

B.Sc. Sem VI

Unit VII: Surface Chemistry

Topic: Adsorption Isotherm

By

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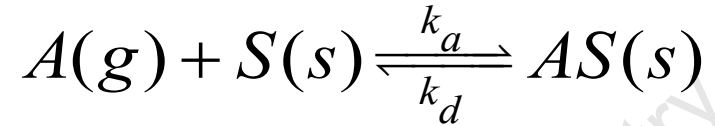
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Langmuir Adsorption Isotherm

Assumptions:

- The dominant force responsible for the adsorption is purely chemical, indicating complete chemisorption.
- Each site on the adsorbent can accommodate a maximum of one molecule, implying the formation of only a monolayer.
- The surface containing the adsorption sites is perfectly smooth & flat
- All active sites are of the same nature and are equivalent.
- There are no lateral interactions between adsorbate molecules on adjacent sites, resulting in the enthalpy of adsorption being independent of surface coverage.

- A dynamic equilibrium exists between the free adsorbate molecules and the adsorbed adsorbate molecules.



A represents a gas-phase molecule

S denotes an unoccupied surface site

AS represents the molecule that has been adsorbed

k_a and **k_d** are the respective rate constants for the adsorption and desorption processes.

$$\theta = \frac{KP}{1 + KP}$$



Expression of Langmuir adsorption Isotherm

Where $K = \frac{k_a}{k_d}$, the equilibrium constant of the adsorption. P represents the Pressure

θ is called the surface coverage. $\theta = \frac{\text{No. of sites occupied at equilibrium}}{\text{Total no. of sites present on surface}}$

$$\theta = \frac{KP}{1 + KP}$$

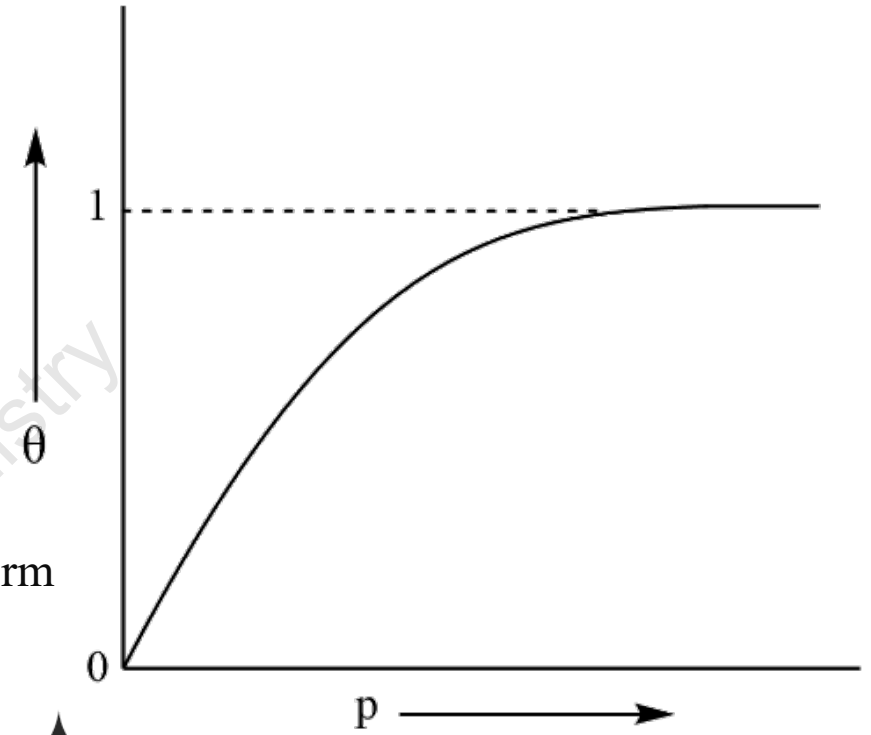
In the limit $KP \ll 1$, when the pressure is significantly low

$$\theta = KP$$

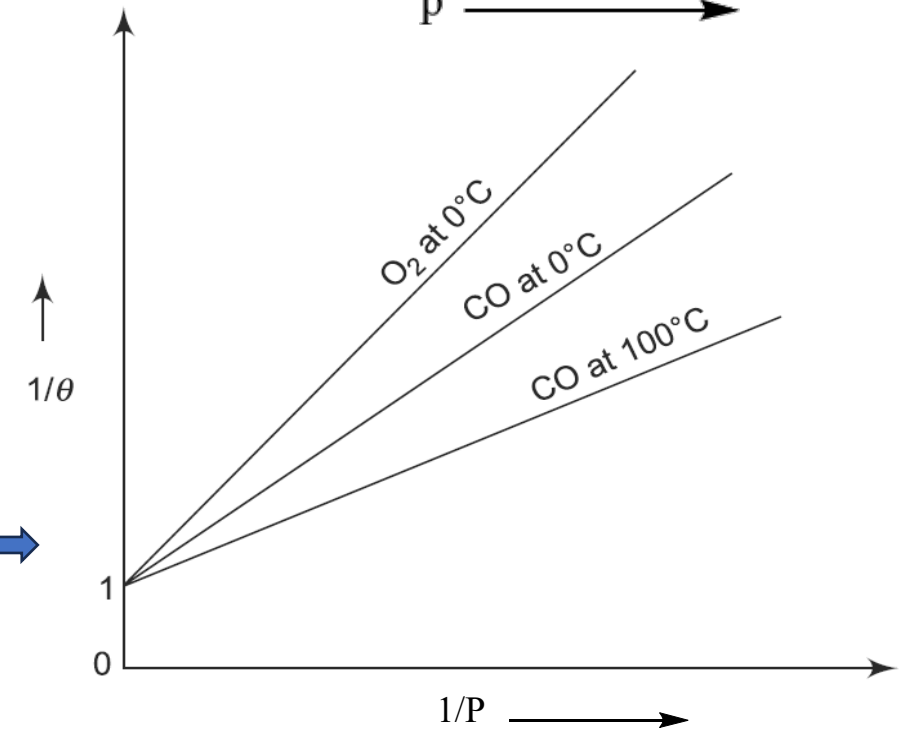
In the limit $KP \gg 1$, when the pressure is significantly high

$$\theta = \frac{KP}{KP} = 1$$

Langmuir isotherm



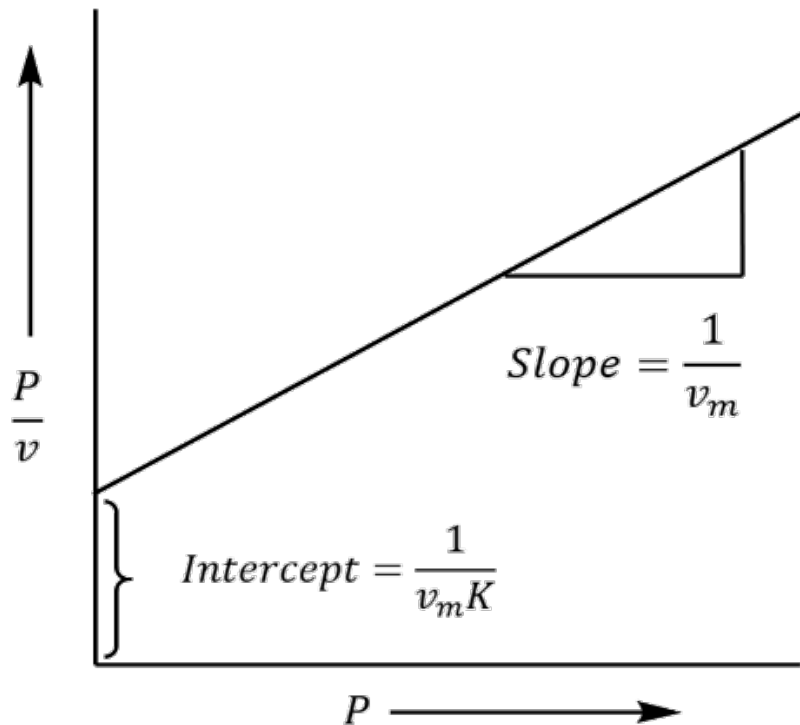
Plot of $1/\theta$ versus $1/P$ for various gases



$$\theta = \frac{v}{v_m} = \frac{KP}{1 + KP}$$

v represents the volume of gas adsorbed at a specific T and P when the surface coverage is θ

v_m is the volume of gas adsorbed at the same T and P when θ equals 1, indicating the formation of a complete monolayer,



$$\frac{P}{v} = \frac{P}{v_m} + \frac{1}{v_m K}$$

$$\text{Slope} = \frac{1}{v_m}$$

$$\text{Intercept} = \frac{1}{v_m K}$$

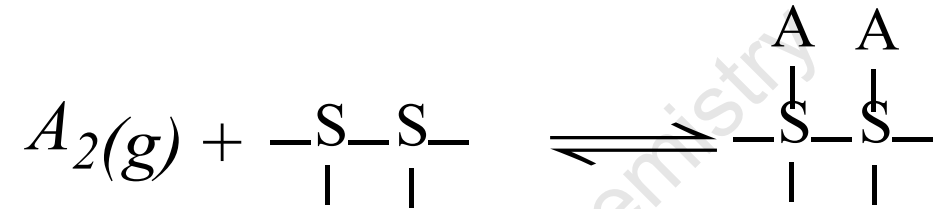


Alternative form of
Langmuir Adsorption
Isotherm

$$K = \frac{\text{Slope}}{\text{Intercept}}$$

verification of Langmuir adsorption isotherm

Langmuir Adsorption Isotherm for a dissociative adsorption



- The adsorption rate remains directly proportional to the pressure P of the overlying gas.
- When two sites are necessary for adsorption, the rate becomes proportional to the square of the number of vacant sites per unit area i.e., $N^2(1 - \theta)^2$

the rate of adsorption:

$$v_a = k_a P N^2 (1 - \theta)^2$$

Similarly, two adsorption sites are required for desorption and therefore, the rate of desorption:

$$v_d = k_d N^2 \theta^2$$

At equilibrium,

$$v_a = v_d$$

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

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

$$\frac{(1 - \theta)^2}{\theta^2} = \frac{1}{KP} \quad \text{where } K = \frac{k_a}{k_d}$$

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

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

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

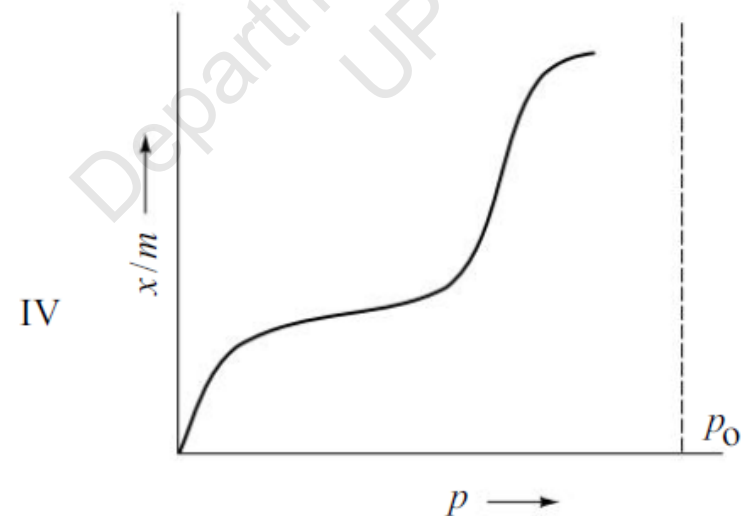
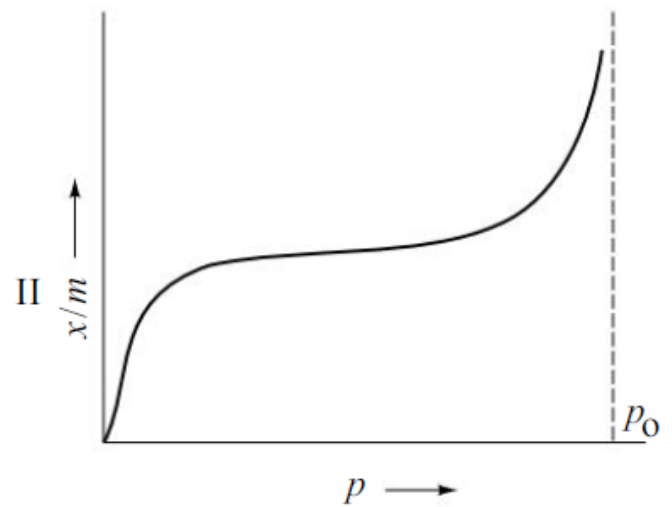
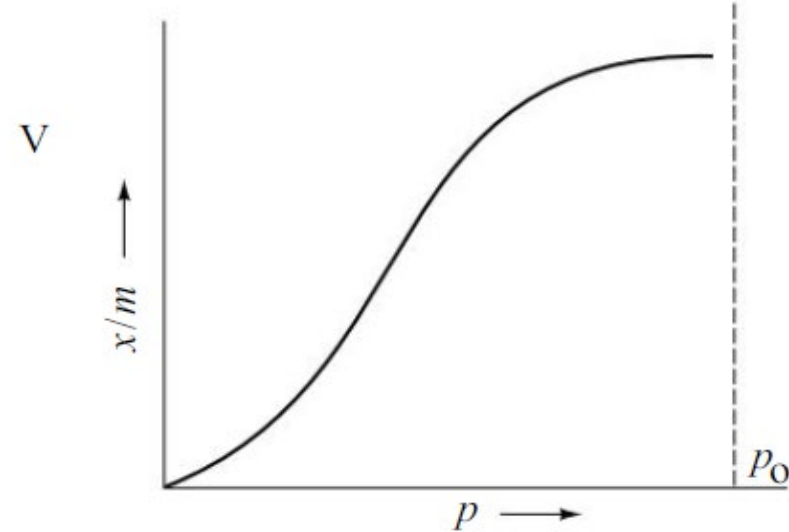
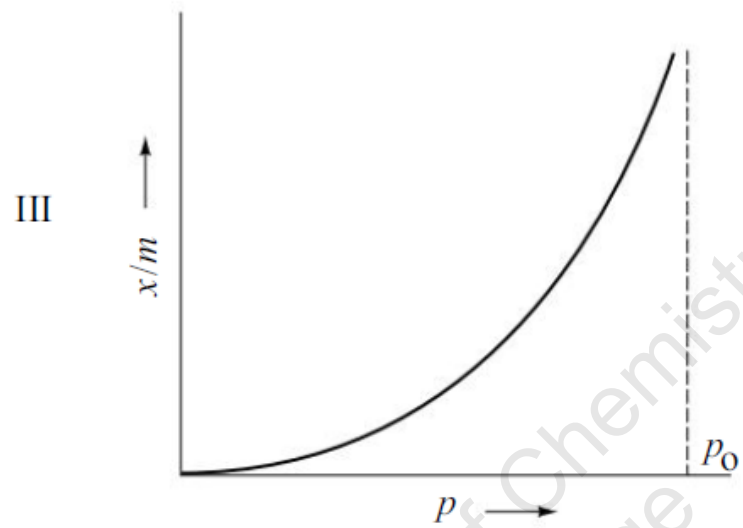
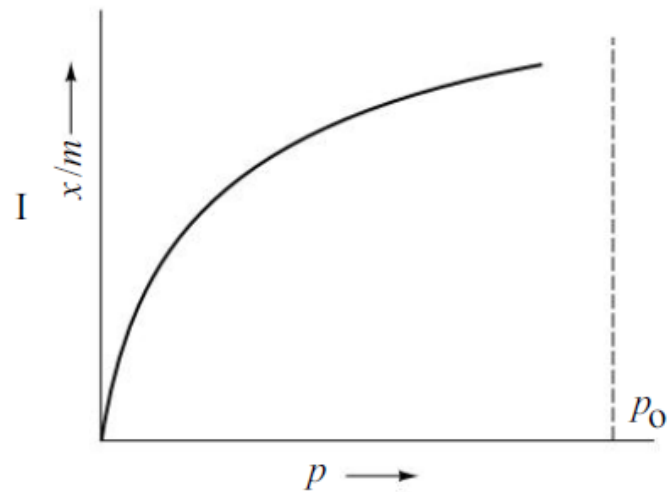
Similarly, when an n atomic molecule undergoes dissociation into atoms during adsorption, The final equation becomes

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

Limitations of Langmuir Adsorption Isotherm

- In the Langmuir adsorption isotherm, only chemisorption is considered, which can elucidate just one of the five distinct types of adsorption isotherms observed in experimental observations. However, both types of adsorptions occur simultaneously in reality.
- If the Langmuir adsorption isotherm holds true, the P/v vs P plot should form a linear relationship across the entire pressure range. However, experimental results indicate that this linearity is preserved only at low pressures, while deviations from linearity become evident in the high-pressure region.
- At sufficiently high pressures, the fraction coverage should theoretically reach a value of 1. However, experimental observations often reveal that in most cases, θ (the fraction coverage) ranges from 0.03 to 0.3.
- While the Langmuir adsorption isotherm suggests no lateral interactions among adsorbed molecules, experiments indicate that these molecules do interact laterally, affecting the enthalpy of adsorption, which varies with surface coverage.

Brunauer–Emmett–Teller (BET) isotherm



Different types of adsorption isotherm

The Brunauer, Emmett, and Teller (BET) theory is based on the following assumptions:

- The adsorbent surface is homogeneous and contains a specific number of equivalent sites.
- The initial layer is formed through chemisorption, and subsequent layers can stack on top of each other. For instance, the second layer adsorbs on top of the first, the third on top of the second, and so on. This stacking is driven by physisorption, specifically Van der Waal forces of attraction.
- A dynamic equilibrium exists between molecules in successive layers. In other words, the rate of evaporation from one layer is equal to the rate of adsorption on the preceding layer.
- The heat of adsorption in the first layer, represented as ΔH_{ad} , depends on the specific adsorbate and adsorbent. In contrast, for subsequent layers (2nd, 3rd, 4th, etc.), it remains constant and is equal to the heat of vapor condensation (H_c).
- There are no lateral interactions among the adsorbed molecules.

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c - 1) p}{v_m c p_0}$$

- Where v represents the volume of gas adsorbed at the pressure p
- v_m is the volume of gas adsorbed, when the surface of the adsorbent is covered completely with a monolayer.
- p_0 is the saturated vapor pressure.
- c is a constant, approximately equal to $e^{(\Delta H_{ad} - \Delta H_c)/RT}$
- ΔH_{ad} is the heat evolved in the adsorption of the first layer of gas molecules and ΔH_c is the heat of condensation of the gas to liquid which is also heat evolved in the absorption of the second or subsequent layer of gas molecules.

BET Adsorption Isotherm

$\frac{p}{v(p_0-p)}$ vs $\frac{p}{p_0}$ → Straight line plot

Slope → $\frac{(c-1)}{v_m c}$

Intercept → $\frac{1}{v_m c}$

From the slope and intercept,
 v_m → the volume required to form a complete monolayer can be calculated.

$$\text{slope} + \text{intercept} = \frac{(c-1)}{v_m c} + \frac{1}{v_m c} = \frac{1}{v_m}$$

$$v_m = \frac{1}{\text{slope} + \text{intercept}}$$

Determination of Surface Area

- v_m is the volume of the gas which is adsorbed when monolayer is fully occupied ($\theta = 1$).
- At STP, the volume occupied by 1 mol of gas is 22414 ml.
- From the value of v_m , the no. of molecules (N) presents in v_m volume of gas is

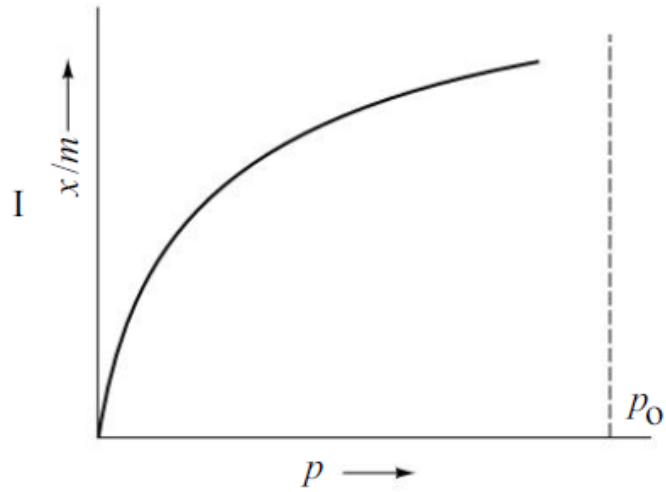
$$N = \frac{v_m(\text{in ml})}{22414 \text{ ml mol}^{-1}} \times N_A \quad N_A \text{ is the Avogadro no.}$$

If the cross-sectional area occupied by each molecule $\rightarrow A$, then the surface area of the adsorbent (S) can be calculated from the following formula

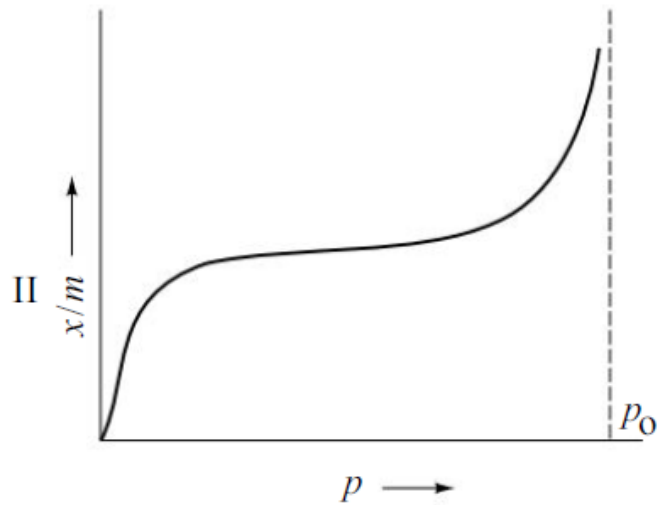
$$S = N \times A$$

$$S = \frac{v_m(\text{in ml})}{22414 \text{ ml mol}^{-1}} \times N_A \times A$$

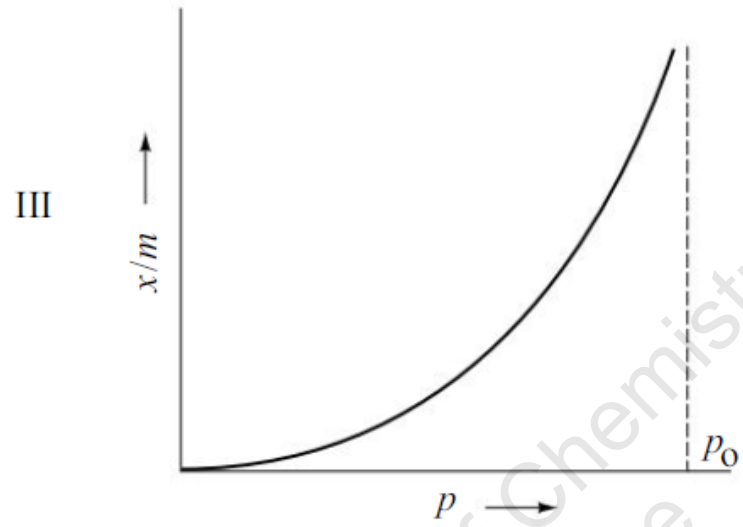
Brunauer–Emmett–Teller (BET) isotherm



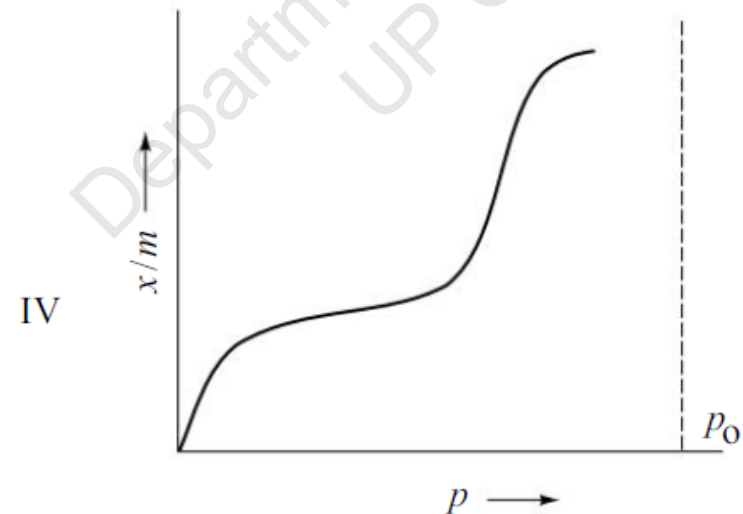
$C \gg 1$ and $p \ll p_0$



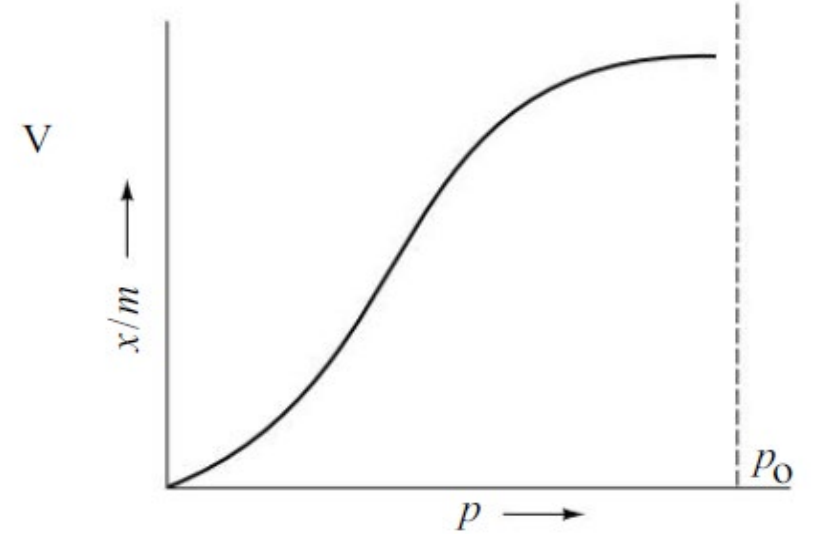
$C > 1$ and multilayer formation takes place



$C < 1$ and physisorption proceeds from beginning



$C > 1$ and indicates the presence of capillary



$C < 1$ and indicates the presence of capillary

Different types of adsorption isotherm

Limitations of BET Adsorption Isotherm

- Except in some ideal situations, a solid surface is usually inhomogeneous.
- In BET adsorption isotherm theory, the interaction between the adsorbed molecules has been neglected. But there must be some lateral interaction.
- In the derivation it has been assumed that the heat of adsorption from second layer onwards is equal, which is not true in real cases
- BET theory is not valid in the entire pressure region. It gives a satisfactory result in the region $0.05 < p/p_0 < 0.3$

Gibbs Adsorption isotherm

- The concentration of a solute at the surface of a liquid might be more than what is found in the overall solution.
- At a specific temperature T , this excess concentration depends on the surface tension of the solution.

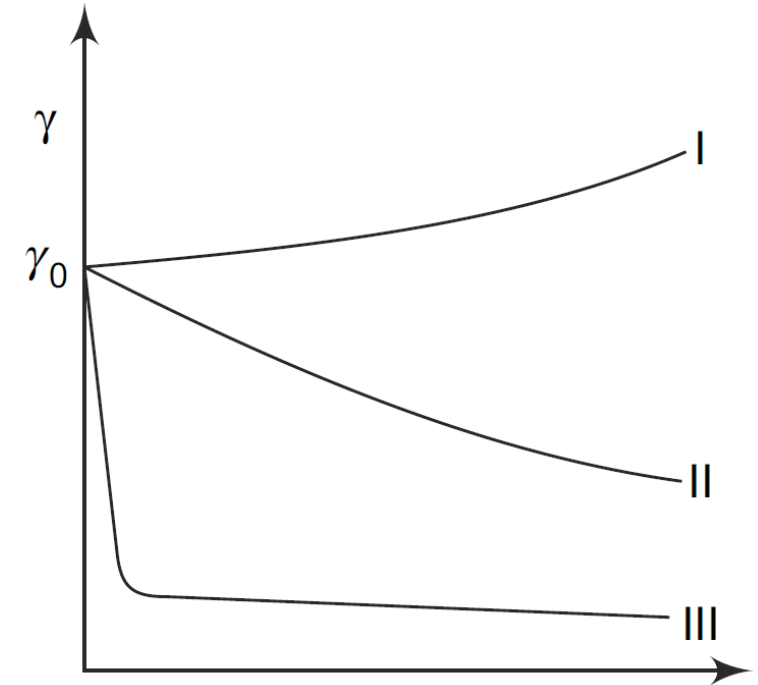
$$\Gamma = -\frac{c_2}{RT} \frac{d\gamma}{dc_2}$$

- Γ is the excess concentration of the solute per unit area of the surface, as compared with that in the bulk of the solution;
- The term $d\gamma/dc_2$ represents the rate at which the surface tension of the solution changes with the concentration of the solute c_2
- R is the universal gas constant
- T is the absolute temperature.

Gibbs Adsorption isotherm

- Depending on the sign of the surface excess concentration (Γ), the surface tension of a solvent changes with the addition of a solute.
- Based on the relationship between γ and c_2 , solutes are generally classified into three categories.

$$\Gamma = -\frac{c_2}{RT} \frac{d\gamma}{dc_2}$$



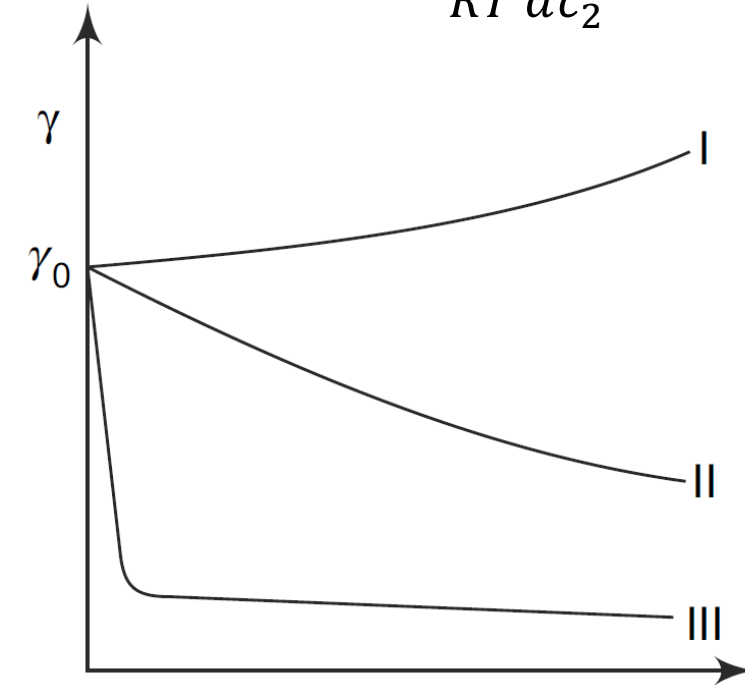
❑ Case I:

- ❑ For solutes such as sucrose and salts like NaCl, KCl, the surface tension increases gradually with an increase in concentration.
- ❑ They have a strong affinity for polar solvents like water.
- ❑ They tend to reside in the bulk rather than at the surface.
- ❑ As a result, the surface excess concentration (Γ) is negative, leading to an increase in surface tension with the addition of solute.

❑ Case II:

- ❑ For solutes such as small organic compounds with polar groups like carboxylic acid group and sulphonic acid group
- ❑ Feature both a polar group and a non-polar hydrophobic part.
- ❑ The polar group exhibits a mild affinity for polar solvents like water, orienting towards the bulk
- ❑ The non-polar hydrophobic part projects outward and occupies the solvent's surface.
- ❑ As a result, the surface excess concentration (Γ) is slightly positive, leading to a decrease in surface tension with the addition of solute.

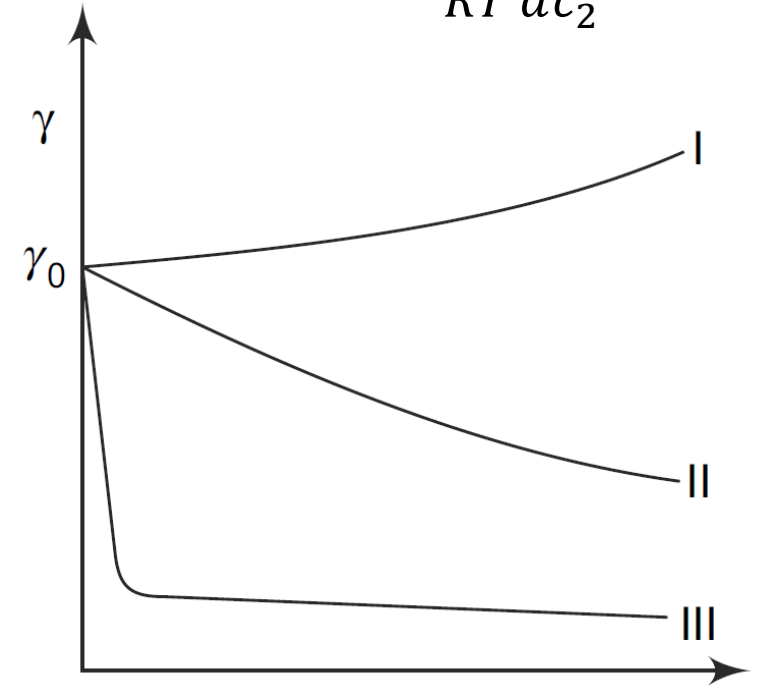
$$\Gamma = -\frac{c_2}{RT} \frac{d\gamma}{dc_2}$$



❑ Case III:

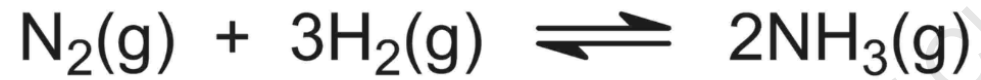
- ❑ For solutes consisting of medium-sized organic molecules with an ionic head, such as Na⁺ or K⁺ salts of carboxylic acids, sulfonic acids, and quaternary amine salts.
- ❑ In this case, the ionic head group exhibits a strong preferential affinity for polar solvents like water
- ❑ The bulky non-polar hydrophobic part orients outward and predominantly occupies the liquid's surface.
- ❑ As a result, the surface excess concentration (Γ) is strongly positive, leading to a rapid decrease in surface tension with the addition of solute.
- ❑ These solutes, which considerably decrease the surface tension by strongly adsorbing at the interface, are called surface-active reagent or surfactants.

$$\Gamma = -\frac{c_2}{RT} \frac{d\gamma}{dc_2}$$

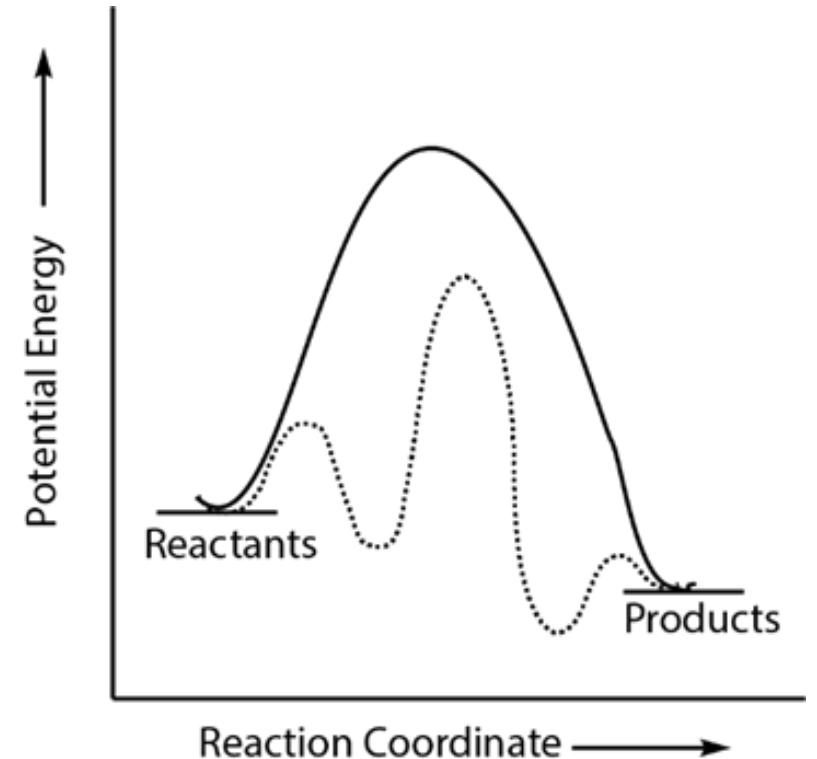


Heterogeneous Catalysis

A heterogeneous catalyst is a catalyst that operates in a phase distinct from that of the reactants and products.



The metal furnishes a surface to which the reactants adhere, preparing them for reaction and facilitating their interactions.

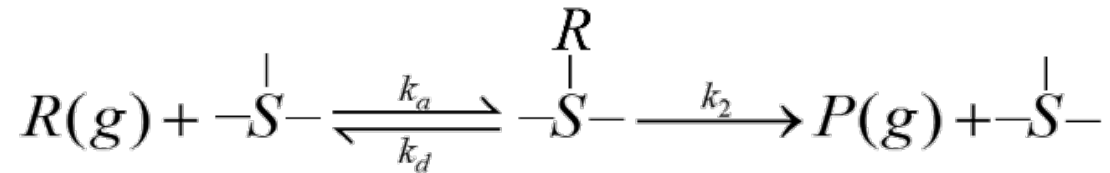


The reaction between gases on the solid surface is common, Majority of catalytic processes falls into this category.

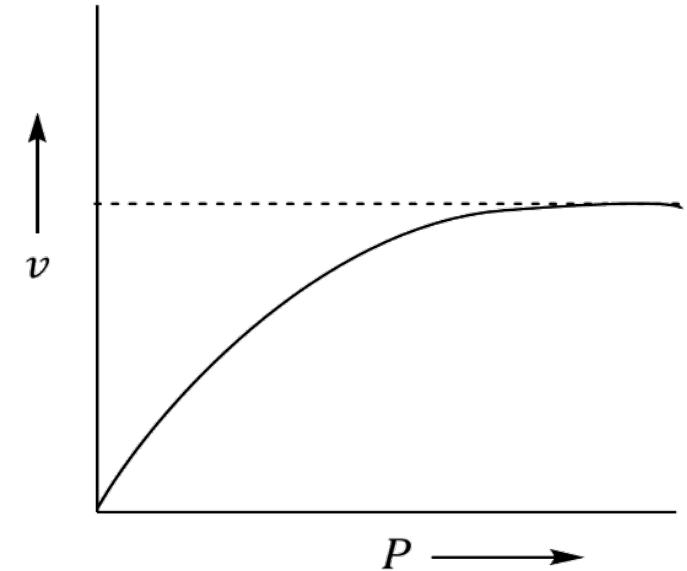
The reactions are expected to proceed in five consecutive steps:

1. Diffusion of the reactant molecules towards the solid surface.
2. Adsorption of the reactant molecules on the surface of catalyst.
3. Reaction on the surface.
4. Desorption of the product molecules from the surface.
5. Diffusion of the desorbed products into the bulk of the gas/liquid phase.

Rate expression for single reactant



- The rate law can be expressed in terms of an adsorption isotherm if it is assumed that the adsorption equilibrium is left undisturbed by the slow reaction of the adsorbed reactant.
- Then, the rate is proportional to the extent of surface coverage.
- The fractional coverage θ is estimated by using the Langmuir isotherm ($\theta = KP/(1 + KP)$), the rate is $v = k_2\theta$



$$v = \frac{k_2KP}{1 + KP}$$

When the pressure is sufficiently low, i.e.,
when $KP \ll 1$

$$v = k_2KP$$

At extremely high pressure, when $KP \gg 1$

$$v = k_2$$