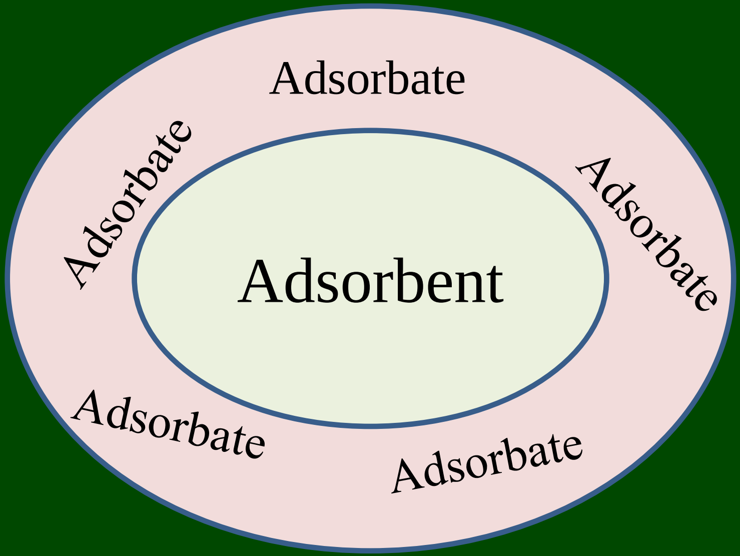
2. Surface Chemistry

- Introduction to surface chemistry –
- Some basic terms related to surface chemistry adsorption,
- Adsorption materials,
- Factors affecting adsorption,
- Characteristics of adsorption,
- Types of adsorption,
- Classification of adsorption isotherms,
- Langmuir adsorption isotherm,
- Freundlich’s adsorption isotherm,
- BET theory (only introduction),
- Application of adsorption, problems.

Introduction to surface chemistry

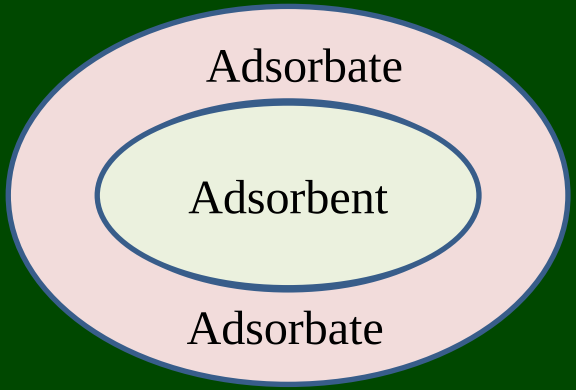
The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as adsorption.



Adsorbent : The solid that takes up a gas or vapour or a solute from a solution

Adsorbent

Adsorbate : The gas or vapour or the solute which is held to the surface of the solid



Adsorbate

Adsorbent

Adsorbate

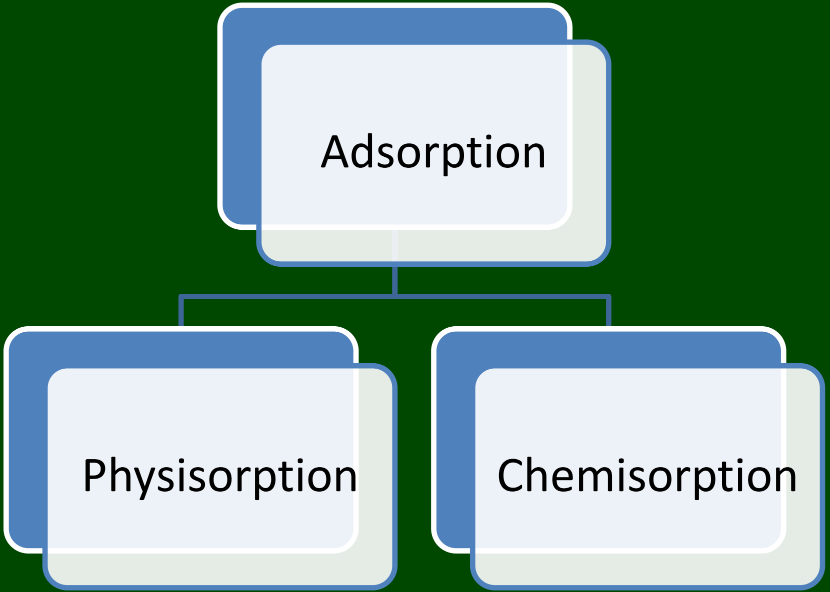
Absorption :

In Absorption substance is uniformly distributed throught the body of a solid or liquid.

Adsorbate

Sorption : The process in which both absorption & adsorption takes place simultaneously.

Types of Adsorption :



Adsorption

Physisorption

Chemisorption

Physisorption :

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

Characteristics of physisorption

1. It arises because of van der Waals’ forces.

2. It is not specific in nature.

3. It is reversible in nature.

4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.

5. Enthalpy of adsorption is low (20-40 kJ mol–1)in this case.

6. Low temperature is favourable for adsorption. It decreases with increase of temperature.

7. No appreciable activation energy is needed.

8. It depends on the surface area. It increases with an increase of surface area.

9. It results into multimolecular layers on adsorbent surface under high pressure.

Chemisorption :

When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed chemical adsorption or chemisorption.

Characteristics of chemisorption

1. It is caused by chemical bond formation.

2. It is highly specific in nature.

3. It is irreversible.

4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.

5. Enthalpy of adsorption is high (80-240 kJ mol–1) in this case.

6. High temperature is favourable for adsorption. It increases with the increase of temperature.

7. High activation energy is sometimes needed.

8. It also depends on the surface area. It too increases with an increase of surface area.

9. It results into unimolecular layer.

Physisorption

Chemisorption

➢ **Factors affecting adsorption**,

1. Temperature
2. Pressure
3. Nature of the gas
4. Nature of the Adsorbent

- **Temperature and Pressure**

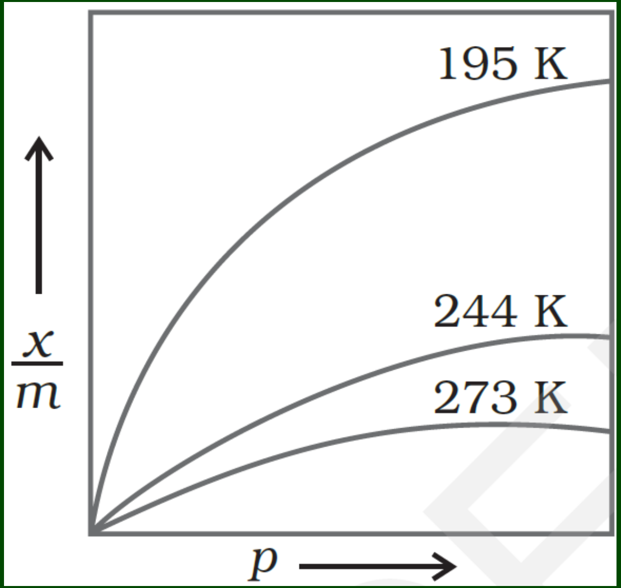
- The decrease of temperature and increase of pressure will increase the magnitude of adsorption of a gas on a solid.

- **Nature of the gas and nature of the adsorbent**

- Readily soluble & easily liquifiable gases such as NH3, HCl, Cl2, SO2 are adsorbed more than H2, N2, O2
- Adsorption is surface phenomenon, as greater the surface area of adsorbent ,the greater is its capacity for adsorption under the given conditions of T & P.

Adsorption Isotherms

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



Classification of adsorption isotherms :

- ☐ Freundlich isotherm
- ☐ Langmuir adsorption isotherm

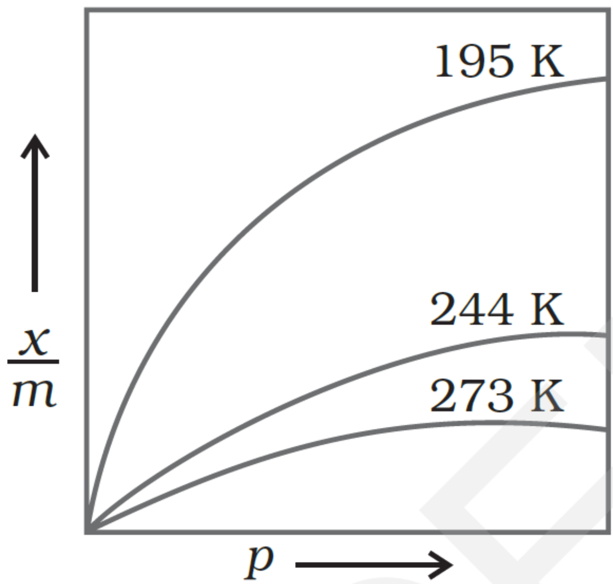
Freundlich isotherm

It gives the relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation

$$\frac{x}{m} = k.p^{\frac{1}{n}} \qquad (n > 1)$$

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.

The relationship is generally represented in the form of a curve where mass of the gas adsorbed per gram of the adsorbent is plotted against pressure as shown in Fig.



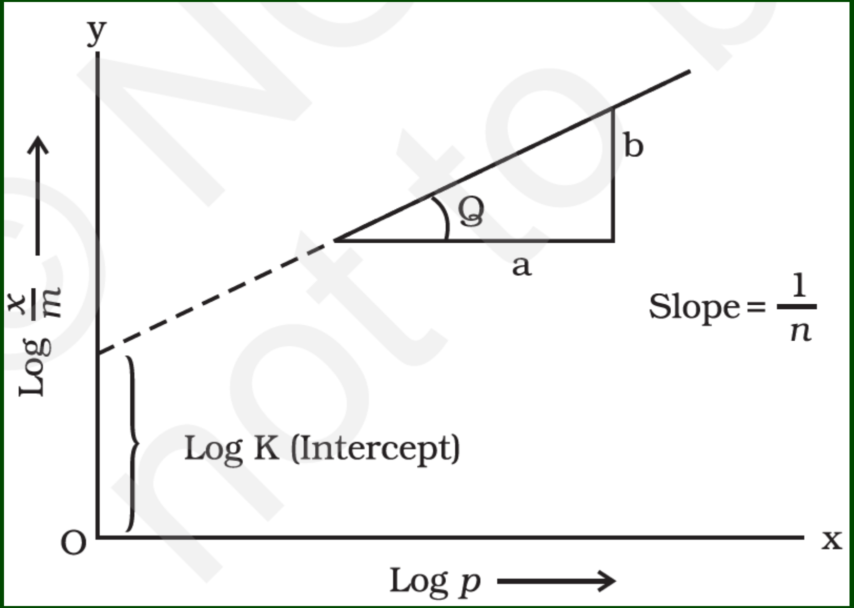
These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

Taking logarithm on both sides

$$log\frac{x}{m} = logk + \frac{1}{n}logp$$

$$log\frac{x}{m} = \frac{1}{n}logp + logk$$

$$y = mx + c$$



Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor $\frac{1}{n}$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation holds good over a limited range of pressure

When $\frac{1}{n} = 0$, $\frac{x}{m}$ = constant, the adsorption is independent of pressure.

When $\frac{1}{n} = 1$, $\frac{x}{m} = k\,p$, i.e. $\frac{x}{m} \propto p$, the adsorption varies directly with pressure.

Both the conditions are supported by experimental results.
The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

Adsorption from Solution Phase

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution.

The following observations have been made in the case of adsorption from solution phase:

(i) The extent of adsorption decreases with an increase in temperature.

(ii) The extent of adsorption increases with an increase of surface area of the adsorbent.

(iii) The extent of adsorption depends on the concentration of the solute in solution.

(iv) The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

Freundlich's equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure, concentration of the solution is taken into account, i.e.,

$$\frac{x}{m} = kc^{\frac{1}{n}}$$

(*C* is the equilibrium concentration, i.e., when adsorption is complete).

On taking logarithm of the above equation, we have

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

Plotting $\log\frac{x}{m}$ against $\log C$ a straight line is obtained which shows the validity of Freundlich isotherm.

Langmuir adsorption isotherm :

In 1916 langmuir proposed his theory of adsorption of gas on the surface of a solid

Assumptions of langmuir theory:

1. Surface of solid is made up of elementry sites each of which could adsorb one gas molecule.
2. All adsorption sites are equivalent.
3. The ability of the gas molecule to get bound to any one site is independent of whether or not the neighbouring sites are occupied.
4. There is dynamic equilibrium exists between the adsorbed molecules and the free molecules.

e.g. If A is the gas molecule & M is the surface site, then

$$A_{(g)} + M(surface) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} AM$$

Where k_a is the rate constant for adsorption
k_d is the rate constant for desorption

The rate of adsorption is proportional to the pressure of A $i.e.$ P_A and no of vaccant sites on the surface i.e. $N(1-\theta)$

Where N is the total no of sites and θ is the fraction of surface sites occupied by the gas molecules.

$$\theta = \frac{Number\ of\ adsorption\ sites\ occupied}{Number\ of\ adsorption\ sites\ available}$$

Thus, the rate of adsorption = $k_a pN(1-\theta)$

The rate of desorption is proportional to no of adsorbed molecules , Nθ

Thus the rate of desorption = $k_d N\theta$

Since at equilibrium , The rate of adsorption is equal to the rate of desorption

rate of adsorption = rate of desorption

$$k_a pN(1-\theta) = k_d N\theta$$

$$Kp(1-\theta)=\theta$$

Where, $K=\frac{k_a}{k_d}$

$$Kp=\frac{\theta}{(1-\theta)}$$

$$\frac{1}{Kp}=\frac{(1-\theta)}{\theta}$$

$$\frac{1}{Kp}=\frac{1}{\theta}-1$$

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

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

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

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

This equation is called the Langmuir adsorption isotherm

Assumptions involved in the derivation of langmuir adsorption isotherm

1. The adsorbed gas behaves ideally in the vapour phase.(*holds at low Pressure)*
2. Only a monolayer is formed by the adsorbed gas.(*Breaks down when the pressure of the gas is increased)*
3. The surface of solid is homogenous so that each binding site has the same affinty for the gas molecules.(*not strictly true bcz real surfaces are hetrogenous , so affinity for gas molecules is different at different sites)*

4. There is no lateral interaction between adsorbate molecules.(*not strictly valid)*

5. The adsorbed gas molecules are loalized , i.e., they do not move around on the surface. (*not strictly valid)*

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

Case 1) At low pressure, $Kp_A << 1$,

$$\theta = Kp$$

Fraction of surface covered is directly proportional to the partial pressure of the gas molecules. This gives first order reaction

Case 2) At high pressure, $Kp_A >> 1$,

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

Therefore we neglect 1

$$\theta = \frac{Kp}{Kp} = 1$$

This equation gives fraction of surface covered is independent of pressure

Therefore this indicate zero order reaction

From Langmuir,
Since at Low P

$$\theta = Kp^{1}$$

At High P

$$\theta = 1 = p^{0}$$

Therefore by logically at intermidiate P

$$\theta = p^{0-1}$$

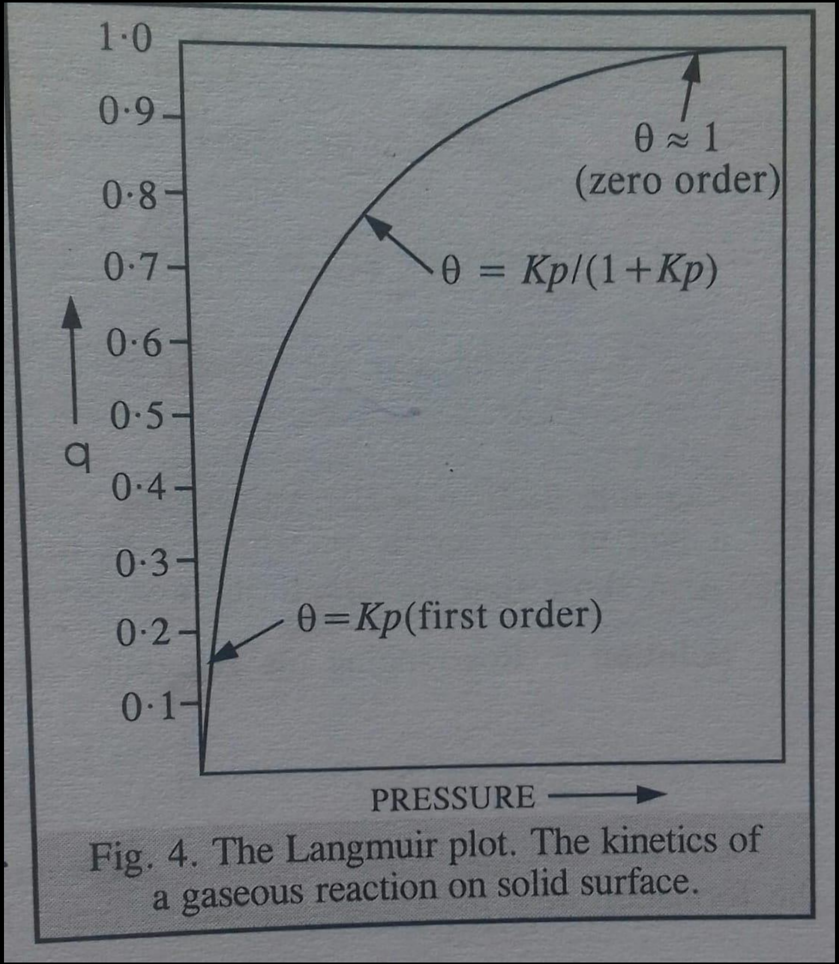


Fig. 4. The Langmuir plot. The kinetics of a gaseous reaction on solid surface.

From Frenluich

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

$$\theta = kp^{\frac{1}{n}}$$

Where n>1

$$\theta = kp^{0-1}$$

Since at intermidiate pressure langmuir adsorption isotherm becomes Frendluich adsorption isotherm.

BET Theory: [Determination of surface area of adsorbent]

It explain physical adsorption of gas molecules on solid adsorbent
This theory proposed in 1938 by Stephen Brunauer, Paul Hugh Emmet & Edward Teller known as BET theory.

Langmuir explain only Monolayer Adsorption
BET theory is an extension of of langmuir theory
BET theory explain Monolayer Adsorption to multi-Molecular layer adsorption with the following assumptions.

Assumptions of BET Theory

1. Gas molecules physically adsorb on a solid in multilayer.
2. Gas molecules only interact with only adjacent layers.
3. Langmuir theory can be applied to each layer.
4. The enthalpy of adsorption for the first layer is constant and greater than the 2nd layer(and higher layers)
5. The enthalpy of adsorption for the 2nd & higher layers is the same as the enthalpy of liquefaction.

Based on the above assumptions BET derived the following equation & it is used to determine the monolayer adsorbed gas volume (V_m)

$$\frac{1}{v[\left(\frac{p_0}{p}\right) - 1]} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

$v = adsorbed\ gas\ quantity$

$P_0 = saturation\ pressure\ of\ adsorbate$

$P = equilibrium\ pressure\ of\ adsorbate$

$C = BET\ constant$

$$\frac{1}{v[\left(\frac{p_0}{p}\right)-1]}=\frac{c-1}{v_m c}\left(\frac{p}{p_0}\right)+\frac{1}{v_m c}$$

$$y=mx+c$$

Applications of adsorption

(1) **Production of high vacuum**

(2) **In Gas masks** :This apparatus is used to adsorb poisonous gases (e.g. oxide of sulphur etc.) and thus purify the air for breathing.

(3) **For desiccation or dehumidification :** These substances can be used to reduce/remove water vapours or moisture present in the air. Silica gel and alumina are used for dehumidification in electronic equipment.

(4) **Removel of colouring matter from solution :**

(i) Animal charcoal removes colours of solutions by adsorbing coloured impurities.

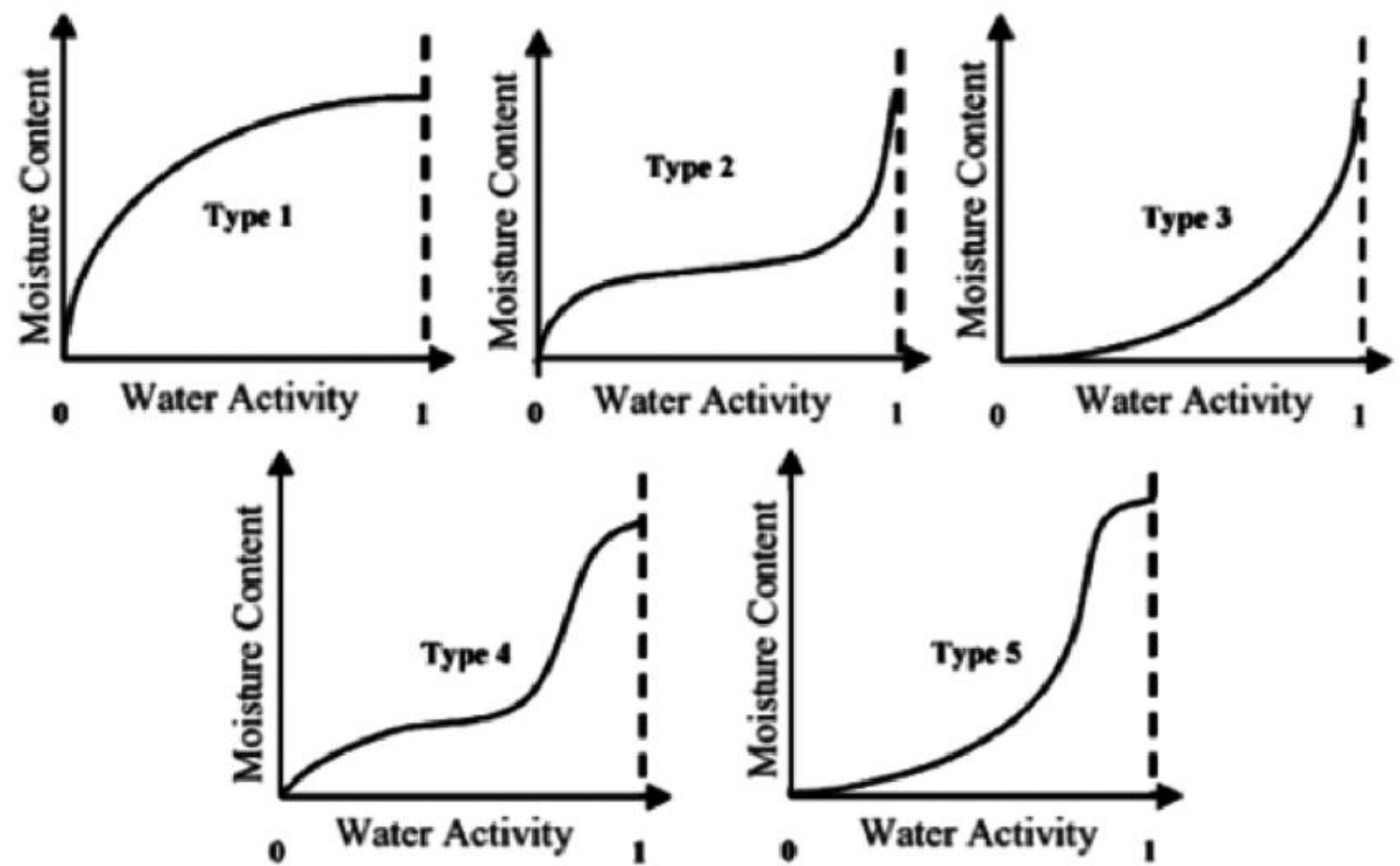
(ii) Animal charcoal is used as decolouriser in the manufacture of cane sugar.

(5) **Heterogeneous catalysis :** Mostly heterogeneous catalytic reactions proceed through the adsorption of gaseous reactants on solid catalyst. For example,

(i) Finely powdered nickel is used for the hydrogenation of oils.

(ii) Finely divided vanadium pentaoxide is used in the contact process for the manufacture of sulphuric acid.

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


Moisture Content
Type 1
Water Activity
0
1
Moisture Content
Type 2
Water Activity
0
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Type 3
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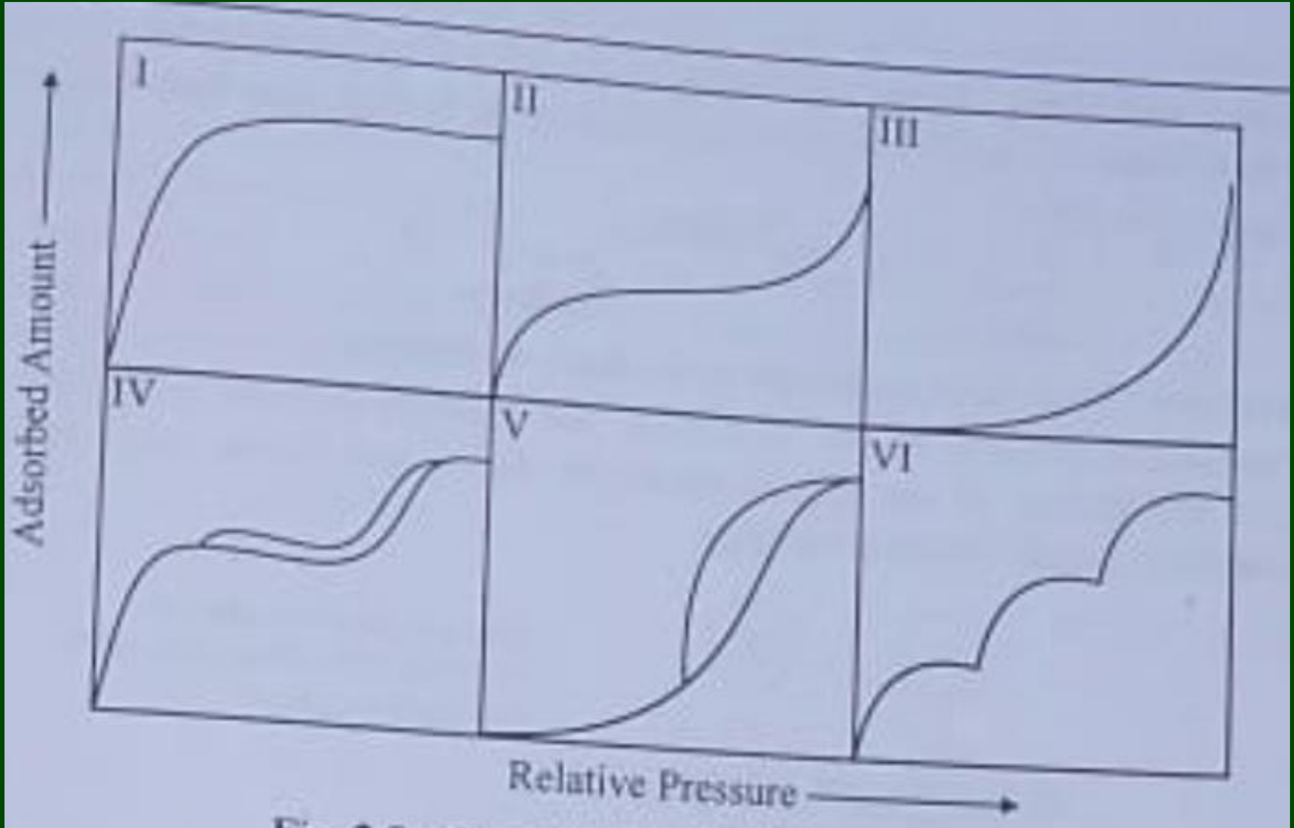

Fig. 2.8 : Classification of adsorption isotherms

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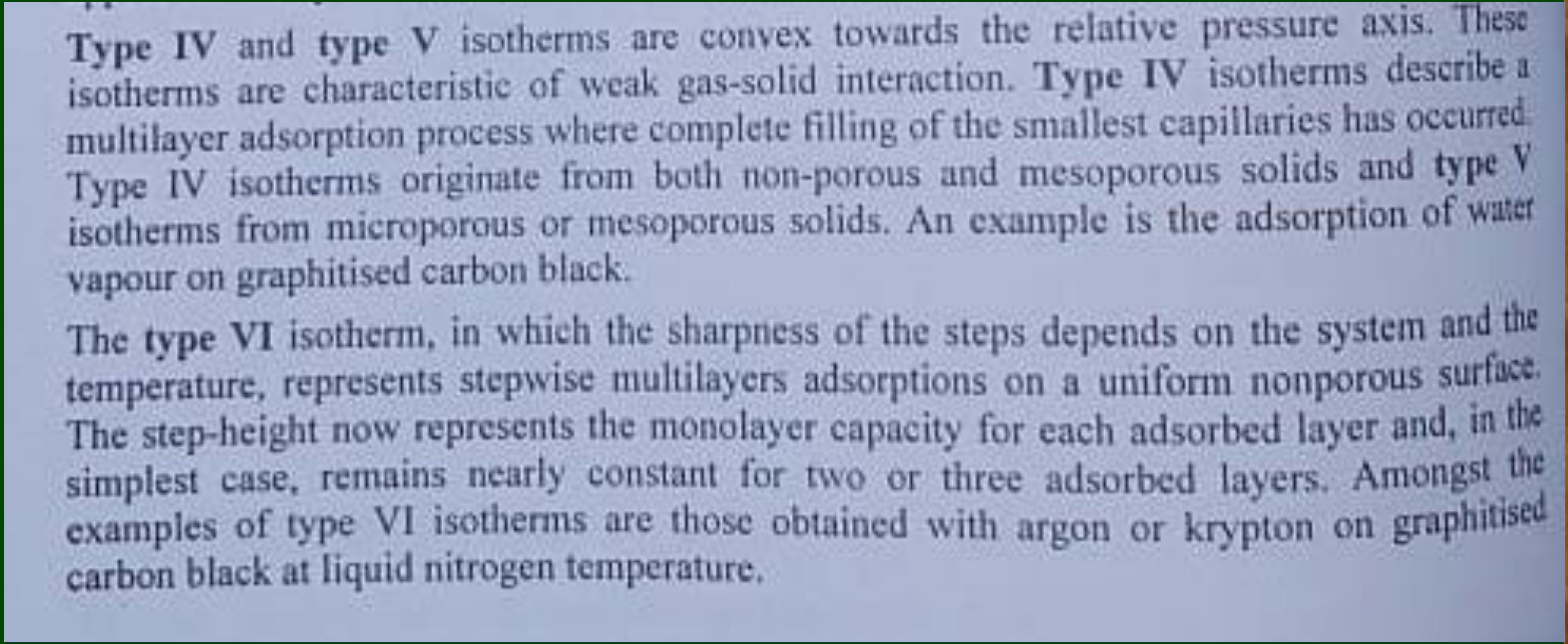

Type IV and **type V** isotherms are convex towards the relative pressure axis. These isotherms are characteristic of weak gas-solid interaction. **Type IV** isotherms describe a multilayer adsorption process where complete filling of the smallest capillaries has occurred. Type IV isotherms originate from both non-porous and mesoporous solids and **type V** isotherms from microporous or mesoporous solids. An example is the adsorption of water vapour on graphitised carbon black.

The **type VI** isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayers adsorptions on a uniform nonporous surface. The step-height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers. Amongst the examples of type VI isotherms are those obtained with argon or krypton on graphitised carbon black at liquid nitrogen temperature.