

\* Differentiate between physisorption and chemisorption.

⇒ Adsorption is often described as a surface phenomenon where particles are attached to the surface of the material. There are two types of adsorption:

(1) Physical adsorption or physisorption

(2) Chemical adsorption or chemisorption

There are some distinct differences between physisorption and chemisorption:

Physisorption	Chemisorption
1. Physisorption occurs due to the formation of van der waals forces.	1. Chemisorption occurs due to the formation of chemical bonds.
2. It is reversible in nature.	2. It is irreversible in nature.
3. It has low adsorption enthalpy.	3. Chemisorption has high adsorption enthalpy.

Physisorption	Chemisorption
4. Physisorption decreases with the increase in temperature.	4. Chemisorption increases with the increase in temperature of bath.
5. It results in a multimolecular layer.	5. It results in a unimolecular layer.
6. Activation energy is less in physical adsorption.	6. Activation energy is very much high in chemical adsorption.

Q2. How does soap help in washing dusty clothes?

⇒ Soap is a surface active agent that has two distinct regions. In its chemical structure, one is hydrophilic (the water loving part) and the other is hydrophobic (the water hating part).

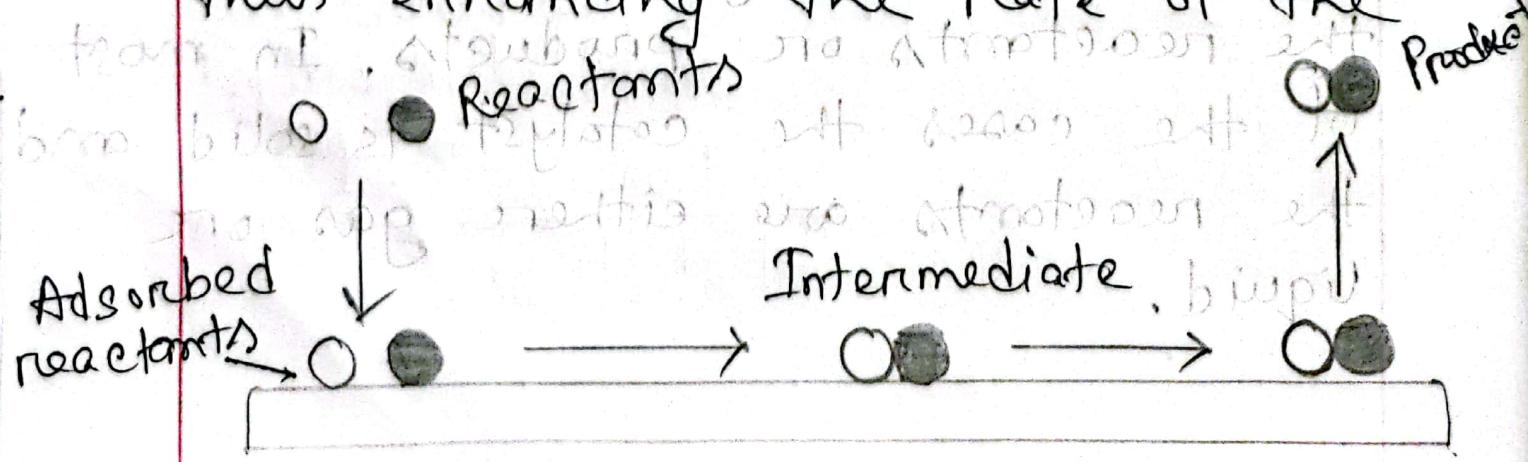
As the soap is rubbed on the dusty fabric, the soaps hydrophobic part gets attached to the dirt molecule of the cloth and the water holds the hydrophilic part. The hydrophobic part holds the dirt and ~~and~~ water pulls the hydrophilic site and ~~the~~ due to the pull, the hydrophobic part draws out the dirt and forms micelle (A soap compound shell with dirt at its core). Thus the soap helps cleaning dusty clothes.

Q3. Describe heterogeneous catalysts based on adsorption theory.

→ Heterogeneous catalysis is the process of catalysis where the catalyst is in a different physical state from the reactants or products. In most of the cases the catalyst is solid and the reactants are either gas or liquid.

As per the old adsorption theory of catalysis, the reactants in their gaseous state or in their dissolved state in a liquid solution get absorbed on the surface of the suitable solid state catalyst. As a result of the increase in the concentration of the reactants on the surface of the catalyst; the availability and probability of the occurrence of a reaction between two species increases and thus the rate of the reaction increases.

Also, the reactants adhere to the surface of the catalyst in some amount of energy is released as the process is exothermic in nature. The heat of combination is utilized in the reaction between the two species, thus enhancing the rate of the



Derive Langmuir equation for adsorption of gas on solid. How does this isotherm explain the kinetics of unimolecular adsorption on solid surface?

→ The Langmuir adsorption isotherm, considers gas molecules striking a solid surface. Then some of these molecules evaporate and a dynamic equilibrium is established between two opposing processes adsorption and desorption.

We consider  $\theta$  as the fraction of the surface covered by adsorbed molecules. The amount of uncovered area is then  $(1-\theta)$ .

i. The desorption rate is directly proportional to the covered surface

i.e.

$$R_d \propto \theta.$$

$$R_d = k_d \theta. \quad (1)$$

where,  $k_d$  is the rate constant for desorption process.

The rate of adsorption  $R_a$  is directly proportional to the uncovered area  $(1-\theta)P$ , and other pressure.

$$R_a \propto (1-\theta)P$$

$$\Rightarrow R_a = k_a(1-\theta)P \quad (2)$$

$k_a$  is the rate at which the gas molecules strike the surface.

Since the adsorption and desorption process remain in a dynamic equilibrium:

$$R_a = R_d$$

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

$$\Rightarrow k_d\theta + k_a\theta P = k_aP$$

$$\Rightarrow \theta(k_d + k_aP) = k_aP$$

$$\Rightarrow \theta = \frac{k_aP}{k_d + k_aP}$$

$$\Rightarrow \theta = \frac{(k_a/k_d) P}{1 + (k_a/k_d) P} \quad \text{--- (3)}$$

Considering

$$\frac{k_a}{k_d} = k_1$$

$$\theta = \frac{k_1 P}{1 + k_1 P} \quad \text{--- (4)}$$

Equation (4) is known as the general form of Langmuir adsorption isotherm.

At very low pressure,  $k_1 P \ll 1$ .

$$1 + k_1 P \approx 1$$

$$\therefore \theta = \frac{k_1 P}{1} = k_1 P$$

That is the extent of adsorption is proportional to pressure. Since the rate of a reaction is directly proportional to  $\theta$ , the heterogeneous unimolecular reaction is kinetically of 1st order, only if pressure is low.

At very high pressure:

$$k_1 P \gg 1.$$

$$\therefore 1 + k_1 P \approx k_1 P.$$

$$\therefore \Theta = \frac{k_1 P}{1 + k_1 P} = 1. \text{ (unity).}$$

That is the entire surface tends to get covered by a mono-molecular thick layer of the gas. Thus the rate of the reaction will be zero independent of the pressure and the reaction is said to be kinetically of zero order.

#5. Explain the following terms on the context of adsorption?

⇒ (1) Surface tension

(2) wetting

(3) contact angle.

⇒ 1. Surface tension : Surface tension is the tension of surface film of a liquid caused by the attraction of the particles in the surface by the bulk of the liquid which tends to minimize surface area.

Adsorption on a surface occurs as a result of residual surface energy due to unbalanced forces on the surface. When the adsorbate molecule comes in contact with the surface of the adsorbent, it tends to reduce the unbalanced force and becomes immobilized at an interphase between two phases without being dissolved in either phase. That's how adsorption occurs due to surface tension.

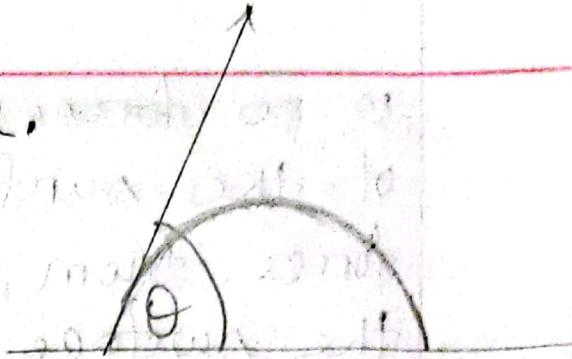
2. Wetting : wetting is the ability of a liquid to maintain contact with a solid surface, resulting from the adsorption of liquid on the surface of the substrate due to intermolecular

interactions when the two are brought together. The more the adhesive is adsorbed on the surface the better is the wetting. Good wetting provides a larger area of contact where the intermolecular forces may act. Consequently, good wetting is crucial for good bond formation.

3. Contact angle: A contact angle (also referred to as wetting angle) is formed when a drop of liquid is placed on a material surface. The surface tension of the liquid and the attraction of the liquid to the surface causes the drop to form a dome shape. It is defined as the angle between a tangent to the liquid surface and the solid surface at the point where they meet.

$\theta$  is the contact angle.

The more the liquid is adsorbed on the solid surface, the more the liquid drop spreads on the surface and the contact angle becomes smaller.



#6. "Solution surface has a natural tendency to adsorb the adsorbate molecules" - validate the statement with proper reason:

⇒ A solid or liquid material has two parts. One is surface, and the other is bulk. In the bulk, ~~the~~ every molecule experience forces from all the directions and the net force is balanced out. But ~~at~~ the surface of a solid or liquid is always in a state of strain due to some unsatisfied valency forces, known as residual force as it experiences ~~pull~~ forces from the bulk, and there

is no force ~~to~~ molecule to on top of the surface to even out the force from the bulk, therefore, the surface has a tendency to attract and retain the adsorbate molecules, when they come in contact with it. This phenomenon is known as adsorption.

\* Discuss the basic assumptions and limitations of Langmuir adsorption isotherm.

→ Assumption: There are some assumptions of Langmuir adsorption isotherm:

(1) The adsorbed layer on the solid adsorbent is assumed to be unimolecular in thickness. (at low pressure and moderate temp.)

(2) The adsorption is taking place on the fixed sites and there is no interaction between the adsorbed molecules on the surface.

(3). The process of adsorption has a dynamic equilibrium which consists of two opposing processes - adsorption (condensation) and desorption (evaporation).

(4) Gas behaves ideally.

(5) surface is uniform and homogeneous energetically.

Limitations: There are some limitations of Langmuir adsorption isotherm!

(1) The adsorbed gas is required to behave ideally in the vapour phase but ~~that~~ real gases don't behave ideally.

(2) The process is required to be fulfilled under low pressure otherwise the isotherms deviate.

(3) Langmuir assumes that the adsorption is monolayer but it is multilayer in some cases.

(4) The surface is not uniform all the time.

(5.) Partial adsorption and some chemical reaction of the adsorbate with the adsorbent deviates the isotherm from (Langmuir's)

# 8. By using Langmuir isotherm, explain the term -

(1) In which condition ~~and~~ the adsorption process, is said to be kinetically of zero order.

→ The general equation of Langmuir adsorption isotherm is:

$$\theta = \frac{K_1 P}{1 + K_1 P}$$

where,  $\theta$  is the fraction of surface area covered at any instant, and

$$K_1 = \frac{K_a}{K_d}$$

At high pressure  $K_1 P \gg 1$ ,

$$\therefore \theta = \frac{K_1 P}{1 + K_1 P} \approx \frac{K_1 P}{K_1 P} = 1$$

∴  $\theta = 1$ . (saturation).

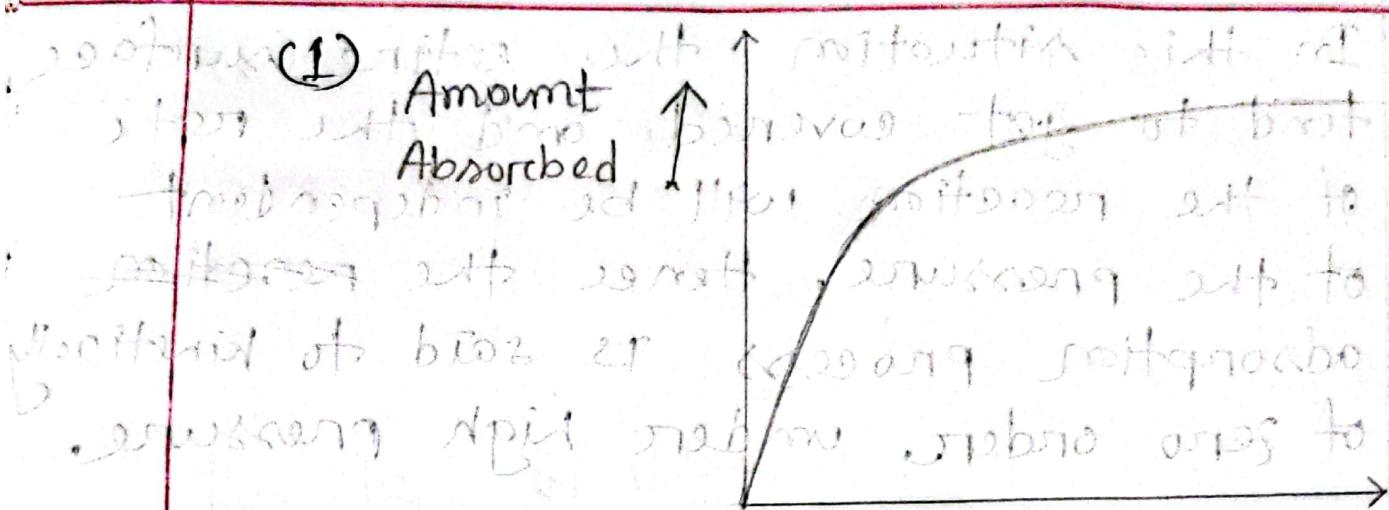
In this situation the entire surface tend to get covered and the rate of the reaction will be independent of the pressure. Hence the ~~reaction~~ adsorption process is said to kinetically of zero order under high pressure.

Q. What is adsorption isotherm? How many experimental adsorption isotherms are possible? Draw and state all these adsorption isotherms.

Ans. An adsorption isotherm is a graph that represents the variation in the amount of adsorbate ( $X$ ) adsorbed on the surface of the adsorbent with the change in pressure (gas) or concentration (liquid) at constant temperature.

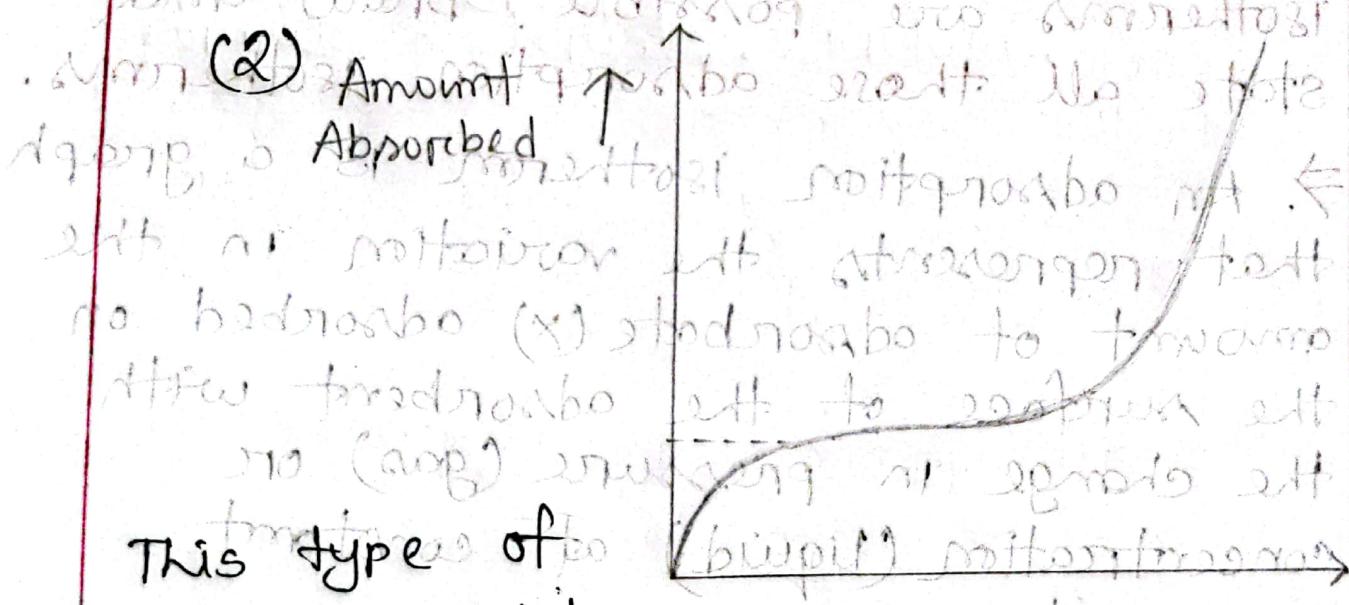
There are five types of adsorption isotherms. The isotherms are drawn on stated below:

(1)



This is a typical Langmuir isotherm, when the adsorption is monolayered with

(2)



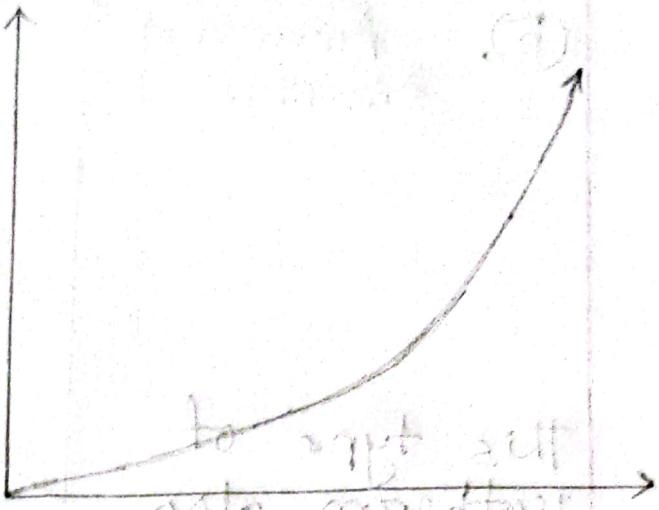
This type of

isotherm that

represents a case of multilayer physical adsorption on non-porous materials.

(3).

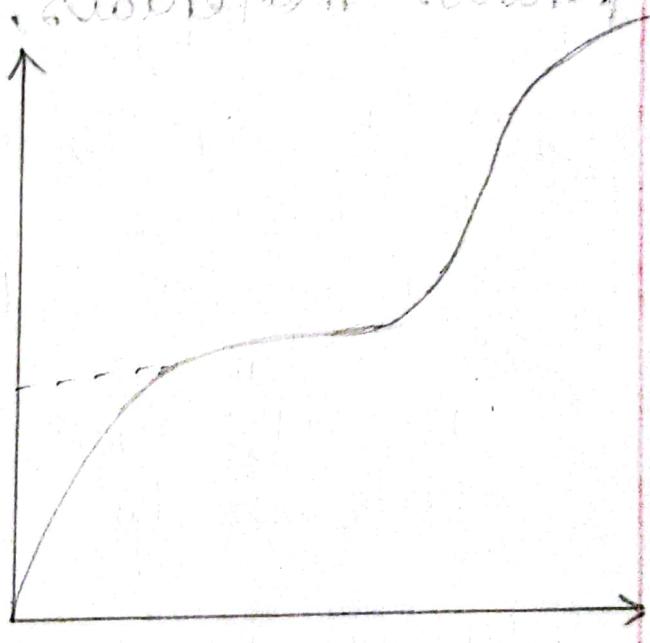
Amount  
Adsorbed ↑



This type of isotherm represents the case of physical adsorption on porous materials. To 2020 isotherm, adsorption aware

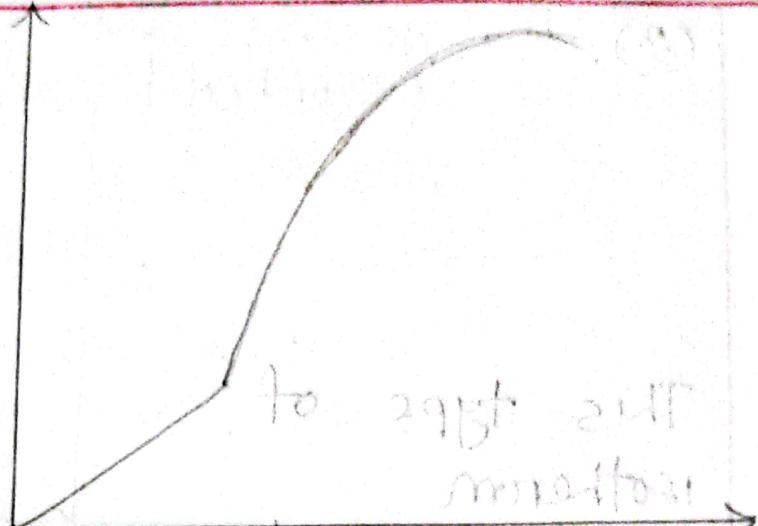
(4)

Amount  
Adsorbed ↑



This type of isotherm represents a case of adsorption on porous material surface accompanied by capillary condensation.

(5). Amount Adsorbed ↑



This type of isotherm also represents the case of physical adsorption on porous materials, surface.

(H)

Amount adsorbed to 99% of monolayer coverage is being made to 2000 mbg by being made to atmospheric pressure among no monolayer to 2000 mbg by being made to 1000 mbg, monolayer, monolayer