

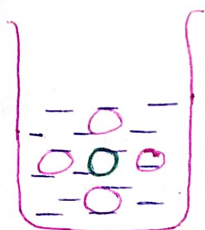
* Surface Chemistry *

Absorption :- Phenomenon in which one substance enters into other and get uniformly distributed throughout the Bulk

Adsorption :- Phenomenon in which one substance concentrate on surface of other than the Bulk.
e.g. Teachers writing on Blackboard

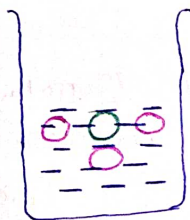
Positive Adsorption	Negative Adsorption
1) Concentration of adsorbate is more at surface as compared to its conc. ⁿ in bulk phase	1) Concentration of adsorbate is less at surface as compared to its conc. ⁿ in bulk phase
2) Solute particle tends to conc. ⁿ on surface of adsorbent	2) Solvent particle tends to conc. ⁿ on surface of adsorbent.

* Why Adsorption take place :-



○ Molecule is ;

- i) Balanced i.e. equal F.O.A. from each side
- ii) Stable
- iii) Consist less energy



○ Molecule is ;

- i) Not balanced
- ii) Unstable
- iii) High energy

→ In order to balance unbalanced force, surface molecule attract outside molecule (through F.O.A.) and get balanced by release in Energy

→ Hence, Adsorption is exothermic phenomenon.

Absorption

- 1) Bulk phenomenon
- 2) Uniform distribution throughout bulk
- 3) Neither exothermic nor endothermic
- 4) Rate of absorption ;
 - a) Uniform
 - b) Independent of surface area

Adsorption

- 1) surface phenomenon
- 2) Not uniform distribution
Generally conc.ⁿ at surface is more than bulk
- 3) Exothermic
- 4) Rate of Adsorption ;
 - a) Rapid in beginning
 - b) Depends on surface area

* Absorption + Adsorption = Sorption

e.g. Dyeing of Fabric

* Removal of Adsorbed molecule = Desorption

* Depends on F.O.A. b/w adsorbate and Adsorbent,
Langmuir classified Adsorption as ;

Physisorption

- 1) Van der Waal's forces are operative / Present
- 2) Relatively weak
- 3) Reversible
- 4) Formation of Multilayers of adsorbed particle
- 5) Not specific in nature i.e. Found in all instances
- 6) Heat of Adsorption is low and lies b/w 20 - 40 kJ mol^{-1}
- 7) Low Activation Energy

Chemisorption

- 1) Chemical forces are operative / Present
- 2) Relatively strong
- 3) Irreversible
- 4) Formation of Monolayer of adsorbed particle
- 5) specific in nature i.e. occurs only when there is tendency to form chemical bond
- 6) Heat of Adsorption is High and 40 - 200 kJ mol^{-1}
- 7) High Activation Energy

Explanation :- In physical Adsorption, Van der Waals Forces present which are weaker than chemical / valance bond and Hence physical adsorption is relatively weak and have low activation Energy.

*** Heat of Adsorption / Molar Enthalpy of Adsorption :-**

→ It is amount of heat released when 1 mole of Adsorbate (Gas or liquid) is adsorbed on surface of Adsorbent.

*** Adsorption Isotherm :-**

→ It is graph of amount of solute adsorbed against the pressure or conc.ⁿ of solute at constant temperature

→ It can also be defined as mathematical relation between the amount adsorbed and pressure or conc.ⁿ at constant temperature.

*** Important :-** physical Adsorption occurs only at low temperature and extent of physical adsorption increases with decrease in temperature, while chemical Adsorption occurs at all temperature and extent of adsorption increases with increase in temperature.

*** Gibbs Free Energy and Adsorption :-**

→ Adsorption is exothermic i.e. when adsorption take place, surface energy decreases

→ When Adsorption take place, entropy (ΔS) decrease because randomness / disorder of Adsorbate and Adsorbent decreases

$$\rightarrow \Delta H = -ve \quad \text{and} \quad \Delta S = -ve$$

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &= -ve - T(-ve) \end{aligned}$$

$$\Delta G = -ve + ve$$

But for spontaneous process, $\Delta G = -ve$ i.e. < 0
Hence, it is evident that ΔH should be have
sufficiently high negative value to make
($\Delta H - T\Delta S$) negative

→ With increase in Temp., Adsorption ↓ and Hence
 ΔH becomes less and less negative and at
one stage, $\Delta H = T\Delta S$

Then, $\Delta G = 0$

→ Equilibrium attained

* Examples of Adsorption :-

- Activated charcoal is use in gas masks to adsorb toxic gases and vapours.
- Animal charcoal is used as decoloriser in the manufacture of cane sugar
- Adsorption also plays important role in heterogeneous catalysis
- High vacuum can be created using cooled charcoal
- Silica and alumina gels are used as adsorbents to remove moisture

* Factors Affecting Adsorption :-

1) Nature of Adsorbent

2) Nature of Adsorbate

3) Temperature

4) Pressure

i) Nature of Adsorbent :-

→ Adsorption is surface phenomena and hence
Rate of Adsorption \propto Surface Area of Adsorbent

→ Finely divided substances are good adsorbents as they provide larger surface area for given mass

→ Rough surface area are good ~~As~~ Adsorbents than Smooth surface.

→ Activated Charcoal $>$ Charcoal

2) Nature of Adsorbate (Gas) :-

→ Easily soluble and easily liquifiable gases are adsorbed to greater extent than so called permanent gases

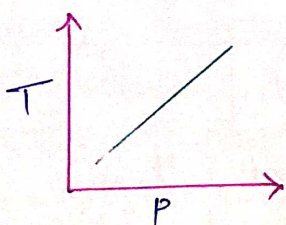
→ Easily liquifiable gas means having higher tendency to become liquid which in turn should have greater intermolecular force of attraction

→ Gases with high value of critical temperature, liquifies easily and hence adsorbed to greater extent

i.e. Adsorption \propto critical Temperature

→ Liquifiable Gases :- NH_3 , HCl , Cl , SO_2

Permanent Gases :- H_2 , N_2 , O_2

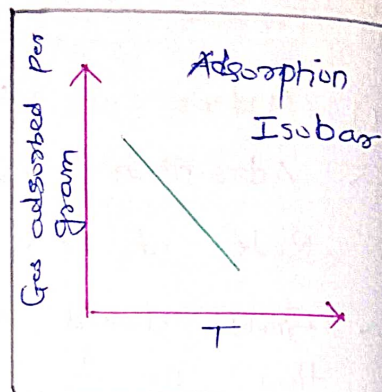


Curve showing variation of pressure and with Temperature for given amount of adsorption is called **Isostere** which is straight line

3) Temperature :-

→ Adsorption is an exothermic process, Acc. to Le-Chatelier principle, it is favoured at low temperature i.e.

$$\text{Adsorption} \propto \frac{1}{\text{Temperature}}$$



4) Pressure :-

Adsorption \propto Pressure

* **Desorption Activation Energy** :- Since adsorbed molecule has low binding energy, it may easily shake itself off the surface. This implies that such molecule will remain on surface for very short time before it desorbed. The rate constant for process of desorption is ;

$$k_{\text{desorption}} = A e^{-E_a/RT}$$

$$\frac{1}{k_{\text{desorption}}} = \frac{1}{A} e^{E_a/RT}$$

$$\tau = \tau_0 e^{E_a/RT}$$

where, τ = Life time, τ_0 = Pre-exponential Factor
 E_a = Desorption activation Energy of adsorbate

$$\ln \tau = \ln \tau_0 + \frac{E_a}{RT}$$

For two different Temperature

$$\ln \tau_1 = \ln \tau_0 + \frac{E_a}{RT_1}$$

$$\ln \tau_2 = \ln \tau_0 + \frac{E_a}{RT_2}$$

$$\ln \left(\frac{\tau_2}{\tau_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

τ_2 = Life time of adsorbed species at T_2

τ_1 = Life time of adsorbed species at T_1

* Freundlich Adsorption Isotherm *

→ Extent of Adsorption of gas per unit mass of Adsorbent is related to pressure of gas.

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

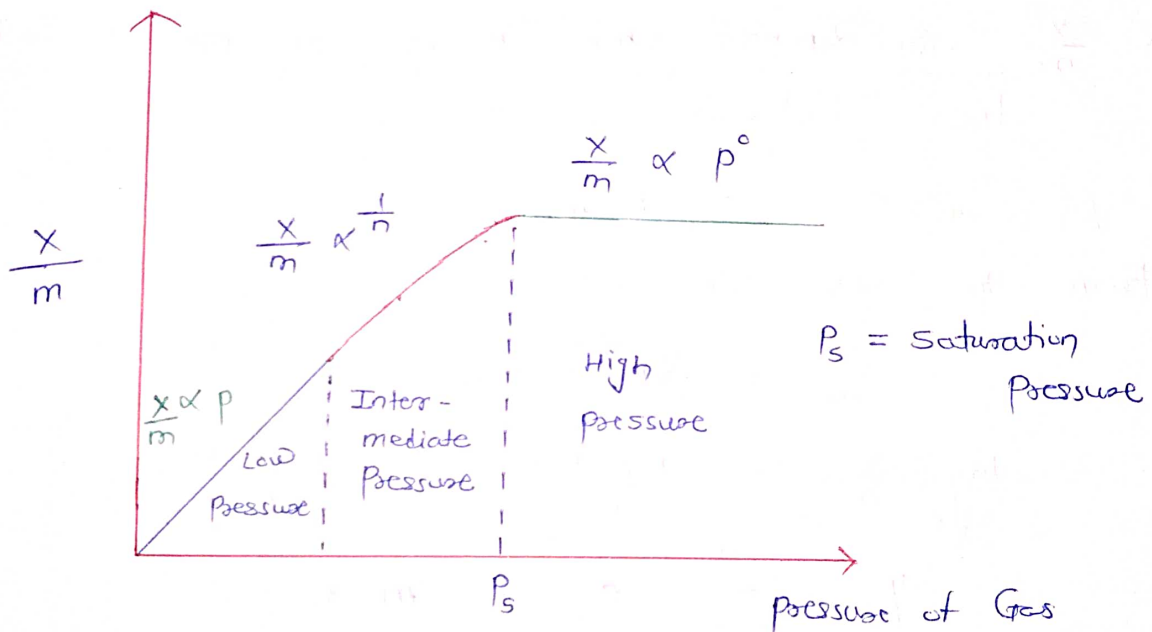
Where, x :- Amount of Adsorbate

m :- Mass of Adsorbent

n :- Integer

p :- Pressure of Gas

$\frac{x}{m}$ is extent of Adsorption i.e. Amount of Gas Adsorbed.



At saturation pressure (P_s) :-

- i) Amount of Gas Adsorbed = Amount of Gas desorbed
- ii) The extent of Adsorption becomes constant even though the pressure is increased. This state also called as saturation pressure.

* Analysis of Isotherm :-

i) At low pressure :-

$$\frac{x}{m} \propto p \Rightarrow \frac{x}{m} = kp$$

$$\Rightarrow \text{slope} = k$$

} Graph is straight line passes through origin

2) At high pressure :-

$$\frac{x}{m} \propto p^0 \Rightarrow \frac{x}{m} = kp^0 \Rightarrow \frac{x}{m} = k$$

⇒ Extent of Adsorption is independent on pressure

⇒ Graph is parallel line to x-axis (i.e. pressure)

3) At Intermediate Pressure :-

$$\frac{x}{m} \propto p^{\frac{1}{n}} \Rightarrow \frac{x}{m} = kp^{\frac{1}{n}} \quad (n \text{ is integer})$$

→ n depends on Adsorbate and Adsorbent

$$1 < n < \infty$$

$$\Rightarrow 1 < \frac{1}{n} < 0$$

⇒ $\frac{x}{m}$ will depends upon power of pressure which lies between 0 to 1

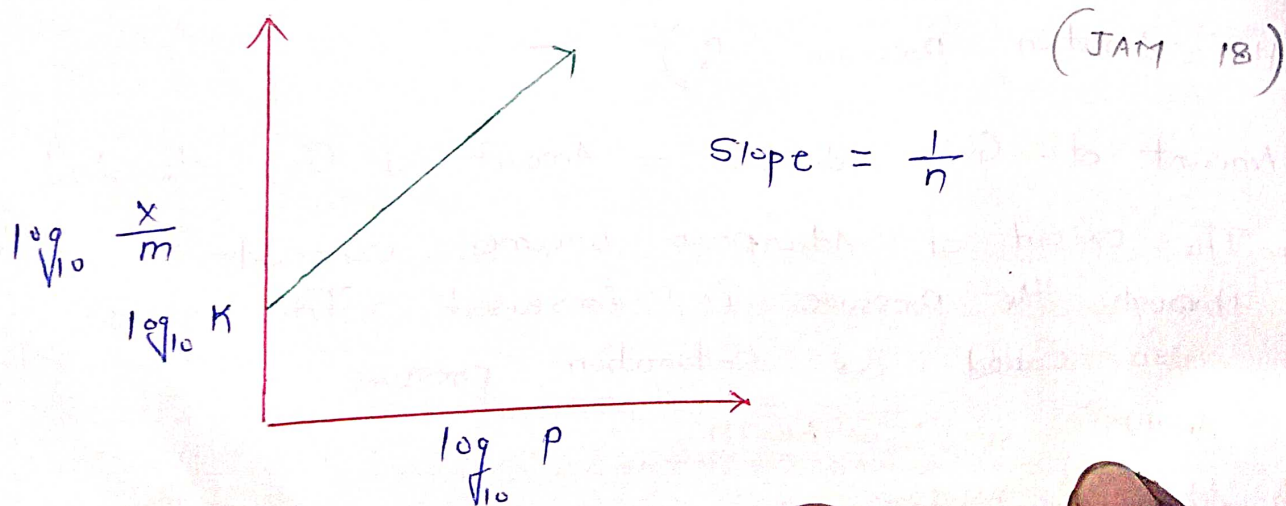
* Verification of Isotherm :-

From the Graph, we get

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

$$\log_{10} \frac{x}{m} = \log_{10} k + \frac{1}{n} \log_{10} p$$

$$y = c + mx$$

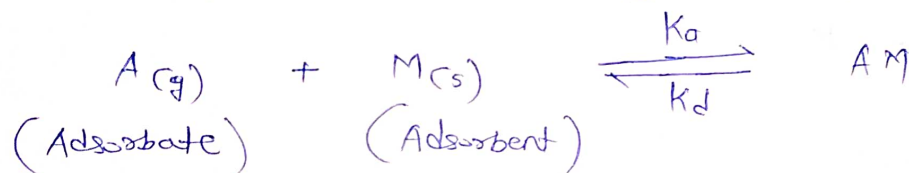


* Langmuir Adsorption Isotherm *

→ Langmuir proposed his theory of Adsorption of Gas on Surface of Solid.

→ It is based on following consideration ;

- 1) In adsorption, formation of monolayer of Adsorbed (i.e. Gas) molecule takes place.
- 2) All Adsorption sites are equivalent and Gas molecule adsorbed on any one site of Adsorbent (i.e. solid surface) and independent on whether neighbouring site is occupied or not.
- 3) He assumes that dynamic equilibrium exists between Adsorbed molecule and Free molecule.



where k_a = Rate constant for Adsorption
 k_d = Rate constant for Desorption

→ Rate of Adsorption is directly proportional to ;

- a) Pressure of Gas Molecule (P_A)
- b) Available Sites

Consider, there are total N sites present on surface

$$\theta = \frac{\text{Site occupied}}{\text{Total site}}$$

where, θ = Fraction of sites occupied by Gas molecule

$$\text{Site occupied} = \theta N$$

$$\text{Available site} = N - N\theta$$

$$\text{But } \theta \approx \frac{x}{n} = \text{Rate of Adsorption}$$

$$\text{Hence R.O.A.} \propto P_A \cdot (N - N\theta)$$

$$R.o.A. = K_a [P_A N (1-\theta)]$$

Now, Rate of Desorption \propto Site occupied

$$R.o.D. \propto N\theta$$

$$R.o.D. = K_d N\theta$$

Now, at equilibrium,

$$R.o.A = R.o.D$$

$$K_a [P_A N (1-\theta)] = K_d N\theta$$

$$\frac{K_a}{K_d} \frac{(1-\theta)}{\theta} = \frac{1}{P_A}$$

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

$$\frac{1-\theta}{\theta} = \frac{1}{K P_A}$$

$$\frac{1}{\theta} - 1 = \frac{1}{K P_A}$$

$$\frac{1}{\theta} = \frac{1}{K P_A} + 1$$

$$\frac{1}{\theta} = \frac{1 + K P_A}{K P_A}$$

$$\theta = \frac{K P_A}{1 + K P_A}$$

Langmuir
Adsorption
Isotherm

$$\frac{x}{y} = \theta = \frac{K P_A}{1 + K P_A}$$

$$\theta = \frac{K_a P_A}{1 + K_b P_A}$$

$$\theta = \frac{A P}{1 + B P}$$

Different
Forms
of Writing

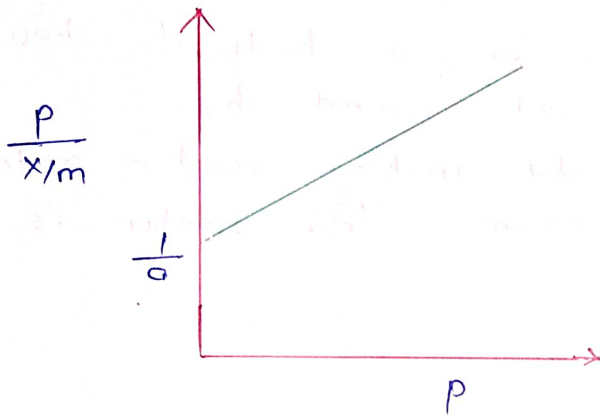
$$\frac{x}{m} = \frac{ap}{1 + bp}$$

where a, b are constant and depends on ;

- i) Nature of Adsorbate Gas
- ii) Nature of Adsorbent
- iii) Temperature

$$\frac{x/m}{p} = \frac{a}{1 + bp}$$

$$\frac{p}{x/m} = \frac{1}{a} + \frac{b}{a} p$$

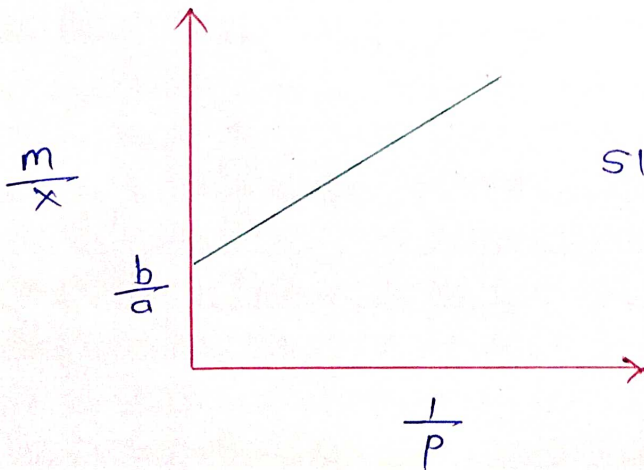


$$\text{slope} = \frac{b}{a}$$

Alternatively,

$$\frac{m}{x} = \frac{1 + bp}{ap}$$

$$\frac{m}{x} = \frac{1}{ap} + \frac{b}{a}$$



$$\text{slope} = \frac{1}{a}$$

* Langmuir Isotherm :-

$$\theta = \frac{K P_A}{1 + K P_A}$$

- i) At low pressure ; ii) At high pressure ;
 $K P_A \ll 1$ $K P_A \gg 1$

$$\theta = K P_A$$

$$\theta = 1 = (P_A)^0$$

i) At low pressure, the fraction of molecule surface covered is directly proportional to partial pressure of Gas. This behaviour corresponds to First order reaction.

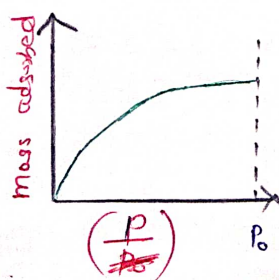
ii) At high pressure, the value of θ tends to become unity i.e. entire surface gets covered by monolayer of gas and thereby making reaction rate independent of partial pressure. This reaction is zero-order.

* B.E.T. Equation *

- There are 5 different types of isotherms are obtained for different gases and solid adsorbents.
- out of which type I is Langmuir isotherm which is based on formation of monolayer
- Remaining 4 adsorption isotherms are based on formation of multilayers of adsorbed molecules on surface of adsorbent.

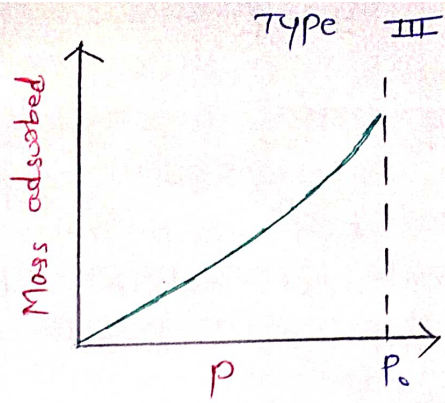
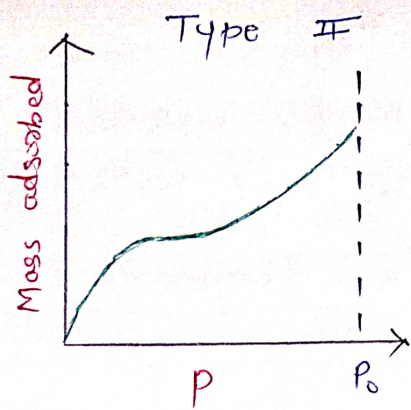
* Postulates of B.E.T. equation :-

- 1) Formation of multilayer of adsorbed molecules.
- 2) Adsorption reaches stage of equilibrium for each layer of adsorbed molecules.
- 3) The first layer of adsorbed molecules differs from the rest as it is in direct contact with the surface.
- 4) Heat of adsorption of first layer is different from the rest, as the layer is in direct contact with surface.
- 5) All other layers of adsorbed molecules are identical in every aspect.
- 6) Heat of adsorption of all subsequent layers will be same and is equal to that heat of condensation of gas to liquid.

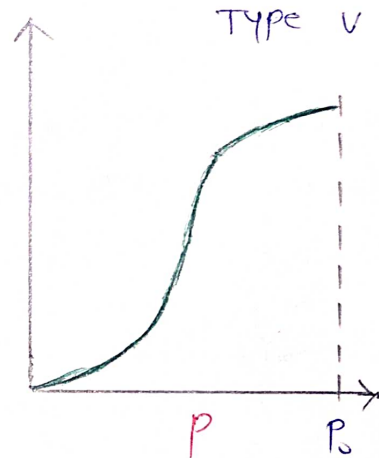
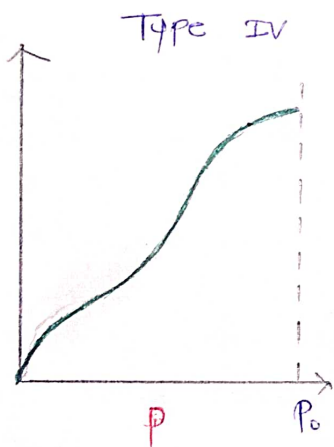


Type I

- Langmuir adsorption isotherm
- $P_0 =$ Saturation pressure
- Monolayer formation



- Type II and III show large deviation from Langmuir model.
- The amount of adsorption keeps on increasing in each case with rise in pressure.
- This leads to formation of additional layers which cause formation of multilayers.
- However for type II, formation of monolayer capacity can be observed but for type III it can't be observed.

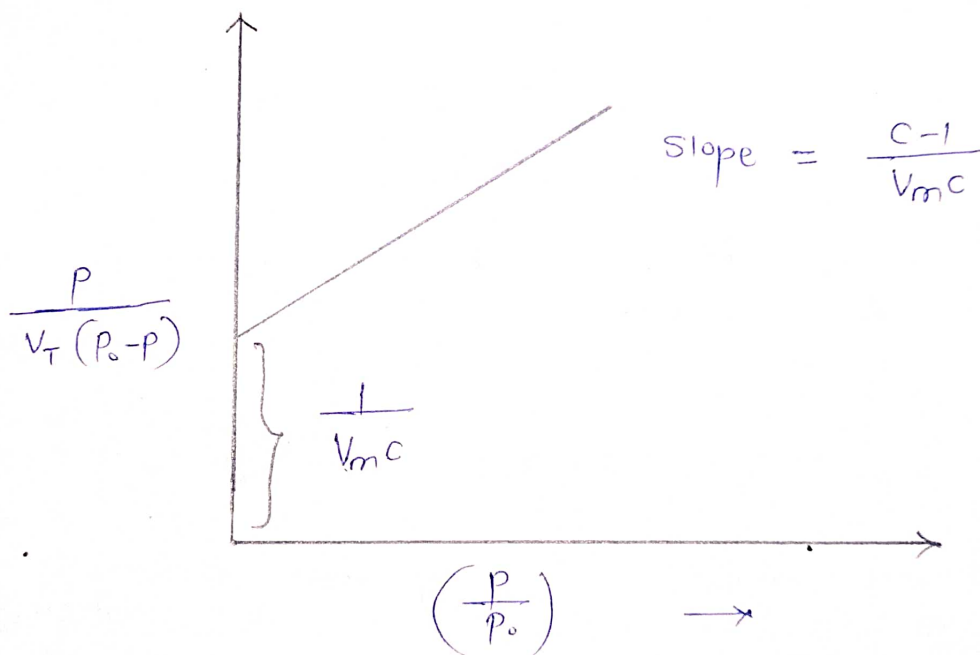


- Type IV and V show similar trend. In both cases amount of adsorption keep increasing with increase in pressure.
- However, there is not only formation of multilayers take place but also condensation of some of the gas molecule take place which is called as capillary condensation of gas.

⇒ A single expression is able to account for four different types of isotherms due to different value of constant c , which is difference b/w heat of adsorption of first layer and heat of condensation of gas.

$$\frac{P}{V_T(P_0 - P)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} \left(\frac{P}{P_0} \right)$$

where, V_T :- Volume of gas adsorbed at pressure P
 V_m :- Volume of gas required for formation of monolayer.
 P_0 :- Saturation pressure
 c :- Diff. b/w. H.o.A. and H.o.C.



→ B.E.T. eqⁿ is used to determine surface area of adsorbent and volume of gas required to cover formation of monolayer.

$$\rightarrow \text{Slope} + \text{Intercept} = \frac{c-1}{V_m c} + \frac{1}{V_m c}$$

$$\begin{aligned} \text{Slope} + \text{Intercept} &= \frac{1}{V_m} \\ \frac{1}{V_m} &= \frac{\text{Slope} + \text{Intercept}}{\rightarrow} \end{aligned}$$

$$V_m = \frac{1}{\text{Slope} + \text{Intercept}}$$

From above eqⁿ, we can determine the volume of Gas required for formation of monolayer.

* Determination of Surface area :-

$$\text{Surface area of adsorbent} = \text{No. of molecules required for formation of monolayer} \times \text{Area of cross section of molecule (A)}$$

$$\rightarrow \text{No. of moles of Gas} = \frac{PV_m}{RT}$$

$$\text{No. of molecules of Gas} = \frac{PV_m}{RT} \times N_A$$

$$\rightarrow \text{Surface area of Adsorbent} = \left(\frac{PV_m}{RT} \times N_A \right) \times (A)$$

9. The volume of N_2 gas measured at STP required to form complete monolayer on sample of silica gel is $129 \text{ cm}^3 \text{ g}^{-1}$. Calculate surface area per gram of silica gel if each Nitrogen molecule occupies $16.2 \times 10^{-20} \text{ m}^2$.

$$\rightarrow V_m = 129 \text{ cm}^3 \text{ g}^{-1} = 0.129 \text{ dm}^3 \text{ g}^{-1}$$

$$\text{At STP, } P = 1 \text{ atm} \quad V = 22.4 \text{ dm}^3, \quad T = 298$$

$$A = 16.2 \times 10^{-20} \text{ m}^2$$

$$\begin{aligned} \rightarrow \text{Surface area} &= \frac{PV_m}{RT} \times N_A \times A \\ &= \frac{1 (0.129)}{0.082 \times 298} \times 6.022 \times 10^{23} \times 16.2 \times 10^{-20} \\ &= 560 \text{ m}^2 \text{ g}^{-1} \end{aligned}$$