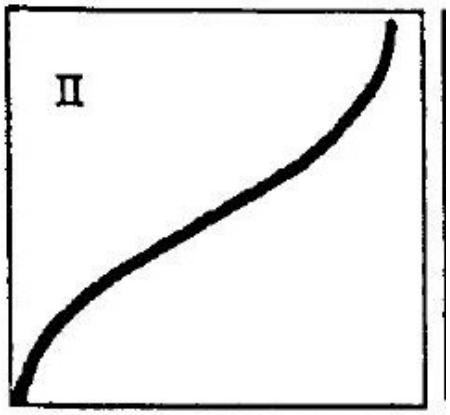






Type I

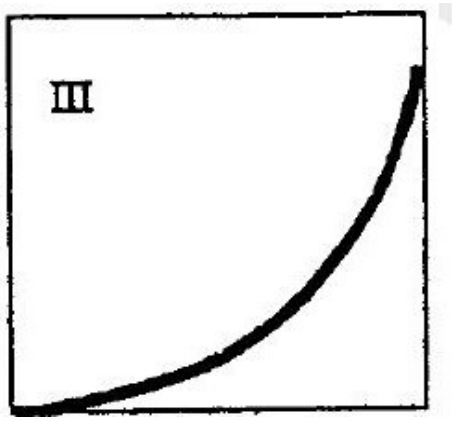
Pores are typically microporous with the exposed surface residing almost exclusively inside the micropores, which once filled with adsorbate, leave little or no external surface for further adsorption.



Type II

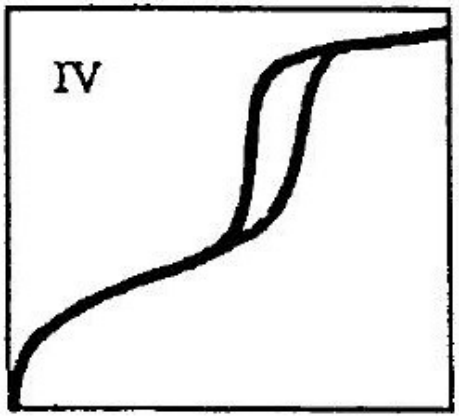
Most frequently found when adsorption occurs on nonporous powders or powders with diameters exceeding micropores.

Inflection point occurs near the completion of the first adsorbed monolayer



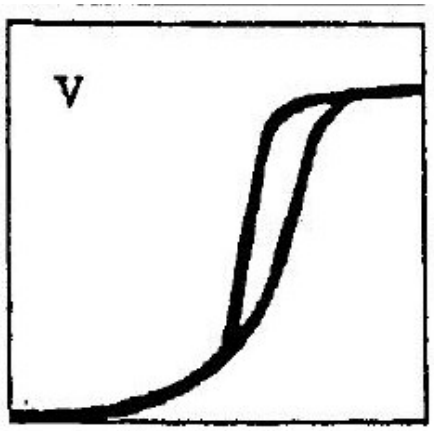
Type III

Characterised by heats of adsorption less than the adsorbate heat of liquification, adsorption proceeds as the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface



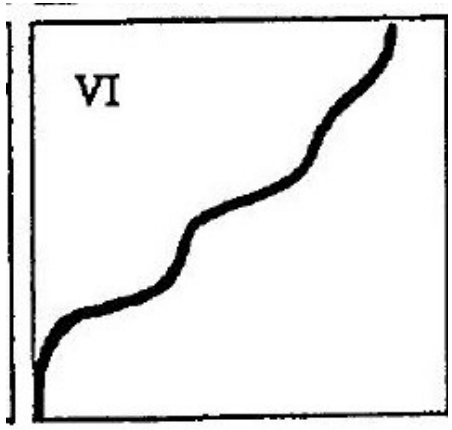
Type IV

Occur on porous adsorbents with pores in the range of 1.5 – 100nm. At higher pressures the slope shows increased uptake of adsorbate as pores become filled, inflection point typically occurs near completion of the first monolayer



Type V

Are observed where there is small adsorbate-absorbent interaction potentials (similar to type III), and are also associated with pores in the 1.5 – 100nm range



Type VI

stepwise multilayer ads. on a uniform, non-porous surface

Type 1 Adsorption Isotherm

The extent of adsorption is measured in terms of the quantity x/m where, x is the mass of the gas (adsorbate) adsorbed at equilibrium on mass m of the adsorbent. The graph showing variation in x/m with pressure(p) at a constant temperature is called adsorption isotherm. Let us see the variation in extent of adsorption in case of gases and of solutes from their solutions.

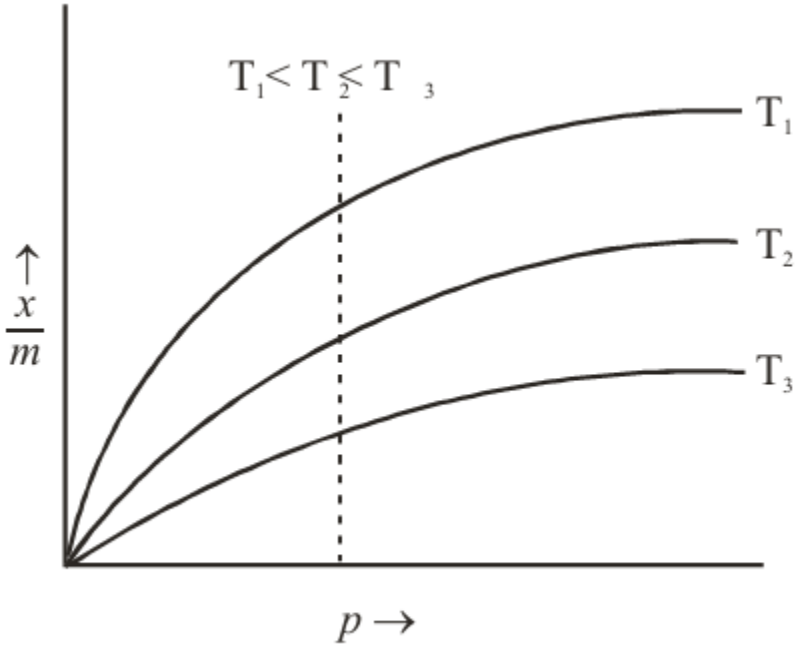


Fig. 17.5 : *Adsorption isotherm of a gas*

Freundlich Adsorption Isotherm

In 1909, Herbert Freundlich gave an expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure.Freundlich adsorption isotherm is an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. The isotherm is given as:

$$\frac{x}{m} = k \, . P^{\frac{1}{n}} \; where \; n > 1$$

Or $log \frac{x}{m} = \log k + \frac{1}{n} \log P$

where x – is mass of adsorbate,

m – is mass of adsorbent,

P – is the equilibrium pressure of adsorbate,

K & n – are constants.

At low pressure, extent of adsorption is directly proportional to pressure:

$$\frac{x}{m} \propto p^{1}$$

At high pressure, extent of adsorption is independent of pressure:

$$\frac{x}{m} \propto p^{0}$$

At intermediate value of pressure, adsorption is directly proportional to pressure raised to power $\frac{1}{n}$. n value is greater than 1.

$$\frac{x}{m} \propto p^{(1/n)}$$

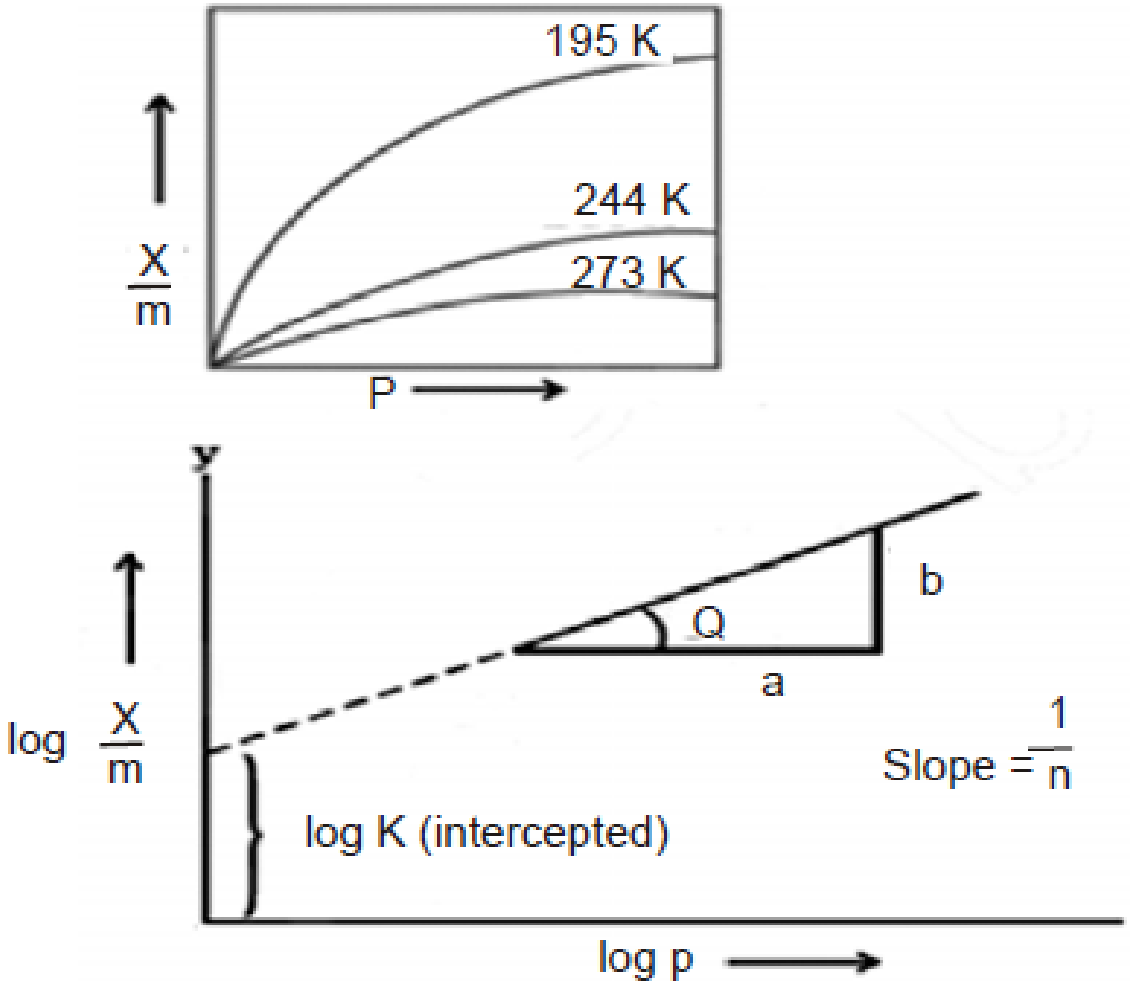


Figure 2.9 : log (*x*/*m*) vs. log p graph

Limitation of Freundlich Adsorption Isotherm

1. Freundlich equation is purely empirical and has no theoretical basis.
2. The equation is valid only upto a certain pressure and invalid at higher pressure.
3. The constants *k* and *n* are not temperature independent, they vary with temperature.
4. Frendilich's adsorption isotherm fails when the concentration of the adsorbate is very high.

LANGMUIR ADSORPTION ISOTHERM

In 1916, Irving Langmuir proposed another adsorption Isotherm which explained the variation of adsorption with pressure

Assumptions of Langmuir Isotherm

Langmuir proposed his theory by making following assumptions.

(i) Surface is energetically uniform. Fixed number of vacant or adsorption sites are available on the surface of the solid.

(ii) All the vacant sites are of equal size and shape on the surface of adsorbent.

Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released.

(iii) Heat of adsorption is constant throughout the surface and it ranges from 0 to 1.

(iv) Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

(v) Adsorption is monolayer or unilayer.

Langmuir Equation depicts the relationship between the extent of adsorption and pressure. Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.

where A(g) – is unadsorbed gaseous molecule

B(s) – is unoccupied metal surface and

AB – is adsorbed gaseous molecule

According to Kinetic theory,

Rate of forward reaction = K_a [A] [B]

Rate of backward reaction = K_d [AB]

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

$$K_a [A] [B] = K_d [AB]$$

A new parameter 'θ' is introduced.

Let θ be the number of sites of the surface which are covered with gaseous molecule and 1-θ be the fraction of surface unoccupied by gaseous molecule. Rate of forward direction depends upon two factors, number of sites available on the surface of adsorbent, $(1 - \theta)$ and pressure, P.

$$\text{Rate of forward reaction} \propto P\,(1 - \theta)$$

$$\text{Rate of adsorption} \propto P\,(1 - \theta) \text{ or}$$

$$\text{Rate of adsorption} = K_a\,P\,(1 - \theta)$$

Rate of backward reaction or rate of desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

$$\text{Rate of desorption} \propto \theta \text{ (or)}$$

$$\text{Rate of desorption} = K_d\,\theta$$

At equilibrium, rate of adsorption is equal to rate of desorption.

$$K_a P (1 - \theta) = K_d \theta$$

The above equation can be written in terms θ.

$$K_a P - K_a P\theta = K_d \theta$$

$$K_a P = K_a P\theta + K_d \theta$$

$$K_a P = (K_d + K_a P)\theta$$

$$\theta = \frac{K_a P}{(K_d + K_a P)}$$

Divide numerator and denominator on RHS by K_d, we get

$$\theta = \frac{\frac{K_a P}{K_d}}{\frac{K_d}{K_d} + \frac{K_a P}{K_d}}$$

But $K = \frac{K_a}{K_d}$

Substituting in the above equation we get

$$\theta = \frac{KP}{1 + KP}$$

This is known as ***Langmuir Adsorption Equation***.