

UNIT II

SURFACE CHEMISTRY AND CATALYSIS

Some important terms involved in surface chemistry

1. Adsorption:

It is the process of concentration of gas/liquid on the surface of solid/liquid due to weak or strong forces of attraction.

(e.g.) Adsorption of H_2 on Nickel.

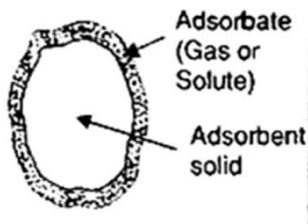


2. Adsorbent:

The surface on which adsorption takes place is known as adsorbent. (e.g.) Nickel, Charcoal.

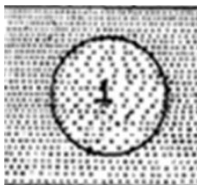
3. Adsorbate:

The substance which gets adsorbed on adsorbent is known as adsorbate. (e.g.) H_2 gas



4. Absorption:

It is a phenomenon in which gas/liquid are slowly penetrate throughout the body of the solid/liquid is known as absorption.



(e.g) Absorption of ink on the surface of a chalk.


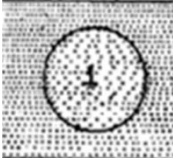
5. Sorption:

It is the process in which both adsorption and absorption take place simultaneously.
Eg. NH_3 in water in presence of charcoal.

6. Desorption:

It is reverse process of adsorption. i.e., removal of adsorbate from the adsorbent surface.

Differences between adsorption and absorption:

NO.	ADSORPTION	ABSORPTION
1	Surface phenomenon	Bulk phenomenon
2	It is the concentration of gas/liquid on adsorbent	It is the concentration of gas/liquid throughout the body of adsorbent
3	Fast process	Slow process
4	Equilibrium is attained easily	It takes some time
5	It depends upon the surface of adsorbent	No such effect
6	Eg. Adsorption of water vapour on silica gel	Absorption of water vapour by CO_2
7		

TYPES OF ADSORPTION**1. Physical adsorption/ Physisorption**

It is a process in which gas/solid/liquid are held on the solid surface through weak vander walls forces it is termed as 'Physisorption'. (e.g) H_2 on charcoal.

2. Chemical adsorption/Chemisorption:

It is a process in which gas/solid/liquid are held on the solid surface through strong chemical covalent bonds, it is chemisorption. (e.g) H_2 on nickel.

Differences between the Physical adsorption and Chemical adsorption:

No	PHYSISORPTION	CHEMISORPTION
1	Adsorption is due to weak Vanderwaal's forces.	Due to strong covalent bonding.
2	Adsorption is multilayer.	Adsorption is monolayer
3	Adsorption is completely reversible	Adsorption is irreversible
4	The Equilibrium is established rapidly	Establishment of equilibrium requires time
5	No surface compound is formed	Surface compound formation is formed
6	Energy of activation (E_a) is low.	Energy of activation (E_a) is High
7	Heat of adsorption (ΔH) is low (20-40kcal/mol)	Heat of adsorption (ΔH) is high (200-400kcal/mol)
8	Temperature increases adsorption decreases	Temperature increases adsorption increases followed by decreases.
9	Pressure increases adsorption increases	It independent of pressure
10	It is nonspecific and non-selective in nature	It is selective and specific in nature
11	e.g - H_2 on charcoal.	e.g., H_2 on nickel.

Factors influencing the adsorption of gases on solid:

(a) *Adsorption of gases on solids*: (Occlusion)

(i). Nature of gases

Easily liquefiable gases like HCl, NH₃ adsorbed more easily than the permanent gases like N₂, H₂, O₂, etc., This is due to (i) Critical temperature (ii) Vander waal's forces. Example,

Gas	SO ₂	NH ₃	CO ₂	N ₂	H ₂
CT (K)	430	406	304	120	33
Amount of gas Adsorbed (mL)	380	180	48	8	4.5

(ii) Nature and surface area of adsorbent

The greater the surface area, larger pores on the adsorbent larger is the adsorption. (eg.) Charcoal and Silica gel.

(iii) Heats (or) Enthalpy of adsorption

The energy liberated when 1 g mole of a gas is adsorbed on the solid surface. In physical adsorption it is small due to weak vander waal's forces, in chemical adsorption it is large due to the formation of chemical bonds.

(iv) Reversible character

Physical adsorption is a reversible process. The gas adsorbed on a solid can be removed under reverse conditions of temperature and pressure.

Chemical adsorption is not a reversible process, because a surface compound is formed.

(v) Effect of pressure

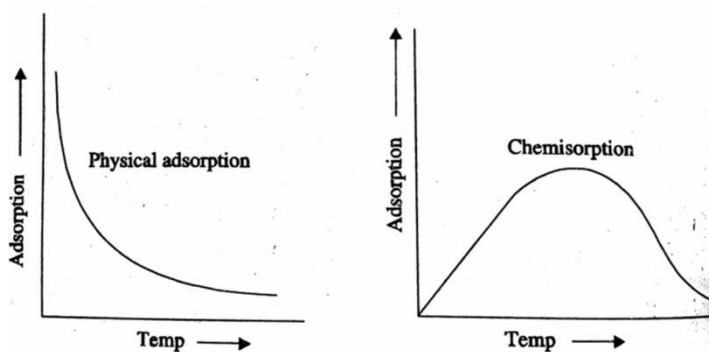
Physical adsorption: It occurs rapidly at lower pressure and increases with increase in pressure.

Chemical adsorption: There is no such effect due to chemisorptions is independent of pressure.

(vi) Effect of temperature

Physical adsorption: It occurs rapidly at lower temperature and decreases with increase in temperature.

Chemical adsorption: It increases with increase in temperature and then decreases.



(vii) Thickness of adsorbed layer of gas

Multilayer adsorption is formed in physisorption. Monolayer adsorption occurs in Chemisorption.

(viii) Effect of activation of adsorbent

Activation leads to increase in the surface.

(1) Creation of rough surface

- (a) by mechanical rubbing,
- (b) by subjecting to some chemical reactions on the solid adsorbent.

(2) Increasing effective area of the surface

- (a) by sub dividing the solid adsorbent into fine particles.
- (b) by heating of solid adsorbent in superheated steam now its pores are opened and adsorption increases.

ADSORPTION OF SOLUTE FROM SOLUTION:

An adsorbent adsorbs substances (solutes) from the solution in two ways.

1. Solid substances adsorb dissolves substances from solutions.
Eg. Activated charcoal adsorbs coloring matter present in sugar solution.
2. An adsorbent also adsorbs certain substance from the solution in preference to other substances.
Eg. Charcoal adsorbs non-electrolytes more readily than electrolytes from a solution.

FACTORS INFLUENCING ADSORPTION OF SOLUTES FROM SOLUTIONS

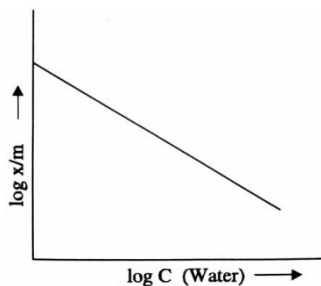
1. Effect of Concentration

Extent of the adsorption of solute from the solution depends on temperature and concentration. Effect of the concentration is explained by the Freundlich adsorption isotherm.

$$\frac{x}{m} = KC^{1/n}$$

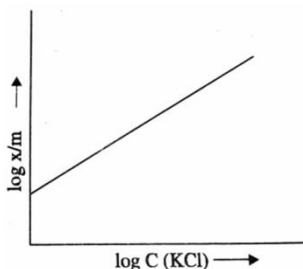
(a) Negative adsorption

Adsorption of solvent from the solution results in increase in the concentration of the solution.



(b) Positive adsorption

Adsorption of solute from the solution results in decrease in the concentration of the solution.



2. The area of adsorbent

In increase in the surface area of adsorbent increases the total amount of solute adsorbed.

3. The nature of the solute adsorbed

The extent of adsorption is usually greater, when the molecular weight of the solute is high.

Adsorption isotherm:

It may be mathematical relationship or of graphical relation between adsorption and pressure at constant temperature is known as adsorption isotherm.

$$\frac{x}{m} = KP^{1/n} \text{ (at constant T)}$$

Where, x = amount of Adsorbate

m = amount of adsorbent

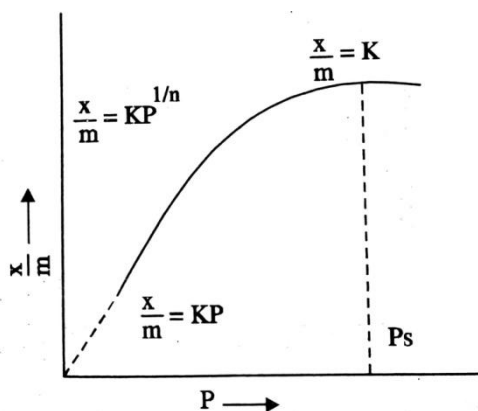
x / m

x/m = extent of adsorption

P = pressure

n = whole number

K = adsorption coefficient



To convert the equation as $y = mx + C$ form, taking log on both sides,

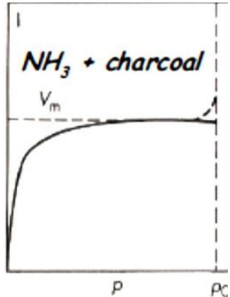
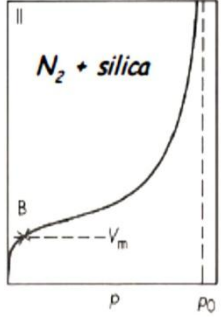
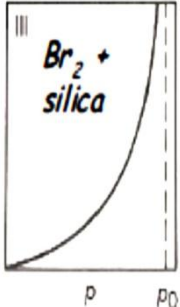
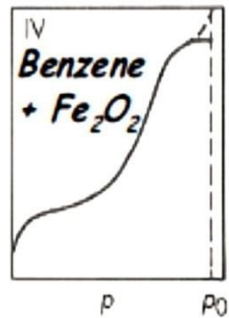
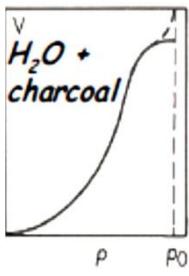

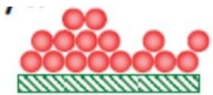
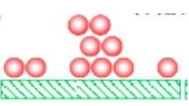

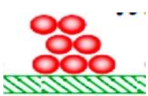
$$\log (x / m) = \log k + (1/n) \log P \quad \text{(at constant T)}$$

Where $y = \log (x / m)$;

$$m = (1/n) ; \quad C = \log k$$

so, the plot will be a line with slope $1/n$ and intercept $\log k$.

Different types of adsorption isotherm curves: (P_0 = Saturation pressure)

Type	I	II	III	IV	V
Model Graph					
Adsorbate	N ₂	N ₂	I ₂ Vapours	Benzene Vapours	Water vapours
Adsorbent	Charcoal	Non porous silica gel	Porous Silica gel	Porous Ferric oxide gel	Porous Charcoal
Temperature	-183 ⁰ C	-195 ⁰ C	83 ⁰ C	50 ⁰ C	100 ⁰ C
Characteristics	Chemisorption (monolayer)	Physisorption (Multilayer)	Physisorption (Multilayer)	Condensation in pores/Capillaries	Condensation in pores/Capillaries
Explanation	Saturation at the monolayer formation	Multilayer forms after the completion of monolayer	Multilayer forms before the completion of monolayer	Saturation at the multilayer formation	Multilayer is formed at the beginning of adsorption process
Diagram					

FREUNDLICH'S ADSORPTION ISOTHERM:

The relation between adsorption and pressure at constant temperature is known as adsorption isotherm. It may be mathematical relationship or of graphical.

$$\frac{s}{N} = KP^{1/n} \text{ (at constant T)}$$

To convert the equation as $y = mx + C$ form, taking log on both sides,

$$\log (x / m) = \log k + (1/n) \log P \quad \text{(at constant T)}$$

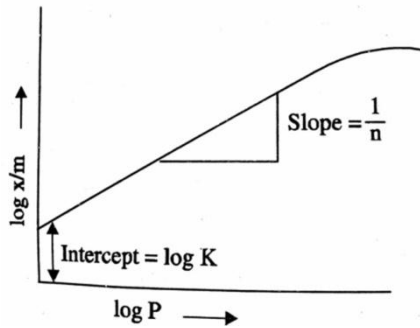
where y axis = $\log (x / m)$;

$m = (1/n)$;

$C = \log k$;

x axis= $\log P$

so, the plot will be a line with slope $1/n$ and intercept $\log k$.



From the above graph, there may be three cases:

Case 1: At low pressure, adsorption is proportional to pressure.

$$\frac{s}{N} \propto P^1$$

$$\frac{s}{N} = KP^1$$

Case 2: At high pressure, adsorption is almost constant.

$$\frac{s}{N} = K$$

$$\frac{s}{N} = K P^0$$

Case 3: At intermediate pressure.

$$\frac{s}{N} = KP^{1/n}$$

This is known as Freundlich adsorption isotherm.

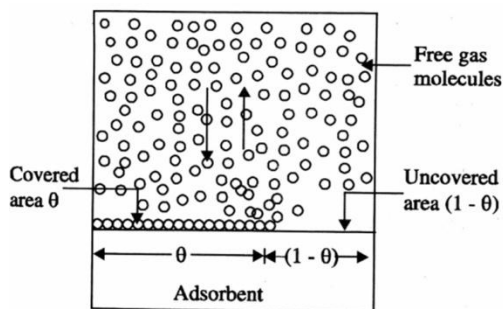
Limitations of Freundlich isotherm:

1. It is only an empirical formula and it has no theoretical basis.
2. It is deviated at high pressure.
3. It is not good at high concentration.
4. n and K are temperature dependent.

DERIVATION OF LANGMUIR ADSORPTION ISOTHERM:

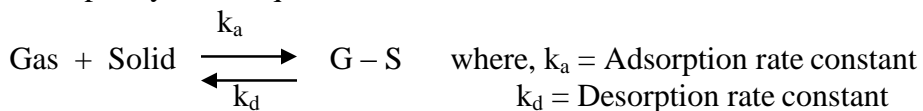
Postulates:

1. In adsorbent, surface valencies are not fulfilled.
2. Adsorbate undergoes monolayer adsorption.
3. Adsorbate is uniformly distributed on the surface.
4. No interaction between adjacent gas molecules.
5. The gas molecules do not move around on the surface.



Derivation:

1. As per dynamic equilibrium,



2. Let us consider,

Total area of adsorbent = 1cm^2

Surface area adsorbed by gas molecule = θ

Then, surface area available for adsorption = $(1-\theta)$

3. Rate of adsorption, $R_a = K_a (1-\theta) P$ --- 1

Rate of desorption, $R_d = k_d \cdot \theta$ --- 2

4. At equilibrium,

$$R_d = R_a \quad \text{--- 3}$$

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

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

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

$$(K_d + K_aP) = K_aP$$

$$\theta = \frac{K_aP}{K_d + K_aP} \quad \text{--- 4}$$

Dividing equation 4 on right hand side by k_d

$$\theta = \frac{\left(\frac{K_a}{K_d}\right)P}{1 + \left(\frac{K_a}{K_d}\right)}$$

As, $\left(\frac{K_a}{K_d}\right) = K$, another constant, known as Adsorption co-efficient,

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

But, amount of gas adsorbed (x) is proportional to θ .

$$x \propto \theta$$

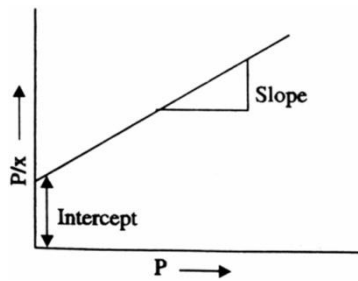
$$x = K' \frac{KP}{1 + KP} \quad \text{-- 5}$$

Where K' is new constant. This equation gives the relation between the amount of gas adsorbed to the pressure of the gas at constant temperature. It is known as langumuir adsorption isotherm.

Rearranging the equation 5.

$$1 + KP = \frac{K'KP}{x}$$

$$\frac{1}{K'K} + \frac{K}{K'K}P = \frac{P}{x} \quad \text{--6}$$



A plot of P vs $\frac{P}{x}$ gives a straight line with a slope of $\frac{K}{K'K}$ and an intercept of $\frac{1}{K'K}$

Case 1: At low pressure, P is very low and $\frac{K}{K'K}P$ term is negligible

$$\frac{1}{K'K} \gg \frac{K}{K'K}P$$

$$\frac{1}{K'K} = \frac{P}{x} \text{ (or) } x = PK'K$$

$$x \propto P \quad \text{-- 7}$$

Amount of gas adsorbed is proportional to P .

Case 2: At high pressure, P is very high hence the term $\frac{1}{K'K}$ negligible

$$\frac{1}{K'K} \ll \frac{K}{K'K}P$$

$$\frac{K}{K'K}P = \frac{P}{x}$$

$$= K'(\text{or}) x = K'P^0 \quad \text{-- 8}$$

Case 3: At normal pressure,

At intermediate pressure equation 8 becomes

$$x = K'P^n, \text{ where } n = 0 \text{ to } 1$$

This proves that at normal pressure, Langmuir adsorption resembles Freundlich isotherm.

Limitations:

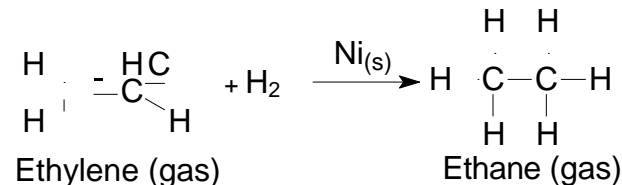
1. Langmuir adsorption holds good at low pressure but fails at high pressure.
2. Langmuir adsorption explains only monolayer adsorption.

ROLE OF ADSORBENT IN CATALYSIS REACTIONS (OR) ADSORPTION (OR) CONTACT THEORY

Action of heterogeneous catalyst

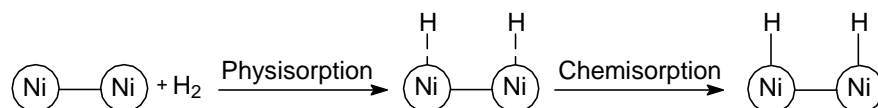
Various steps involved in the heterogeneous catalysis are explained with an example

Hydrogenation of ethylene using Ni catalyst

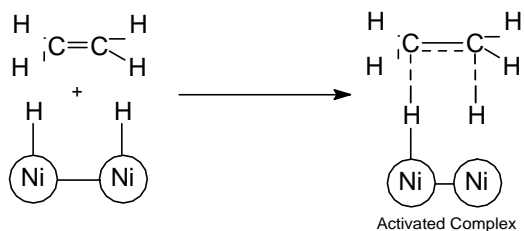


Step I Adsorption of reactant molecules

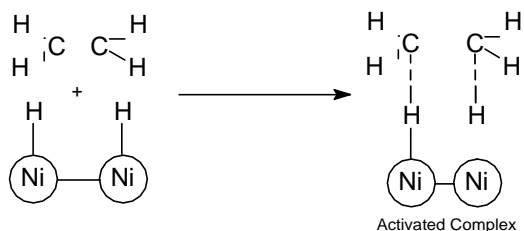
Active centers in the catalyst surface adsorbs the gaseous reactant.



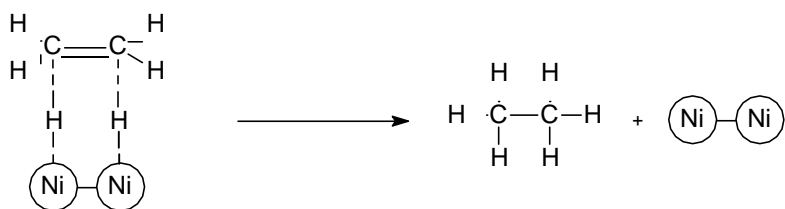
Step II Formation of activated complex



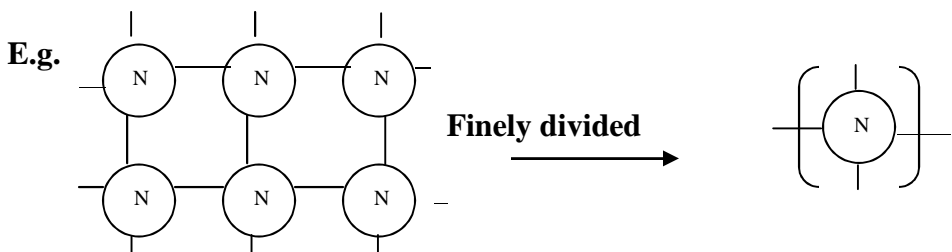
Step III Decomposition of activated complex



Step IV Desorption of activated complex



2. Finely divided state of catalyst is more efficient

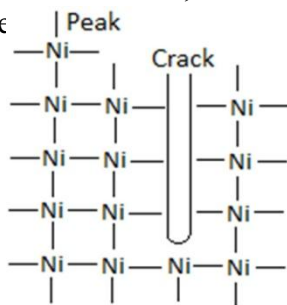


Free valencies in combined state = 10 Divided state valencies = (6 x 4)=24

Fineness of the catalyst increase, the free surface area gets increases, thereby free valencies increases.

3. Enhanced activity of a rough surfaced catalyst

It possess “Cracks”, “Peaks”, “Corners” etc., and consequently have larger number of active centers. These active centre



reaction.

4. Action of promoters

Promoters are defined as the substances, which increase the activity of a catalyst. Promoters change the lattice spacing



Promoters increases the peaks and cracks

5. Action of catalytic poisons

Catalytic poison is defined as a substance which destroys the activity of the catalyst. This process is called catalytic poisoning. Number of free valencies (or) active centres of catalysts are reduced by the preferential adsorption of the poison. So the rate of reaction decreases.

6. Specific action of the catalyst

The adsorption depends on the nature of both the adsorbent (catalyst) and the adsorbate (reactants). So, different catalysts cannot possess the same affinity for the same reactants. Thus, the action of the catalyst is specific.

7. Ion exchange method (Demineralisation)

Ion exchange resins adsorb the cations and anions present in hard water.

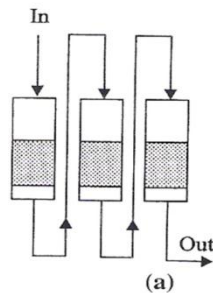
ROLE OF ADSORBENTS IN POLLUTION ABATEMENT TREATMENT OF POLLUTED WATER AND AIR Using Granular Activated Carbon (GAC)

A fixed – bed column is often used for contacting polluted water or air with GAC. It can be operated singly, in series or in parallel. Among the various type two are important.

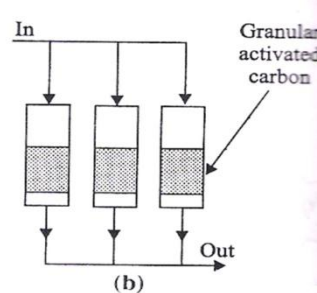
1. Down flow carbon contactors.
2. Upflow carbon contactors.

(a) Down flow Carbon Contactors

It usually consist of two (or) three columns operated in series (or) in parallel.



Down flow in series



Down flow in parallel

The water or air is applied to the top of the column and withdrawn at the bottom. The AC is held in place with an under drain system at the bottom of the column. Provision for back washing and surface washing is usually necessary to limit the headless build up due to the removal of particle material with the carbon column.

Advantage

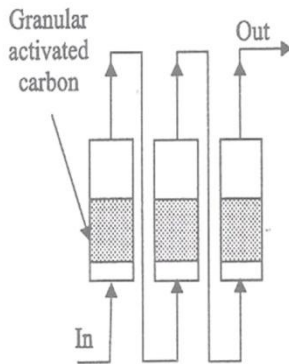
Adsorption of organic materials and filtration of suspended solids are accompanied in a single step.

Disadvantages

- ◆ Down flow filters may require more frequent back washing because of the accumulation of suspended materials on the surface of the contactor.
- ◆ Plugging of carbon pores may require premature removal of the carbon for regeneration, thereby decreasing the useful life of the carbon.

(b) Upflow Carbon Contactors

In the upflow columns, the polluted water or air moves upward from the base of the column .



Up flow expanded in series

Advantage

- ♦ As the carbon adsorbs organic materials, the apparent density of the carbon particles increases and encourages migration of the heavier or spent carbon downward.

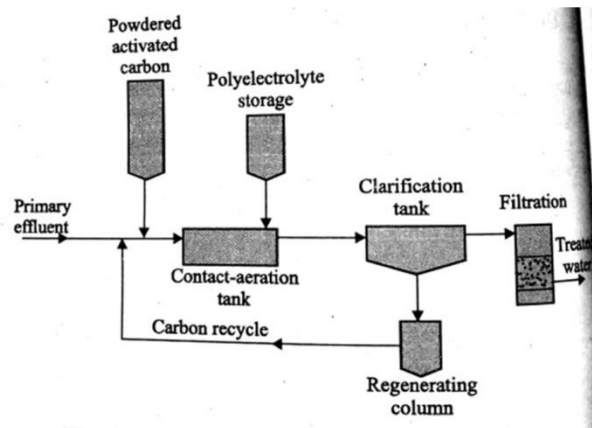
Disadvantage

- ♦ Upflow columns may have more carbon fines in the effluent than downflow columns, because upflow tends to expand, not compress, the carbon.
- ♦ Bed expansion allows the fines to escape through passage ways created by the expanded bed.

2. Using Powdered Activated Carbon

In this method powdered activated carbon is added directly into the effluent.

- The powdered activated carbon and a coagulant are mixed in the contact aeration tank.
- It is then sent to the clarification tank where the heavier carbon settle down due to gravity.
- The spent carbon can be regenerated.
- The water clarification filtration



from the tank is filtered in a column.

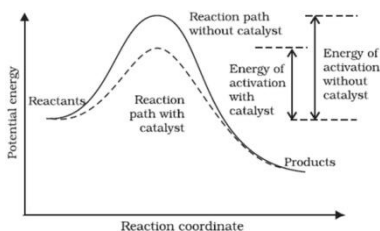
Flow diagram of water treatment using powdered activated carbon

Catalysis

The process of altering (increasing or decreasing) the rate of a chemical reaction with the help of a catalyst is known as catalysis.

Effect of catalyst

A catalyst increases the rate of reaction by lowering the energy barrier between the reactant and product.



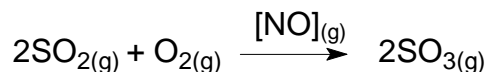
Types of catalysis

1. Homogeneous catalysis

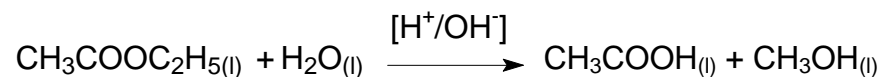
It is a process in which the catalyst and the reactants are in the same phase.

Examples

(a) *Homogeneous catalysis in gas phase*



(b) *Homogeneous catalysis in liquid phase*

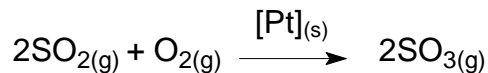


2. Heterogeneous catalysis

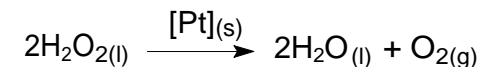
It is a process in which the catalyst and the reactants are in different phase.

Examples

(a) *Heterogeneous catalysis in gaseous and solid phase*



(b) *Heterogeneous catalysis in liquid and solid phase*



Difference between homogeneous and heterogeneous catalysis

S.No.	Homogeneous catalysis	Heterogeneous catalysis
1.	Reactant, product and catalyst are in one phase	Reactant, product and catalyst are in different phase
2.	Catalyst cannot be regenerated.	Catalyst can be regenerated.
3.	Thermal stability of catalyst is low.	Thermal stability of the catalyst is low.
4.	Reactions are carried out at low	Reactions are carried out at high

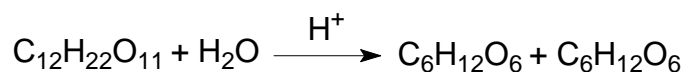
	temperature and pressure.	temperature and pressure.
5.	Temperature increases the rate of the reaction.	Temperature increases the rate of the reaction.
6.	Selectivity of the catalyst does not depend on the physical nature.	Selectivity of the catalyst depend on the physical nature.

Acid-Base Catalysis

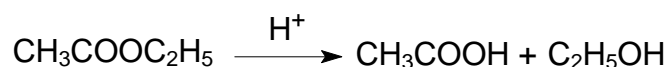
A large number of homogeneous catalytic reactions are catalyzed by acids or bases. The study of kinetics of these reactions is called acid-base catalysis.

Examples

1. Inversion of cane sugar



2. Hydrolysis of an ester



Classification of acid base catalysis

Acid catalysis

A reaction may be catalyzed by a proton (H^+)- Specifically proton catalyzed.

or

A reaction may be catalyzed by a bronsted acid (proton donors)- General acid catalysis.

Base catalysis

A reaction may be catalyzed by a hydroxide ion (OH^-)- Specifically hydroxide catalyzed.

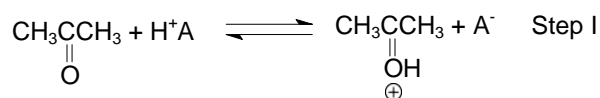
or

A reaction may be catalyzed by a bronsted base (proton donors)- General base catalysis.

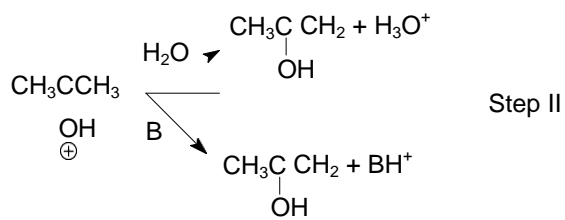
Mechanism of Acid-Base catalysis

Acid catalysis

Step I: Addition of H^+ ion to the substrate forming intermediate complex. (E.g. keto-enol tautomerism of acetone)

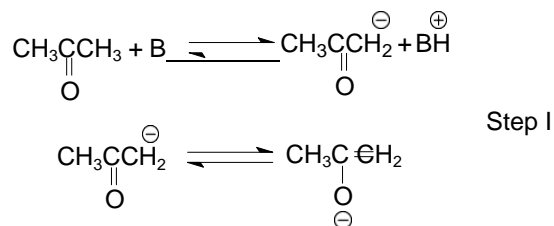


Step II: Removal of proton from intermediate complex by water or base.

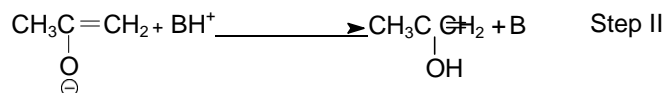


Base catalysis

Step I: Removal of H^+ ions from the reactant forming intermediate complex.



Step II: Addition of proton to the intermediate complex.

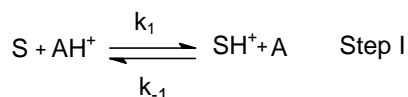


Kinetics of acid-base catalysis

Kinetics of acid-base catalysis is explained by the following mechanism.

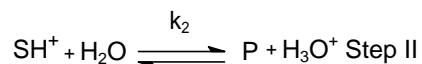
Step I

Involves transfer of the H^+ ions from an acid AH^+ to the substrate S.



Step II

Involves reaction of the acid form of the substrate with water to give products.



Applying steady state approximation to the intermediate $[\text{SH}^+]$

$$\frac{d[\text{SH}^+]}{dt} = 0 = k_1[\text{S}][\text{AH}^+] - k_{-1}[\text{A}][\text{SH}^+] - k_2[\text{SH}^+] \quad \text{---1}$$

The reactions are carried out at low concentration hence concentration of water is not taken into account in equation 1.

$$k_1[\text{S}][\text{AH}^+] = k_{-1}[\text{A}][\text{SH}^+] + k_2[\text{SH}^+]$$

$$[\text{SH}^+] = \frac{k_1[\text{S}][\text{AH}^+]}{k_{-1}[\text{A}] + k_2} \quad \text{---2}$$

The rate of formation of product is given by

$$\frac{d[\text{P}]}{dt} = k_2[\text{SH}^+] \quad \text{---3}$$

Substituting 2 in 3

$$\text{Rate} = \frac{d[\text{P}]}{dt} = \frac{k_2 k_1 [\text{S}][\text{AH}^+]}{k_{-1}[\text{A}] + k_2} \quad \text{---4}$$

Two cases are applied on equation 4.

Case 1 When $k_2 \gg k_{-1}[A]$, $k_{-1}[A]$ is negligible, so the above equation 4 becomes

$$Rate = \frac{k_2 k_1 [S][AH^+]}{k_2}$$

$$Rate = k_1 [S][AH^+] \quad \text{---5}$$

In this case the reaction is general acid catalyzed

Case II

When $k_{-1}[A] \gg k_2$, k_2 is negligible, the equation 4 becomes

$$Rate = \frac{k_2 k_1 [S][\text{EK}^+]}{k_{-1}[A]} \quad \text{---6}$$

The ionization constant of the acid AH^+ is

$$AH^+ \rightleftharpoons [H^+] + [A]$$

$$K = \frac{[H^+][A]}{[AH^+]}$$

$$[A] = \frac{K[\text{EK}^+]}{[K^+]} \quad \text{---7}$$

Equation 7 is substitute in 6

$$Rate = \frac{k_2 k_1 [S][AH^+]}{K [AH^+]} \cdot \frac{K}{[H^+]}$$

$$Rate = \frac{k_2 k_1 [S][H^+]}{k_{-1} K}$$

In this case the reaction is specifically hydrogen-ion catalyzed, because the equation contains $[H^+]$

General applications of catalysis

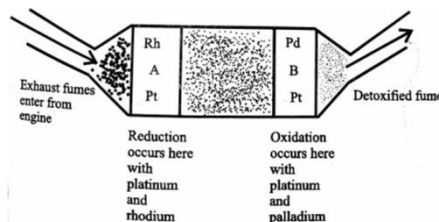
1. It increases the efficiency of industrial processes.
2. Many fine chemicals are prepared by employing catalysts.
3. Shape selective catalysis is possible.
4. Zeolites are used as catalyst in cracking of hydrocarbon.
5. Catalysts are used in catalytic cracking of petroleum.
6. They are used in functioning of fuel cells.
7. Nickel catalyst is used in hydrogenation of oils.
8. Catalysts are used in green chemistry.

Catalytic converter

- It is a device used to reduce the emission from IC engine.
- Reduced supply of oxygen in IC engine causes emission of toxic gases.
- These gases are oxidized and reduced to less harmful byproducts by catalytic converters

Construction

- It has a metal housing with a ceramic honey comb like interior with insulating layers.
- The honey comb interior is coated with aluminium oxide.
- It is porous and it contains metals such as platinum, palladium and rhodium.



Working

- The exhaust fumes are allowed inside compartment A where the reducible impurities are reduced.
- The remaining gases are allowed through the compartment B where all the oxidisable impurities are oxidized.
- The outgoing fume contains no toxic byproducts.

Function of catalytic converter

1. Reduction of nitrogen oxides into elemental nitrogen and oxygen



2. Oxidation of CO to CO₂

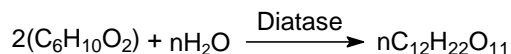
3. Oxidation of hydrocarbons into CO₂ and H₂O

Enzyme catalysis

Enzymes (or) biological catalyst are complex organic substances of high molecular weight proteins derived from living organisms.

Examples

1. Conversion of starch into maltose

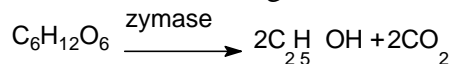


2. Inversion of cane sugar

The enzyme invertase catalyses the conversion of sugar into glucose and fructose.

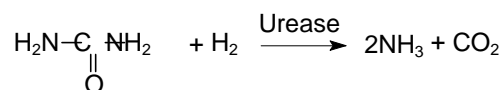
3. Conversion of glucose into ethanol

The enzyme zymase catalyses the conversion of glucose into ethanol.



4. Hydrolysis of urea

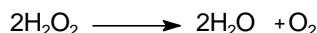
The enzyme urease converts urea in ammonia.



Characteristics of enzyme catalysis

1. Enzymes are most efficient catalysts

Enzyme catalyzed reactions proceed at higher rates than the reactions catalyzed by inorganic catalysts. Enzymes lower the activation energy of a reaction.



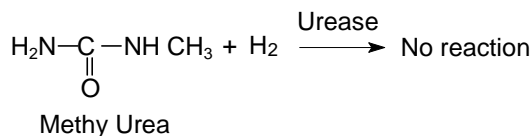
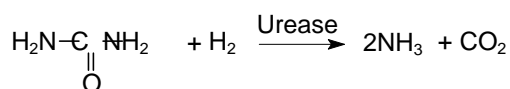
Activation energy without catalyst = 18 kCal/mol

Activation energy with colloidal platinum = 11.7 kCal/mol

Activation energy with enzyme catalyst > 2 kCal/mol

2. Enzyme catalyzed reactions are more specific

Enzymes are highly specific in catalyzing reactions. An enzyme catalyzes only a particular reaction.



3. Rate of the enzyme catalyzed reactions is maximum at optimum temperature.

Rate of the enzyme catalyzed reactions increases with increase in temperature and enzymes are denatured at high temperature. Rate is maximum at optimum temperature.

e.g. The optimum temperature of enzymatic reactions in human body is 37 °C. The enzymatic reactions will not happen at high temperature hence high body temperature is dangerous.

4. Rate of the enzyme catalyzed reactions is maximum at optimum pH.

The rate of the enzyme catalyzed reactions is maximum at a particular pH, known as optimum pH. The rate decreases below and above the optimum pH.

e.g. Many enzymes in human body are highly active at pH 7.4.

5. Catalytic activity of the enzymes is enhanced by activators (or) Co-enzymes.

If activators (metal ions Na^+ , Mn^{2+} , Co^{2+} , Cu^{2+} , etc.,) (or) co-enzymes (small molecules) are added to enzymes, they increase the catalytic activity.

6. Enzymes are poisoned by other substances

The catalytic activity is inhibited by the addition of other substances.

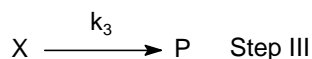
e.g. Heavy metal ions (Ag^+ , Hg^{2+}) react with the SH group of the enzyme and inhibit the enzyme activity.

Michaelis-Menten Equation

The following mechanism is proposed by Michaelis and Menten to explain the enzyme catalyzed reactions.

Let the enzyme E react with the substrate S resulting in the formation of intermediate complex X in first step.

The intermediate complex $E + S \xrightarrow{k_1} X$ Step I may dissociate back into E and S (or) may form product P.



k_1 , k_2 and k_3 are rate constant of the respective reactions.

The rate of formation of complex X is given by the following equation.

$$\begin{aligned} \frac{d[X]}{dt} &= k_1[E][S] - k_2[X] - k_3[X] \\ &= k_1[E][S] - (k_2 + k_3)[X] \quad \text{---1} \end{aligned}$$

Where, $[E][S]$ and $[X]$ = Molar concentrations of the enzyme, substrate and intermediate complex.

Rate of formation of the product is given by the following

$$\frac{d[P]}{dt} = k_3[X] \quad \text{---2}$$

$$\text{Since, } [E_0] = [E] + [X] \quad \text{---3}$$

Applying equation 3 in 1 gives,

$$\frac{d[X]}{dt} = k_1\{[E_0] - [X]\}[S] - (k_2 + k_3)[X] \quad \text{---4}$$

Where, $[E]$ = molar concentration of the unreacted enzyme

$[X]$ = concentration of the enzyme in the complex

$[E_0]$ = total concentration of the enzyme

The intermediate complex is unstable, it decomposes instantaneously hence

$$\frac{d[X]}{dt} = 0 \quad \text{---5}$$

Applying steady state, equation 5 may be applied on 4

$$k_1\{[E_0] - [X]\}[S] = (k_2 + k_3)[X] \quad \text{---6}$$

$$k_1[E_0][S] - k_1[X][S] = (k_2 + k_3)[X]$$

$$k_1[E_0][S] = k_1[X][S] + (k_2 + k_3)[X]$$

$$k_1[E_0][S] = \{k_1[S] + (k_2 + k_3)\}[X]$$

$$[X] = \frac{k_1[E_0][S]}{k_1[S] + k_2 + k_3} \quad \text{---7}$$

Dividing equation 7 by $k_1[E_0]$ gives

$$[X] = \frac{[E_0]}{1 + \frac{k_2 + k_3}{k_1[S]}} \quad \text{---8}$$

Substituting [X] in equation 2 gives

$$\frac{d[P]}{dt} = k_3 \frac{[E_0]}{1 + \frac{k_2 + k_3}{k_1[S]}} \quad \text{---9}$$

$$\frac{k_2 + k_3}{k_1} = K_m = \text{Michaelis constant}$$

$$\frac{d[P]}{dt} = \frac{k_3[E_0]}{1 + \frac{K_m}{[S]}} \quad \text{--10 (or)} \quad \text{Rate} = \frac{k_3[E_0][S]}{[S] + K_m}$$

Equation 10 is called Michaelis-Menten equation

Case (i) At low concentration of substrate

When the concentration of the substrate [S] is less than K_m
 $[S] \ll K_m$ then

$$\frac{d[P]}{dt} = \frac{k_3[E_0][S]}{K_m} \quad \text{---11}$$

Case (ii) At high concentration of substrate

When the concentration of the substrate [S] is higher than K_m
 $[S] \gg K_m$ then

$$\frac{d[P]}{dt} = \frac{k_3[E_0][S]}{[S]} \quad \text{---12}$$

$$\frac{d[P]}{dt} = k_3[E_0]$$

Effect of substrate concentration on rate

The order of the reaction changes with increase in the concentration of substrate.

(i) At low concentration of substrate

When the substrate concentration is low most of the active sites in the enzyme are unoccupied. At this moment, rate of the reaction increase with increase in the concentration of the substrate. It is a first order reaction with respect to substrate.

(i) At high concentration of substrate

When all the active sites are occupied, further increase in concentration of enzyme has no effect on the rate. The reaction becomes zero order with respect to substrate.

Significance of Michaelis-Menten equation

The equation can be simplified by assuming that all the enzyme has reacted with the substrate. In that case the rate is maximum.

$$[E_0] = [X]$$

Substituting the above equation in equation 2 gives

$$\frac{d[P]}{dt} = k_3 [E_0] = v_{\text{Nas}} \quad \text{---13}$$

Where, v_{Nas} = maximum rate

The Michaelis-Menten equation can be written as

$$\text{Rate} = \frac{v_{\text{Nas}}[S]}{[S] + K_N}$$

If $K_N = [S]$, then

$$\text{Rate} = \frac{v_{\text{Nas}}[S]}{[S] + [S]}$$

$$\text{Rate} = \frac{v_{\text{Nas}}[S]}{2[S]}$$

$$\text{Rate} = \frac{1}{2} v_{\text{Nas}}$$

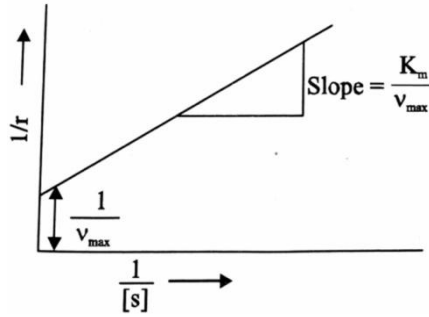
When the Michaelis-Menten constant is equal to concentration of the substrate, rate of the reaction is half the maximum rate.

Determination of the Michaelis-Menten constant (K_m)

Lineweaver-Burk equation is used to determine the value of the Michaelis-Menten constant.

$$\frac{1}{\text{rate}} = \frac{1}{v_{\text{Nas}}} + \frac{K_N}{v_{\text{Nas}}[S]}$$

The plot of reciprocal of rate vs concentration of substrate gives a straight line with intercept ($\frac{1}{\text{rate}}$) and slope $\frac{K_N}{v_{\text{Nas}}}$

**Turn over number (k_3)**

The number of molecules of substrate converted into products in unit time by one molecule of enzyme.

Factors affecting enzyme catalysis**1. pH**

Enzymes work well in the neutral pH but they get denatured at low and high pH values.

2. Temperature

Enzymes work faster at high temperature.

3. Salt Concentration

High concentration of salts increases the activity of the enzyme.

4. Activators and Inhibitors

Activators are small molecules that increase the activity of the enzyme. Inhibitors are small molecules that decrease the activity of the enzyme.