Unit□II

SURFACE CHEMISTRY AND CATALYSIS

Introduction - Terminologies in surface chemistry - Difference between adsorption and absorption - Types of adsorption - Adsorption isotherm- Freundlich Adsorption Isotherms- Langmuir Adsorption Isotherm - Contact Theory (or) Mechanism of Heterogeneous Catalysis - Kinetics of Surface Reaction - Kinetics of Bimolecular Reaction (Langmuir-Hinshelwood) - Types of Adsorption Isotherm - Application of Adsorption- Terms - Mechanism of Catalytic Reaction- Criteria (or) Characteristics for Catalyst Types of Catalysis - Homogeneous Catalysis - Heterogeneous Catalysis- Catalytic Poisoning and Promoters Application of Catalysis- Biological Catalyst— —Enzymes - Kinetics of Enzyme Catalysed Reaction Or Michaelis and Menten equation - Factors Affecting Enzyme Activity

CHAPTER 2: Surface Chemistry

INTRODUCTION

Surface Chemistry is closely related to interface and colloidal science. Surface chemistry is important in many criticalchemical processes, such as enzymatic reactions at biological interfaces found in cell walls and membranes, in electronics at the surfaces and interfaces of microchips used in computers, and the heterogeneous catalysts found in the catalytic converter used for cleaning emissions in automobile exhausts.

DEFINITION

Surface science is the study of chemical phenomena that occur at the interface of two phases (solid–liquid interfaces, solid–gas interfaces, solid–vacuum interfaces, and liquid-gas interfaces). **(or)**

It is defined as the ***study of chemical reactions at interfaces***.

TERMINOLOGIES IN SURFACE CHEMISTRY

- **Adsorbate:** The substance which gets adsorbed on any surface is called ***adsorbate.***
- **Adsorbent:** The substance on the surface of which adsorption takes place is called **adsorbent**.
- **Adsorption**: The process whereby molecules of gases or liquids adhere chemically to the surface of a solid.

  (Eg.) Occlusion of Hydrogen gas on Palladium where palladium is adsorbent and hydrogen gas is adsorbate.

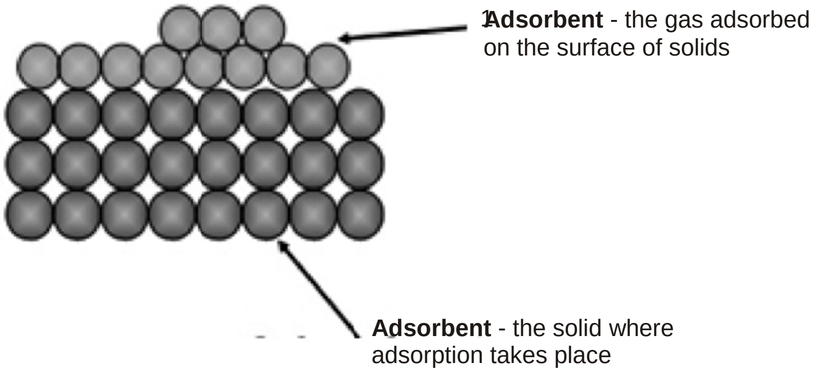


Figure 2.1 : Adsorption Process

- **Desorption:** The removal of the adsorbed substance from a surface is called ***desorption***.
- **Interface:** The plane which separates any two phase is generally called an ***interface.***
- **Absorption:** When the molecules of a substance are uniformly distributed throughout the body of a solid or liquid. This phenomenon is called ***absorption***.
- **Sorption:** The phenomenon in which adsorption and absorption occur simultaneously is called ***sorption.***
- **Occlusion:** When adsorption of gases occurs on the surface of metals it is called ***occlusion.***

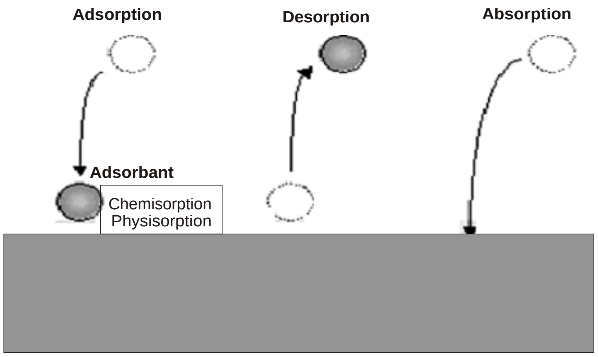


Figure 2.2 : Occlusion Process

- **Positive adsorption:** When the concentration of solute adsorbed on the solid adsorbent surface is greater than in the bulk it is called *positive adsorption.*

  (Eg.) Concentrated solution of KC*l* is shaken with blood charcoal, it shows positive adsorption

- **Negative adsorption:** When the solvent from the solution may be absorbed by the adsorbent so that the concentration of the solute decreases and the concentration of solution increases than the initial concentration and it is called *negative adsorption***.**

  (Eg.) Dilute solution of KC*l* is shaken with blood charcoal it shows negative adsorption.

Enthalpy or heat of adsorption

Amount of heat evolved when 1 mole of an adsorbate gets adsorbed on the surface of an adsorbent is called ***Molar Heat*** **or** ***Molar Enthalpy of Adsorption***.

DIFFERENCE BETWEEN ADSORPTION AND ABSORPTION

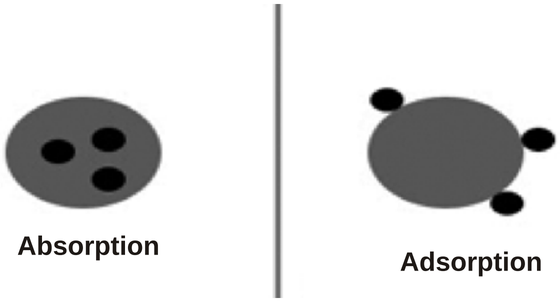
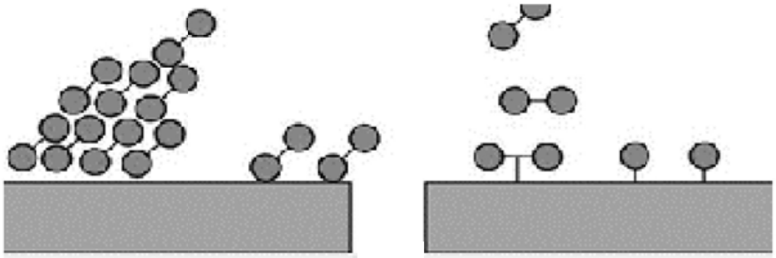


Figure 2.3 : Illustration of Absorption and Adsorption

S.No.	ABSORPTION	ADSORPTION
1.	It is a bulk phenomenon	It is a surface phenomenon
2.	It is a slow process	It is a fast process
3.	Substance uniformly distributed throughout the surface	Higher concentration of molecular species in the surface than in the bulk
4.	Attainment of equilibrium takes time	Equilibrium attained easily
5.	Eg.: Ammonia adsorbed in charcoal	Eg.: Ammonia adsorbed in water

TYPES OF ADSORPTION



Physical Adsorption **Chemical Adsorption**

Figure 2.4 : Illustration of Physical and Chemical Adsorption

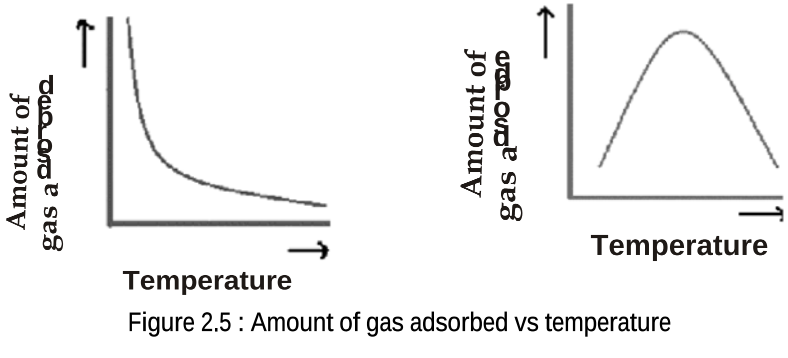


Figure 2.5 : Amount of gas adsorbed vs temperature

S.No	Physical adsorption or Physisorption	Chemical adsorption or Chemisorption
1.	Caused by intermolecular vanderwaal's forces	Caused by chemical bond formation
2.	Not specific in nature	Highly specific in nature
3.	Reversible in nature	Irreversible in nature
4.	Multimolecular layers are formed on the adsorbed surface	Unimolecular layers are formmed on the surface
5.	Heaat of adsorption is less (20 to 40 KJ/mole)	Heat of adsorption is large (80 to 240 KJ/mole)
6.	No activation energy is required	High activation energy is required
7.	Depends on nature of gas. Easily Liquefiable gases are adsorbed easily	Depends on nature of adsorbent and adsorbate
8.	Occurs at low temperature	Increases with increase in temperature
9.	Increase in pressure increase adsorption	High pressure is favourable. Decrease in pressure does not cause desorption

Adsorption of Gases on Solids

In adsorption of gases on solid surface, the solid surface is called the adsorbent and the gas adsorbed is called **adsorbate**. The extent of adsorption depends on many factors.

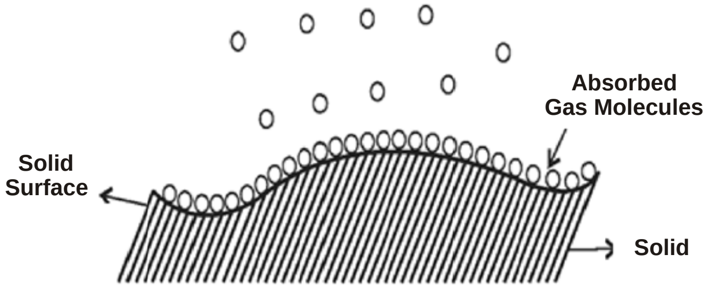


Figure 2.6 : Adsorption of gases on solids

2.2 FACTORS AFFECTING THE EXTENT OF ADSORPTION

(i) Nature of Adsorbent

The adsorption depends on the type of adsorbents used. When the adsorbent is highly porous the rate of adsorption increases. Activated carbon, metal oxides like aluminum oxide, silica gel and clay are commonly used adsorbents. The rate of adsorption can be increased by activation process. It helps in enhancing the pores in the adsorbent **Eg. charcoal adsorbs 0.011 gms of CCl_4 at 24°C and activated charcoal adsorbs 1.48 gm of at 24°C.**

Activation of adsorbent

During activation, the adsorbent is heated in steam to about 1500°C. Heating drives out all impurities and leads to a lager free surface for adsorption. It can be done in 3 given ways

- By making the surface of adsorbent rough.
- By heating the adsorbent in vacuum so that the water vapour present in pores leave those pores.
- By increasing the surface area of adsorbent

(ii) Surface area of adsorbent

Increase in surface area of the adsorbent increases the adsorption of gases and the extent of adsorption depends on two factors

- Greater the surface area greater the adsorption-Increase in surface area increases the number of adsorbing sites.
- Larger the porosity greater the adsorption-Finely divided and highly porous materials acts as good adsorbents.

  Eg. Charcoal and silica gel (excellent adsorbents).

(iii) Nature of Gases

The amount of gas adsorbed by a solid depends on the nature of the gas. Easily liquefiable gases like HI, NH_3, CI_2, SO_2 etc., are adsorbed more easily then the permanent gases like H_2, N_2, and O_2 etc. Physical adsorption is non-specific in nature, so any gas will be adsorbed on the surface under any given conditions of temperature and pressure. Chemisorption is specific in nature so only those gases which forms chemical bonds will be adsorbed.

The nature of gas depends on two factors:

- **Critical Temperature** (maximum temperature above which the gas cannot be liquefied). Liquefactions of gases depend on critical temperature. When the critical temperature is more the gases will be liquefied and more adsorption occurs.
- **Van der Waal's forces**: Easily liquefiable gases possess greater Vander Waal's forces than permanent gases, so they are adsorbed more readily.

(iv) Exothermic Nature

Heat of adsorption is defined as the energy liberated when 1 g mol of a gas is adsorbed on a solid surface. Increase in temperature increases the kinetic energy of the gas molecules and it results in more number of collisions of gas molecules over the adsorbent surface.

(v) Pressure

When pressure is increased then the rate of adsorption increases initially. The extent of adsorption is expressed as x/m where 'x' is amount of adsorbate; 'm' is mass of adsorbent when the dynamic equilibrium is established between free gas and the adsorbed gas. But after some time it reaches appoint where no more adsorption occurs and at this point adsorption is independent of pressure.

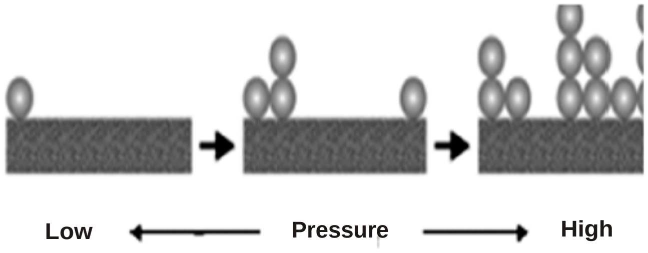


Figure 2.7 : Rate of adsorption

3. ADSORPTION OF SOLUTE FROM SOLUTIONS

The process of adsorption of solutes on solid surface can take place from solutions. For example the activated animal charcoal adsorbs colouring matter present in sugar solution and clarifies the sugar solution. It also has the capacity to adsorb acetic acid and oxalic acid from water thereby reducing the concentration of acids in water.

There are two (or more) components present in a solution namely**solute** and **solvent.** The solute may be present in the molecular or ionic form. The extent of adsorption from solution depends upon the concentration of the solute in the solution, and can be expressed by the **Freundlich Isotherm**.

$$\frac{x}{m} = k \cdot c^{(1 \cdot n)}$$

(or)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

where, x- is the mass of the solute adsorbed,

m -is the mass of the solid adsorbent,

c -is the concentration of the solute in the solution &

n -is a constant having value greater than one,

k -is the proportionality constant.

The value of k depends upon the nature of solid, its particle size, temperature, and the nature of solute and solvent etc. It the graph is plot between x/m against c which gives a straight line which is similar to Freundlich adsorption isotherm.

FACTORS AFFECTING ADSORPTION OF SOLUTES FROM SOLUTION

Nature of adsorbent

Adsorption ofsolute from solution is highly specific. Adsorption depends mainly on nature of adsorbent.

Temperature

Adsorption from solution decreases with rise in temperature.

Concentration of solute

Adsorption from solution decrease with decrease in concentration of solution.eg charcoal adsorbs water from dilute KCl solution whereas charcoal adsorbs KCl from concentrated KCl solution.

4. ADSORPTION ISOTHERM

The process of adsorption is usuallystudied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure (P) at constant temperature.

$$\text{Adsorbent} + \text{Adsorbate} \Longleftrightarrow \text{Adsorption}$$

Adsorption isotherm shows the amount of molecules adsorbed on the solid surface as a function of the equilibrium partial pressure at constant temperature.

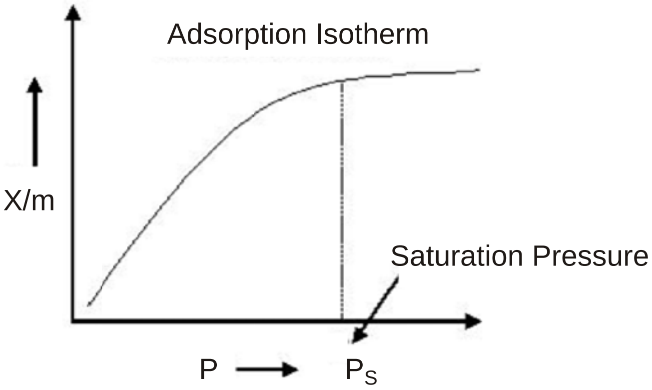


Figure 2.8 : Adsorption Isotherm

A plot of x/m vs P is plotted to obtain adsorption at constant temperature, P_s is called the ***saturation pressure.***

FREUNDLICH ADSORPTION ISOTHERMS

In 1909, Herbert Freundlich gave an expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure.Freundlich adsorption isotherm is an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. The isotherm is given as:

$$\frac{x}{m} = k \cdot p^{\left(\frac{1}{n}\right)} \qquad [n > 1]$$

(or)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

where x – is mass of adsorbate,

m – is mass of adsorbent,

P – is the equilibrium pressure of adsorbate,

K & n – are constants.

At low pressure, extent of adsorption is directly proportional to pressure:

$$\frac{x}{m} \propto p^1$$

At high pressure, extent of adsorption is independent of pressure:

$$\frac{x}{m} \propto p^0$$

At intermediate value of pressure, adsorption is directly proportional to pressure raised to power $\frac{1}{n}$· n value is greater than 1.

$$\frac{x}{m} \propto p^{(1/n)}$$

To remove proportionality a proportionality constant 'k' is used which is known as adsorption constant and we get

$$\frac{x}{m} = k \cdot p^{\left(\frac{1}{n}\right)}$$

The above equation is known as **Freundlich Adsorption equation**.

Plotting of Freundlich Adsorption Isotherm

$$\frac{x}{m} = k \cdot p^{\left(\frac{1}{n}\right)}$$

Taking log both sides of equation, we get,

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

The equation is comparable with equation of straight line, $y = mx + c$ where, m represents slope of the line and c represents intercept on y axis. Plotting a graph between log (x/m) and log p, we will get a straight line with value of slope equal to $1/n$ and log k as y-axis intercept.

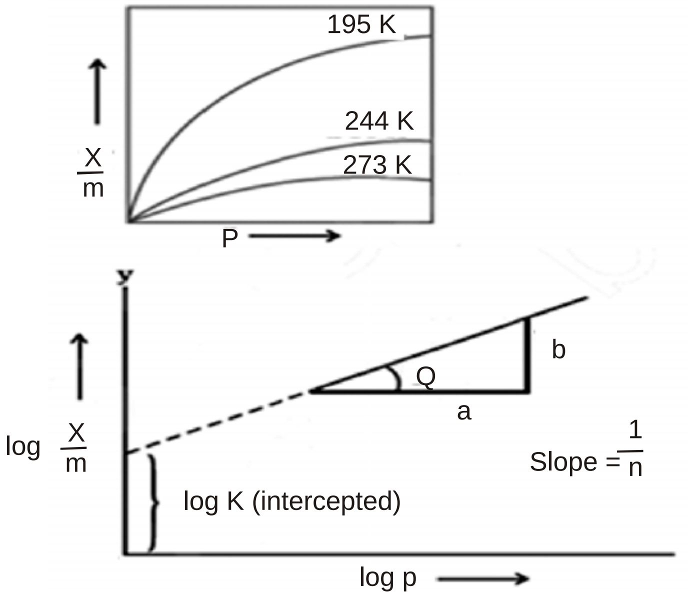


Figure 2.9 : log (*x*/*m*) vs. log p graph

Limitation of Freundlich Adsorption Isotherm

1. Freundlich equation is purely empirical and has no theoretical basis.
2. The equation is valid only upto a certain pressure and invalid at higher pressure.
3. The constants *k* and *n* are not temperature independent, they vary with temperature.
4. Frendilich's adsorption isotherm fails when the concentration of the adsorbate is very high.

LANGMUIR ADSORPTION ISOTHERM

In 1916, Irving Langmuir proposed another adsorption Isotherm which explained the variation of adsorption with pressure

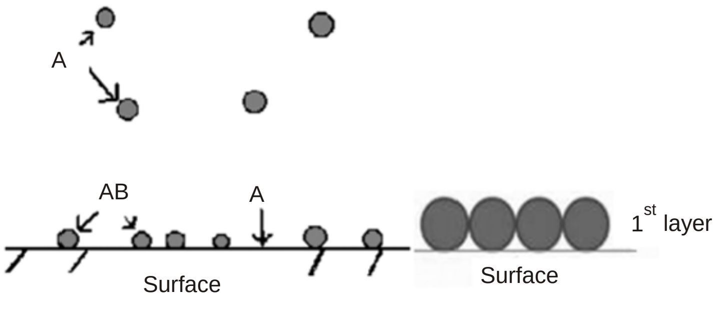


Figure 2.10 : Equilibrium between tree molecule and adsorbed molecules

Assumptions of Langmuir Isotherm

Langmuir proposed his theory by making following assumptions.

(i) Surface is energetically uniform. Fixed number of vacant or adsorption sites are available on the surface of the solid.

(ii) All the vacant sites are of equal size and shape on the surface of adsorbent.

Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released.

(iii) Heat of adsorption is constant throughout the surface and it ranges from 0 to 1.

(iv) Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

(v) Adsorption is monolayer or unilayer.

Derivation

Langmuir Equation depicts the relationship between the extent of adsorption and pressure. Langmuir proposed that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. Using the equilibrium equation, equilibrium constant can be calculated.

$$A(g)+B(s) \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\square}} AB$$

where $A(g)$ – is unadsorbed gaseous molecule

$B(s)$ – is unoccupied metal surface and

AB – is adsorbed gaseous molecule

According to Kinetic theory,

Rate of forward reaction = $K_a [A] [B]$

Rate of backward reaction = $K_d [AB]$

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

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

A new parameter ‘θ’ is introduced.

Let θ be the number of sites of the surface which are covered with gaseous molecule and (1–è) be the fraction of surface unoccupied by gaseous molecule. Rate of forward direction depends upon two factors, number of sites available on the surface of adsorbent, (1 – θ) and pressure, P.

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

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

Rate of adsorption $= K_a P(1-\theta)$

Rate of backward reaction or rate of desorption depends upon number of sites occupied by the gaseous molecules on the surface of adsorbent.

Rate of desorption $\propto \theta$ (or)

Rate of desorption $= K_d \theta$

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

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

The above equation can be written in terms 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_d, we get

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

But $K = \dfrac{K_a}{K_d}$

Substituting in the above equation we get

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

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

Alternate form of Langmuir Adsorption Equation

Langmuir adsorption equation can be written in an alternate form in terms of volume of gas adsorbed. Let V be volume of gas adsorbed under given sets of conditions of temperature and pressure and V_{mono} be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecule.

$$\theta = \frac{V}{V_{mono}}$$

Substituting the value of θ in Langmuir equation

$$\frac{V}{V_{mono}} = \frac{KP}{1 + kP}$$

(or) $$V_{mono} = 1 + \frac{1}{kP}$$

in terms of pressure P we get, Langmuir Adsorption Equation in alternate form.

Thus, if we plot a graph between P/V vs P, we will obtain a straight line with Slope = $1/V_{mono}$ and intercept $=1/KV_{mono}$.

Limitations of Langmuir Adsorption Equation

(i) The adsorbed gas has to behave ideally in the vapour phase. Langmuir equation is valid under low pressure only.

(ii) 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.

(iii) Another assumption is the surface of solid is homogeneous but in real solid surfaces is heterogeneous.

(iv) 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.

(v) In adsorption liquefaction of gases taking place, which results in decrease in randomness but the value is not zero.

5. CONTACT THEORY (OR) MECHANISM OF HETEROGENEOUS CATALYSIS (OR) ADSORPTION THEORY

This theory postulated by Faraday in 1883. It explains the action of heterogeneous catalysis. Heterogeneous catalysis has five steps.

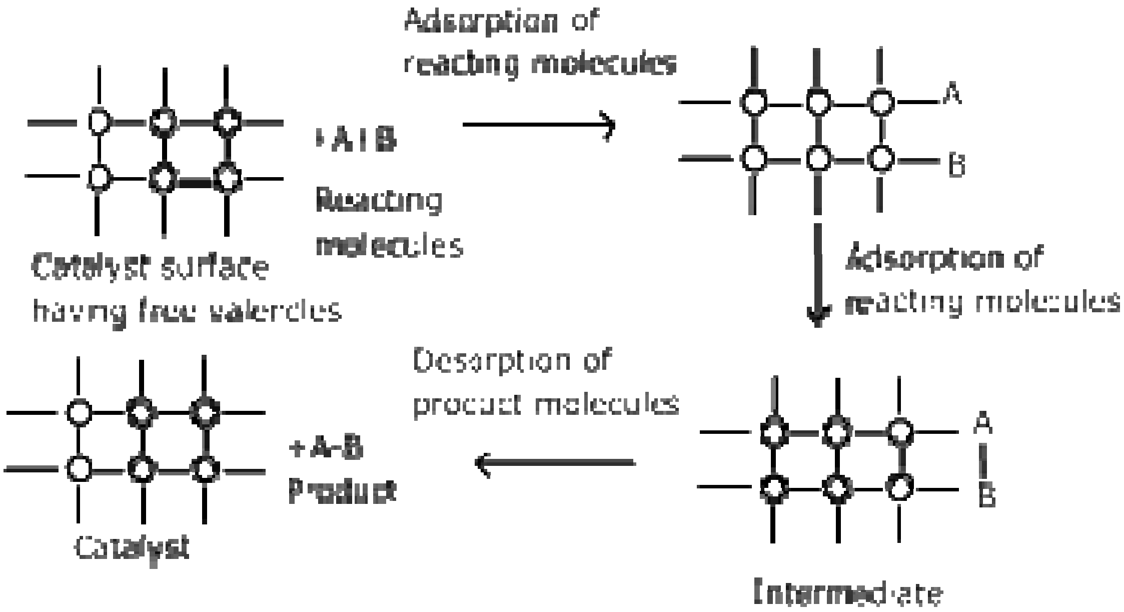


Figure 2.11 : Mechanism of heterogeneous catalysis

(i) **Diffusion of Reactant(s) to the Surface**: The reactants diffuse to the surface of the catalysts. Some of the reactant cross the barrier and enter the interior exposed surface that includes paths and cracks on the external surface.

(ii) **Adsorption of reactants**: Bonds are formed as the reactant(s) are adsorbed onto the surface of the catalyst. The ability for an atom or molecule to stick to the surface is known as the Sticking Co-efficient.

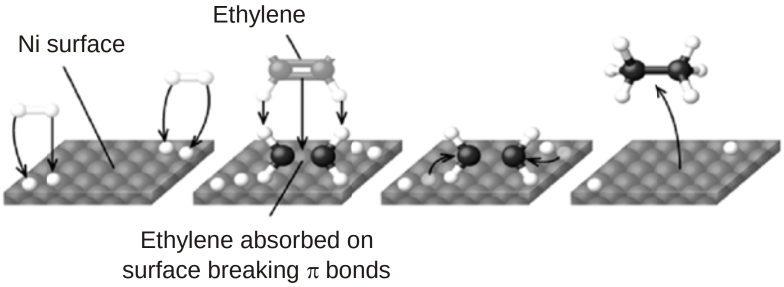
(iii) **Reaction**: The reactants, when bound to the surface have a higher probability of reacting with each other, and after the reaction, they forman intermediate compound.

(iv) **Desorption of products**: The intermediate compound gets desorbed fromthe surface, which again becomes available for adsorption for other molecules

(v) **Diffusion of Product(s)**: The intermediate compound then disintegrates to form the final products and the products are then desorbed from the surface of the catalyst.

For example,

1. Conversion of ethylene to ethane



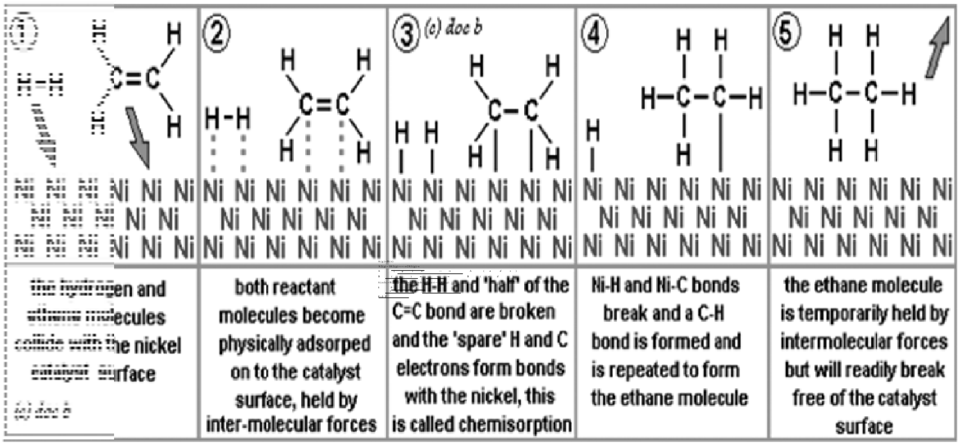


Figure 2.12 : Conversion of ethylene to ethane

2. Haber–Bosch reaction

The original Haber–Bosch reaction chambers used osmium as the catalyst, less expensive iron-based catalyst, which is still used today.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

The reaction mechanism, involving the heterogeneous catalyst, is believed to involve the following steps:

1. $N_2(g) \rightarrow N_2(\text{adsorbed})$
2. $N_2(\text{adsorbed}) \rightarrow 2\,N(\text{adsorbed})$
3. $H_2(g) \rightarrow H_2(\text{adsorbed})$

4. H_2 (adsorbed) → 2 H (adsorbed)

5. N (adsorbed) + 3 H (adsorbed) → NH_3 (adsorbed)

6. NH_3 (adsorbed) → NH_3 (*g*)

6. KINETICS OF SURFACE REACTION

The kinetics of heterogeneously-catalyzed reactions might vary with the partial pressures of the reactant gases above the catalyst surface which can be predicted by using the Langmuir isotherm.

6.1 KINETICS OF UNIMOLECULAR DECOMPOSITION

Examples of unimolecular decomposition

1. Decomposition of NH_3 to N_2 and H_2 on metal surfaces,

2. Decomposition of Phosphine on glass,

3. Decomposition of Formic acid on glass, P*t*, A*g*, A*u*, or T*i*O_2.

Consider the surface decomposition of a molecule A, i.e. the process

$$\text{A}(g) \longrightarrow \text{A (adsorbed)} \longrightarrow \text{Product}$$

Assumption

1. The decomposition reaction occurs uniformly across the surface sites. Molecule 'A' may be adsorbed and is not restricted to a limited number of specific sites.
2. The products are very weakly bound to the surface and, they can be easily deformed.
3. The rate determining step is the surface decomposition step.

According to Langmuir adsorption isotherm molecule 'A' adsorbed on the surface is in equilibrium with the gas phase and the surface concentration is represented as:

$$\theta = \frac{b \cdot P}{(1 + b \cdot P)}$$

The rate of the surface decomposition is given by an expression :

$$\text{Rate} = k\,\theta$$

Substituting, θ , in the rate expression we get:

$$\text{Rate} = \frac{k\,b\,\text{P}}{(1 + b\,\text{P})}$$

The reaction is expressed within two limits:

a. Low pressure limit: $b \cdot \text{P} << 1$(First order reaction with a first order constant $k' = k \cdot b$)

$$\text{Rate} = \frac{k' \cdot \text{P}}{(1 + b\text{P})}$$

$$\text{Rate} = \frac{\text{K}' \cdot \text{P} + \text{K}'}{b}$$

So $\text{Rate} \;\square\; k \cdot b \cdot \text{P}$ as $\frac{\text{K}'}{b}$ is constant.

Under low pressure 'è' is very small and rate is directly proportional to pressure

b. High pressure limit: $b \cdot \text{P} >> 1$ (Zero order reaction)

$$\text{Rate} = \frac{k \cdot b \cdot \text{P}}{(1 + b\text{P})}$$

$$\text{Rate} = \frac{k}{(1 + b\text{P})}$$

Therefore

$$(1 + b \cdot \text{P}) \sim b \cdot \text{P} \quad \text{and} \quad \text{Rate} \sim k$$

Under high pressure θ is almost unity.

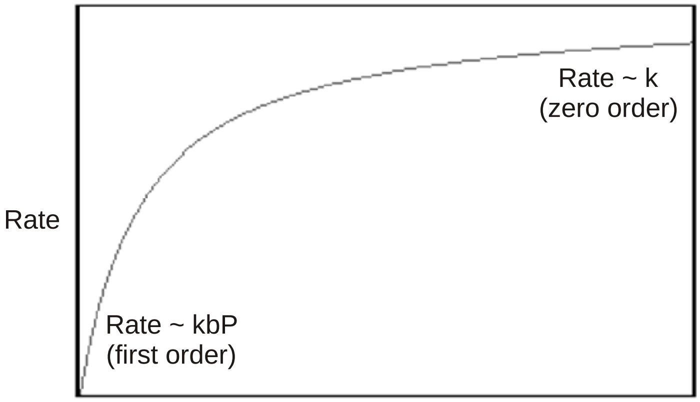


Figure 2.13 : Graphical representation of unimolecular surface decomposition

6.2 KINETICS OF BIMOLECULAR REACTION (Langmuir-Hinshelwood)

Between molecular adsorbates.

Consider the reaction:

$$A(g) \longleftrightarrow A(ads)$$

$$B(g) \longleftrightarrow B(ads)$$

$$A(ads) + B(ads) \xrightarrow{rds} AB(ads) \xrightarrow{\text{fast}} AB(g)$$

Assumption:

The surface reaction between the two adsorbed species is the rate determining step. The rate of the reaction of the two adsorbed molecules for biomolecular surface will be given by:

$$\text{Rate} = k\,\theta_A\,\theta_B$$

According to Langmuir adsorption isotherm:

$$\theta = \frac{b \cdot P}{(1 + b \cdot P)}$$

where two molecules (A & B) are competing for the same adsorption sites then

$$\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B} \quad \text{and} \quad \theta_B = \frac{b_B P_B}{1 + b_A P_A + b_B P_B}$$

Substituting these into the rate expression gives:

$$\text{Rate} = k\,\theta_A\,\theta_B = \frac{k\,b_A P_A \cdot b_B P_B}{\left(1 + b_A P_A + b_B P_B\right)^2}$$

Condition

1. Reactant Aand B in first order then

$b_A P_A << 1$ and $b_B P_B << 1$

θ_A & θ_B are very low.

Hence, Rate $\rightarrow k\, b_A P_A b_B P_B = k' P_A P_B$

2. First order in A, but negative first order in B then

$b_A P_A << 1 << b_B P_B$

$\theta_A \rightarrow 0,\ \theta_B \rightarrow 1$ so Rate $= \dfrac{k\, b_A P_A}{(b_B P_B)} = \dfrac{k' P_A}{P_B}$

7. TYPES OF ADSORPTION ISOTHERM

Adsorption process is usually studied through graphs known as adsorption isotherm. After saturation pressure P_s, adsorption does not occur anymore, as there are limited numbers of vacancies on the surface of the adsorbent. At high pressure when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, adsorption is independent of pressure. There are 5 different types of adsorption isotherms and each of them has specific characteristics.

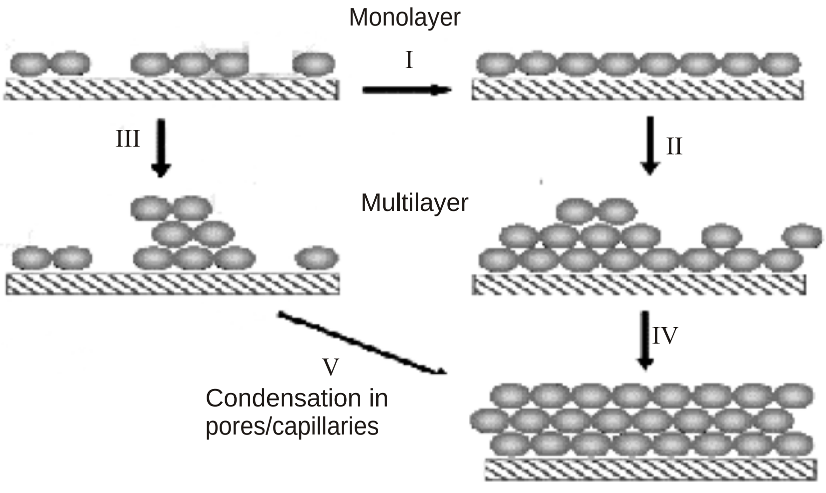


Figure 2.14 : Illustration of different types of Adsorption Isotherm

Type I Adsorption isotherm is for very small pores or microporous adsorbents. Adsorption occurs by filling of micropores and it mainly depicts Monolayer adsorption.

Eg. Adsorption of Nitrogen or Hydrogen on charcoal around –1800°C.

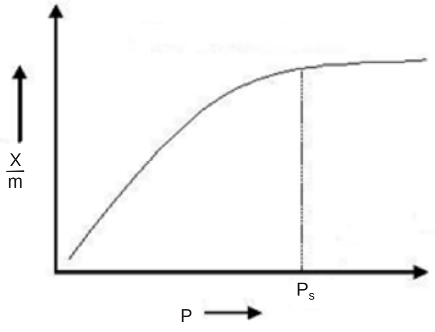


Figure 2.15 : Type I

Type II Adsorption isotherm shows large deviation from Langmuir model of adsorption. They are most frequently encountered when adsorption occurs on nonporous powders or macroporous adsorbents with unrestricted monolayer -multilayer adsorption.

The intermediate flat region in the isotherm corresponds to monolayer formation. When the monolayer formation of the adsorbed molecules are complete, multilayer formation starts to take place corresponding to the **'sharp knee'** of the isotherms.

Eg: Iron (Fe) catalyst and Nitrogen (N_2 (g)) adsorbed at –1950°C on silica gel.f

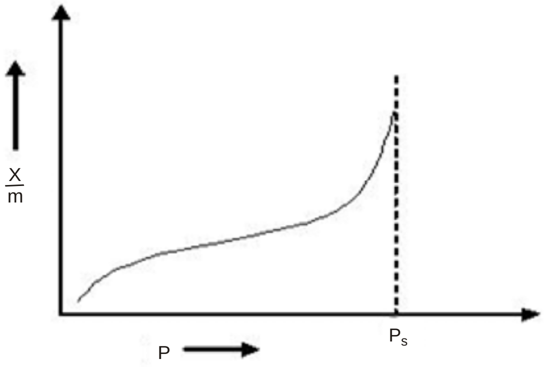


Figure 2.16 : Type II

Type III Adsorption Isotherm also shows large deviation from Langmuir model. This isotherm explains the formation of multilayer. They are characterized principally by heats of adsorption which are less than the adsorbate heat of liquefaction.

Eg: Bromine (Br_2) at 790°C on silica gel or Iodine (I_2) at 790°C on silica gel.

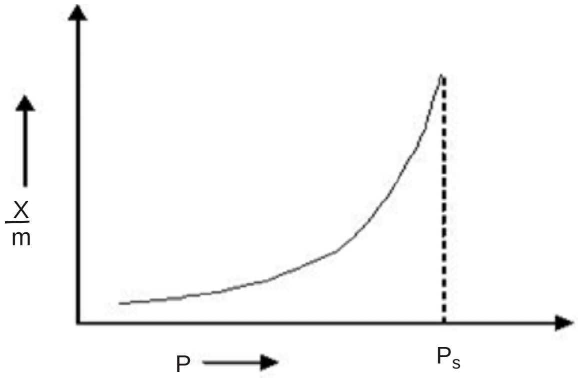


Figure 2.17 : Type III

Type IV Adsorption Isotherm occur on porous adsorbents possessing pores in the range of approximately 15-1000 angstroms (A). At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer.

The intermediate flat region in the isotherm corresponds to monolayer formation.

The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure (P_S) of the gas.

Eg. Adsorption of Benzene on Iron Oxide (Fe_2O_3) at 500°C and adsorption of Benzene on silica gel at 500°C.

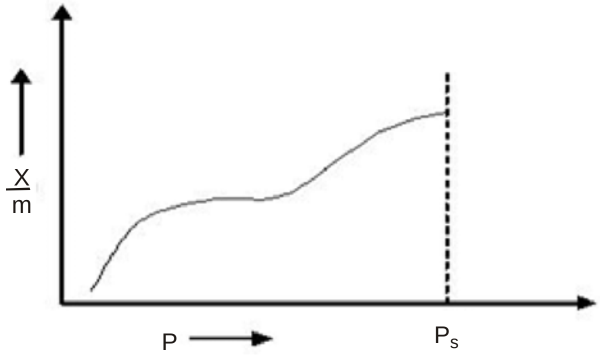


Figure 2.18 : Type IV

Type V Adsorption Isotherm results from small adsorbate-adsorbent interaction potentials similar to the Type III isotherms. However, Type V isotherms are also associated with pores in the same range as those of the Type IV isotherms.

Eg: Adsorption of Water (vapors) at 1000°C on charcoal.

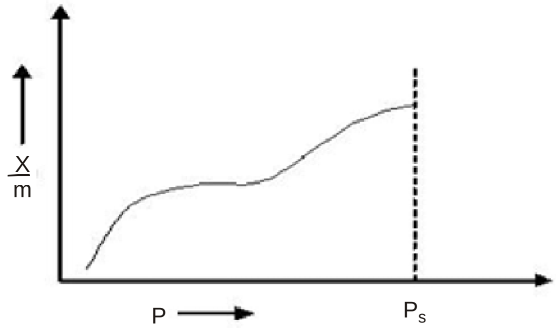


Figure 2.19 : Type V

Type III and Type V isotherms do not have the **'sharp knee'** shape implying stronger adsorbate – adsorbate interactions than adsorbate-adsorbent interaction.

Type IV and V shows phenomenon of capillary condensation of gas.

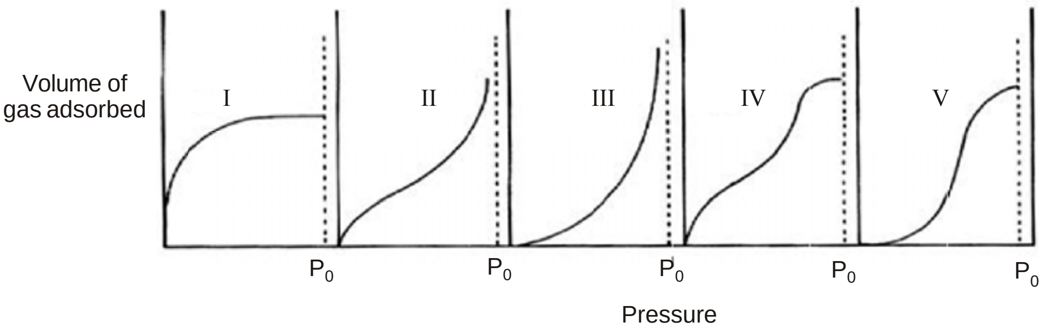


Figure 2.20 : Different types of adsorption isotherms

8. APPLICATION OF ADSORPTION

Extensive application of adsorption is been listed below

(i) Production of high vacuum

In Dewar flasks activated charcoal is placed between the walls of the flask so that gas entering into the annular space gets adsorbed.

(ii) In Gas masks

Activated carbon is used in gas masks to adsorb poisonous gases (e.g. oxide of sulphur, NO*x* etc.) and purifies air for breathing.

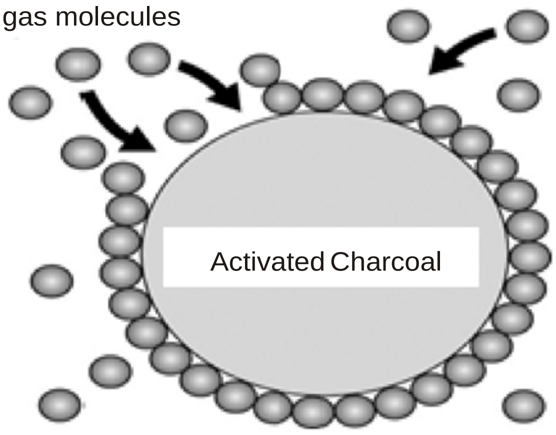


Figure 2.21 : Adsorption of poisonous gases using activated charcoal

(iii) In desiccation or dehumidification

Certain substances can be used to remove water vapour or moisture present in the air. Silica gel and alumina are used for dehumidification in electronic equipment.

(iv) In clarification of sugar

Sugar is decolorized by treating sugar solution with animal charcoal powder which removes the colour producing substances.

(v) In paint industry

The paint should not contain dissolved gases as it inhibits the adherence capacity of paint to the surface to be coated. The dissolved gases are therefore, removed by suitable adsorbents. This is done by adding suitable liquids which adsorbs these films. Such liquids are called wetting agents. Eg. Use of spirit as wetting agent in furniture painting..

(vi) Adsorption chromatography

Analytical method, in which molecules are separated according to their adsorptive properties, where a mobile fluid phase is passed over an immobile solid adsorptive stationary phase.

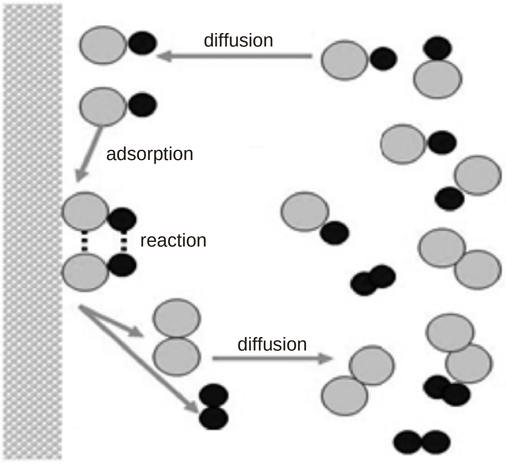
(vii) In adsorption indicators

Various dyes which possess adsorption property have been introduced as indicators mainly in precipitation titrations. For example KBr is titrated with $AgNO_3$ using eosin as an indicator

(viii) Heterogeneous Catalysis

In heterogeneous catalytic reactions adsorption of gaseous reactants on solid catalyst occurs. The adsorption mechanism is responsible for the greater efficiency of the catalyst in the finely divided state and helps us to understand the action of catalyst promoters and poisons. eg,

1. Finely powdered nickel is used for the hydrogenation of oils.
2. In manufacture of sulphuric acid finely divided vanadium pentaoxide (V_2O_5) is used in the contact process.



(i) **diffusion** of reactants to surface;
(ii) **adsorption** of reactants to surface;
(iii) **reaction** on the surface;
(iv) **desorption** of products from surface;
(v) diffusion of products away from the surface**.**

Figure 2.22 : Process of Heterogeneous Catalysis

(ix) In adsorption indicators

In many precipitation titrations many dyes are used as indicators which work on the principle of adsorption.

(x) In curing diseases

Some pharmaceutical drugs have the capacity to adsorb the germs on them and kill them and protect us from diseases.

(xi) Lake test for aluminium

It is based on adsorption of litmus paper by $Al(OH)_3$ precipitate

(xii) Separation of inert gases

Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

(xiii) In softening of hardwater

The use of ion exchangers for softening of hard water is based upon the principle of adsorption chromatography. The ion exchange resins helps to remove hardness causing ions from water and make it useful for industrial and domestic applications.

(xiv) Arsenic Poisoning

Colloidal ferric hydroxide is administered which adsorbs arsenic and removes it from body by vomiting

(xv) Formation of stable emulsions in cosmetics and syrups etc.

(xvi) Froth floatation method

Used for concentration of sulphide ores is based on adsorption.

(xvii) In cleaning action of soaps and detergents

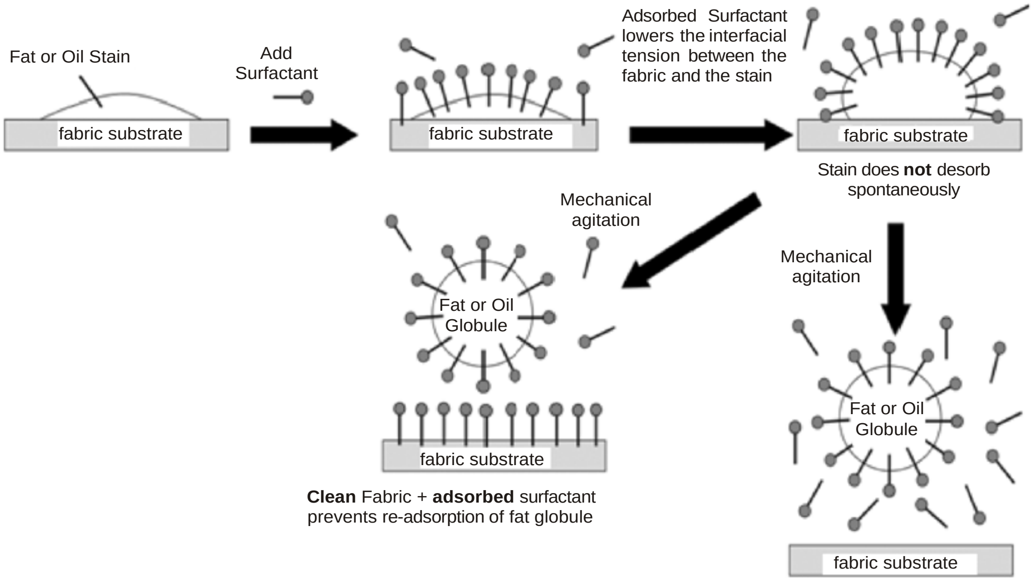


Figure 2.23 : Cleaning actions of soaps and detergents

(xviii) *Application of adsorbents on pollution abatement*

- Many pollutants, both natural and synthetic, are gaseous in nature and it need to be effectively removed from the exhaust.
- Gaseous industrial pollutants include HC*l*, H_2SO_4, H_2S, SO_x, NO_x, NH_3, Ethylene, Benzene, Ethanol, and HAP's. Adsorption is a mass transfer process in which a porous solid comes in contact with a liquid or gaseous stream to selectively remove pollutants or contaminates by adsorbing them onto the solid.
- The most common adsorbents used in industry are activated carbon, silica gel, activated alumina (alumina oxide), and zeolite. Activated carbon is the most common non-polar adsorbent. Polar adsorbents have a great attraction to absorb moisture.
- Most industrial exhaust streams contain moisture the use of polar adsorbents is significantly limited for air pollution control systems. There are two main types of adsorption systems; fixed bed or continuous.

[1] Fixed Bed or Packed Bed Systems

These are quite simple devices. The fixed bed or packed bed reactors are most commonly used for study of solid catalyst. A fixed bed reactor usually consists of a cylindrical vessel packed with the adsorbent material (eg. activated carbon) and it contains more surface area for adsorption. The contaminated or the polluted air enters the fixed bed system at the side, where there is an exhaust distributor. The exhausted air exits the fixed bed adsorber clean of pollutants or contaminates. Once the adsorbent is fully saturated with adsorbate the system requires change-out of the spent materials, which is then packed with new adsorbent material. The spent adsorbent will be thermally cleaned.

Advantages

1. Ideal plug flow behavior
2. Lower maintenance cost

Disadvantage

1. Plugging of bed due to coke deposition which results in high pressure drop.

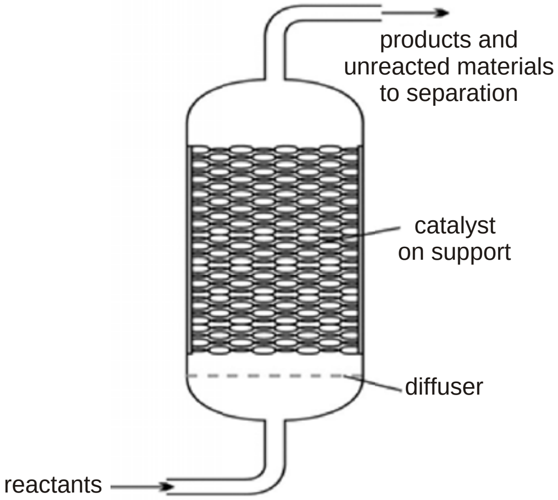


Figure 2.24 : Fixed Bed Reactor Device

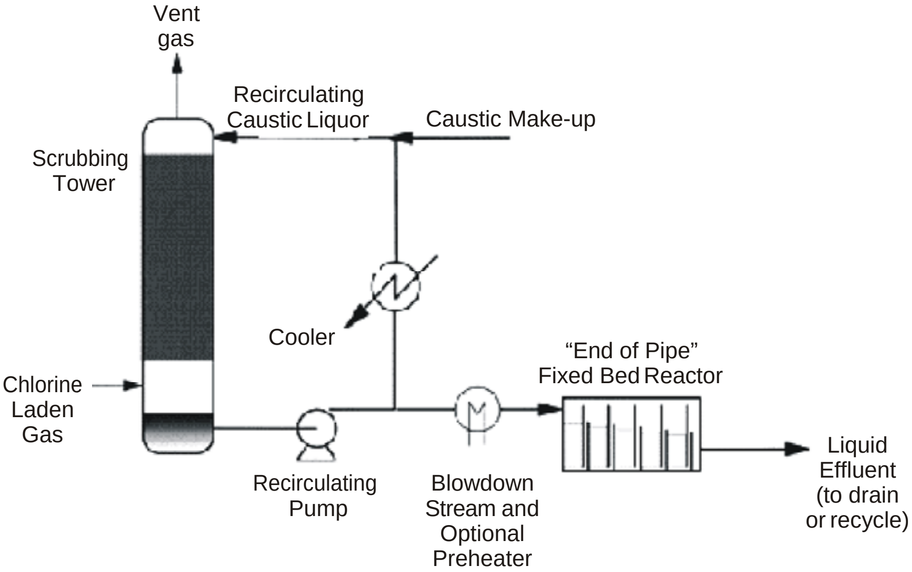


Figure 2.25 : Schematic representation of fixed bed reactor

[2] Continuous Flow Reactor Systems

Continuous-flow reactors are almost always operated at steady state. These are more complex and provide continuous operations. These systems provide in-situ desorption of the adsorbates from the adsorbent. This can be done with superheated or saturated steam. The adsorbate can be condensed, collected, and re-used in the process. There are two adsorber units in the system. The gases are being adsorbed in one unit as the other unit is being desorbed with steam. The exhaust from the desorbed bed can be condensed for solvent reuse or other beneficial purpose.

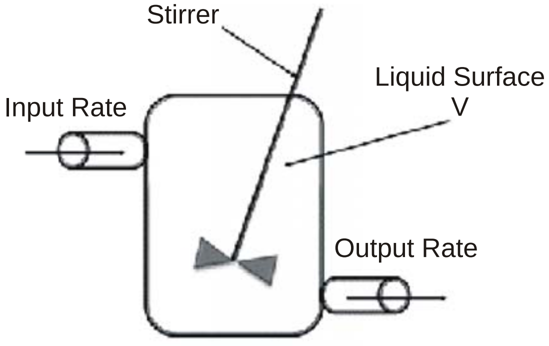


Figure 2.26 : Continuous Flow Reactor

[3] Special Type of Continuous System (Zeolite Concentrator, or Rotary Concentrator)

A hydrophobic zeolite is designed in a monolithic rotor in which the contaminated air flows. An integrated thermal oxidizer is used to provide desorption of the solvents from the zeolite. They have wide acceptance in industrial air pollution control applications.

CHAPTER 3: Catalysis

A catalyst is defined as a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the end of the reaction. The process is called catalysis.

3.1 INTRODUCTION

The word "catalyst" was introduced into science by the great Swedish chemist Jons Jakob Berzelius (1779-1848) who also determined the atomic and molecular weights of thousands of substances, discovered several elements including selenium, first isolated silicon and titanium, and created the present system of writing chemical symbols and reactions.

Catalysts are of immense importance in chemistry and biology. All enzymes are catalysts that expedite the biochemical reactions necessary for life. (eg) Enzymes in saliva accelerate the conversion of starch to glucose.

3.1.1 DEFINITION

The process by which a substance speeds up a chemical reaction without being consumed or altered in the process.

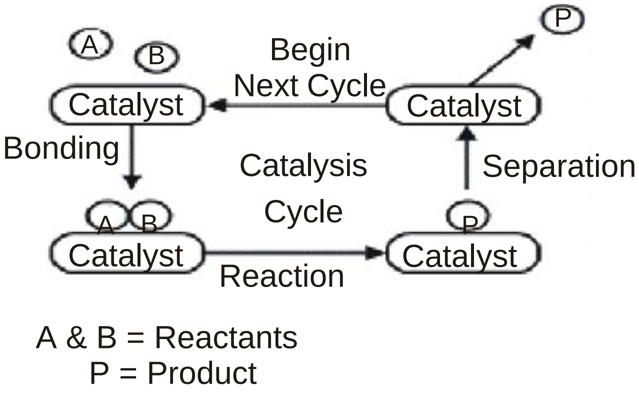


Figure 3.1 : Catalysis Cycle

1. TERMS

1. *Catalyst*

A catalyst is a substance that decreases the activation energy of a chemical reaction without itself being changed at the end of the chemical reaction

(or)

It is the small amount of substance which alters the velocity of reaction without altering in any change in mass and composition at the end of the reaction.

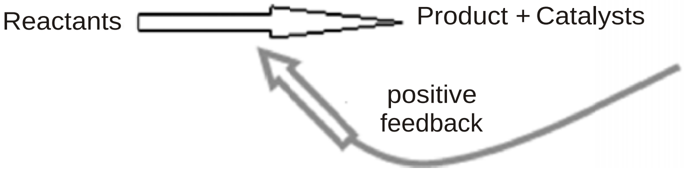
2. *Positive and negative catalyst*

Catalyst helps in altering the velocity of the reaction and the catalyst is called as positive catalyst.eg.MnO_2 acts as catalyst in decomposition of $KClO_3$ into KCl and O_2.Some catalyst have the capacity to retard the chemical reaction and they are called as negative catalyst .eg Alcohol retards the conversion of chloroform to phosgene.

3. *Auto Catalysis*

If the products of a reaction act as a catalyst for the reaction, it is referred to as autocatalysis

Eg. $$RCOOR' + H_2O \longrightarrow RCOOH + R'OH$$



2. MECHANISM OF CATALYTIC REACTION

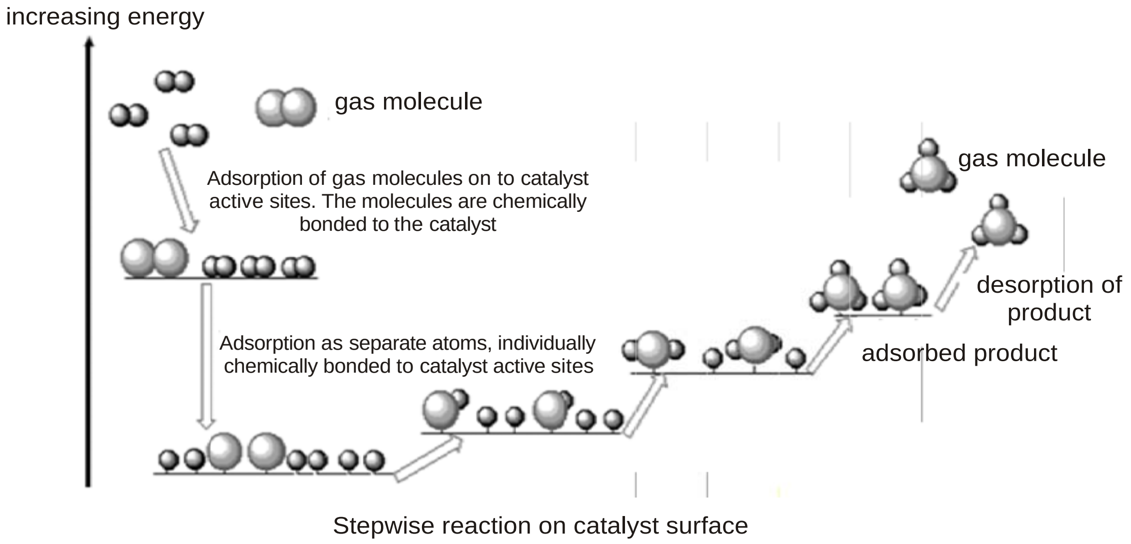


Figure 3.2 : Mechanism of catalytic reaction

3. CRITERIA (OR) CHARACTERISTICS FOR CATALYST

(i) A catalyst remains unchanged in mass and chemical composition at the end of the reaction qualitative and quantitative analysis show that a catalyst undergoes no change in mass of chemical nature. However, it may undergo a physical change. Thus granular manganese dioxide (MnO_2) used as a catalyst in the thermal decomposing of potassium chlorate is left as a fine powder at the end to the reaction.

(ii) A small quantity of catalyst is generally needed to produce almost unlimited reaction Sometimes a trace of a metal catalyst is required to affect very large amounts of reactants. For example, one ten-millionth of its mass of finely divided platinum is all that is needed to catalyse the decomposition of hydrogen peroxide.

On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus in Friedel-Crafts reaction,

$$C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$$

anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 per cent of the mass of benzene. For the acid and alkaline hydrolysis of an ester

$$\underset{\text{ester}}{\text{RCOOR}} + H_2O \xrightarrow{H^+ \text{ or } OH^-} \text{RCOOH} + \text{R}'\text{OH}$$

the rate of reaction is proportional to the concentration of the catalyst (H^+ or OH^-)

(iii) A catalyst is more effective when finely divided In heterogeneous catalysis, the solid catalyst is more effective when in a state of fine subdivision than it is used in bulk. Thus a lump of platinum will have much less catalytic activity than colloidal or platinised asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel.

(iv) A catalyst is specific in its action While a particular catalyst works for one reaction, it will not necessarily work for another reaction. Different catalysts, moreover, can bring about completely different reactions for the same substance. For example, ethanol (C_2H_5OH) gives ethene (C_2H_4) when passed over hot aluminium oxide,

$$C_2H_5OH \xrightarrow{Al_2O_3} \underset{\text{ethene}}{CH_2{=}CH_2} + H_2O \qquad \text{(Dehydration)}$$

but with hot copper it gives ethanal (CH_3CHO)

$$C_2H_5OH \xrightarrow{Cu} \underset{\text{ethanol}}{CH_3CHO} + H_2 \qquad \text{(Dehydrogenation)}$$

(v) A catalyst cannot, in general, initiate a reaction In most cases a catalyst speeds up a reaction already in progress and does not initiate (or start) the reaction. But there are certain reactions where the reactants do not combine for very long period (perhaps years). For example, a mixture of hydrogen and oxygen, which remains unchanged almost indefinitely at room temperature, can be brought to reaction by the catalyst platinum black in a few seconds.

$$H_2 + O_2 \xrightarrow{\text{room temp.}} \text{No reaction}$$

$$2H_2 + O_2 \xrightarrow{\text{Pt black}} 2H_2O$$

Thus it is now considered that the catalyst can initiate a reaction. According to this view, the reacting molecules (in the absence of catalyst) do not possess minimum kinetic energies for successful collisions. The molecules rebound from collision without reacting at all

(vi) A catalyst should remain unchanged in mass and chemical composition during end of the reaction.

(vii) Catalyst can alter only the speed of the reaction but it should not affect the equilibrium of the reaction.

(viii) Catalysts are more active at its optimum temperature. Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction without a catalyst.

(ix) The catalytic activity can be altered by adding a small amount of foreign substance. Such substances which catalyse the catalyst are called as **promoters** and the substance which inhibits the reaction are called as **catalytic poisons or anti-catalyst.**

4. TYPES OF CATALYSIS

Catalytic reactions can be broadly divided into the following types,

HOMOGENEOUS CATALYSIS

When the reactants and the catalyst are in the same phase (i.e. solid, liquid or gas) it is said to be **homogeneous**.

Examples of Homogenous Catalysis

1. The depletion of ozone (O_3) in the ozone layer of the Earth's atmosphere by chlorine free radicals (C*l*□) is a an example where the reactant and product exist in gaseous phase. Slow breakdown of manmade chlorofluorohydrocarbons (CFCs), release chlorine free radical into the atmosphere, which converts gaseous ozone to gaseous oxygen (O_2).
2. **Fischer esterification:** Reaction of carboxylic acid with an alcohol involves the use of sulfuric acid as the catalyst and is an example where everything is contained in a liquid phase.

HETEROGENEOUS CATALYSIS

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

Examples of Heterogeneous Catalysis

1. The catalytic converters in automobiles convert exhaust gases such as carbon monoxide (CO) and nitrogen oxides (NO*x*) into more harmless gases like carbon dioxide (CO_2) and nitrogen (N_2). Metals (solids) like platinum (P*t*), palladium (P*d*) and rhodium (R*h*) are used as the catalyst.

2. Manufacturing of sulfuric acid (H_2SO_4) involve solid vanadium pentoxide (V_2O_5) as the catalyst to convert gaseous sulfur dioxide (SO_2) into gaseous sulfur trioxide (SO_3).
3. Catalytic hydrogenation of liquid Unsaturated hydrocarbons (alkenes) reacts with gaseous hydrogen (H_2) to produce liquid saturated hydrocarbons (alkanes) where metals like platinum (P*t*) and palladium (P*d*) as the catalyst..
4. **Haber Process**

$$H_2(g) + 3H_2(g) \longrightarrow 2H_3(g)$$

The catalyst is porous iron prepared by reducing magnetite, Fe_3O_4, with potassium hydroxide (KOH) added as a promoter.

Positive Catalysis: When the rate of the reaction is accelerated by the foreign substance, it is said to be a **positive catalyst** and phenomenon as **positive catalysis.** Examples of positive catalysis are given below.

(i) Decomposition of $KClO_3$

$$2\ KClO_3 \xrightarrow[370^o\ C]{MnO_2\ (S)} 2\ KCl + 3O_2$$

Negative Catalysis: There are certain, substance which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called **negative catalyst** or **inhibitors** and the phenomenon is known as **negative catalysis**.

Some examples are as follows.

(i) Oxidation of sodium sulphite

$$2\ Na_2SO_3 + O_2 \xrightarrow{\text{Alcohol}} 2\ Na_2SO_4$$

(ii) Tetra Ethyl Lead (TEL) is added to petrol to retard the ignition of petrol vapours on compression in an internal combustion engine and thus minimize the **knocking effect.**

5. AUTOCATALYSIS

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

In autocatalysis the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily (Figure). The curve plotted between reaction rate and time shows a maximum when the reaction is complete

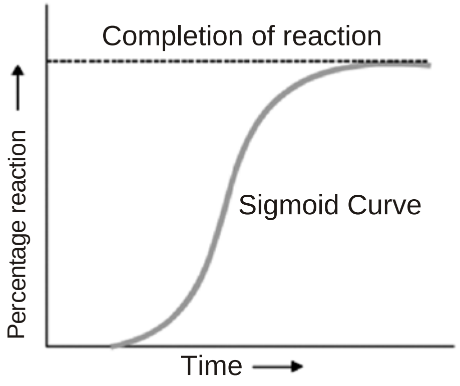


Figure 3.3 : Rate of autocatalytic reaction

A chemical reaction is said to have undergone autocatalysis, or be autocatalytic, if the reaction product is itself the catalyst for that reaction.

Examples of Autocatalysis

(1) **Hydrolysis of an Ester.** The hydrolysis of ethyl acetate forms acetic acid (CH_3COOH) and ethanol. Of these products, acetic acid acts as a catalyst for the reaction.

$$CH_3COOC_2H_5 + H_2O \longrightarrow \underset{\text{catalyst}}{CH_3COOH} + C_2H_5OH$$

(2) **Oxidation of Oxalic acid**. When oxalic acid is oxidised by acidified potassium permanganate, manganous sulphate produced during the reaction acts as a catalyst for the reaction.

$$2\,KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow 2\,\underset{\text{catalyst}}{MnSO_4} + K_2SO_4 + 8\,H_2O + 10\,CO_2$$

(3) **Decomposition of Arsine.** The free arsenic produced by the decomposition of arsine (AsH_3) autocatalyses the reaction.

$$2\,AsH_3 \longrightarrow \underset{\text{catalyst}}{2\,As} + 3H_2$$

6. CATALYTIC POISONING AND PROMOTERS

Promoters

The activity of a catalyst can often be increased by addition of a small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble catalyst.

A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter. They are substances when added in small concentration can increase the activity of a catalyst.

Example of Promoters

Molybdenum (Mo) or aluminium oxide (Al_2O_3) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.

$$N_2 + \quad 3H_2 \underset{Mo}{\overset{Fe}{\square}} 2NH_3$$

In some reactions, mixtures of catalysts are used to obtain the maximum catalytic efficiency. For example, in the synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen, a mixture of zinc and chromium oxide is used as a catalyst.

$$CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$$

Explanation of Promotion Action

The theory of promotion of a catalyst is not clearly understood. Presumably:

(1) **Change of Lattice Spacing.** The lattice spacing of the catalyst is changed thus enhancing the spaces between the catalyst particles. The absorbed molecules of the reactant (say H_2) are further weakened and cleaved. This makes are reaction go faster.

(2) **Increase of Peaks and Cracks.** The presence of the promoter increases the peaks and cracks on the catalyst surface. This increases the concentration of the reactant molecules and hence the rate of reaction.

The phenomenon of promotion is a common feature of heterogeneous catalysis.

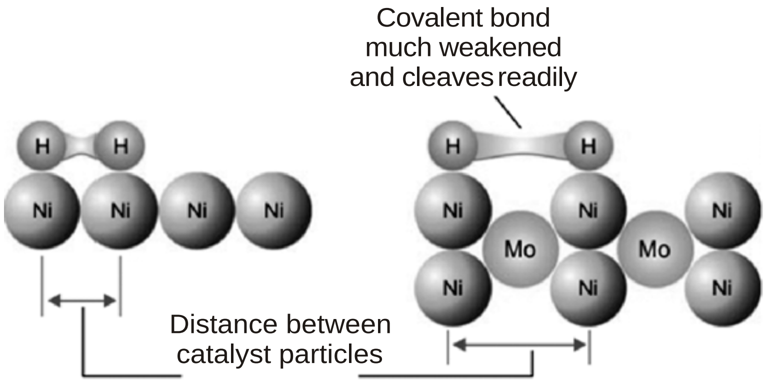


Figure 3.4 : How the change of crystal lattice spacing of catalyst makes the reaction go faster.

CATALYTIC POISONS

Small amounts of substances can reduce the activity of catalyst. If the reduction in activity is reversible, the substances are called inhibitors. Inhibitors are sometimes used to increase the selectivity of a catalyst by retarding undesirable reactions.

A substance which destroys the activity of the catalyst to accelerate a reaction is called a poison and the process is called Catalytic Poisoning.

Examples of Catalytic Poisoning

(1) The platinum catalyst used in the oxidation of sulphur dioxide (Contact Process), is poisoned by arsenic oxide (As_2O_3)

$$SO_2 + O_2 \xrightarrow[As_2O_3]{Pt} 2SO_3$$

(2) The iron catalyst used in the synthesis of ammonia (Haber Process) is poisoned by H_2S.

$$N_2 + 3H_2 \xrightarrow[H_2S]{Fe} 2NH_3$$

(3) The platinum catalyst used in the oxidation of hydrogen is poisoned by carbon monoxide

$$2H_2 + O_2 \xrightarrow[CO]{Pt} 2H_2O$$

Types of Catalytic Poison

(i) Temporary Poisoning

Catalyst regains its activity when the poison is removed from the reaction

(ii) Permanent Poisoning

a. Catalyst cannot regain its activity even if the catalytic poison is removed.

b. Eg.AS_2O_3 poisons catalyst Pt permanently in manufacturing of SO_3.

Explanation of Catalytic Poisoning

(1) The poison is adsorbed on the catalyst surface in preference to the reactants. Even a monomolecular layer renders the surface unavailable for further adsorption of the reactants. The poisoning by As_2O_3 or CO appears to be of this kind.

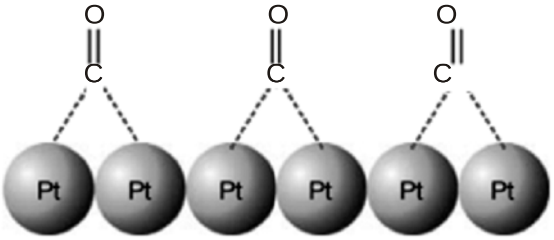


Figure 3.5 : Poisoning of platinum catalyst by carbon monoxide

(2) The catalyst may combine chemically with the impurity. The poisoning of iron catalyst by H_2S falls in this class

$$Fe + H_2S \longrightarrow FeS + H_2$$

7. ACID AND BASECATALYSIS

A number of homogeneous catalytic reactions are known which are catalysed by acids or bases, or both acids and bases. These are often referred to as Acid-Base catalysts. Arrhenius pointed out that acid catalysis was, in fact, brought about by H^+ ions supplied by strong acids, while base catalysis was caused by OH^- ions supplied by strong bases.

Many reactions are catalyzed by both acids and bases. Typical reactions catalysed by proton transfer are esterification and aldol reaction. Catalysis by either acid or base can be in two different ways (Specific catalysis and general catalysis).

Example

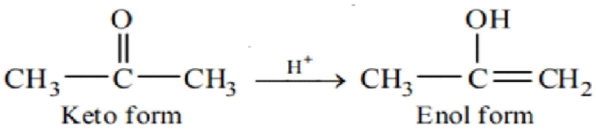
- Acid-specific (acid catalysis) — Decomposition of Sucrose into glucose and fructose occurs in presence of sulfuric acid
- Base-specific (base catalysis) — Addition of hydrogen cyanide to aldehydes and ketones in the presence of sodium hydroxide.

Examples of Acid-Base Catalysis

(1) Inversion of Cane Sugar:

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2 \xrightarrow{H+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(2) Keto-Enol Tautomerism of Acetone :



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{H^+} CH_3-\overset{\overset{OH}{|}}{C}=CH_2$$

(3) Decomposition of Nitramide :

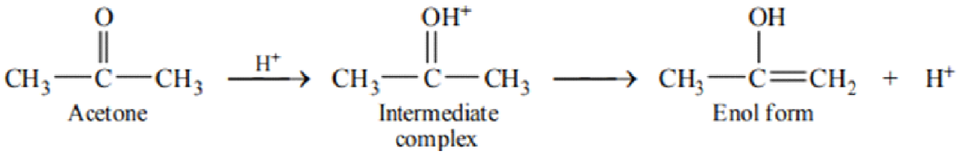
$$NH_2NO_2 \xrightarrow{H^+} N_2O + H_2O$$

(4) Hydrolysis of an Ester :

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} \xrightarrow[\text{or OH}^-]{H^+} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{C_2H_5OH}$$

Mechanism of Acid-Base Catalysis

(a) In acid catalysis, the H+ (or a proton donated by Bronsted acid) forms an intermediate complex with the reactant, which then reacts to give back the proton. For example, the mechanism of keto-enol tautomerism of acetone is:



$$\underset{\text{Acetone}}{CH_3-\overset{\overset{\Large O}{\|}}{C}-CH_3} \xrightarrow{H^+} \underset{\substack{\text{Intermediate}\\\text{complex}}}{CH_3-\overset{\overset{\Large OH^+}{\|}}{C}-CH_3} \longrightarrow \underset{\text{Enol form}}{CH_3-\overset{\overset{\Large OH}{|}}{C}=CH_2} + H^+$$

(b) **In base catalysis, t**he OH– ion (or any Bronsted base) accepts a proton from the reactant to form an intermediate complex which then reacts or decomposes to regenerate the OH– (or Bronsted base). For example, the decomposition of nitramide by OH– ions and CH_3COO– ions may be explained as follows: *By* OH^- *ions*:

$$NH_2NO_2 + OH^- \longrightarrow H_2O + \underset{\substack{\text{Intermediate}\\\text{Complex}}}{NHNO_2^-}$$

$$NHNO_2^- \longrightarrow N_2O + OH^-$$

8. APPLICATION OF CATALYSIS

1. Catalytic Converters

A device incorporated in the exhaust system of a motor vehicle, containing a catalyst for converting pollutant gases into less harmful ones.

Catalytic converters are used for mitigating automobile exhaust emissions. Catalytic converters are used within internal combustion engines fueled by either petrol (gasoline) or diesel. It converts three harmful substances into harmless ones carbon monoxide (a poisonous gas) into carbon dioxide, nitrogen oxides (cause acid rain and smog) into nitrogen and oxygen, and hydrocarbons (cause smog and respiratory problems) into carbon dioxide and water.

Catalytic converters consist of a stainless steelbox attached to the muffler and containing ceramic beads or honeycomb coated with catalysts (Expensive metals like platinum, Palladium, Rhodium are used. Alumina, Ceria can also be used when combined with expensive metals.)

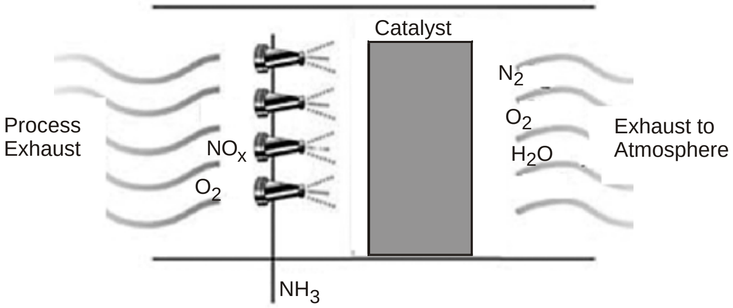
Eg: Consider the reaction

$$2\,CO + 2\,NO \longrightarrow 2\,CO_2 + N_2$$

Carbon monoxide and Nitrogen monoxide will be adsorbed on the surface of catalyst where they get adsorbed to catalyst and result in formation of carbon dioxide and nitrogen which gets desorbed.

Catalytic converters can be affected by catalytic poison.

Eg. Lead is a very good example for catalytic poisoning. It gets adsorbed to the honey comb of expensive metals and inhibits the function of catalyst. Catalytic converter has also forced the removal of lead from petrol.



$$4\ NO + 4\ NH_3 + O_2 \longrightarrow 4\ N_2 + 6H_2O$$

$$2\ NO_2 + 4\ NH_3 + O_2 \longrightarrow 3\ N_2 + 6H_2O$$

Figure 3.6 : Basic Catalytic Converter

2. Petroleum Refining

(i) ***Fluid catalytic cracking***: Breaking large hydrocarbon into smaller hydrocarbons.

(ii) ***Catalytic reforming***: Reforming crude oil to produce high quality gasoline component

(iii) ***Hydrodesulfurization***: Removing sulfur compounds from refinery intermediate products

(iv) ***Hydrocracking***: Breaking large hydrocarbon molecules into smaller ones

(v) ***Alkylation:*** Converting isobutane and butylenes into a high-quality gasoline component

(vi) ***Isomerization:*** Converting pentane into a high-quality gasoline component

3. Chemicals and petrochemicals

(i) Haber process for ammonia production

(ii) Styrene and Butadiene synthesis for use in producing synthetic rubber

(iii) Contact process for production of sulfuric acid

(iv) Ostwald process for production of nitric acid

(v) Methanol synthesis

(vi) Production of different plastics and synthetic fabrics

4. Other

(i) Fischer-Tropsch and Coal gasification processes for producing synthetic fuel gases and liquid fuels

(ii) Various processes for producing many different medicine

9. BIOLOGICAL CATALYST——ENZYMES

Numerous organic reactions are taking place in the body of animals and plants to maintain the life process. These reactions being slow remarkably catalysed by the organic compounds known as **Enzymes.** All enzymes have been found to be complex protein molecules. Thus: Enzymes are protein molecules which act as catalysts to speed up organic reactions in living cells. The catalysis brought about by enzymes is known as Enzyme Catalysis.

Each enzyme is produced in a particular living cell to catalyse a reaction occurring in that cell. Many enzymes have been identified and obtained in pure crystalline state from the cells to which they belong. However the first enzyme as prepared by synthesis in the laboratory in 1969.

Enzymes are substances found in biological systems that act as catalyst for specific biochemical process. Enzymes are usually protein or steroid which is synthesized in the living cells of animals and plants. Enzymes catalyze reactions inside organism. Enzymes possess a incredible capacity to carry out complex chemical reactions like hydrolysis, oxidation, reduction etc.

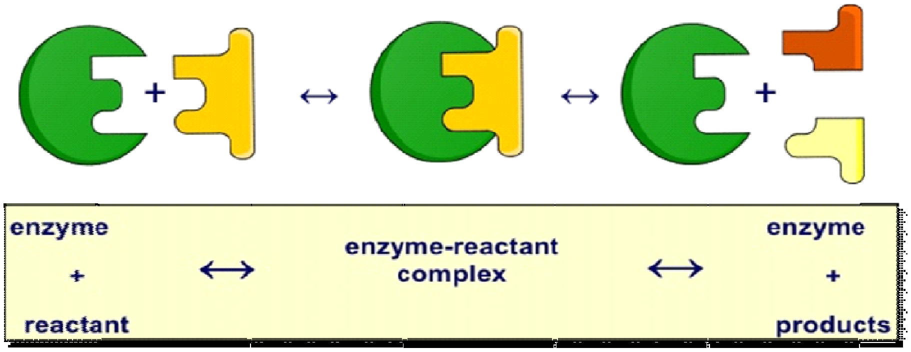
Eg.(i) Amylase is an enzyme which breaks down starch into glucose.

$$\left(C_6H_{10}O_5\right)_n + nH_2O \longrightarrow nC_{12}H_{22}O_{11}$$

(ii) Diastase converts starch to maltose and maltase converts maltose to glucose

$$2\left(C_6H_{10}O_5\right)_n + nH_2O \longrightarrow nC_{12}H_{22}O_{11}$$

$$nC_{12}H_{22}O_{11} + nH_2O \longrightarrow nC_{12}H_{22}O_{11}$$



Enzymes speed up reactions by lowering activation energy. Many enzymes change shape when substrates bind. This is termed as ***"induced fit".*** Enzymes have active sites. The enzyme active site is the location on the enzyme surface where substrates bind, and where the chemical reaction catalyzed

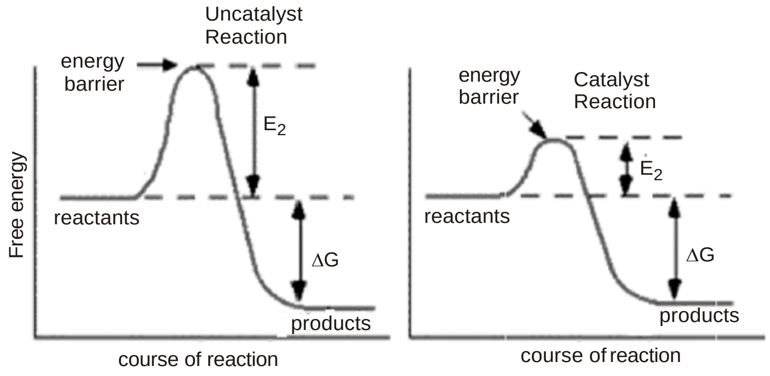


Figure 3.7 : Rate of free energy vs course of reaction

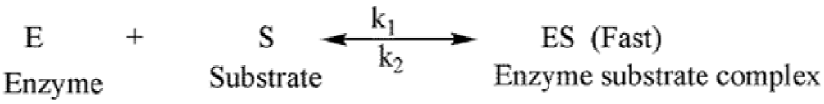
Enzymes do not

- Change the equilibrium constant for a reaction
- Change ΔG for a reaction
- Convert a nonspontaneous reaction into a spontaneous reaction.

KINETICS OF ENZYME CATALYSED REACTION OR MICHAELIS AND MENTENEQUATION

Consider the enzyme catalyzed reaction:

Step 1: Formation of enzyme substrate complex



$$\underset{\text{Enzyme}}{E} + \underset{\text{Substrate}}{S} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \underset{\text{Enzyme substrate complex}}{ES} \text{ (Fast)}$$

Step 2: Decomposition of enzyme substrate complex

$$ES \xleftrightarrow{k_3} \underset{\text{Product}}{P} + \underset{\text{Enzyme}}{E} \text{ (Slow)}$$

It can be expressed as follows:

$$V_0 = \frac{V_{max}[S]}{K_m + [S]}$$

where the terms V_0, V_{max} and [S] and there is a constant K_m, which is known as **Michaelis constant.**

Rate of formation of ES = k_1 [E]×[S]

Rate of breakdown of ES = $(k_2 + k_3) \times$ [ES]

At steady state, the formation and the breakdown are equal. This steady state would onlybe temporary.

$$k_1 \text{ [E]} \times \text{[S]} = (k_2 + k_3) \times \text{[ES]}$$

Rearranging the above equation :

$$\text{[ES]} = K_1 \frac{\text{[E] } x\text{[S]}}{(K_2 + K_3)}$$

(or)

$$\text{[ES]} = \frac{\text{[E] } x\text{[S]}}{(K_2 + K_3) / K_1}$$

But $K_m = \frac{(K_2 + K_3)}{K_1}$ and substituting in above equation and we get

$$\text{[ES]} = \text{[E] [S]} / Km$$

The total amount of enzyme equals the free and that bound to substrate

$$[E_T] = [E] + [ES]$$

$$[E] = [E_T] - [ES]$$

Substitute the value of E

$$[ES] = \frac{\{[E]\, x[S]\}}{([S] + K_m}$$

Then $[ES] = \dfrac{\dfrac{\{[Et][S]\}}{K}}{1+[S] / K_m}$

This simplifies to:

$$[ES] = \{[Et]\, x[S] / ([S]+ K_m\}$$

Multiplying both sides by the kinetic constant k_3 gives the velocity of the reaction

$$V = k_3 \times [ES] = k_3 \times [E_T] \times(([S] ([S] + K_M)$$

and substituting V_{max} for $k_3 \times [E_T]$ leads to the familiar form of the Michaelis Menten Equation:

$$\boxed{V = V_{max} \frac{X[S]}{[S] + K}}$$

The above equation is called **Michaelis –Menton equation**. This equation is applicable to enzyme catalysed reaction having a single substrate. Aquantitative estimation of initial rate of reaction, maximum velocity and substrate concentration is combined through a constant called Michaelis constant.

Case 1: First order reaction-When concentration of substrate is low.

If $K_m >> S$ then s is neglected and then the equation becomes

$$\text{Rate } (v) = V_{max} \times [S] \mid (K_M)$$

Case 2: Zero order reaction-When concentration of substrate is high.

If $K_m << S$ then Km is neglected and equation becomes

$$\text{Rate } (v) = V_{\max} \times [S] \mid [S] \text{ so } V_{\max} = \text{Constant}$$

Case 3: If $K_m = [S]$ then

$$\text{Rate (V)} = \frac{V_{\max}[S]}{[S]+[S]} = \frac{1}{2} V_{\max}$$

Reciprocating the above equation

$$\frac{1}{\text{Rate}(v)} = \frac{K_m}{V_{\max}[S]} + \frac{[S]}{V_{\max}[S]}$$

Rearranging the above equation:

$$\frac{1}{\text{Rate}(v)} = \frac{K_m}{V_{\max}[S]} + \frac{[S]}{V_{\max}[S]}$$

The above equation is similar to an equation of straight line $y = mx + c$. A graph is plotted between 1/rate and 1/[S] we get a straight line.

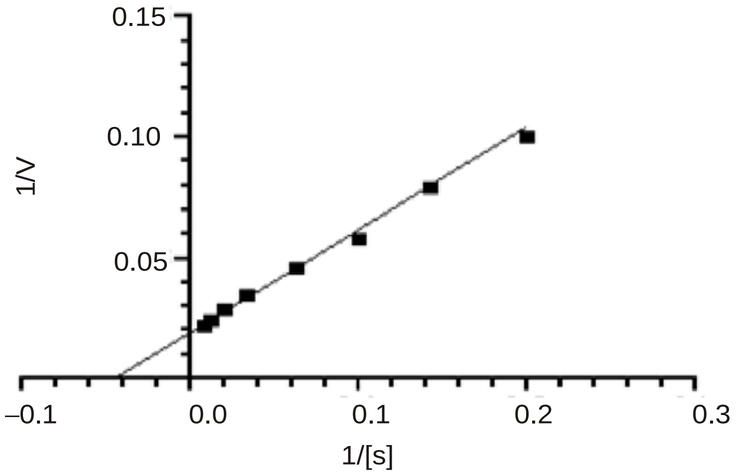


Figure 3.8

where slope = $K_m/V_{\max}$ and Intercept $=1/V_{\max}$

FACTORS AFFECTING ENZYME ACTIVITY

a. Enzyme Concentration

- If we keep the concentration of the substrate constant and increase the concentration of the enzyme, the rate of reaction increases linearly. (That is if the concentration of enzyme is doubled, the rate doubles.)
- This is because in practically all enzyme reactions the molar concentration of the enzyme is almost always lower than that of the substrate.

b. Substrate Concentration

- If we keep the concentration of the enzyme constant and increase the concentration of the substrate, initially, the rate increases with substrate concentration, but at a certain concentration, the rate levels out and remains constant.
- So at some point, increasing the substrate concentration does not increase the rate of reaction, *because the excess substrate cannot find any active sites to attach to.*

c. Temperature

- For enzyme-catalyzed reactions, like all chemical reactions, rate increases with temperature. However, enzymes are proteins, and at higher temperatures proteins become denatured and inactive. Thus, every enzyme has an optimum temperature.
- Optimum temperature - the temperature at which enzyme activity is highest-usually about 25^oC–40^oC.

d. Effect of pH

- Small changes in pH can result in enzyme denaturation and loss of catalytic activity.
- Because the charge on acidic and basic amino acid residues located at the active site depends on pH. Most enzymes only exhibit maximum activity over a very narrow pH range.
- Most enzymes have an optimum pH that falls within the physiological range of 7.0-7.5.
- Notable exceptions are the digestive enzymes pepsin and trysin.
- pepsin (active in the stomach) - optimum pH of 1.5
- trypsin (active in the small intestine) - optimum pH of 8.0

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