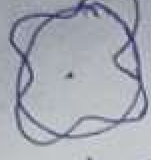
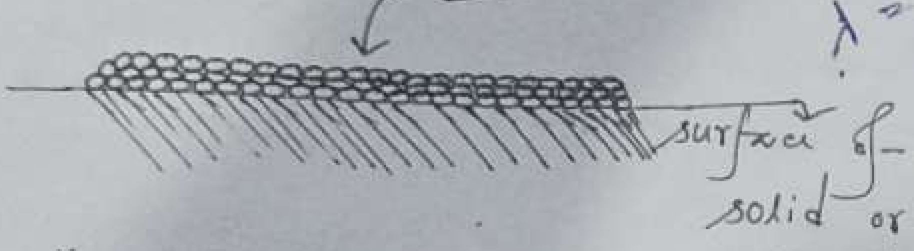
Adsorption phenomena

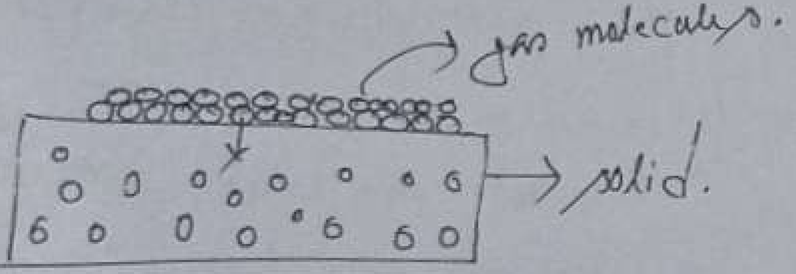


$\lambda = \frac{h}{mv}$

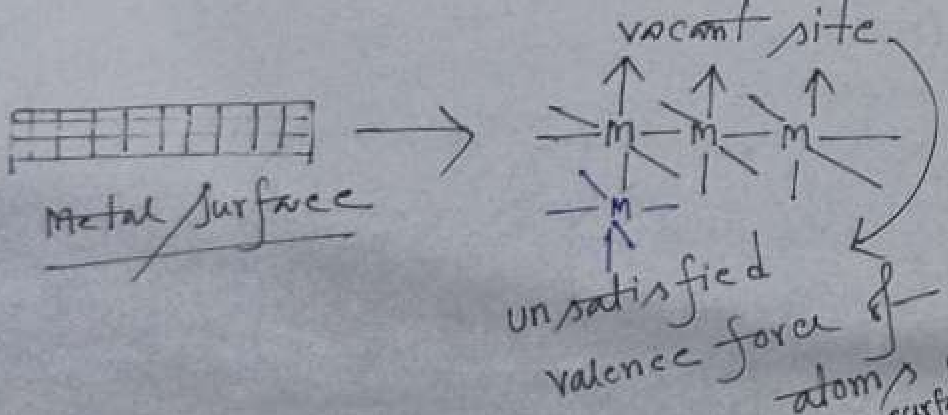


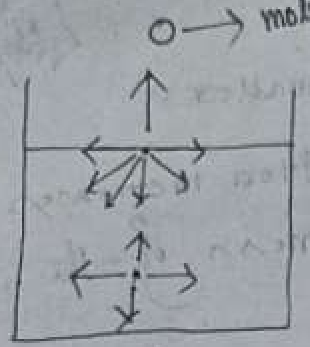
* Adsorption on solid or Liquid surface.

* Absorption: when the substance is not only retained on the surface but also passed through the surface into the bulk of a liquid or solid.



Why this phenomena happend.

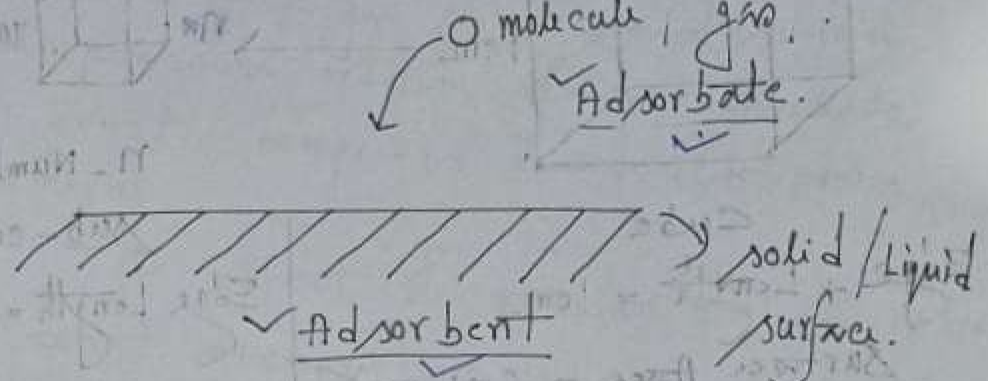




Liquid system.

✓ non-uniform distribution of molecules in both sides of surface.

✓ Residual force.



The affecting factors

i) The nature of the adsorbent and its subdivision →

ii) The nature of the adsorbate and its conc. and Pressure →

iii) Temperature →

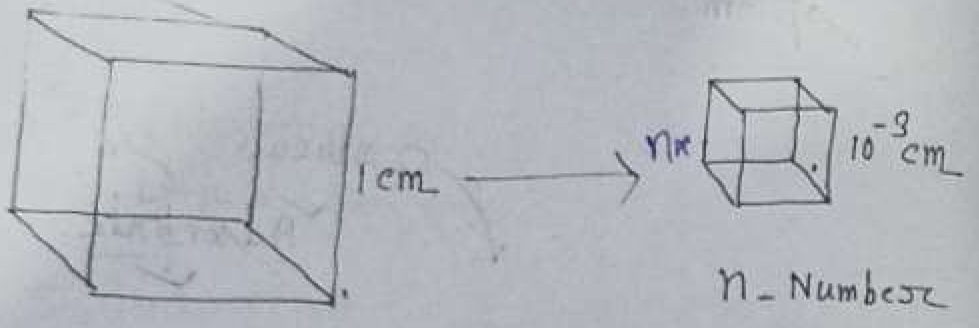
———— x ———— x ———— x ————

⟨i⟩ surface area of the adsorbent and residual force or active site.

More and more residual force or active site are created when the adsorbent size becomes more and more smaller.

Thus the extent of adsorption increases with the degree of fineness of the adsorbent particles.

example



sub-cube

cube

Edge - Length = 1cm

Surface Area = 6×1 cm^2

Edge Length = 10^{-3} cm

Surface Area = 6×10^{-6} cm^2 of each sub-cube

volume $1 = n \times (10^{-3})^3$

NO. of cubelets (sub-cube) $n = \frac{1}{(10^{-3})^3} = 10^9$

Total surface area

$= 10^9 \times 6 \times 10^{-6}$ cm^2

$= 6 \times 10^3$ cm^2

Due to degree of fineness, the surface area increase from

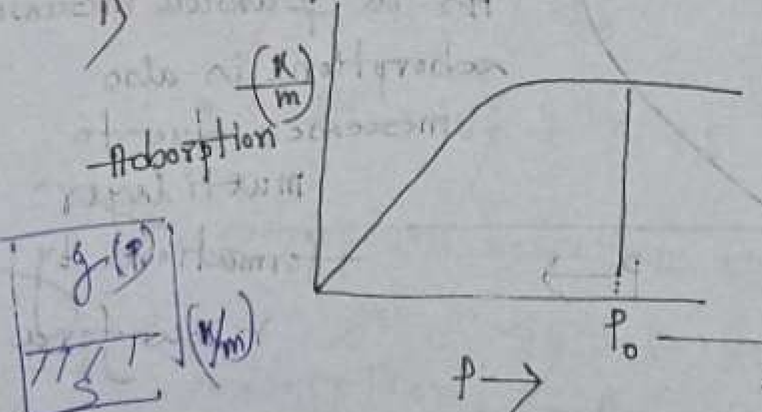
6×1 cm^2 $\longrightarrow$ 6×10^3 cm^2. $\Delta = (6000 - 6)$ cm^2

⟨ii⟩ Adsorption → depends on the nature of Adsorbate → (cohesive force)

The relationship between the extent of adsorption of a gas on the solid surface and pressure or conc. of the adsorbate at const. tempr is called adsorption isotherm.

The effect of pressure on adsorption at const. tempr. are shown by various adsorption isotherm ~~curves~~ curves.

i)



T = const

P_0 ⟶ saturated pressure

a) $P = 0$, No gas in the vessel/reactor ie $\left(\frac{x}{m}\right) = 0$

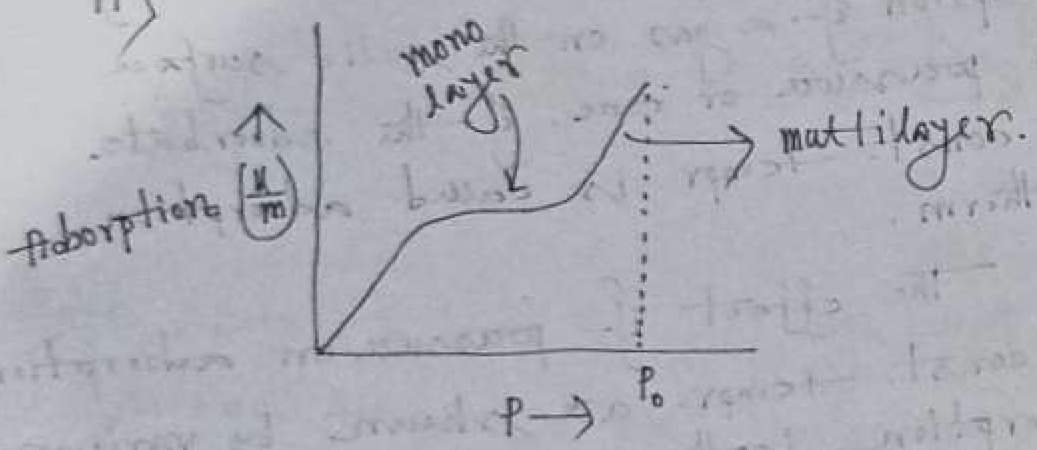
b) P increases, $\left(\frac{x}{m}\right)$ increases

c) At a certain P, adsorption totally saturated.

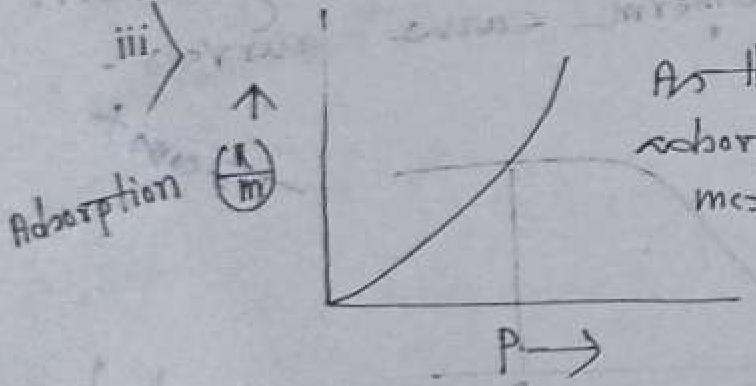
The extent of adsorption $= \left(\frac{x}{m}\right)$

it means, x gm of adsorbate retained on m gm of the adsorbent.

ii)

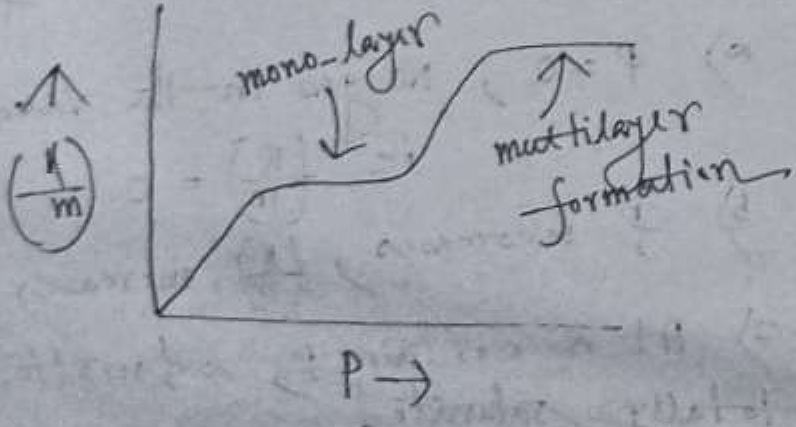


iii)



As the pressure increases adsorption is also increases due to multilayer formation by V.D.W force

IV)



At const tempr, with increase of pressure (P), the extent of adsorption is also increases. According to Le-chatelier principle

$$\underset{\text{(gas molecule)}}{G} + \underset{\text{vacant site.}}{S} \rightleftharpoons \underset{\text{Adduct.}}{G-S}$$

With increase of pressure, the forward reaction occurs i.e the extend of adsorption increases.

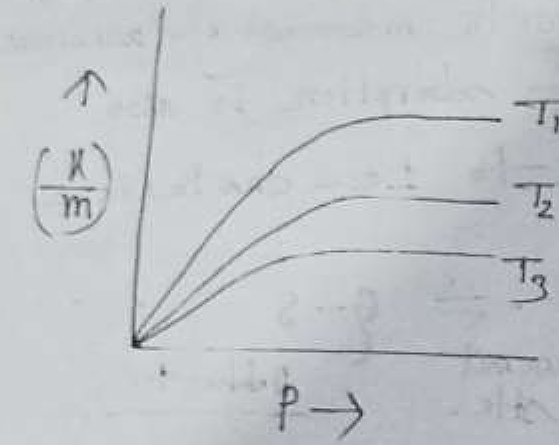
⟨III⟩ The extent of adsorption decreases with increase of tempr.

$$\Delta G = \Delta H - T\Delta S$$

$$\therefore \Delta H = \Delta G + T\cdot\Delta S$$

The adsorption reaction is spontaneous so, $\Delta G = (-)ve$. Again, due to adsorption, the randomness of the system decreases and hence $\Delta S = (-)ve$.

So, $\Delta H = (-)ve + (-)ve$
$= (-)ve$
= Exothermic in nature.



$T_1 < T_2 < T_3$

With rise in tempr, the thermal energy of the adsorbate increases, and lesser no. of molecules will be held to the surface of the solid by residual force and hence adsorption decreases with increase of tempr.

Freundlich Adsorption isotherm

$$\left(\frac{x}{m}\right) = K\cdot P^{n}$$

n → const

extent of adsorption

const.

pressure of the gas.

K and n are const and they depend on the nature of the adsorbate and adsorbent and tempr.

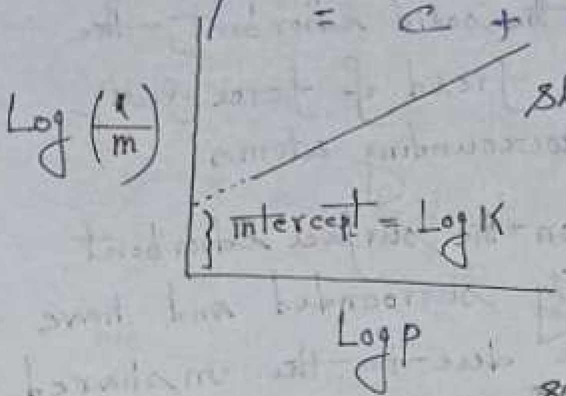
n = fraction

$$\left(\frac{x}{m}\right) = K\,P^{n}$$

Taking Log on both side, we get

$$\log\left(\frac{x}{m}\right) = \log K + n\cdot\log P$$

$$y = c + mx$$



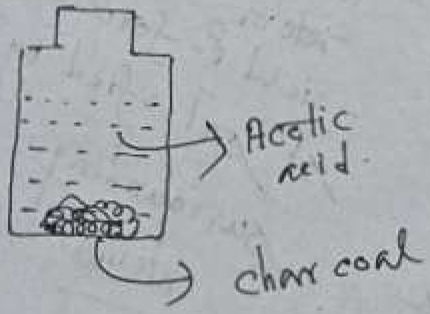
$\log\left(\frac{x}{m}\right)$ vs $\log P$ gives st. line

Experimental values, however when plotted show some deviation specially at low T and high P.

This isotherm is also used for adsorption of solute in solution on solid powders added to it and has been found satisfactory. only P is replaced by equil^{m} conc. (C) of the solute.

$$\log\left(\frac{x}{m}\right) = \log K + n\log C$$

Example :



at 298°K

n = 0.425

A = ε.c.l

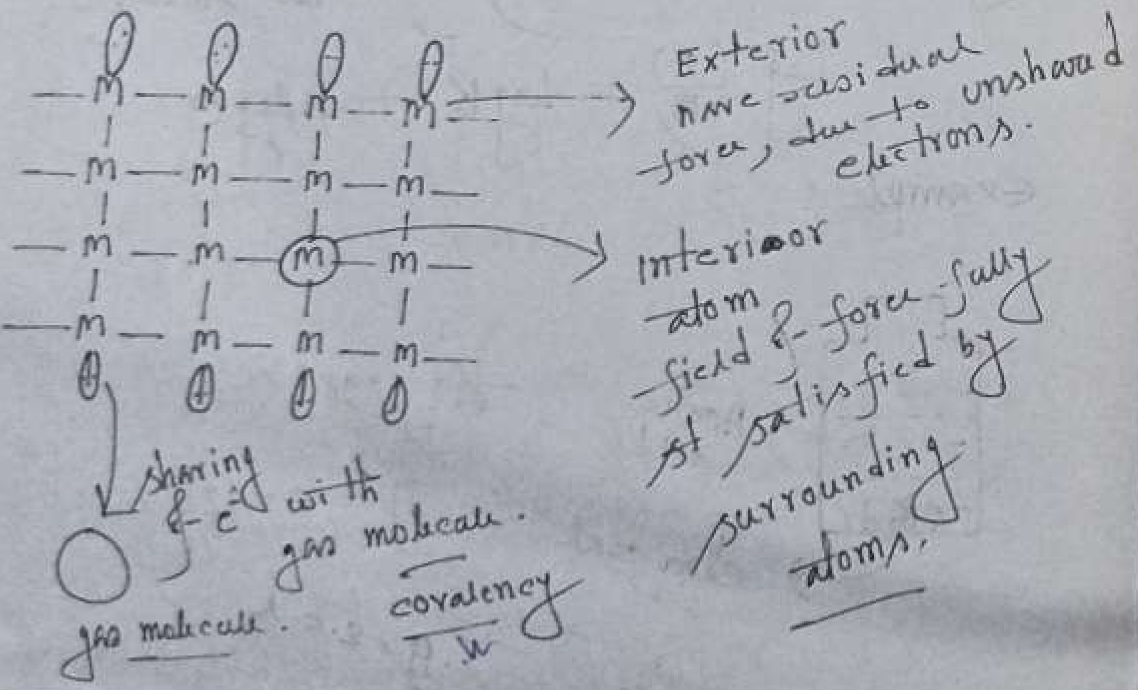
Langmuir_ Adsorption isotherm

New concept → chemical forces responsible for adsorption

The interior of the solid adsorbent, the atoms have the field of force fully satisfied by surrounding atoms

But the atoms on the surface adsorbent are not completely surrounded and have residual force due to the unshared electrons [illegible] towards the exterior.

This residual force leads to sharing of electrons with the striking gas molecules and a sort of covalency linkage is formed between the adsorbate gas molecules and the surface atoms.

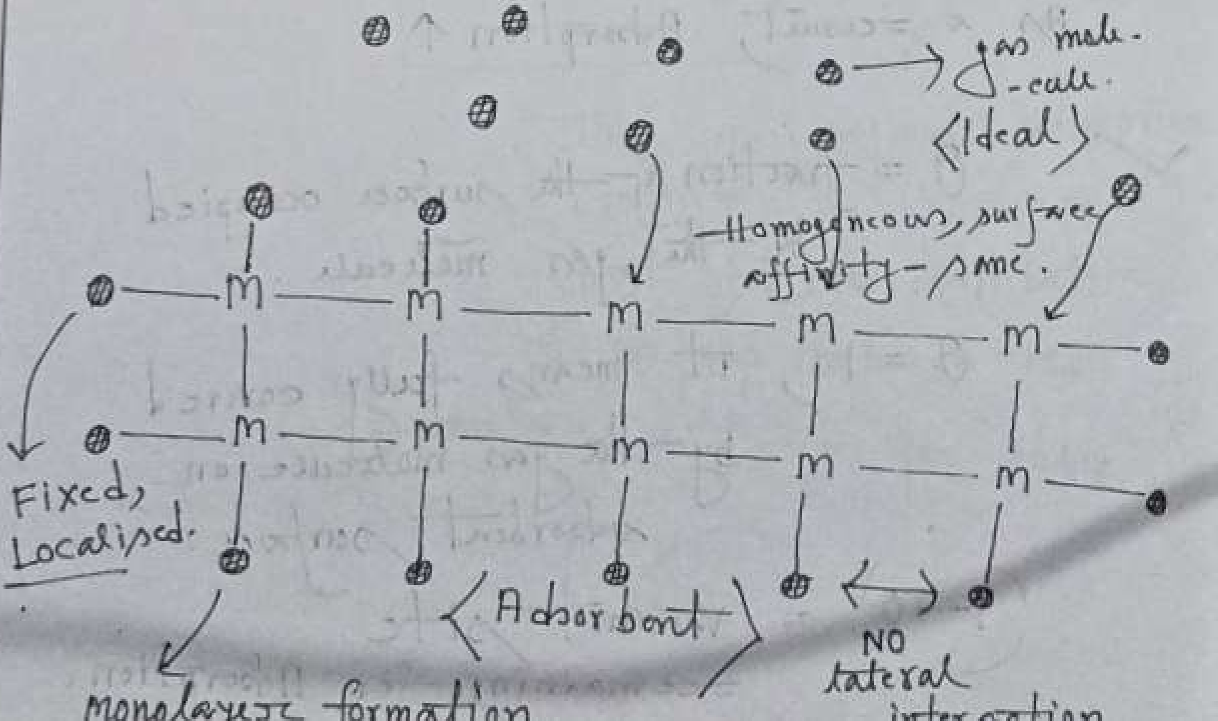


This adsorption is thus chemical in nature and is called chemical adsorption or chemisorption.

Langmuir derived an expression for the variation of adsorption with pressure using the chemical adsorption.

Assumptions of the theory :

i) The adsorbed gas — Ideally in vap. phase
ii) — monolayer
iii) Homogeneous surface → Adsorption site
iv) No lateral interaction between the adsorbed molecules.
v) Adsorbed molecules → Localised.



$$G + S \underset{K_d}{\overset{K_a}{\rightleftharpoons}} G\text{--}S$$

Forward reaction, Adsorption

gas molecule (P)

vacant sites on the surface (θ)

Adsorbed gas molecules.

Backward reaction, desorption.

The rate of Adsorption $\propto P$

$\propto (1-\theta)$

So, The rate of Adsorption $= K_a \cdot P \cdot (1-\theta)$

✓ P ↑ increases

sticking rate on Adsorbent surface increases ↑

As a result, Adsorption ↑

✓ θ = fraction of the surface occupied by the gas molecule.

$\theta = 1$, it means fully covered by the gas molecule on adsorbent surface.

$(1-\theta)$ = vacant site remaining for Adsorption.

Again, the rate of desorption $\propto \theta$

$= K_d \cdot \theta$

At equil^m, the rate of adsorption = the rate of desorption.

So, $K_a \cdot P \cdot (1-\theta) = K_d \cdot \theta$

$\Rightarrow K_a \cdot P = [K_a \cdot P + K_d] \cdot \theta$

$$\Rightarrow \theta = \frac{K_a \cdot P}{K_a \cdot P + K_d} = \frac{\left(\frac{K_a}{K_d}\right) \cdot P}{1 + \left(\frac{K_a}{K_d}\right) \cdot P}$$

K_1 = equil^m const. $= \frac{K_a}{K_d}$

$$\boxed{\theta = \frac{K_1 \cdot P}{1 + K_1 \cdot P}} \quad \text{....①}$$

This is Langmuir adsorption isotherm. K_1 is an equil^m const for the distribution of the gas between the surface and the gas phase.

✓ The extent of adsorption,

$$\frac{x}{m} \propto \theta$$

θ = The fraction of the surface occupied by the gas molecules.

or, $$\left(\frac{x}{m}\right) = K_2 \cdot \theta$$

~~putting~~ the value of θ,

or, $$\left(\frac{x}{m}\right) = K_2 \cdot \frac{K_1 \cdot P}{1 + K_1 \cdot P}$$

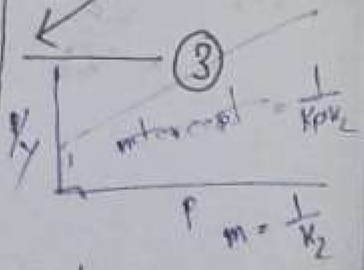
or, $$\boxed{\left(\frac{x}{m}\right) = \frac{K_1 K_2 \cdot P}{1 + K_1 \cdot P}} \quad ②$$

$\left(\frac{x}{m}\right) = y$ = Extent of adsorption.

or, $$y = \frac{K_1 K_2 \cdot P}{1 + K_1 \cdot P}$$

or, $$\boxed{\frac{P}{y} = \frac{1}{K_1 K_2} + \frac{1}{K_2} \cdot P} \quad ③$$

$$Y = C + mx$$



✓ Again from equation ⟨1⟩, we get

$$\theta = \frac{V}{V_m} = \frac{K_1 \cdot P}{1 + K_1 \cdot P}$$

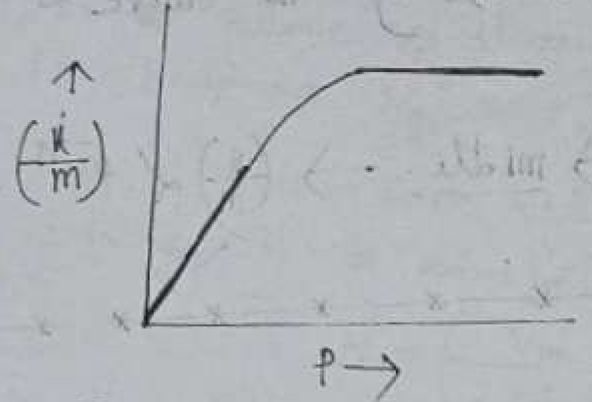
Where,
V = volume of adsorbed gas at a given tempr. and pressure (P).
V_m = That at sufficiently high P and at the expl. Tempr, so as to give a complete coverage of the surface with mono-layer.

$$\frac{V}{V_m} = \frac{K_1 \cdot P}{1 + K_1 \cdot P}$$

or, $$\frac{P}{V} = \frac{1}{K_1 \cdot V_m} + \left(\frac{1}{V_m}\right) \cdot P \quad \text{—— } ⟨4⟩$$

✓ $$\left(\frac{x}{m}\right) = \frac{K_1 K_2 \cdot P}{1 + K_1 P} \quad \text{—— } ②$$

We can plot $\left(\frac{x}{m}\right)$ vs. P



Plot — ①

We can explain plot ① from consideration of the three cases of equation 2

case — ①
When P is low
such that, $K_1 \cdot P << 1$
The equation (2), reduced to

$$\frac{x}{m} = K_1 K_2 \cdot P$$

ie, $\frac{x}{m} \propto P$

so $\left(\frac{x}{m}\right)$ is directly proportional to P.

case — ② When P is high, $K_1 P >> 1$

so, $$\frac{x}{m} = \frac{K_1 K_2 P}{K_1 P} = K_2 = \text{const.}$$

or, $$\left(\frac{x}{m}\right) = K_2$$

or, $$\left(\frac{x}{m}\right) \propto P^0.$$

The adsorption attains limiting value and this explain the horizontal portion of the curve.

case ③ When the pressure is moderate, then $\left(\frac{x}{m}\right) = K\cdot P^{\frac{1}{n}}$ $\frac{1}{n} = 0$ to 1

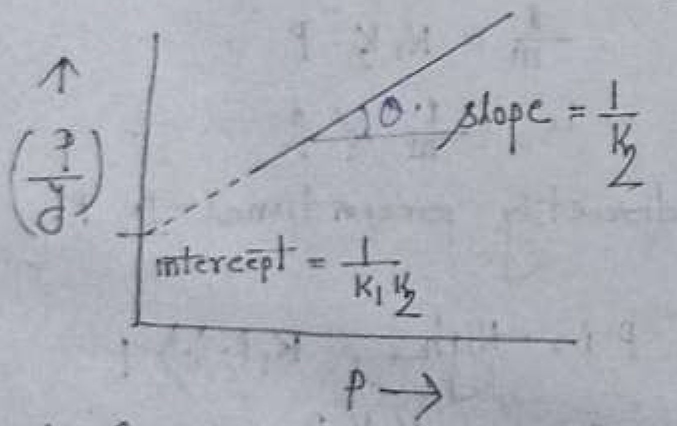
This explain the bending portions of the curve

① $\left(\frac{x}{m}\right) \propto P^{1}$ ——

② $\left(\frac{x}{m}\right) \propto P^{0}$ → midle → $\left(\frac{x}{m}\right) \propto P^{\frac{1}{n}}$

* * * * * * * * * * * *

⇒ $$\left(\frac{P}{y}\right) = \frac{1}{K_1 K_2} + \frac{1}{K_2}\cdot P \quad \text{......③}$$



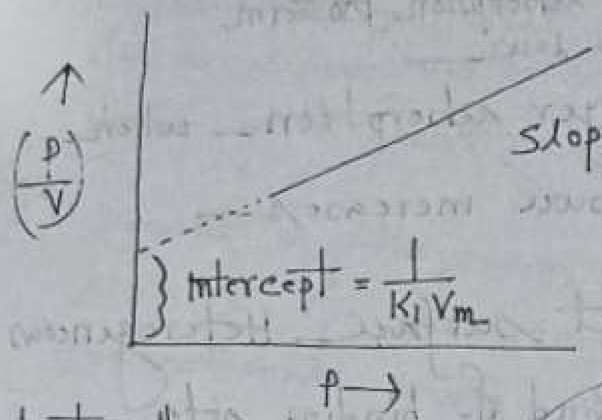
$y = c + mx$

From this plot, K_1 and K_2 can be determined.

$K_2 = \frac{1}{\text{slope}}$, $K_1 = \frac{\text{slope}}{\text{intercept}}$

$$\underset{y}{\frac{P}{V}} \underset{=}{=} \underset{c}{\frac{1}{K_1\cdot V_m}} \underset{+}{+} \underset{m}{\left(\frac{1}{V_m}\right)}\cdot P \quad \text{———— ④}$$

Now we can plot $\left(\frac{P}{V}\right)$ vs P



slope = $\frac{1}{V_m}$ or, $V_m = \frac{1}{\text{slope}}$

Let the volume V_m is reduced to STP and it becomes V_m° cc.

No. of adsorbate molecules for complete coverage of the adsorbate surface

$$N = \left(\frac{V_m^{\circ}}{22414} \times N_0\right)$$

Where N_0 = Avogadro's number.

22414 cc — N_0
1 cc — $\frac{N_0}{22414}$
V_m° cc — $\left(\frac{V_m^{\circ}}{22414}\right) \times N_0$.

If β is the surface area occupied by a single molecule

β = Surface area/single molecule.

so, Total Surface area of the adsorbate

$$= \left(\frac{V_m^{\circ}}{22414}\right) N_0 \times \beta$$

if m g. adsor$\overset{\text{bent}}{\text{bate}}$ used, then surface area per gm of adsor$\underset{\text{bent}}{\text{bate}}$

$$S = \left(\frac{V_m^{\circ} N_0 \beta}{22414 \times m} \right)$$

Deviation of Langmuir adsorption isotherm

⟨i⟩ P is low —

⟨ii⟩ multi-layer adsorption — when Pressure increases —

⟨iii⟩ Adsorbent surface — Heterogeneous — Dif. kind of binding site created by edges, cracks and crystal imperfections.

⟨iv⟩ Heat of adsorption decreases with increase of θ. This points to the initial occupation of energetically most favourable sites and presence of interaction of the adsorbed molecules.

⟨v⟩ The surface films may be mobile.

UG 6th sem - Internal Examination - 2021
Achhruram Memorial College, Jhalda
Sub: chemistry (Hons), course code: BCEMCCHC C02 | F.M. = 10
course title: Physical chemistry IV

Answer any four from the following questions 4×2½ = 10

① Explain the fact that pure rotational spectra of a linear rotor consists of series of lines with const. separation. m = 2½

② Draw a diagram showing relative spacing of electronic, vibrational and rotational energy levels. m = 2½

③ a) Which of the following diatomic molecules will show pure rotational spectra and why?
i) HCl ii) H_2 iii) HD and iv) CO, m = 1½

b) Explain why the symmetrical stretching vibration of CO_2 is IR inactive. m = 1

④ Which one of the following vibrational transitions i) $V=0 \rightarrow V=1$ and $V=1 \rightarrow V=2$ will be more intense and why? m = 2½

⑤ Define molar absorption co-efficient. Derive its dimension from the equation of its absorbance. m = 2½

⑥ What is Franc-Condon principle? Explain its significance? m = 2½

BET Adsorption Equation | This is an improved equation and include the formation of multilayer adsorption layer.

$$\frac{P}{V_t\,(P^\circ - P)} = \frac{1}{V_m \cdot C} + \frac{C-1}{V_m \cdot C} \cdot \frac{P}{P^\circ}$$

V_t = volume of the gas under pressure P

P° = saturated vap. pressure of the gas.

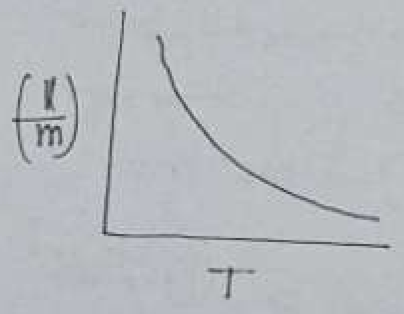
C = const. for the given adsorbate.

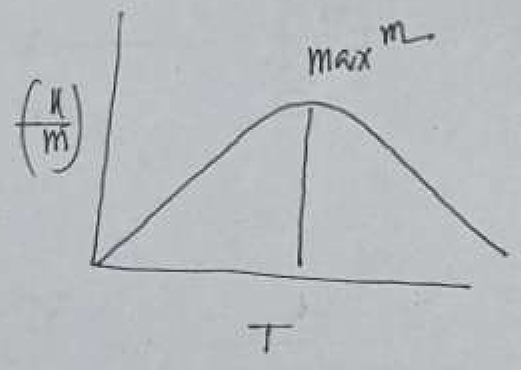
Distinction of Physical Adsorption and chemical Adsorption

⟶ Physical adsorption occurs when the adsorbate gas molecules are held by physical force like VDW forces.

⟶ chemical adsorption or chemisorption occurs when the adsorbate molecules are held on the adsorbent surface by chemical forces. Some sort of covalent linking occurs by sharing of electron.

Physical Adsorption	Chemical Adsorption
i) Heat of adsorption Low (5 Kcal/mole)	(i) Heat of adsorption High (20 – 100 Kcal/mole)
ii) Low tempr dominate	ii) High tempr. dominate
iii) Multi-layer formed	iii) mono-layer formed
iv) V.D.W force	iv) gas + surface nature.
v) Heat of activation Low	v) Heat of activation High
vi) quike process	vi) slow process – T = low quike process – T = high
vii) Adsorption isobar effect of T on x/m at const P.	vii) Adsorption isobar





7/1/2021

1) Chaitak.
2) Dipankar.
3) Sourav
4) Subhajit.