

Surface Chemistry

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✓ Adsorption :- When the rxn takes place on the surface of reactant is called adsorption.

✓ Absorption :- When rxn take place in the bulk of reactant is called absorption.

✓ Adsorbate :- foreign particles react with reactant is called

Chemical adsorption

- Irreversible
- strong bond
- chemical ads. needs more pressure doesn't exist.

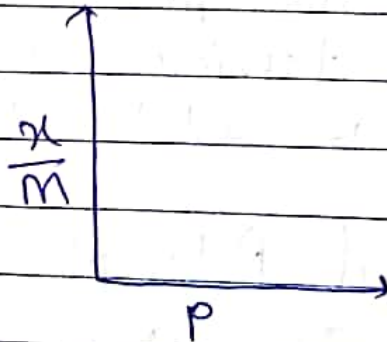
- Multimolecular
Unimolecular
- Chemical ads. needs more energy to break bonds.

Physical

reversible
weak bond
The effect of pressure exist @ an in physical

Unimolecular
Multimolecular
It doesn't need much energy.

★ Adsorption Isotherm :- Is the study of extent of adsorption with reference of pressure under constant temp.



Freundlich → low pressure
Langmuir → high pressure → monolayer

$$\left[\frac{x}{m} \propto P \right]$$

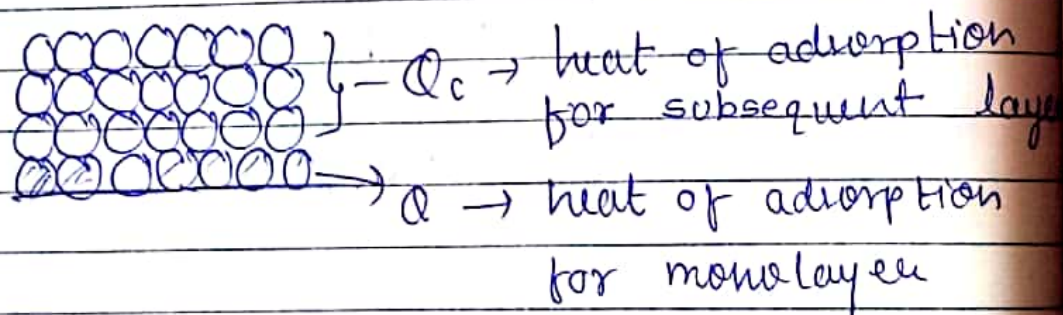
~~Arav~~ Dr. Kuldeep sir

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BET adsorption isotherm :-

In 1938, Brunauer, Emmet, and Teller presented the multilayer adsorption theory. based on the Langmuir model. The basic assumption of the BET theory is the Langmuir eqⁿ applied to each layer with addⁿ postulate

The first layer the heat of adsorption (Q_1) have special value which is diff from all other subsequent layers (Q_2) which is different from heat of adsorption of all other subsequent



molecules get-into adsorb on adsorbent surface. form an adsorption can with a layer where molecules (adsorbate molecules) has already being adsorb. when vapour pressure increase and reach at the saturate vapour pressure P_0 the no. of vacant site of adsorbent is zero. and remaining adsorbent molecules form

Saturated pressure \rightarrow maximum pressure

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double or triple adsorption complex
free surface + vapour \rightarrow single complex
Single complex + vapour \rightarrow double complex
double complex + vapour \rightarrow triple complex

from these all assumptions and the basis of some kinetic experiments following formula has been derived by Brunauer, Emmet and Teller

$$Q = \frac{C \frac{P}{P_0}}{\left(1 - \frac{P}{P_0}\right) \left[1 + (C-1) \frac{P}{P_0}\right]} \quad (1)$$

above formula gives the information of amount of adsorption (Q) of 1st layer with the reference of saturated pressure P_0 and difference of heat of adsorption (C).

\rightarrow for multilayer adsorption following formula is derived.

$$Q = \frac{a_m C \frac{P}{P_0}}{\left(1 - \frac{P}{P_0}\right) \left[1 + (C-1) \frac{P}{P_0}\right]} \quad (2)$$

where a = amount of adsorption
 a_m = monolayer capacity of

Importance of formula :-

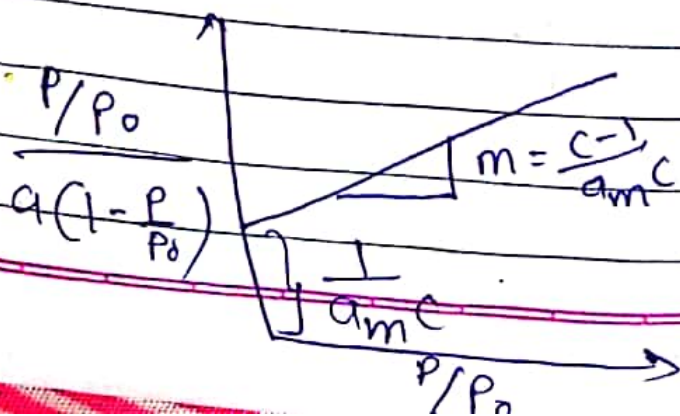
$$a = a_m c \cdot P/P_0$$

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

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

$$\frac{\frac{P}{P_0}}{a \left(1 - \frac{P}{P_0}\right)} = \frac{1}{\underbrace{a_m c}_c} + \frac{c-1}{\underbrace{a_m c}_m} \frac{P}{\underbrace{P_0}_x}$$

$$y = mx + c$$



→ presenting adsorption isotherm in the coordinate system $(y = \frac{P/P_0}{a(1-P/P_0)})$

$(x = \frac{P}{P_0})$ can be used to determine a_m and C constant from slope of straight line and intercept of y axis

→ knowing the value of a_m the specific surface area of adsorbent material can be calculated by using following eqⁿ

$$S = a_m \cdot N \cdot W_m$$

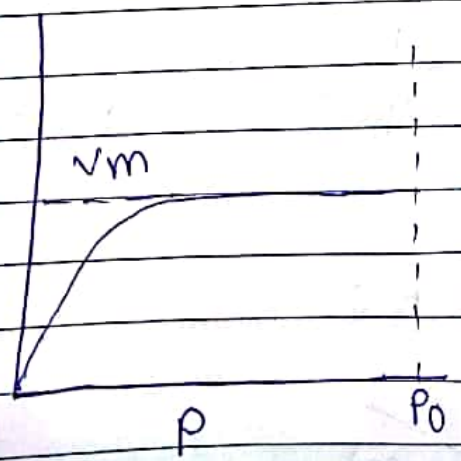
a_m - monolayer capacity of adsorption

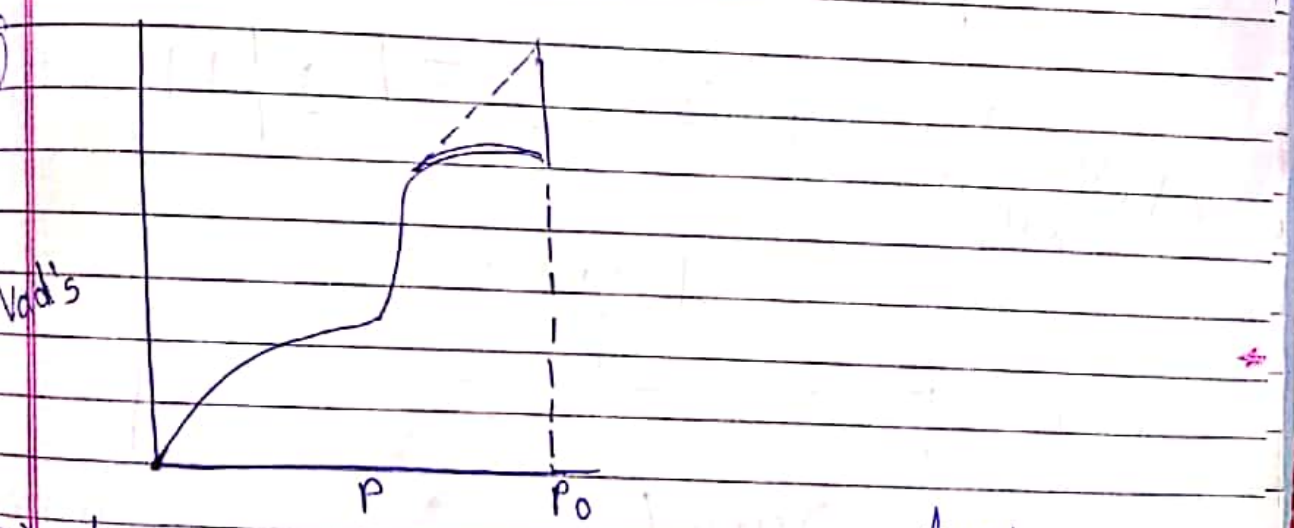
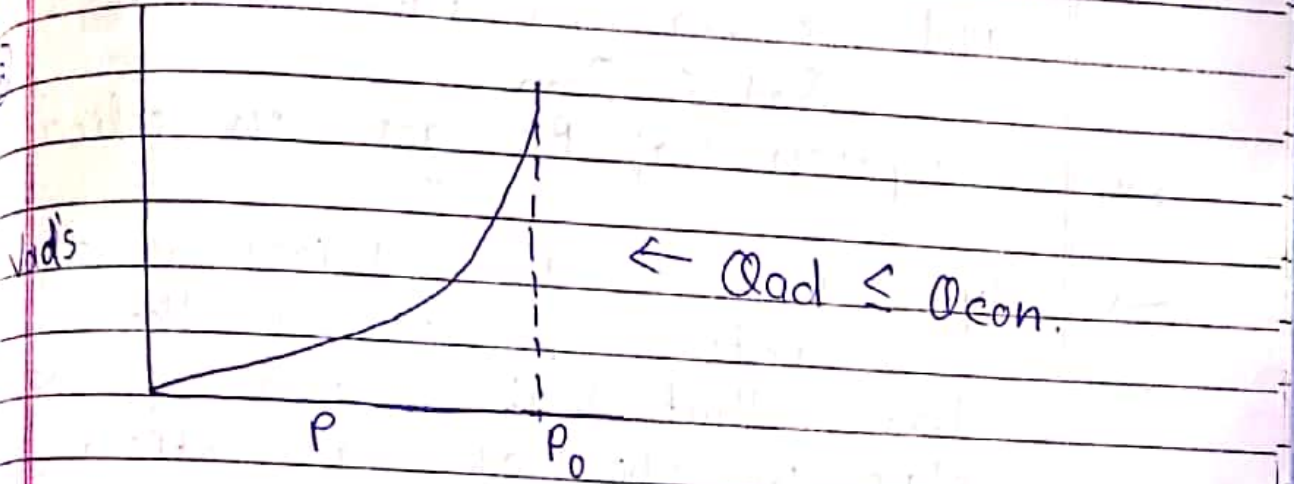
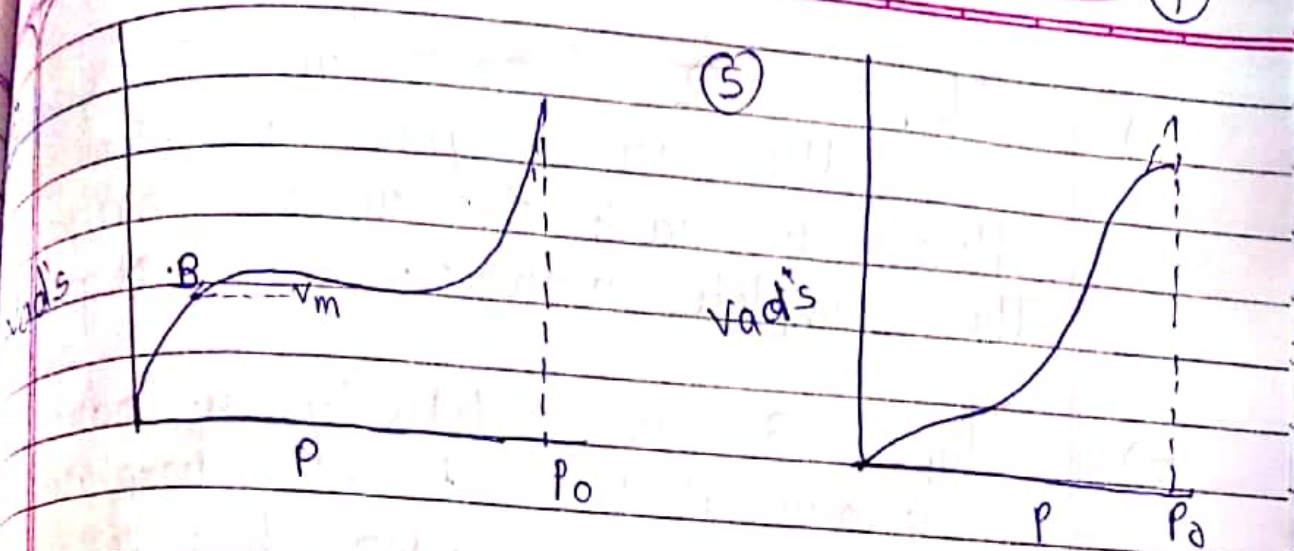
W_m = surface occupied by molecule of molecule

N = Avogadro no.

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Jad's





(B) Acc. to BET isotherm five ^{types} kind of graph has been developed after the experiment

Type - I Graph :- I Graph shows the monolayer adsorption process hence it is also called Langmuir adsorption type

Ex. Adsorption of ammonia gas on charcoal.

⇒ Type - 2 :- Type 2 graph the multilayer adsorption. Here B mark on curve corresponds the complete monolayer. Ex → N gas adsorption

⇒ Type - 3 is relatively rare and shows that heat of adsorption is equal to or less than heat of condensation

$$Q_{ad} \leq Q_{con}$$

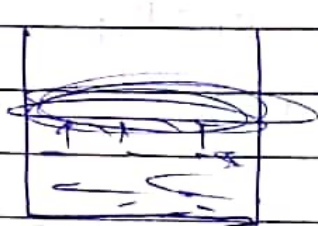
Ex adsorption of Br₂ gas on silica

⇒ Type : 4 & 5 are consider as capillary condensation phenomena that it shows that adsorption process take place in case of adsorption

★ ✓ Gibbs's Adsorption Isotherm (J.W. Gibbs)

n_1 solvent n_2 solute

→ This adsorption isotherm gives the information regarding liquid (solvent & solute) phase



In the liquid phase Gibbs free energy depends on no. of moles of solvent n_1 potential of solvent μ_1

→ no. of moles of solute n_2 & further liquid phenomena it is also dependent on surface tension (σ), ^{surface} energy

$$G = \mu_1 n_1 + \mu_2 n_2 + \sigma \delta$$

→ If we differentiate above formula

$$dG = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \sigma d\delta + \delta d\sigma$$

→ When in the system solvent is in liquid phase and solute is in a solid phase at that time Gibbs's free energy depend on the

$$\frac{d}{dt} = C$$

function of $f(T, P, n_1, n_2, \delta)$

$$dG = \left(\frac{dG}{dT}\right)_{P, n_1, n_2, \delta} dT + \left(\frac{dG}{dP}\right)_{T, n_1, n_2, \delta} dP$$
$$+ \left(\frac{dG}{dn_1}\right)_{T, P, n_2, \delta} dn_1 + \left(\frac{dG}{dn_2}\right)_{T, P, n_1, \delta} dn_2$$
$$+ \left(\frac{dG}{d\delta}\right)_{T, P, n_1, n_2} d\delta$$

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\delta$$

→ practically during the experiment in the system of solid solute and liquid solvent pressure and temperature remains constant hence $dP = 0$ and $dT = 0$ put this value in above eqⁿ.

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\delta \quad \text{--- (2)}$$

→ When compare eqⁿ (1) with eqⁿ (2) we found that value of

$$n_1 d\mu_1 + n_2 d\mu_2 + \delta d\gamma = 0 \quad \text{--- (3)}$$

⇒ In bulk system n_1^0 & n_2^0 are no. of moles of solvent and solute respectively - dy in

$$G = 0$$

$$0 = n_1^0 du_1 + n_2^0 du_2$$

$$0 = n_1^0 du_1 + u_1 dn_1^0 + n_2^0 du_2 + u_2 dn_2^0$$

$$0 = n_1^0 du_1 + n_2^0 du_2$$

$$du_2 = - \frac{n_1^0 du_1}{n_2^0} \quad \text{--- (4)}$$

By putting the value of eqⁿ (4) in eqⁿ

$$n_1 du_1 = - n_1 \left(\frac{n_2^0}{n_1^0} \right) du_2 + n_2 du_2 + \sigma dr$$

$$\left(n_2 - \frac{n_1 n_2^0}{n_1^0} \right) du_2 + \sigma dr = 0$$

$$- \sigma dr = \left(n_2 - \frac{n_1 n_2^0}{n_1^0} \right) du_2$$

$$- \frac{dr}{du_2} = \left[\frac{n_2 - \frac{n_1 n_2^0}{n_1^0}}{\sigma} \right] \quad \text{--- (5)}$$

In eqⁿ (5), n_2 is total mole of solute and $\frac{n_1 n_2^0}{n_1^0}$ = total no. of molecule into bulk.

remaining surface of liquid adsorbent

$$\Gamma_2 = - \frac{dr}{dU} \quad \text{--- (1)}$$

$$U = U^0 + RT \ln a$$

in above given condition

$$dU = RT \ln a_2$$

put this value in eqⁿ (1)

$$\Gamma_2 = - \frac{dr}{RT \ln a_2}$$

$$\Gamma_2 = \frac{a_2}{a_2} \left(- \frac{dr}{RT \ln a_2} \right)$$

Q If we convert activity into the conc. at constant temp. we can write down the above formula like as under.

$$\Gamma_2 = \frac{-C_2}{RT} \left(\frac{dr}{dC_2} \right)_T$$

$$\Gamma = \frac{-C}{RT} \left(\frac{dr}{dC} \right)_T$$

This is the final con. of Gibb's adsorptive isotherm

If we take log on the both side

$$\log \Gamma = \frac{-\log C}{R} + \log \left(\frac{dr}{dC} \right)_T$$

Assumption of result from Gibbs adsorption isotherm

→ If with the increasing of conc. of solute the surface tension decrease. it means solute adsorbs on the surface of soln.

$$\left(\frac{d\sigma}{dc \text{ solute}} \right)_T < 0 \text{ and } \Gamma_{\text{solute}} > 0 \text{ [positive adsorption]}$$

→ If increase in conc. of solute can increase the surface tension of solution it means solute adsorbs inside (pore) the soln.

$$\left(\frac{d\sigma}{dc \text{ solute}} \right)_T > 0 \text{ and } \Gamma_{\text{solute}} < 0 \text{ [negative adsorption]}$$

→ If the surface tension of soln. does not change or affected by conc. of solute then adsorption process does not exist.

$$\left(\frac{d\sigma}{dc \text{ solute}} \right)_T = 0 \text{ and } \Gamma_{\text{solute}} = 0 \text{ [no adsorption]}$$

★ Benton - white method surface area determination

→ In 1931, the sh a sharp break point had been obs observe by Benton and white in the S shape isotherm for the adsorption of nitrogen at -191.5°C on iron ads surface at 120 mm pressure. This result indicate complete normal monolayer formation on the surface of adsorbent

→ In addⁿ they also found that the product of no. of molecules in the monolayer and the molecular cross section would give the surface area

→ from this conclusion Benton - white gave following formula to find out surface area of adsorbent.

$$A = 4.866 \left(\frac{M}{4.2N d} \right)^{2/3}$$

- ∴ A = surface area
- M = molecular weight of gas which is observed
- d = density of liquified or solidified adsorbent gas
- N = avogadroes no.

Gravimetric & Volumetric adsorption of process

adsorb amount of gas or vapour or liquid on solid adsorbent are can determine by two method (i) static (e) dynamic

→ Static & dynamic → static method is also called gravimetric analysis of adsorption

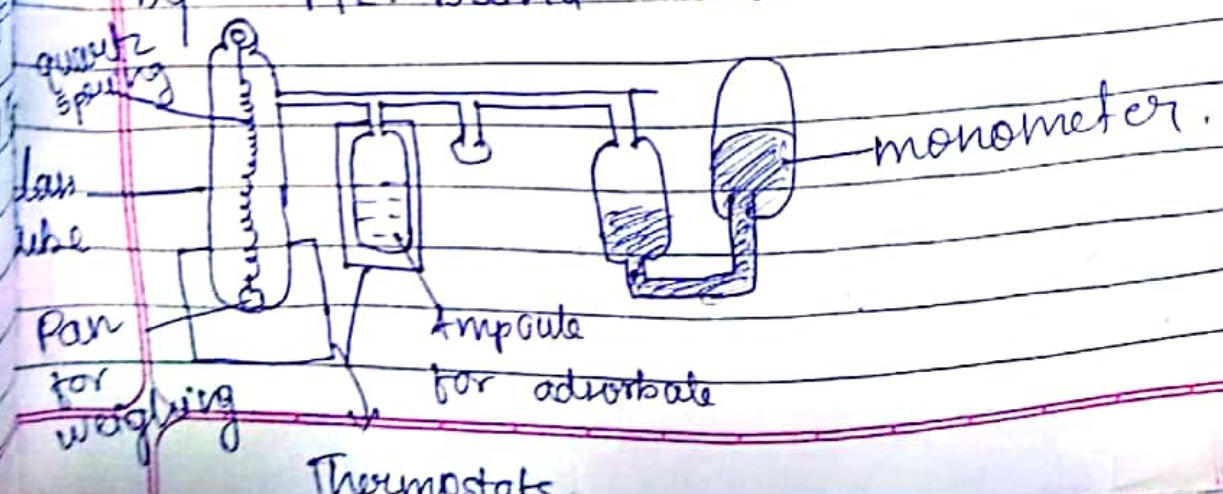
→ This method is based on mass of adsorbent, adsorb on ^{surface of} adsorbent

→ In this method adsorbent place in a close gas set vessel with some amount of gas or liquid vapour.

→ when equilibrium take place pressure and adsorbent amount are measure by measuring of the mass of adsorbent.

→ If the mass of ^{adsorbent} initial and point after adsorption are different then we can say that adsorption is not completed

→ Measurement of mass of adsorbent before and after ^{adsorption} process can be determine by Mc. Bain balance.



$$\frac{\% \text{ gm/litre}}{100 \times 2 \times 1000} \Rightarrow \text{mg/litre}$$

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adsorption process can be also determined by volumetric process with the help of gas liquid chromatography.