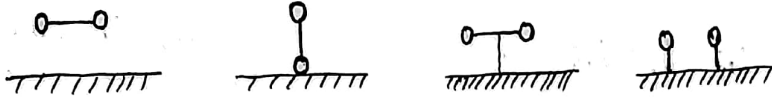


Adsorption :- The molecules at the surface of a material experience imbalanced forces of intermolecular interaction which contribute to the surface energy. It causes accumulation of molecules of a solute or gas in contact with the substance. The preferential <sup>accumulation</sup> of ~~substance~~ substrate molecules at the surface is called adsorption.



- Surface chemistry of the materials as a whole is critically dependent upon the nature and types of surfaces exposed on different crystal lattices.  
eg. The (100) plane of fcc surface exposes five atoms showing greater adsorption than the bcc crystal lattice (4 atoms at the surface)  
Pd, Rh, Pt belong to fcc crystal ~~lattice~~ structures.  
Fe, W, Mo " " bcc "

\* Physisorption: The only bonding between the ~~sub~~ substrate and the adsorbent is van der Waals forces. There is no significant redistribution of electron density in either the molecule or at the surface of the substrate.

\* Chemisorption :- A chemical bond involving substantial rearrangement of electron density is formed between the adsorbate and adsorbent. The nature of the bond may lie between the ~~examples of extremes~~ of virtually complete ionic or complete covalent character.

#### Properties

① Material specificity  
(variation bet<sup>n</sup> substrates of different chemical composition)

② Crystallographic specificity  
(variation bet<sup>n</sup> different surface planes of the same crystal)

Physisorption  
Slight dependence on the substrate composition

Virtually independent of substrate geometry

Chemisorption  
Substantial variation bet<sup>n</sup> the materials.

Marked variation bet<sup>n</sup> crystal planes.

## Properties

③ Temp range  
(over which adsorption occurs)

④ Adsorption enthalpy

⑤ Nature of adsorption

⑥ Saturation uptake

⑦ Kinetics of adsorption

## Physisorption

Near or below the condensation temp. of the gas (e.g.  $N_2 < 100K$ ,  $CO_2 > 200K$ )

Typically 5-40 kJ/mol  
(similar to heat of liquefaction)

No dissociative reversible

Limited to monolayer

Fast - since it is a non-activated process.

## Chemisorption

Virtually ~~unlimited~~ unlimited.  
(but a given molecule may effectively adsorb over a small range)

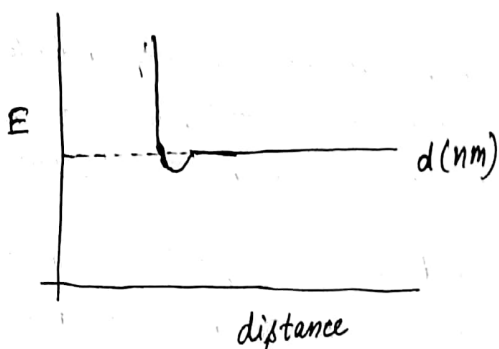
Typically bet<sup>n</sup> 40-400 kJ/mol  
(depends on the chemical bond)

Often dissociate, may be irreversible.

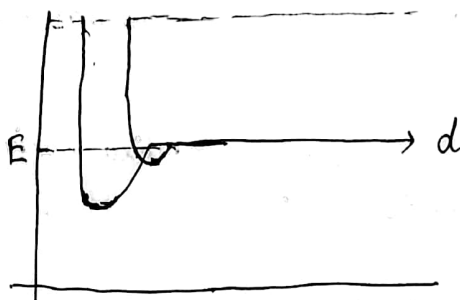
Multilayer uptake possible

Highly variable - ~~often~~ often an activated process.

## PE curves and energetics of adsorption

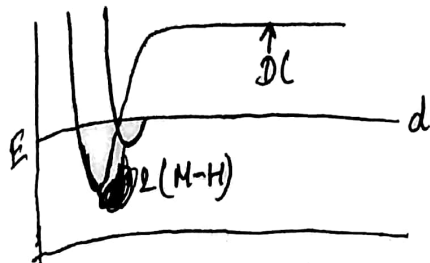


Here, van der Waal forces give rise to a shallow minimum in the PE curve at a relatively large distance (typically  $> 0.3nm$ ) before strong repulsive forces arising due to overlap electron density cause rapid increase in total energy.



## Physisorption + molecular chemisorption.

Here PE curve due to physisorption and chemisorption shown separately - any real molecule capable of undergoing chemisorption is best described by combination of two curves - ~~overlapping~~ - the crossing point where chemisorption forces begin to dominate over the forces arising due to physisorption.

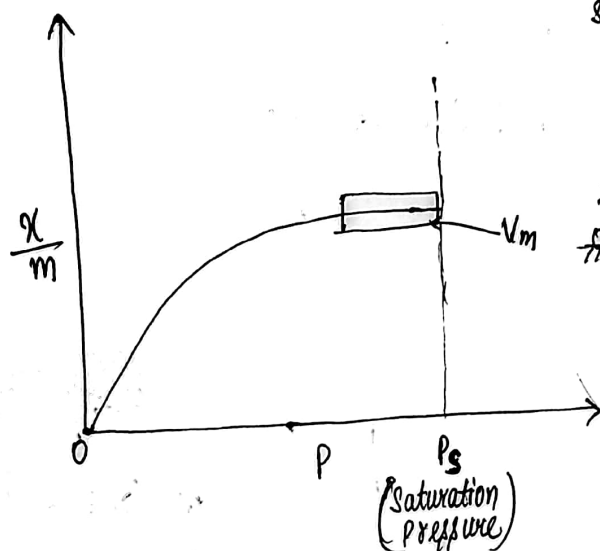


In this case, a molecule such as  $H_2$  may be treated as isolated (when the distance is very large) then. dissociative energy needed to break the ~~bond~~ molecule chemisorption of H atoms leads to decrease in energy

Application of adsorption:

\* Types of adsorption isotherm :- TYPE I, TYPE II, TYPE III, TYPE IV, TYPE V

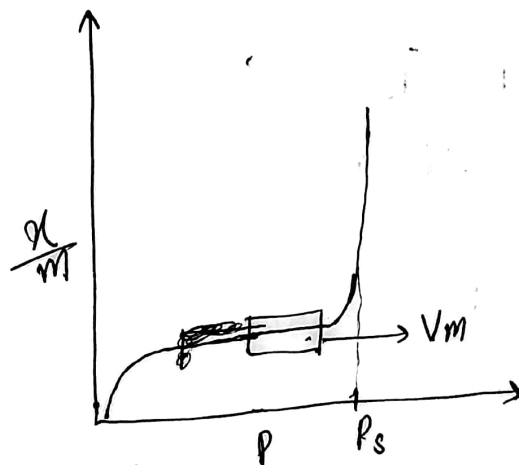
TYPE-I:-



Single layer formation

Eg:  $N_2$  or  $H_2$  on charcoal at  $-180^\circ C$

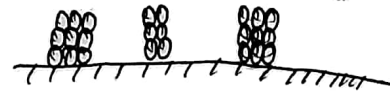
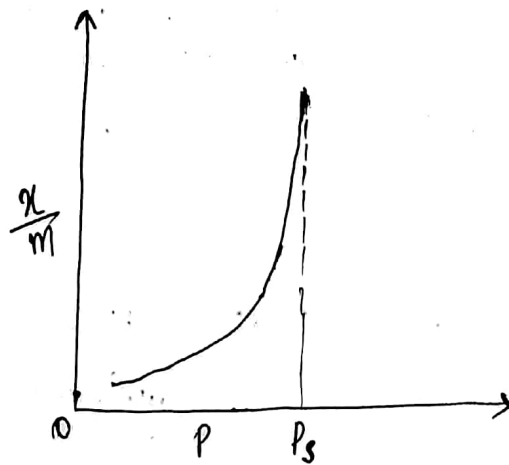
TYPE-II:-



Multi-layer formation

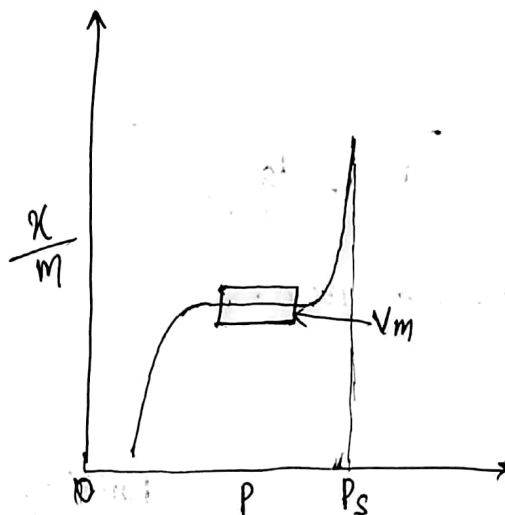
Eg:  $N_2$  on Fe or Pt at  $-195^\circ C$

### • TYPE-III.



Eg:-  $\text{BX}_2$  on silica at  $180^\circ\text{C}$

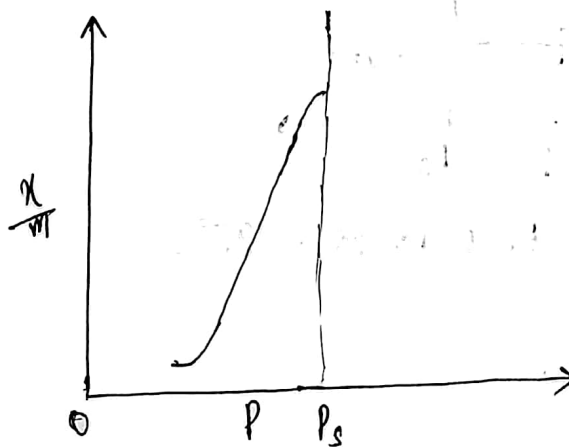
### • TYPE-IV.



At first, ~~the~~ monolayer is formed and after increasing pressure multilayer is formed and molecules fill the holes also.

Eg:- Benzene on silica at  $50^\circ\text{C}$

### • TYPE-V.



No monolayer is formed.

Capillary adsorption

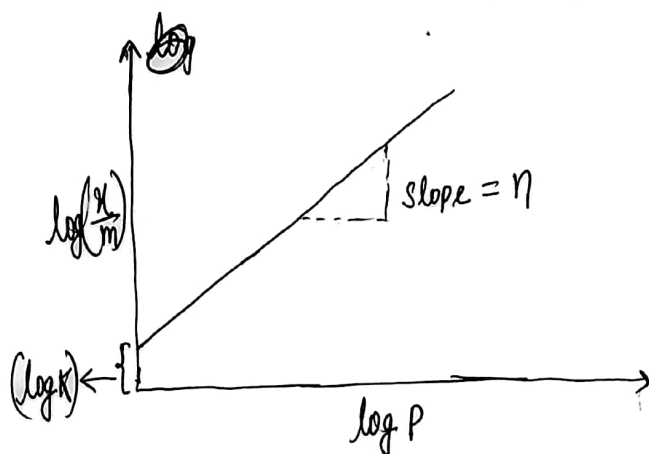
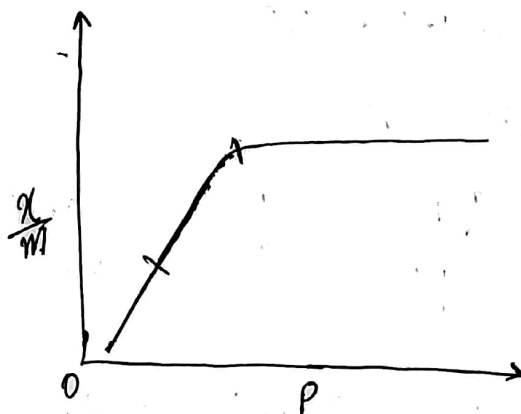
Eg:-  $\text{H}_2\text{O}$  vapour on activated charcoal at  $100^\circ\text{C}$

\* Freundlich isotherm :-

$$\frac{x}{m} = K P^n \quad (0 < n < 1)$$

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

$$Y = C + mX$$



\* Langmuir isotherm :-

Assumptions :-

1. There are fixed sites on the ~~adsorbent~~ adsorbent. At a given temp<sup>r</sup> and pressure, a fraction of these sites are occupied, called  $\theta$ .
2. Each site on the surface can hold only one molecule.
3. The heat of adsorption is the same on each site and is independent of  $\theta$ .
4. There is no interaction between molecules ~~and~~ on the adsorbed sites.
5. At equilibrium, rate of adsorption will be equal to rate of desorption.

Rate of adsorption :  $\gamma_a \propto P(1-\theta)$

$\gamma_a = K_a P(1-\theta)$  ;  $K_a \rightarrow$  proportionality const for adsorption.

Rate of desorption:

$$Y_d \propto \theta$$

$$Y_d = K_d \theta$$

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

At equilibrium,  $Y_a = Y_d$

$$\Rightarrow \cancel{K_d P} K_a P (1 - \theta) = K_d \theta$$

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

$$\Rightarrow \theta = \frac{\frac{K_a}{K_d} P}{1 + \frac{K_a}{K_d} P}$$

$\frac{K_a}{K_d} = K = \text{Langmuir constant}$

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

Langmuir adsorption isotherm

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

$$\frac{K P}{V} = \frac{1 + K P}{V_m}$$

$$\Rightarrow \frac{V}{V_m} = \frac{K P}{1 + K P}$$

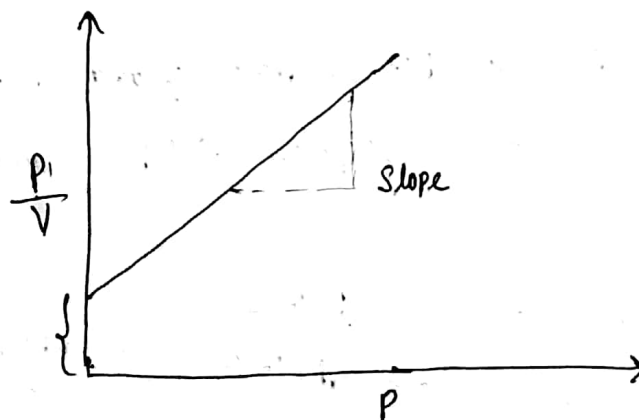
$$\frac{P}{V} = \frac{1}{K V_m} + \frac{K P}{V_m K}$$

$$\Rightarrow V_m K P = V \theta (1 + K P)$$

$\Rightarrow$

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{K V_m}$$

$$Y = \frac{1}{V_m} P + \frac{1}{K V_m}$$



Q. Slope =  $0.02 \text{ g/cm}^3$   
 intercept =  $2.05 \text{ torr g/cm}^3$   
 $V_m = ?$ ,  $K = ?$

Ans  $V_m = \frac{1}{\text{slope}} = 50 \text{ cm}^3/\text{g}$

$\frac{1}{KV_m} = 2.05 \text{ torr g/cm}^3$

$\Rightarrow K = \frac{1}{V_m \times 2.05} = \frac{1}{50 \times 2.05} \text{ torr}^{-1}$   
 $= 9.75 \times 10^{-3}$