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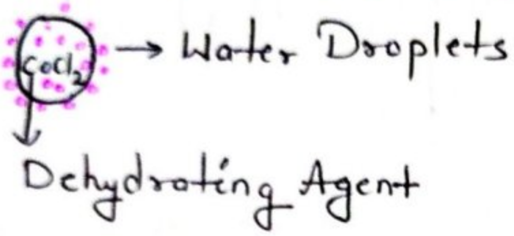
# Surface chemistry

**Introduction:-** Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface is represented by seperating the bulky phase by hypen or a slash.

**Absorption:-** When gas or liquid particle get absorb uniformely at the bulk of the solid

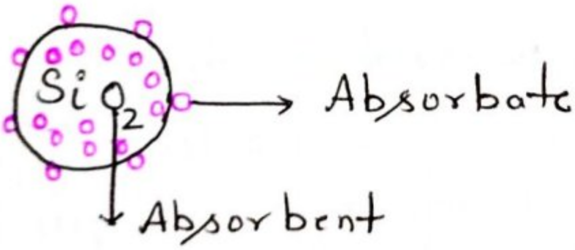
Ex- Tea - Biscuit, Gulab Jamun, chalk in water

Ex:-



**Some Dehydrating Agent:-** $P_2O_5$, $H_3PO_4$, $CaO$, $CaCl_2$, $H_2SO_4$

**Adsorption:-** When concentration of liquid or gas particle are more on interfaces (surface) than bulk then the phenomena is called adsorption.



**De-Adsorption:-** Reverse phenomena of Adsorption is called de-adsorption.

**Sorption:-** When both Adsorption or Absorption both takes simultanousely.

Ex:- cotton dippen in Ink.

**Examples of Adsorption:-**

Activated charcal, Silica Gel, Alumina Gel etc --

bsorbent :- The substance which ABSORBS

Absorbate :- The substance which is being ABSORBED

Ex- silica Gel, charcol Gel, Activated charcal etc.

Types of Adsorption :- These are two types

(1) Positive Adsorption :- If concn of absorbate is more at the surface as compared to its concn in the bulk phase

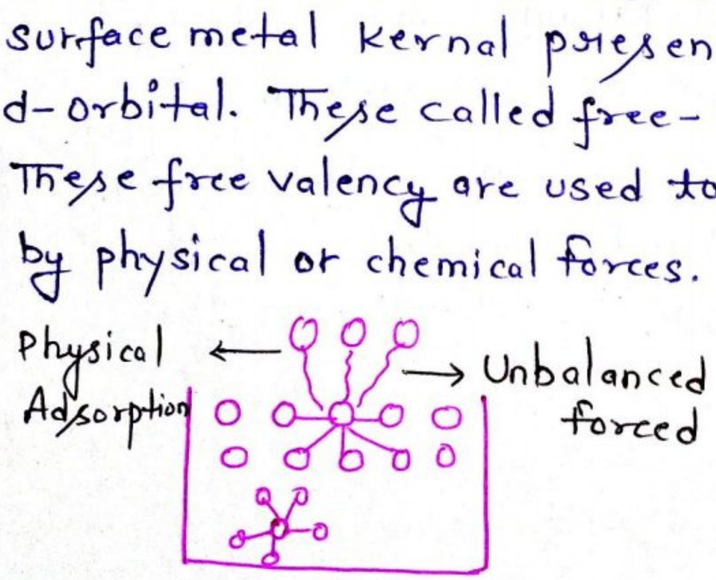
$$\boxed{C_S > C_B}$$

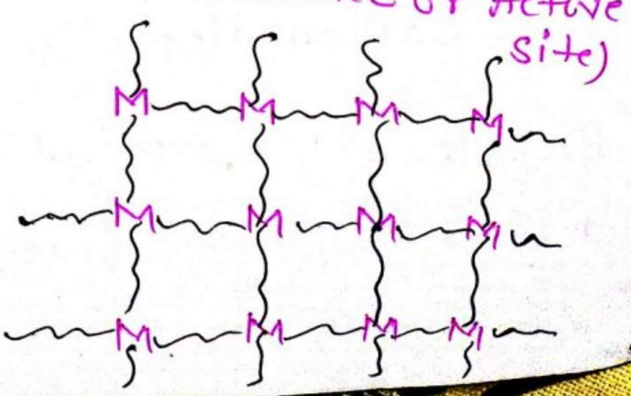
(2) Negative Adsorption :- If concn of adsorbate is less in the surface layer then in the bulk phase.

$$\boxed{C_B > C_S}$$

Mechanism of Adsorption :-

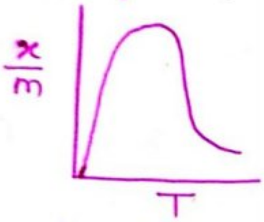
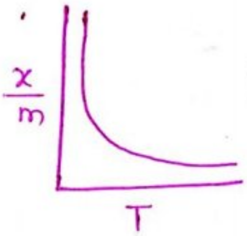
Molecule or Atom present at the surface of the adsorbent have unbalence force, this unbalence force balence by the particle of absorbate through physical interaction like H-bonds or Von-Der walls force. In case of metallic surface metal kernal present at surface have incomplete d-orbital. These called free-valency or Active site, These free valency are used to bind absorbate molecule by physical or chemical forces.





Occulation :- Gas Absorbed on metal surface.

# Classification of Adsorption on the basis of interaction b/w the Absorbate & Absorbent :-

| Chemical Adsorption | Physical Adsorption |
|---|---|
| 1. It is specific in nature | It is non-specific in nature |
| 2. Reversible in nature | Reversible in nature |
| 3. High Entholphy of Adsorption | Low Enthalpy of Adsorption |
| 4. Need of Activation Energy | No Need of Activation Energy. |
|  |  (At constant P) |
| 5. Covalent Bonds | Hydrogen bonds, Van Derwall forme |

Note :-

Extant Adsorption $= \frac{x}{m}$

Whrer $x =$ Amount of Absorbate
$m =$ Amount of Absorbent

Factor Affecting of Adsorption :-

1. Nature of Adsorbate :-

Extant of Adsorption depend on the ease of the liquification of absorbate [or absorbing Gases]

Extant of Adsorption $\propto$ Inter particle forces (H. Bonding)
$\propto T_c = \frac{3}{2} T_b$ [Goldbarg Rule]
$\propto$ Ease of liquification
$\propto$ Molecular Weight

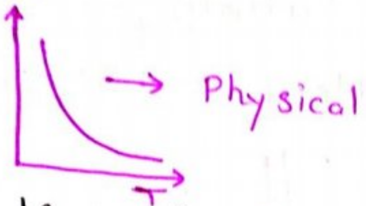
$H_2O > SO_2 > NH_3 > CO_2 > O_2 > N_2 > H_2$

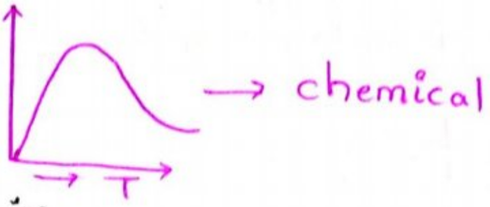
(2) Nature of Adsorbent:-

Extant of Adsorption is directly proportional to the surface Area.

collidal solⁿ > Powder > solid

(3) Effect of Temp:- Physical adsorption favourable at Low temp. chemical adsorption changes firstly incresing on incresing T then starts to decrease.





## Application of Adsorption :-

1. A very good method to creating a high vacum is to connect a bulb of charcol cooled in liquid air to vessel which has already been exhasuted as far as possible by a vacom pump. since the magnitude of adsorption at such low temp. is quite high, the remaining traces of air, in spite of the low presssure, are absorbed by the charcoal almost completely.

2. Activated charcoal is used in gas masks in which all toxic gases and vapours are absorbed by the charcoal while pure air passes through it pores practically unchanged.

3. Silica And alumina gels are used as adsorbents for removing moisture and for controlling humidity of rooms.

4. Animal charcol (Bone charcoal) used as a decoloriser in the manufacturing of cane sugar.

5. Adsorption also plays an important role in hetrogeneous catalysis, Ex- The role of finely divided in iron in the manufacture of ammonia and that of finely divided in the hydrogenation of oils.

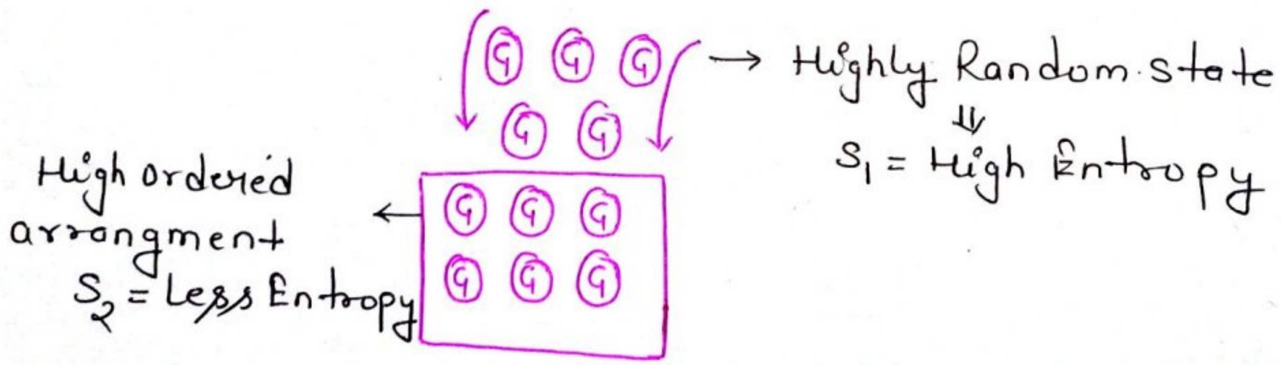
6. Different inert gas are adsorbed to different extents on cocunut charcoal.

7. Many dyes have become useful due to adsorption. These dyes have been introduced as indicators especially in precipitation titrations. Ex – KBr is easily titrated with $AgNO_3$ using eosin as the indicator.

8. The selective adsorption of some adsorption of some substances by a solution helps us seperate components of a mixture. Ex – All the dyes in ink.

9. Some drugs can adsorb the germs on them and hence kill them saving us from disease.

Thermodynamics of Adsorption:-



$$\therefore \text{change Entropy} = (S_2 - S_1) \quad (S_1 > S_2)$$
$$= -ve$$

* Adsorption is an Exothermic process than change in Enthalpy = –ve

* For spontaneous the free energy $(\Delta G) = -ve$

From Gibbs Helmhotz Eq :-

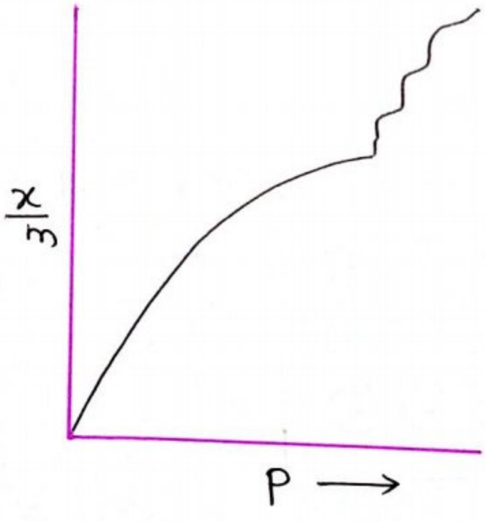
$$\text{Useful Work done} \leftarrow \underset{\downarrow\ -ve}{\Delta G} = \overset{\text{Total Energy}}{\underset{\downarrow\ -ve}{\Delta H}} - \underset{\downarrow\ -ve}{T\Delta S} \rightarrow \text{unavilable Energy}$$

## Adsorption Isotherm :-

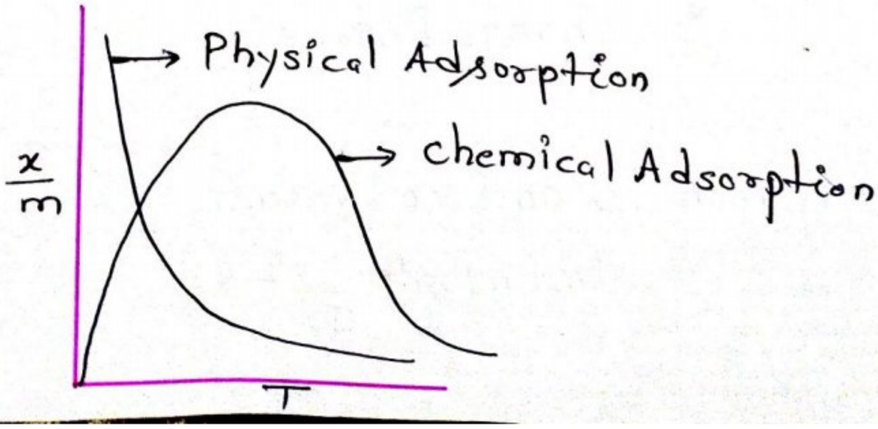
In Adsorption Isotherm three are three variable

1. $\frac{x}{m}$ = Extant Adsorption [x gm adsorbate absorb m gm of adsorbent]
2. P = Pressure
3. T = Temperature

Graph plotted b/w the x/m and P at constant temp called isothermal.

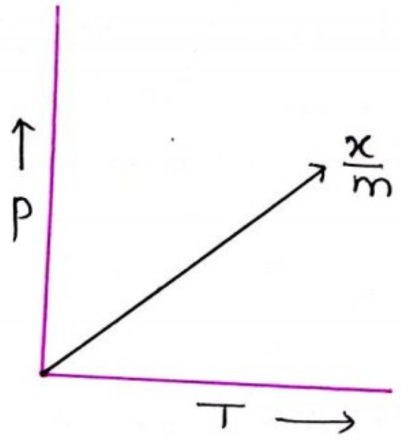


## Isobar :-



Graph b/w the $\frac{x}{m}$ and T at constant P.

Iso: Graph plotted b/w P and v at constant $\frac{x}{m}$ called isoter.



## Freundlich Isotherm:-

It gives an empirical relation b/w the x/m and pressure at const. Temp for a physical Adsorption. This ~~is~~ relation given as,

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

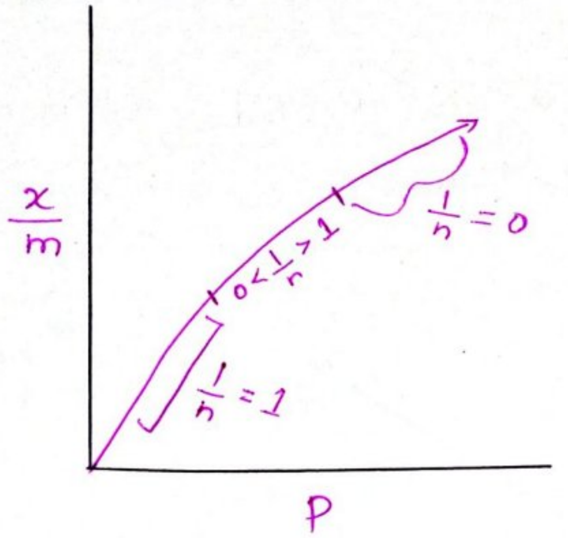
$$\boxed{\frac{x}{m} = k\, p^{1/n}}$$

If $1/n = 0$

$$\boxed{\frac{x}{m} \propto p^{0}} \longrightarrow$$ (order of Rec$^n$ is zero)

If $1/n = 1$

$$\boxed{\frac{x}{m} \propto p^{1}} \longrightarrow$$ (order of Rec$^n$ is one)

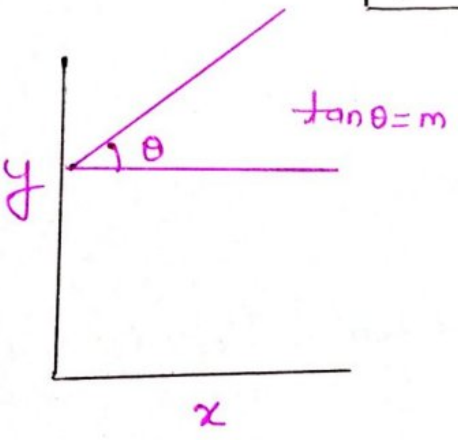


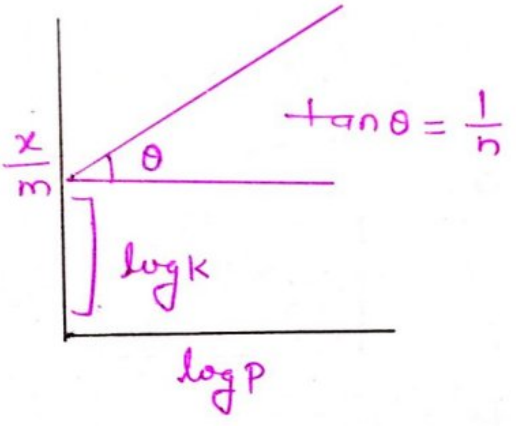
| P | order |
|---|---|
| High | 0 |
| Low | 1 |

Taking log of both sides of $\frac{x}{m} = kP^{1/n}$

$$\underbrace{\log\frac{x}{m}}_{y} = \underbrace{\log K}_{c} + \underbrace{\log P^{1/n}}_{mx}$$

$$\boxed{y = mx + c}$$





## The Langmuir Theory of Adsorption:-

In 1916 Irwing Langmuir proposed another adsorption isotherm which explain the variation of extant of adsorption with pressure. Based on his theory he derived Langmuir equation, which depicted a relationship between the no. of active site and pressure.

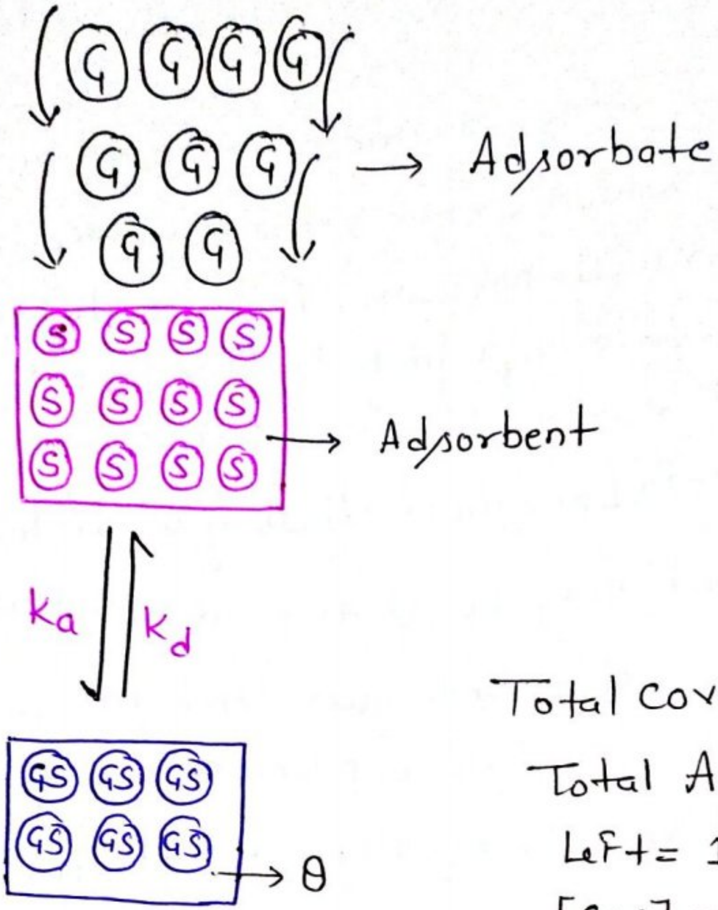
Postulate of Langmuir theory all listed below :-

1. Adsorbent surface at fix no of Active sites.
2. All active sites are equivalent in respect of their size, volume and adsorption capacity.
3. Each active site equally proable for adsorption.
4. One active site occupy one molecules and adsorb molecules are independent from neighbouring sites
5. According to the Langmuir adsorption is an mono-layer adsorption.
6. Adsorption and De- Adsorption process exists in dynamic Equilibrium.

Dynamic Equilibrium :- वह Equilibrium जब दो process होते भी रहे और पता भी ना चले।

7. Each Active sites produce same amount of enthalpy of adsorption.

Derivation of Langmuir $Eq^n$ of Monoatomic gas:-



Total coverage $= \theta$

Total Area $= 1$

Left $= 1-\theta$

$[gas] = P$

Where $k_a \rightarrow$ Rate constant of Adsorption (Depend vacant sites)

$k_d \rightarrow$ " " " De-Adsorption (Depends on occupied sites)

$$G + S \underset{k_d}{\overset{k_a}{\rightleftharpoons}} GS$$

From Rate Law

$$r_a \propto [G][S] \Rightarrow r_a = k_a [G][S] = k_a P(1-\theta) \text{ — ①}$$

$$r_d \propto [G][S] \Rightarrow r_d = k_d [GS] = k_d \theta \text{ — ②}$$

At Equilibrium, $r_a = r_d$

$$k_a P(1-\theta) = k_d \theta$$

[From eqn (1) & eqn(2)]

$$\frac{k_a}{k_d} = \frac{\theta}{P(1-\theta)}$$

Here

$K = \frac{k_a}{k_d}$ = Molar cofficient or Langmuir cofficien

$$K = \frac{\theta}{P - P\theta}$$

$$K.P - KP\theta = \theta$$

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

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

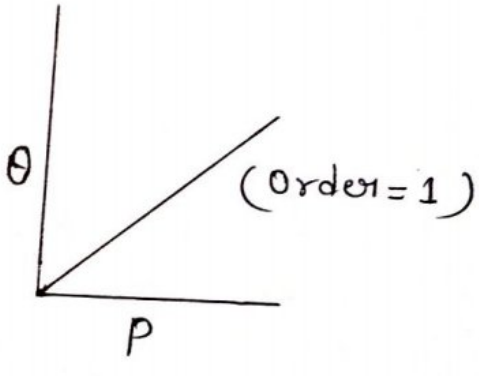
(The above Eq$^n$ Represent Langmuir Equation)

Case I:- At low pressure

$Kp << 1$ ∴ $1 + Kp \simeq 1$

$$\theta = Kp$$

$$\boxed{\theta = K(P)^1}$$



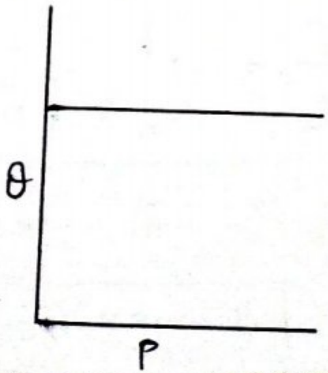
case II:- At high Pressure

$KP >> 1$ ∴ $1 + Kp \simeq Kp$

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

$$\boxed{\theta = P^0}$$

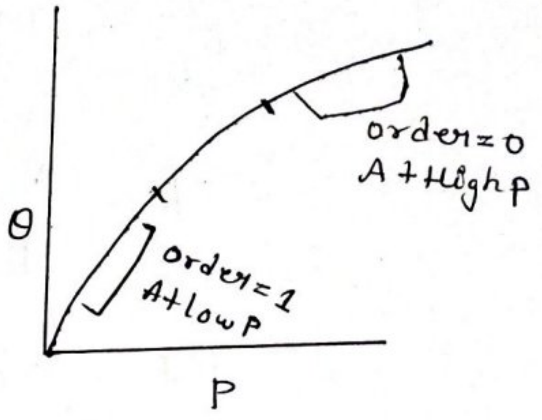
(Order = zero)



## Case III – At Modrate Pressure

$$1 \simeq Kp$$

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



Another form of Langmuir Equation:-

θ is written as

$$\theta = \frac{V_a}{V_m}$$

$V_a$ → Adsorbate volume at normal P

$V_m$ → Volume of coverage at high P

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

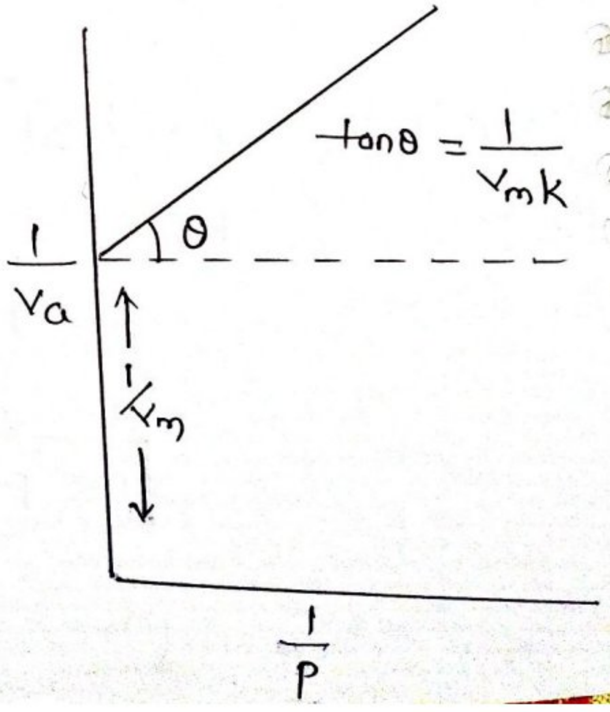
$$\frac{1+Kp}{V_m} = \frac{Kp}{V_a}$$

$$\frac{1}{V_m} + \frac{Kp}{V_m} = \frac{Kp}{V_a}$$

$$\frac{1}{V_m Kp} + \frac{1}{V_m} = \frac{1}{V_a}$$

$$\underset{\substack{\downarrow \\ y}}{\frac{1}{V_a}} = \underset{\substack{\downarrow \\ m}}{\frac{1}{V_m K}} \underset{\substack{\downarrow \\ x}}{\left(\frac{1}{P}\right)} + \underset{\substack{\downarrow \\ c}}{\frac{1}{V_m}}$$

$$\boxed{y = mx + c}$$



Desociative Langmuir Isotherem (M.Imp) for Di-atomic gas molecule:-

$$G_2 + 2S \underset{k_d}{\overset{k_a}{\rightleftharpoons}} 2GS$$

Here
$$r_a = [G_2][S]^2 = k_a P(1-\theta)^2$$

$$r_d = [GS]^2 = k_d(\theta)^2$$

At Equilibrium

$$r_a = r_d$$

$$\therefore k_a P(1-\theta)^2 = k_d \theta^2$$

$$\frac{k_a}{k_d} = k = \frac{\theta^2}{P(1-\theta)^2}$$

$$kp = \frac{\theta^2}{(1-\theta)^2}$$

$$\sqrt{kp} = \frac{\theta}{1-\theta}$$

$$\sqrt{kp} - \sqrt{kp}\,\theta = \theta$$

$$\theta(1+\sqrt{kp}) = \sqrt{kp}$$

$$\theta = \frac{\sqrt{kp}}{1+\sqrt{kp}}$$

$$\boxed{\theta = \frac{(kp)^{1/2}}{1+(kp)^{1/2}}}$$

If gas molecule have n atom,

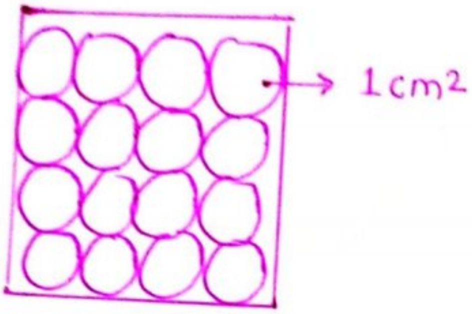
$$\boxed{\theta = \frac{(Kp)^{1/n}}{1+(Kp)^{1/n}}}$$

Limitations of Langmuir Adsorption:-

1. The adsorb gas has to have ideally in a vapour phase condition can be fully filled at low P conditions only. Thus langmuir adsorption valid only low P.
2. Langmuir eqn assumed that at adsorption is monolayer but at high condition, multi layerformation occur, it is explain by BET Theory.
3. Another assumption was that all the site on the solid surface are equal in size and shape and have equal iffinity of adsorbate molecule, that is the surface of solid is homogenous but we all know that in real adsorption is hetrogenous.
4. Langmuir eqn assumed that mole do not introact with each other this impossible work force of attraction exists of same type.
5. The adsorb mol to have is to localized, that is decrease in the randomness is zero.
6. This not possible because on adsorption liquification of gases also take place, which result increase in rondomness but the value is not zero ($\Delta S = -ve$)

# Determination of Surface Area of Absorbent Surface:-

The total surface Area can be determined from the No. of molecules in the monolayer volume and the surface were corresponding to the one molecule



Total surface Area = No. of molecules corresponding to complete monolayer coverage × Area occupied by one molecules —— ①

$$A = \pi \times r^2 \text{ —— } ②$$

$$1 \text{ Mole} = 22.4 \text{ lit.}$$
$(N_A)$

22.4 lit contains = $N_A$ molecules

$$1 \text{ lit.} = \frac{N_A}{22.4} \text{ Molecules}$$

$$\text{for } V_m \text{ lit} = \frac{V_m . N_A}{22.4} \text{ molecules}$$

$$\boxed{N' = \frac{N_A . V_m}{22.4} \text{ — } ③}$$

We know that

$$\rho = \frac{\text{Mass}}{\text{Volume}} = \frac{\text{Mass}}{\text{Volume occupied by 1 molecule} \times \text{No. of molecule} \times N_A}$$

$$\boxed{V = \frac{M}{N_A \times \rho}} \quad \text{—} \quad ④$$

If particle is sphere

$$V = \frac{4}{3}\pi r^3 \quad \text{—} \quad ⑤$$

From eqn ④ and ⑤

$$\frac{4}{3}\pi r^3 = \frac{M}{N \times \rho}$$

$$r^3 = \frac{3}{4\pi} \cdot \frac{M}{N \times \rho}$$

$$\boxed{r = \left[\frac{3}{4\pi} \cdot \frac{M}{N\rho}\right]^{1/3}} \quad \text{—} \quad ⑥$$

By first

$$A = \pi \left[\frac{3}{4\pi} \cdot \frac{M}{N\rho}\right]^{2/3} \quad \text{—} \quad ⑦$$

Put the value in eq ①

$$\boxed{\begin{aligned} T.S.A. &= A \times N \\ T.S.A. &= \left[\frac{N_A \cdot V_m}{22.4\,lit}\right] \pi \left[\frac{3}{4\pi} \cdot \frac{M}{N\rho}\right]^{2/3} \end{aligned}}$$

# Desorption Activation Energy:-

In case of physical adsorption the gaseous adsorbate molecule are weakly bonded on the solid adsorbate surface that is they have very low binding energy on the surface and therefore they can be easily remove from the surface. The amount of energy required to the cause the adesorption of Adsorbate molecules from the adsorbent surface is called desorption activation energy and it can be determine by Arhenius Equation-

$$K = A \cdot e^{-E_a/RT} \qquad \text{——} \quad ①$$

Where

$K$ = Rate constant of De$\overset{ad}{\wedge}$sorption

$(E_a)_D$ = Activation energy of deadsorption

$T$ = Temperature

$R$ = Gas constant $= 8.314 \times \frac{J}{mole\text{-}k} = 0.0821 \times \frac{L\,atm}{mole\text{-}k}$

$\frac{1}{K} = \tau$ = Times of Residential Adsorption = $sec^{-1}$

$$\frac{1}{A} = \tau_A$$

From the eq$^n$ ①

$$\frac{1}{K} = \frac{1}{A} \cdot e^{\frac{(E_a)_D}{RT}}$$

$$\tau = \tau_A \, e^{\frac{(E_a)_D}{RT}}$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \times \left[\frac{T_2 - T_1}{T_1 \times T_2}\right]$$

$$\log \frac{T_2}{T_1} = \frac{E_a}{2.303R} \times \left[\frac{T_2 - T_1}{T_1 \times T_2}\right]$$

[Liquification → Pressure → Temp. Low]

## BET Equation :-

The longmuir theorey of Adsorption is limited to the formation of monolayer of Adsorbate molecule on solid surface. This theory does not accept the posibilites the formation of monolayer.

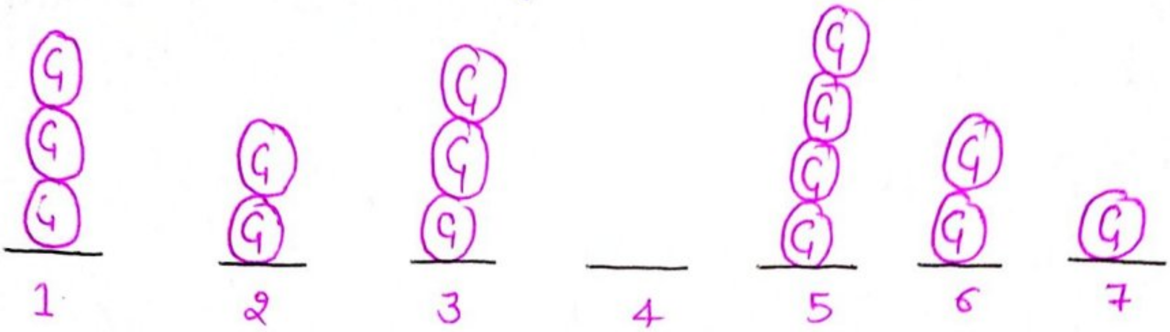
Brunour, Emett and Taellor in 1958 extended the longmuir concept to multilayer adsorption and proposed a theory known as BET.

After the investigate of these scientist the main postulate this theory given below:-

1. The adsorbate layer may be multilayer thickness.
2. Longmuir Assumptions are applicable to everylayer.
3. Rate of evaporation equal to the Rate of the condensation. → (गैस को liquid मे)
4. The Heat of adsorption in the first layer remains constant and heat of adsorption in proceeding layer is equal to heat of liquification of the gas. (गैस को liquid मे करना)
5. Rate of evaporation (Liquid → Vapour → B.P↓) from the first layer is equal to the rate condensation an proceeding layer.
6. condensation forces are principal forces in adsorption The surface area avilable for the $n^{th}$ layer is equal to the $(n-1)^{th}$ layer.
7. The surface of the solid has uniform localised sites and the adsorption at one site does not effect adsorption of the neighbour sites.

# Derivation of BET Equation :-

The formation of multilayer can be represent as -



(Solid ~~state~~ Adsorbent Surface)

$$S + G \rightleftharpoons GS \quad , \quad K_1 = \frac{[GS]}{[G][S]}$$

$$GS + G \rightleftharpoons G_2S \quad , \quad K_2 = \frac{[G_2S]}{[G][GS]}$$

$$G_2S + G \rightleftharpoons G_3S \quad , \quad K_3 = \frac{[G_3S]}{[G_2S][G]}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$G_{n-1}S + G \rightleftharpoons G_nS \quad , \quad K_n = \frac{[G_nS]}{[G_{n-1}S][G]}$$

Where

$G \rightarrow$ Unabsorbed gaseous molecule

$S \rightarrow$ Vacant sides on Adsorbent surface

$GS \rightarrow$ One gaseous molecule Adsorp persite

$G_2S \rightarrow$ Two " " " " "

$G_3S \rightarrow$ Three " " " " "

$G_nS \rightarrow$ n " " " " "

Let us assume

$S \propto \theta_0 \rightarrow$ Total coverage when no gas molecule Absorbed

$q_1 S \propto \theta_1$ → " " " one " " "

$q_2 S \propto \theta_2$ → " " " two " " "

$q_3 S \propto \theta_3$ → " " " three " " "

$q \propto p$ , so

$$K_1 = \frac{\theta_1}{P\theta_0}, \quad K_2 = \frac{\theta_2}{P\theta_1}, \quad K_3 = \frac{\theta_3}{P\theta_2}, \quad K_n = \frac{\theta_n}{P\theta_{n-1}}$$

$K_1$ will be maximum when the rest of the equilibrium constant because the force of attraction b/w the adsorbent surface and adsorbate molecule decrease very fastly at distance from the adsorbate surface increases.

$$K_1 >>> K_2 > K_3 > K_4 - - - - K_n$$

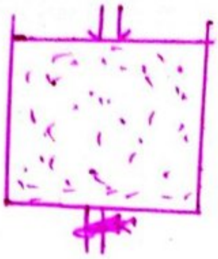
$$\begin{matrix} 1.00 & 0.19 & 0.18 & 0.11 \end{matrix}$$

$$\underbrace{K_2 = K_3 = K_4 = K5 = K_n = K_L}$$

$$K_1 >>>> K_L$$ , $K_L$ → Equilibrium Constant for Liquification

However all the other equilibrium constant $K_1, K_2, K_3 - - - - K_n$ are not exactly same but the difference b/w any two of them is very small, and due to this they are consider as equal to $K_L$.

$K_L$ can also be corelated with the equilibrium for the equilibrium in b/w the ~~substrate~~ vapour and liquid for the same gas which being absorbed.



$$\text{Saturated} \overset{k_L}{\rightleftharpoons} \text{Liquid}$$

$P_0$ = saturated vapour pressure

$$k_L = \frac{[\text{Liquid}]}{[\text{Sat. Vapour}]} = \frac{1}{P_0}$$

$$k_1 = \frac{\theta_1}{P\theta_0}, \quad k_2 = \frac{\theta_2}{P\theta_1}, \quad k_3 = \frac{\theta_3}{P\theta_2}, \quad k_n = \frac{\theta_n}{P\theta_{n-1}} \quad — ①$$

Now,

$$\theta_1 = k_1 P\theta_0$$

$$\theta_2 = k_2 \cdot P\theta_1 = k_L P k_1 P\theta_0 \quad [k_2 = k_3 = k_4 = k_L]$$

$$\theta_3 = k_3 \cdot P\theta_2$$

$$= k_3 P k_2 P \theta_1$$

$$= k_L P k_L P \cdot k_1 P\theta_0$$

$$= (k_L)^2 \cdot P^2 \cdot k_1 P\theta_0$$

$$= \left(\frac{P}{P_0}\right)^2 \cdot k_1 P\theta_0$$

$$\theta_n = (k_L P)^{n-1} \cdot k_1 P\theta_0 \qquad \left[k_L = \frac{1}{P_0}\right]$$

Two $$\theta_n = \left[\frac{P}{P_0}\right]^{n-1} \cdot k_1 P\theta_0 \quad — ②$$

Total coverage = 1

$$\theta_{total} = \theta_0 + \theta_1 + \theta_2 + \theta_3 + --- + \theta_n$$

$$= \theta_0 + \theta_1 + K_1 P\theta_0 + K_L P K_1 P\theta_0 + (K_L P)^2 K_1 P\theta_0 + (K_L P)^3 K_1 P\theta_1 + --- + (K_L P)^{n-1} K_1 P\theta_0 \quad ③$$

In eqn (3) We put $K_L = \frac{1}{P_0}$, We get

$$\theta_{total} = \theta_0 + K_1 P\theta_0 + \left(\frac{P}{P_0}\right) K_1 P\theta_0 + \left(\frac{P}{P_0}\right)^2 K_1 P\theta_0 + --- + --- \left[\frac{P}{P_0}\right]^{n-1} K_1 P\theta_0$$

$$\theta_{total} = \theta_0 \left[1 + K_1 P + K_1 P\left(\frac{P}{P_0}\right) + \left(\frac{P}{P_0}\right)^2 K_1 P + \left(\frac{P}{P_0}\right)^3 K_1 P + --- + \left(\frac{P}{P_0}\right)^{n-1} K_1 P\right]$$

$$\theta_{total} = \theta_0 \left[1 + K_1 P \left\{1 + \left(\frac{P}{P_0}\right)^1 + \left(\frac{P}{P_0}\right)^2 + \left(\frac{P}{P_0}\right)^3 + --- \left(\frac{P}{P_0}\right)^{n-1}\right]\right.$$

from Mathematics

$$(1-x)^{-1} = 1 + x + x^2 + x^3 + - - - + x^{n-1}$$

$$\theta_{total} = \theta_0 +$$

$$1 = \theta_0 \left[1 + \frac{K_1 P}{\left(1 - \frac{P}{P_0}\right)}\right]$$

$$\theta_0 = \frac{1}{1 + K_1 P\left(\frac{1}{1 - P/P_0}\right)} \quad ⑤$$

Now the total volume of Adsorb gas collect at STP will be given by

$$V_{total} = V_{mono}\left[\theta_1 + 2\theta_2 + 3\theta_3 + - - - + n\theta_n\right]$$

$$V_{total} = V_{mono}\left[k_1 P\theta_0 + 2K_L P K_1 P\theta_0 + 3(K_L P)^2 K_1 P\theta_0 + - - - + n\left[K_L P\right]^{n-1} K_1 P\theta_0\right]$$

Putting the value of $K_L = \frac{1}{P_0}$

$$V_{total} = V_{mono}\left[K_1 P\theta_0 + 2\left(\frac{P}{P_0}\right)^1 K_1 P\theta_0 + 3\left(\frac{P}{P_0}\right)^2 K_1 P\theta_0 + - - - + n\left(\frac{P}{P_0}\right)^{n-1} K_1 P\theta_0\right]$$

$$V_{total} = V_{mono}\left[K_1 P\theta_0\left[1 + 2\left(\frac{P}{P_0}\right) + 3\left(\frac{P}{P_0}\right)^2 + - - - - + n\left(\frac{P}{P_0}\right)^{n-1}\right]\right] \quad ⑥$$

From Mathematics

$$1 + 2x + 3x^2 + 4x^3 + - - - + nx^{n-1} = \frac{1}{(1-x)^2}$$

$$V_{total} = V_{mono} \times \frac{K_1 P\theta_0}{\left(1 - \frac{P}{P_0}\right)^2} \quad - ⑦$$

Now from eq$^n$ (5)

$$\theta_0 = \frac{1}{1 + K_1 P\left(\frac{1}{1 - P/P_0}\right)}$$

$$\theta_0 = \frac{1 - P/P_0}{1 + K_1 P - \frac{P}{P_0}}$$

Now from eq$^n$ (7)

$$V_{total} = \frac{V_{mono} \times K_1 P \times \dfrac{\cancel{\left(1-P/P_0\right)}}{1 + K_1 P - P/P_0}}{\cancel{\left(1-P/P_0\right)}\left(1-P/P_0\right)}$$

$$V_{total} = \frac{V_{mono} \times K_1 P}{\left(1 + K_1 P - \frac{P}{P_0}\right)\left(1 - \frac{P}{P_0}\right)} \quad \text{--- (8)}$$

On putting in this eq$^n$ $P = \frac{1}{K_L} \cdot \frac{P}{P_0}$

$$V_{total} = \frac{V_{mono} \times \left[\frac{K_1}{K_L} \cdot \frac{P}{P_0}\right]}{\left(1 - \frac{P}{P_0}\right) \cdot \left(\frac{K_1}{K_L} \cdot \frac{P}{P_0} - \frac{P}{P_0} + 1\right)}$$

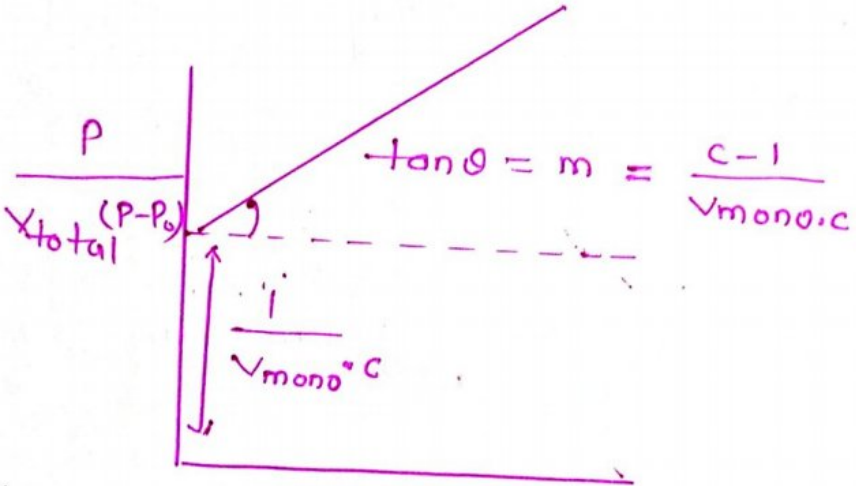
$$V_{total} = \frac{V_{mono} \times C \times \frac{P}{P_0}}{\left(1 - \frac{P}{P_0}\right) \cdot \left(C \cdot \frac{P}{P_0} - \frac{P}{P_0} + 1\right)} \quad \text{--- (9)}$$

Eq$^n$ (9) Known as another form of BET equation and eq$^n$ (9) can be written by the rearranging in the following manner.

$$\frac{P}{X_{total}(P_0-P)} = \frac{1}{X_{mono}\cdot C} + \frac{C-1}{V_{mono}\cdot C}\left(\frac{P}{P_0}\right) \quad — \text{⑩}$$

If we plot a graph b/w the $\left(\frac{P}{P-P_0}\right)$ Vs $\frac{P}{P_0}$ We get

$$\underbrace{\frac{P}{V_{total}(P-P_0)}}_{y} = \underbrace{\frac{C-1}{V_{mono}\cdot C}}_{m}\underbrace{\left(\frac{P}{P_0}\right)}_{x} + \underbrace{\frac{1}{V_{mono}\cdot C}}_{c}$$



Intersect $= \frac{1}{V_{mono}\cdot C}$

Slope $= m = \frac{C-1}{V_{mono}\cdot C}$

## Limitations of BET Equation:-

1. BET Equation is Failed a related pressure of $P/P_0$ of 0.005 and its also failed, Hence $P/P_0$ is above the point. $0.005 \le \frac{P}{P_0} \le 0.35$
2. The assumptions that the adsorbate the liquid property are not correct.

co-ordination of the molecule in the higher

# Temklin Isotherm:-

In longmuir isotherm it was assumed that all the adsorption sites are equally proable per this coverage, each site involve the constant amount of heat of adsorption, But in real deviation are absorbed inorder to account for the derivation of temklin suggests a new eqn

$$\theta = c_1 \ln (c_2 P)$$

$c_1$ & $c_2$ → Temklin Constant

$P$ → Pressure

$\theta$ → total coverage

Graph b/w $\theta$ and $c_2 P$