

VIVEKANANDA COLLEGE  
THAKURPUKUR  
KOLKATA-700063

NAAC ACCREDITED 'A' GRADE



Topic : Catalytic Reactions  
Course Title : Enzymes  
Paper : CC4  
Unit : 1  
Semester : 2  
Name of the Teacher : Dr. Kakali Roy  
Name of the Department : Biochemistry

## Catalytic Reaction :

The chemical phenomenon which is influenced by a substance or a set of substances that remains unchanged at the end of the phenomenon is called catalytic reaction. The influencing substances are called catalyst. For example - In Fischer-Tropsch synthesis Ru (Ruthenium) is used as a catalyst.  $(2n+1)H_2 + n CO + [Ru] = C_nH_{(2n+2)} + nH_2O + [Ru]$  - A catalyst increases the forward reaction as well as backward reaction and reduces the activation energy of a reaction corresponding to the non catalytic reaction of the reactants.

According to the phase of reactant, product and catalyst, catalytic reaction are 2 types.

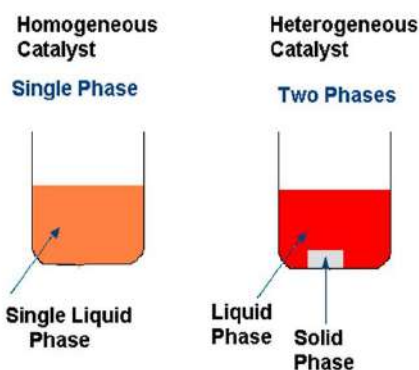
- a) **Homogeneous Catalysis:** The reactants and catalyst remain in the same phase.  
For example – In the decomposition of excited  $NO_3^*$ ,  $NO_2$  is used as catalyst.  
 $NO_3^*(g) + [NO_2(g)] = NO^*(g) + O_2(g) + [NO_2(g)]$   
 $2 SO_2(g) + O_2(g) + NO(g) \rightarrow 2 SO_3(g) + NO(g)$  where NO acts as catalyst
- b) **Heterogeneous Catalysis:** The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis.  
Some of the examples of heterogeneous catalysis are given below:
- Oxidation of  $SO_2$  to  $SO_3$  in the presence of Pt metal or  $V_2O_5$  as catalyst in the contact process for the manufacture of sulphuric acid.  
 $2SO_2(g) + O_2(g) + Pt(s) = 2SO_3(g) + Pt(s)$
  - Combination between nitrogen and hydrogen to form ammonia in the presence of finely divided iron in Haber's process.  
 $N_2(g) + 3H_2(g) + Fe(s) = 2NH_3(g) + Fe(s)$

## Catalysts

Catalysts may be either homogeneous or heterogeneous

A **homogeneous** catalyst is in the same phase as the substances reacting.

A **heterogeneous** catalyst is in a different phase



## Homogeneous catalysis

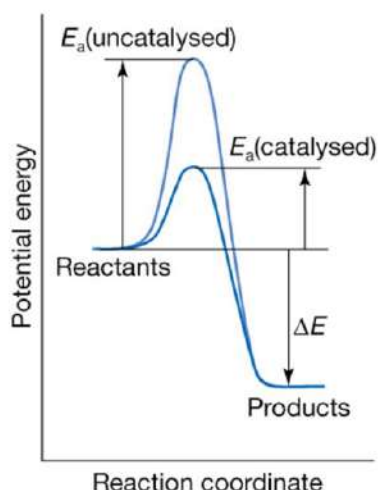
Homogeneous catalysis is catalysis in a solution by a soluble catalyst. Homogeneous catalysis refers to catalytic reactions where the catalyst is in the same phase as the reactants. Homogeneous catalysis applies to reactions in the gas phase and even in solids.

Enzymes are examples of homogeneous catalysts.

Enzymes are homogeneous catalysts that are essential for life but are also harnessed for industrial processes. A well-studied example is carbonic anhydrase, which catalyses the release of  $\text{CO}_2$  into the lungs from the bloodstream.

### 23.5 Features of homogeneous catalysis

- A Catalyst is a substance that accelerates a reaction but undergoes **no net chemical change**.
- Enzymes are biological catalysts and are **very specific**.
- *Homogeneous catalyst*: a catalyst in the same phase as the reaction mixture.
- *heterogeneous catalysts*: a catalyst exists in a different phase from the reaction mixture.



## Primary salt effect

It has been observed that the rate of a reaction can be altered by the presence of non-reacting or inert ionic species in the solution. This effect is profound when the reaction takes place between ions, even at low concentrations.

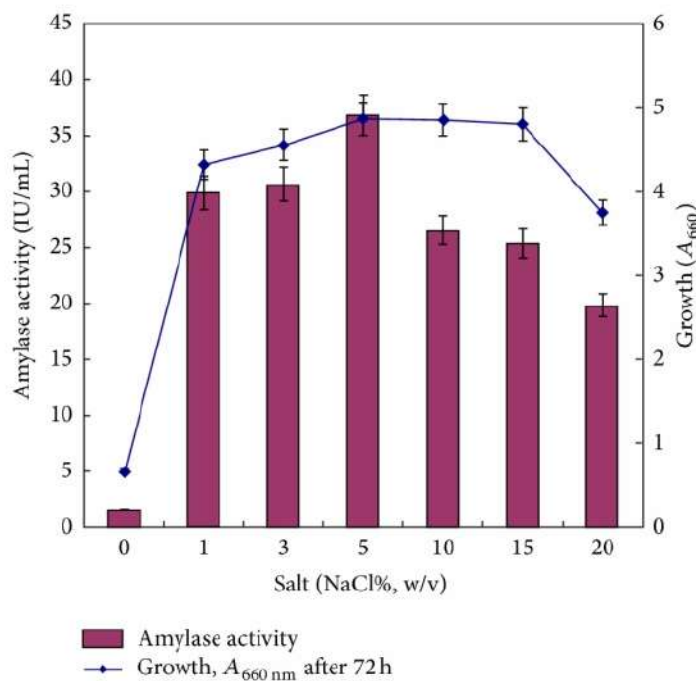
The general effect of an added electrolyte (i.e. an effect other than, or in addition to, that due to its possible involvement as a reactant or catalyst) on the observed rate constant of a reaction in solution. At low concentrations the effect on a given reaction is determined only by the ionic strength of the solution and not by the chemical identity of the ions.

At higher concentrations, the effect of an added electrolyte depends also on the chemical identity of the ions. Such specific action can usually be interpreted as the incursion of a reaction path involving an ion of the electrolyte as reactant or catalyst, in which case the action is not properly to be regarded just as a kinetic electrolyte effect. Kinetic electrolyte

effects are usually (too restrictively and therefore incorrectly) referred to as 'kinetic salt effects'. A kinetic electrolyte effect ascribable solely to the influence of the ionic strength on activity coefficients of ionic reactants and transition states is called a 'primary kinetic electrolyte effect'.

The presence of salt usually affect the conformation, folding, stability and activities of enzymes, including those from the snake venom. Some enzymes are affected by monovalent cations, other and in most cases are affected by divalent cations. Not only the type of cations, but different concentrations would also affect the substrate enzyme interactions.

For example, enzyme such as specific DNA polymerase require 2 - 5 mM of MgCl for catalytic activity, but in addition, the presence of 100mM NaCl would stabilized the enzyme substrate reaction.

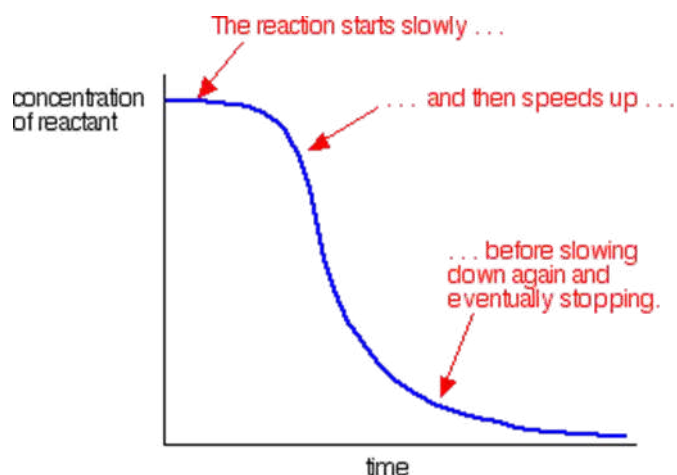


Effect of salt concentration on Amylase activity

## Autocatalysis

A chemical reaction is called autocatalytic if at least one of the reaction products acts as a catalyst in the same or in one of the coupled reactions. Reactions of this type have the property that the rate equations are nonlinear, that is, the reaction is very slow in the beginning but steadily increases as more product is formed.

The simplest autocatalysis is a reaction in which the product acts as a catalyst for its own production: If the products of a reaction act as a catalyst for the reaction, it is referred to as autocatalysis



. Reactions that show autocatalysis start slowly and as more of the reactants get converted to the products, there is an increase in the rate of the reaction. Later, there is a fall in the rate as the concentration of the reactants decreases and the reaction finally comes to an end.

Autocatalysis describes reactions having a rate acceleration as a function of time. These reactions are characterized by an S-shape conversion curve

The reaction proceeds very slowly at the start (induction period) because there is very little catalyst present, increases steadily as the reaction proceeds and the amount of catalyst increases, and slows down again at the end when the reactant gets depleted.

### Auto Catalysis

When one of the products of a reaction itself acts as a catalyst for that reaction the phenomenon is called autocatalysis.

Examples of autocatalysis: -  
(a) Hydrolysis of an ester

$$\text{CH}_3\text{COC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$$

*Here CH<sub>3</sub>COOH is acting as a catalyst.*

An **example of an autocatalytic reaction** is the ester hydrolysis. Each bond cleavage of an ester group in the polymer backbone produces an organic acid which catalyses hydrolytic bond cleavage.

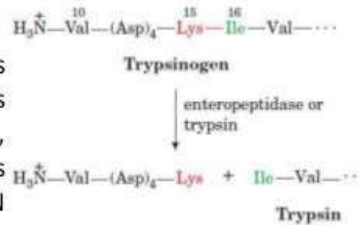
### Autocatalytic activation of trypsinogen by trypsin:

The zymogen of trypsin is trypsinogen, which is activated by a very specific protease, enterokinase, secreted by the mucosa of the duodenum. The trypsin, once activated, can also cleave other trypsinogens as well as the precursors of other proteases such as chymotrypsin and carboxypeptidase to activate them.

# Trypsin

- The activation of **trypsinogen** : two-stage process.

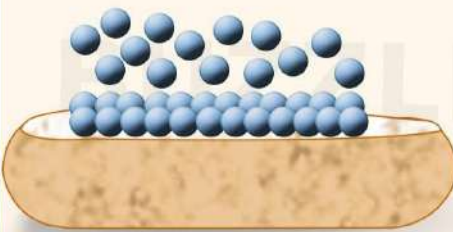
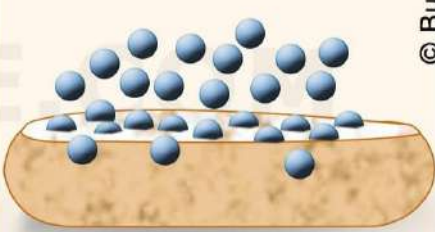
- **Enteropeptidase**, a single-pass transmembrane serine protease that is located in the duodenal mucosa, specifically hydrolyzes trypsinogen's **Lys 15-Ile 16** peptide bond at its N terminal end, forming an hexapeptide.



- Formed small amount of trypsin cleaves trypsinogen to form its active form. I.e. trypsinogen activation is **autocatalytic**

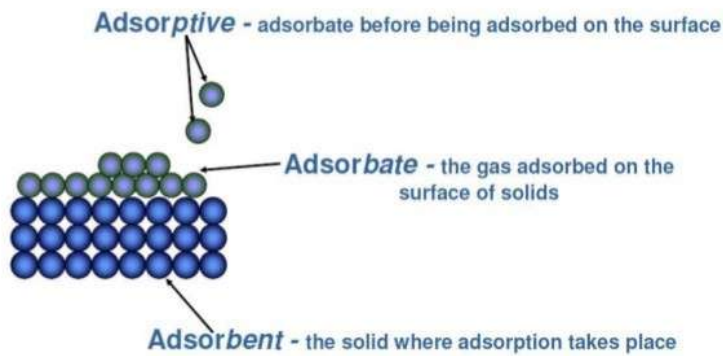


## Adsorption of gases on solids

<p><b>ADSORPTION</b></p>  <p>Molecules adhere to the surface of the phase.</p>	<p><b>ABSORPTION</b></p>  <p>Molecules are drawn into the bulk of the phase.</p>
---	--

© Buzzle.com

# Adsorption Process



CHE4001 Lecture Notes 13 (Page 30)

## Catalysis & Catalysts

### Adsorption On Solid Surface

#### □ Adsorption process

##### Adsorbent and adsorbate

- **Adsorbent** (also called *substrate*) - The solid that provides surface for adsorption
  - > high surface area with proper pore structure and size distribution is essential
  - > good mechanical strength and thermal stability are necessary
- **Adsorbate** - The gas or liquid substances which are to be adsorbed on solid

##### Surface coverage, $\theta$

The solid surface may be completely or partially covered by adsorbed molecules

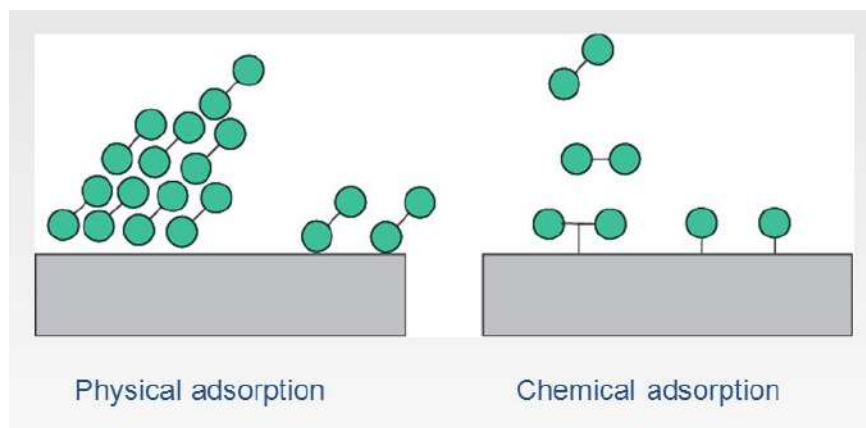
$$\text{define } \theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}} \quad \theta = 0 \sim 1$$

##### Adsorption heat

- Adsorption is usually exothermic (in special cases *dissociated* adsorption can be endothermic)
- The heat of chemisorption is in the same order of magnitude of reaction heat; the heat of physisorption is in the same order of magnitude of condensation heat.

## Types of Adsorption

- **Types of Adsorption:** Depending on the nature of the forces between adsorbate & adsorbent, Adsorption is of two types.
- 1. **Physical Adsorption or physisorption:** Forces of attraction between adsorbate and adsorbent are Van der Waal's forces, they are weak.
- 2. **Chemical Adsorption or chemisorption:** Forces of attraction between adsorbate and adsorbent are as strong as chemical bonds, they are strong. This type of adsorption cannot be easily reversed.



Physical adsorption	Chemical adsorption
1. The forces operating in this case are weak Vander wall's forces.	1. The Forces operating are chemical bonds (ionic or covalent bond).
2. The heat of adsorption is low about 20-40 KJ mol <sup>-1</sup>	2. The heat of absorption are high about 40-400 KJ mol <sup>-1</sup>
3. The process is reversible, desorption can be occur by increasing tem. Or decreasing pressure.	3. The process is irreversible. Efforts to free the adsorbed gas give different Compounds.
4. It does not require any activation energy.	4. It requires activation chergy.
5. It takes place at the low temperature and decreases with increase in the temperature.	5. This type of adsorption first increases with increase in temperature
6. It is not specific in nature all gases adsorbes on all solids to same extent.	6. It is highly specific in nature occurs only by the possibility of formation of chemical bond.
7. It increases with the increase insurface area of the adsorbent.	7. It also increases with the increases with the increase in surface area of adsorbent.
8. It forms multimolecular layer.	8. It forms unimolecular layer.

## Factors affecting adsorption of gases on solids

When a solid surface is brought in contact with a gas or liquid, molecules from the gas or liquid starts to collect at the surface of the solid. This phenomenon of collection of gas or liquid molecules on the surface of the solid is known as adsorption. A substance which accumulates on the solid surface is known as adsorbate and the solid surface on which it occurs is known as adsorbent.

Following are the factors which influence the adsorption of gases by solids.

1. Surface area
2. Nature of gas
3. Temperature
4. Pressure

### 1. Surface Area of adsorbent

Adsorption being a surface phenomenon, the extent of adsorption depends upon the surface area. Increase in the surface area of the adsorbent, increases the total amount of gas adsorbed. Larger the surface area of adsorbent more will be active centres and faster will be the rate of adsorption. Thus finely divided metals (nickel, platinum) and porous substances (Charcoal, silica gel) provides large surface area and are best solid adsorbents.

### 2. Nature of Gas

The amount of gas adsorbed by a solid depends upon the nature of gas. In general, more easily liquefiable a gas is the more readily will it be adsorbed. For example, Gases like  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{CO}_2$ , which can be liquefied easily are more readily adsorbed on the solids surface rather than permanent gases like  $\text{O}_2$ ,  $\text{H}_2$ , etc. Thus 1gm of activated charcoal adsorbs 380 ml of sulphur dioxide, 16 ml of methane and 4.5 ml of hydrogen. This is valid for physical adsorption only. In chemisorption only those gases will be adsorbed which form chemical bonds with it.

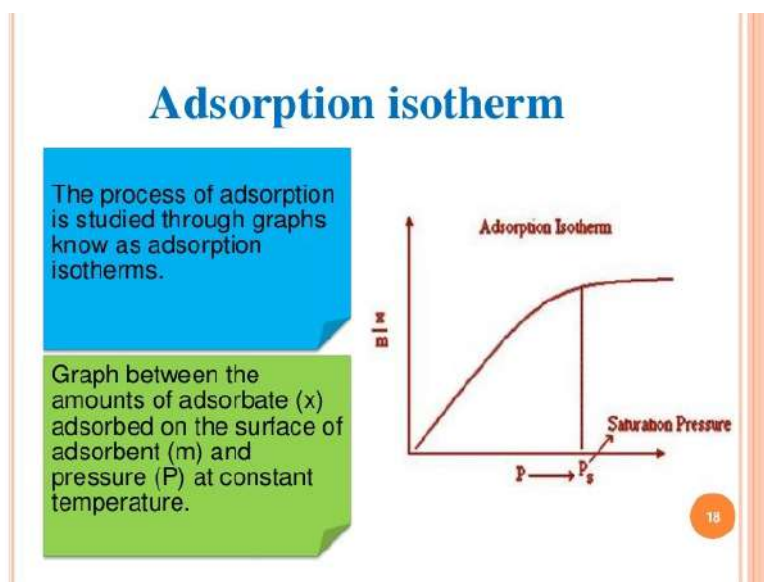
### 3. Effect of temperature

As adsorption is accompanied by evolution of heat, so according to the Le-Chatelier's principle, the magnitude of adsorption should decrease with rise in temperature. When the temperature is increased the kinetic energy of the gas molecules also increases which results in more number of collisions between the molecules and the surface.

#### 4. Pressure

On the solid surface, there is a fixed number of adsorption sites where gas molecules can be adsorbed. Initially when the pressure has increased the rate of adsorption increases due to an increase in the gas molecules striking on the surface. Thus an increase in the pressure increases the rate of adsorption linearly. But after sometime, it will reach a point when the pressure has no effect on the rate of adsorption as the number of adsorption sites is fixed and no more adsorption can happen in those sites. Hence at that point, the extent of adsorption will be independent of the pressure.

**Adsorption Isotherm** is a curve that expresses the variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature.



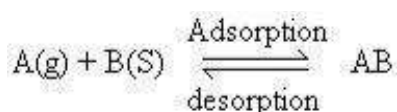
### Langmuir Adsorption Isotherm

In 1916, Irving Langmuir proposed another Adsorption Isotherm which explained the variation of Adsorption with pressure. Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

## Assumptions of Langmuir Isotherm :

Langmuir proposed his theory by making following assumptions.

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.



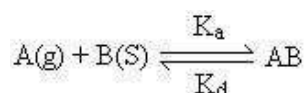
Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

5. Adsorption is monolayer or unilayer.

## Derivations of the Langmuir Adsorption Equation

Calculation of Equilibrium Constant

Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.



Where  $K_a$  represents equilibrium constant for forward reaction and  $K_d$  represents equilibrium constant for backward direction.

According to Kinetic theory,

$$\text{Rate of forward reaction} = K_a [A] [B]$$

$$\text{Rate of backward reaction} = K_d [AB]$$

At equilibrium, Rate of forward reaction is equal to Rate of backward reaction

$$K_a [A] [B] = K_d [AB]$$

$$\text{Or, } \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

$$K = \frac{K_a}{K_d} = \frac{[AB]}{[A][B]}$$

The above equation represents the equilibrium constant for distribution of adsorbate between the surface and the gas phase.

## Derivation

Langmuir Equation which depicts a relationship between the number of active sites of the surface undergoing adsorption (i.e. extent of adsorption) and pressure.

To derive Langmuir Equation and new parameter 'θ' is introduced. Let θ the number of sites of the surface which are covered with gaseous molecules. Therefore, the fraction of surface which are unoccupied by gaseous molecules will be (1 - θ).

Now, Rate of forward direction depends upon two factors: Number of sites available on the surface of adsorbent, (1 - θ) and Pressure, P. Therefore rate of forward reaction is directly proportional to both mentioned factors.

$$\text{Rate of forward reaction} \propto P (1 - \theta)$$

$$\text{Rate of adsorption} \propto P (1 - \theta)$$

$$\text{Or, Rate of adsorption} = K_a P (1 - \theta)$$

Similarly, Rate of backward reaction or Rate of Desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

$$\text{Rate of desorption} \propto \theta$$

$$\text{Or, Rate of desorption} = K_d \theta$$

At equilibrium, rate of adsorption is equal to rate of desorption.

$$K_a P (1 - \theta) = K_d \theta$$

We can solve the above equation to write it in terms of θ.

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

$$K_a P = K_a P \theta + K_d \theta$$

$$K_a P = (K_d + K_a P) \theta$$

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

Divide numerator and denominator on RHS by K<sub>d</sub>, we get

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

Now put

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

in above equation we get

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

**This is known as Langmuir Adsorption Equation.**

## The Langmuir Equation

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

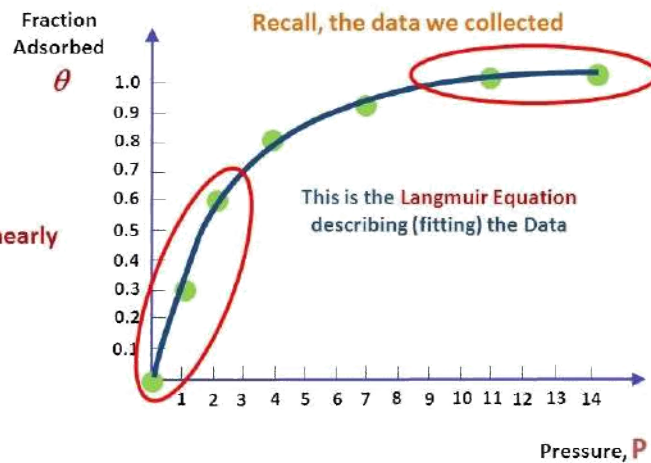
**Notice...**

when  $P \rightarrow 0$ ,  $\theta \rightarrow 0$

**And** at low concentration, adsorption is **linearly proportional to  $P$**

when  $P \rightarrow \infty$ ,  $\theta \rightarrow 1$

i.e. reaches a **monolayer**



## Limitations of Langmuir Adsorption Equation

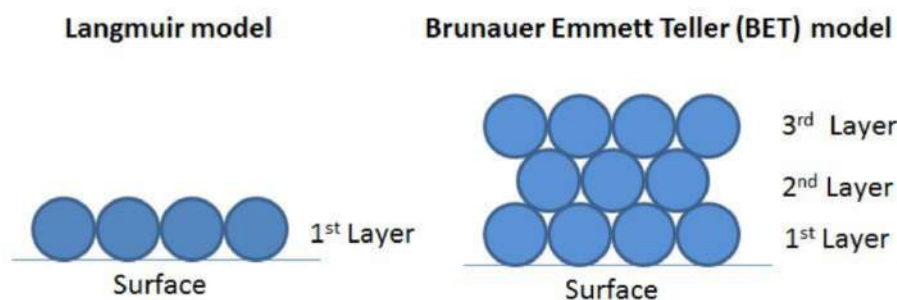
The adsorbed gas has to behave ideally in the vapour phase. This condition can be fulfilled at low pressure conditions only. Thus Langmuir Equation is valid under low pressure only. Langmuir Equation assumes that adsorption is monolayer. But, monolayer formation is possible only under low pressure condition. Under high pressure condition the assumption breaks down as gas molecules attract more and more molecules towards each other. BET theory proposed by Brunauer, Emmett and Teller explained more realistic multilayer adsorption process.

Another assumption was that all the sites on the solid surface are equal in size and shape and have equal affinity for adsorbate molecules i.e. the surface of solid is homogeneous. But we all know that in real solid surfaces are heterogeneous.

Langmuir Equation assumed that molecules do not interact with each other. This is impossible as weak force of attraction exists even between molecules of same type.

The adsorbed molecules has to be localized i.e. decrease in randomness is zero ( $\Delta S = 0$ ). This is not possible because on adsorption liquefaction of gases taking place, which results into decrease in randomness but the value is not zero.

From above facts we can conclude that, Langmuir equation is valid under low pressure conditions.

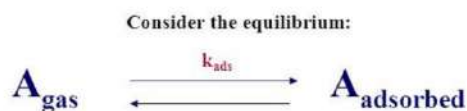


### Langmuir Isotherm

Langmuir's "checkerboard" model of chemisorption assumes that a surface is composed of a finite number of equivalent adsorption sites.

So the maximum coverage is obtained when all sites are filled. The coverage  $\theta$  is expressed in terms of the the number of molecules adsorbed in relation to the number of available sites. i.e.

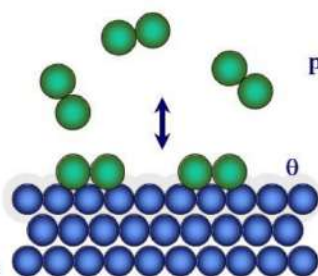
When all sites are filled,  $\theta = 1$ .



The Rate of adsorption is proportional to:

- 1) The number of surface collisions  $n$  from the gas phase per second, which is proportional to the pressure  $p$ .
- 2) area of bare surface available for adsorption  $(1 - \theta)$ .

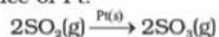
ie. rate of adsorption =  $k_{\text{ads}} p (1 - \theta)$



## Heterogeneous Catalysis

The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis.

For e.g -: Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt.



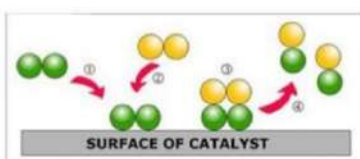
The reactant is in gaseous state while the catalyst is in the solid state.

### Advantages

- There is little difficulty in separating and recycling the catalyst.

### Disadvantages

- There is a lower effective concentration of catalyst since the reaction occurs only on the exposed active surface. ([www.knockhardy.org.uk](http://www.knockhardy.org.uk))

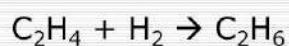


Heterogeneous catalysis also refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Phase here refers not only to solid, liquid, vs gas, but also immiscible liquids, e.g. oil and water.

Examples of Heterogeneous Catalysts:

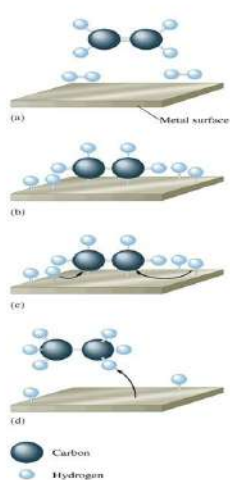
There are several processes which use heterogeneous catalysts to help speed up the reaction. ... Vanadium oxide ( $\text{V}_2\text{O}_5$ ) is a brown/yellow solid on which the oxygen and sulphur dioxide can adsorb in order to react with each other to form sulphuric acid.

## Heterogeneous Catalysis



with a metal catalyst

- reactants
- adsorption
- migration/reaction
- desorption



Reference :

1. [www.google.com](http://www.google.com)
2. [www.chemguide.co.uk>catalysis>introduction](http://www.chemguide.co.uk/catalysis/introduction)
3. [Catalysis-ed.org.uk/Principles/mechanism.htm](http://Catalysis-ed.org.uk/Principles/mechanism.htm)
4. [Industrial catalyst-Lessons-Tes Teach—tes.com](http://Industrial%20catalyst-Lessons-Tes%20Teach—tes.com)