UNIT - III Adsorption and Catalysis

1 **Adsorption :-**

The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption

The adsorption of gas on a solid is sometimes called occulsion.

2. **Adsorbate :-**

The substance which is held on the surface of the solid is called adsorbate

3. **Adsorbent :-**

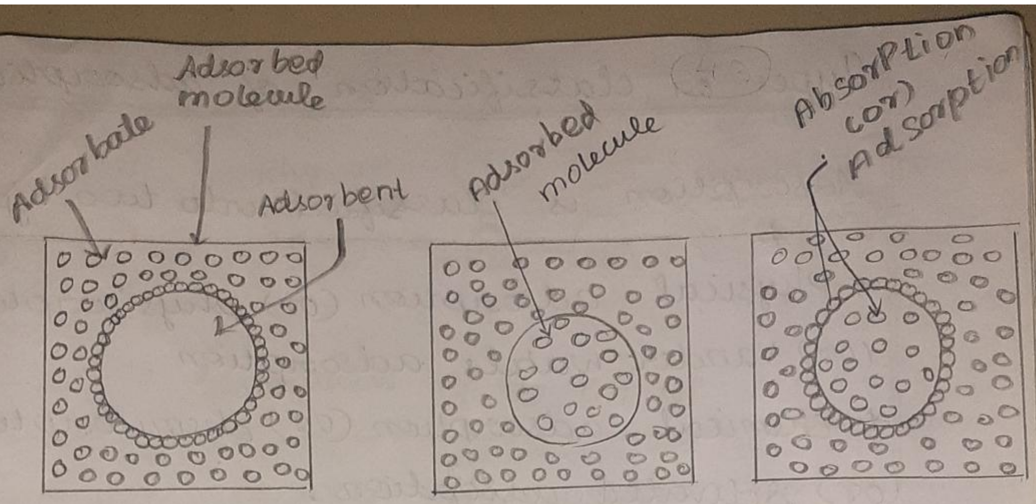
The solid that takes up a gas or a solute from the solution is called the adsorbent.

4. **Adsorption :-**

Adsorption is a process in which a substance is uniformly distributed throroughout the body of the solid or liquid.

5. **Sorption :-**

Sorption is the process in which both adsorption and absorption takes place simultaneously.



Adsorption Absorption Sorption

Illustration of adsorption, absorption and sorption.

Difference between adsorption and absorption

Adsorption	Absorption.
Adsorption is a surface phenomenon.	Absorption is a bulk phenomenon
It is a rapid process.	It is a slow process
Equilibreium is attained easily.	Equilibrium is attained slowly.
The concentration of molecules are more on the surface and less in the bulk.	But, distribution is uniform.

Types or classification of adsorption.

Adsorption is classified into two types.

- Physical adsorption (or) physisorption (or) Vander waal's adsorption.
- Chemical adsorption (or) chemisorption (or) Activated adsorption.

* Physical adsorption (or) physisorption:-

Physical adsorption is the one, in which the absorbed molecules are held on the surface of the absorbednt by weak physical (or) Vander wall's forces of attraction.

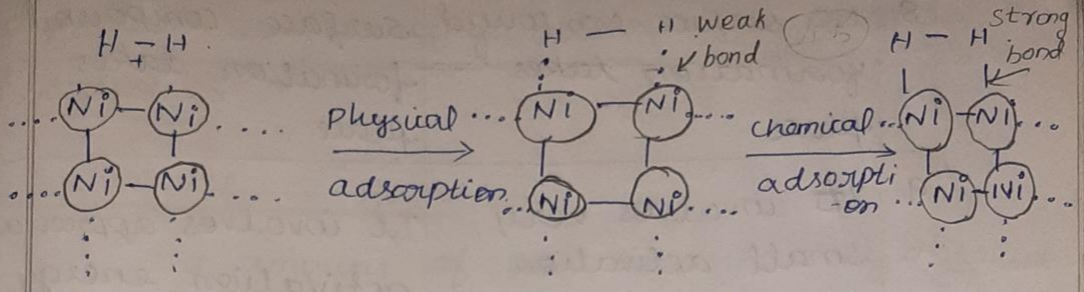
Example: Adsorption of H_2 (or) O_2 on charcol

* Chemical adsorption (or) chemisorption:-

Chemical adsorption is the one, in which the adsorbed molecules are held on the surface of the adsorbent by chemical bonds (covalent bond (or) ironic bond).

Example:- Adsorption of H_2 on Ni.

H_2 molecule is first ~~abso~~ adsorbed by vander wall's forces and then undergoes dissociation to hydrogen atoms. Then the H-atoms are chemisorbed on Ni



Adsorption of H_2 on Ni.

Differences between Physisorption and chemisorption

	Physisorption	chemisorption
1.	It is caused by intermolecular vander Waal's forces (weak)	It is caused by chemical bond formation (Strong)
2.	Heat of adsorption is low (0-40 k.cal/mol)	Heat of adsorption is high (40-400 k.cal/mol)
3.	Adsorption is completely reversible.	Adsorption is irreversible
4.	Adsorption decrease with increase in temperature	Adsorption increases with increase ~~in~~ with temperature
5.	Multilayer adsorption occurs.	Only ~~monomaly~~ monolayer adsorption occurs.
6.	The rate of adsorption increases with the increase of pressure and concentration	The rate of adsorption decreases with increase of pressure and concentration.
7.	Equilibrium is established rapidly.	But it requires time

8.	NO surface compound formation takes place	Surface compound formation takes place.
9.	It involves very small activation energy	It involves appreciable activation energy.
10.	It is not specific in nature.	But it is highly specific in nature.

Characteristics of Adsorption :-

* Adsorption on surface of a solid is always spontaneous.

* Adsorption is always accompanied by evolution of heat.

* Adsorption is accompanied both by decrease in enthalpy and entropy of the system.

* Adsorption is a selective process.

* The rate of adsorption depends on temperature.

* Adsorption is a physical phenomenon, but accompanied by a chemical change.

* Adsorption is specific, it depends on the nature of adsorbent and adsorbate.

Factors influencing adsorption of gases on solids:-

* Nature of gases:-

The amount of gas absorbed by a solid depends on the nature of the gas.

Easily liquefiable gases like HCl, NH_3, Cl_2, SO_2, etc,..., are absorbed more easily than the permanent gases like H_2, N_2, O_2 etc,... This is due to the following ~~gases~~. reasons

i) critical temperature: The case of liquefication depends on its critical temperature (i.e, the minimum temperature above which a gas cannot be liquefied). Thus if the critical temperature of the gas is more, it will be liquified and absorbed more readily.

Example:- Adsorption of various gases on 1 g of activated charcol.

Gases.	SO_2	NH_3	CO_2	N_2	H_2
critical temperature (K)	430	406	304	126	33
Amount of gas absorbed (in ml)	330	180	48	8.0	4.5

ii) Vander Waal's forces:- Easily liquefiable gases posses greater vander Waal's forces than permanent gases, so they are absorbed more readily.

* Nature and surface area of substance absorbent :-

Since the adsorption is surface phenomenon, the extent of adsorption depends on the surface area.

i) The greater the surface area, the greater is the adsorption.

ii) Larger pores on the adsorbent, larger is the adsorption. This is because, pores permit the diffusion of gases.

Charcol and silica gel: These are excellent absorbents, because their structure is highly porous and possess large surface area.

* Heats (or) Enthalpy of adsorption:

Adsorption is always accompanied by the evolution of heat i.e., it is an exothermic. Heat of adsorption is defined as " The energy liberated when 1 gm mole of a gas is absorbed on the solid surface.

In Physical adsorption, the attraction between gas molecules and solid surface are due to relatively weak Vander Waal's forces, The heat of adsorption is small (about 5 K.cal/mol).

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In chemical adsorption, the attractive forces are due to the formation of chemical bonds. The heat of adsorption is large (about 100 k. cal/mol).

* **Reversible character of absorbed gases:-**

Physical adsorption: It is a ~~rever~~ reversible process. The gas absorbed on a solid can be removed (desorbed) under reverse conditions of temperature and pressure.

$$\text{Gas} + \text{Solid} \rightleftharpoons \text{Gas/solid} + \text{Heat.}$$

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

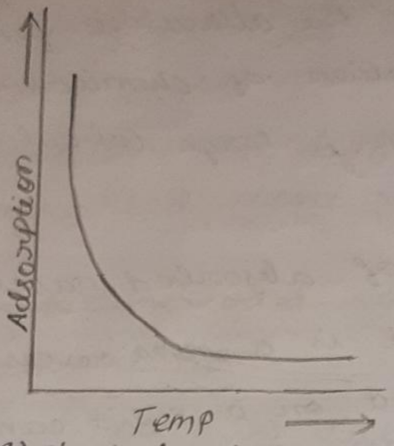
* **Effect of pressure of gas:-**

Since dynamic equilibrium exists between the absorbed gas and the gas in contact with the solid, increase of pressure increases adsorption and decrease of pressure causes desorption (decrease of adsorption)

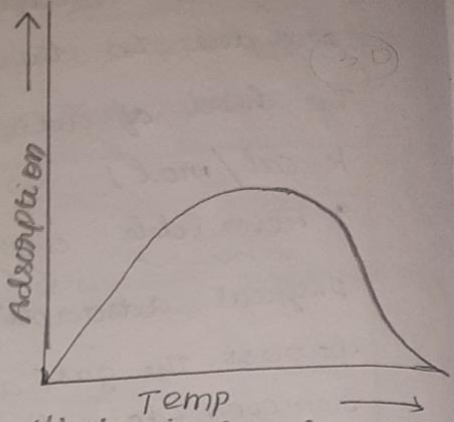
* **Effect of temperature of gas:-**

Physical adsorption:- It occurs rapidly at lower temperature and decreases with increase in temperature [Fig(a)]

Chemical adsorption:- It increases with increase in temperature and then decreases (Fig b)



(a) Physical adsorption Vs temperature



(b) Chemical adsorption Vs temperature

* Thickness of adsorbed layer of gas:-

Langmuir showed that at low pressure, the physically adsorbed gas forms one molecule thick layer. But, above a certain pressure, multimolecular thick layer is formed.

In chemisorption, the adsorbed gas is one-molecule thick. since chemical combination takes place with the adsorbent surface only directly.

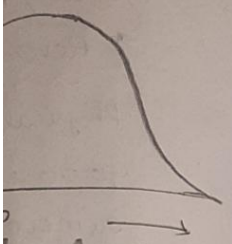
* Activation of adsorbent:-

Activation leads to increase in the surface area of the adsorbent, which increases adsorption. Activation is achieved by the following ways.

i) creation of rough surface:-

(a) by mechanical rubbing of solid adsorbents in1(w)1,

(b) by heating of solid adsorbent in superheated steam, now its pores are opened and adsorption increases.



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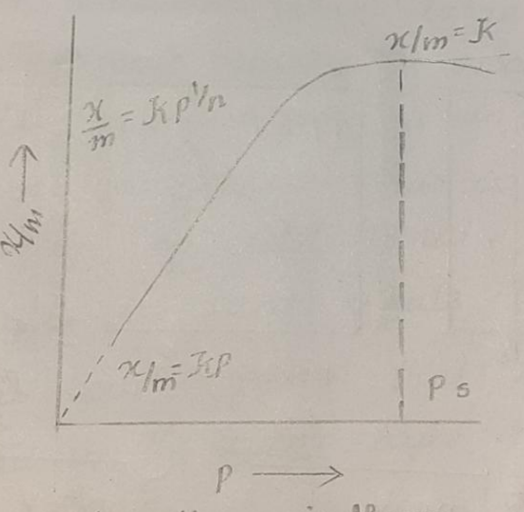
Adsorption isotherms:-

The extent of adsorption (x/m) (where, x = mass of adsorbate; m = mass of adsorbent) depends on pressure (P) and temperature (T). This can be understood by plotting a graph between (x/m) against (P).

Deffinition:-

Adsorption isotherm is a relationship (or a grap) between magnitude of adsorption with pressure at contand temperature (Fig a).

i.e., $x/m = KP^{1/n}$.



Adsorption isotherm. fig a

* From the graph, it is clear that the extent of adsorption (x/m) increases with increases of pressure (P) and becomes
* maximum at P_s (saturation pressure
* at P_s the rate of adsorption becomes equal to rate of desorption, thereby

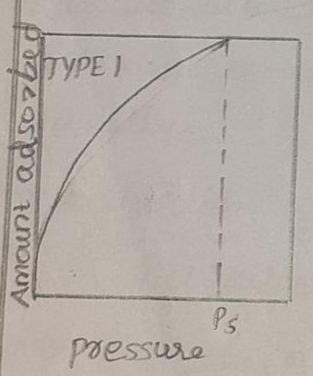
* dynamic equilibrium is reached.

Free gases $\rightleftharpoons$ Gas adsorbed on solid

* Further increase of pressure does not alter the equilibrium

Types of Adsorption isotherms:-

A large number of adsorption isotherms of gases on a variety of adsorbents at different temperatures have been studied. Their results are given into five different types of adsorption isotherms (Fig b). In each type, the saturation pressure where the maximum adsorption occurs, is indicated by "P_s".



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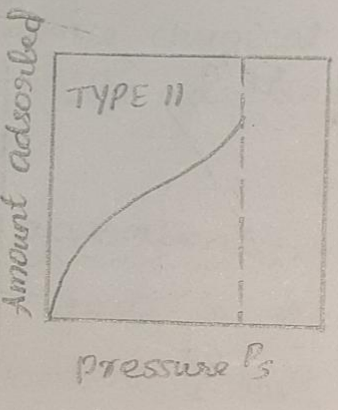

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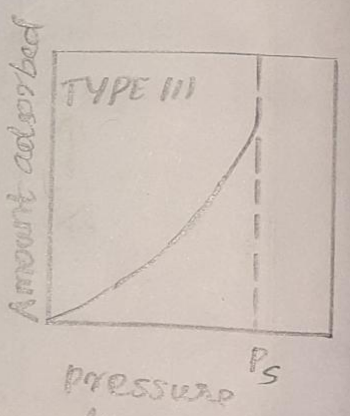

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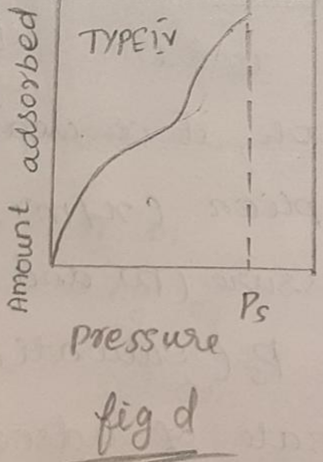

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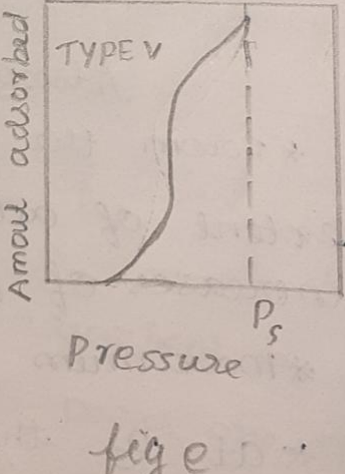


fig e

Type I :-

As postulated by Langmuir * it corresponds to monomolecular adsorption * The volume of the gas adsorbed approaches a limiting values "P_s", which is just enough to complete a monomolecular layer even when the gas pressure is low * Further increase in pressure will not increase the amount of adsorption.

Example :-

Adsorption of N_2 on H_2 On charcol at 180°C.

Type II and III :-

* These isotherms show large deviations from Langmuir model. * The amount of adsorption in each type, is going on increasing with increase in pressure. This is due to the formation of additional layers over the monolayers by vander waal's forces of attraction. It has been suggested that, the gas molecules absorbed in the first layes may hold a second layer of gas molecules by weak vander Waals forces (Physical bond), which in turn, may hold a third layer and so on.

Example :-

For type II :- Adsorption of N_2 on Fe or Pt catalyst at 195°c.

For type III :- Adsorption of Br_2 on Sili ca (or) Alumina gel at 80°c.

Type IV and V :

These isotherms indicate a possibility of condensation of gases in the minute capillary pores of the adsorbent at the pressures even below the saturation pressure "P_s". This is not only due to multi molecular adsorption layers of the gas molecules but also due to condensation of some of the gas molecules with in the capillary pores of the adsorbent. This is known as capillary condensation of the gas.

Example :-

For type IV: Adsorption of Benzene on silica gel at 50°c.

For type V :- Adsorption of H_2O vapour on activated carbon at 100°c.

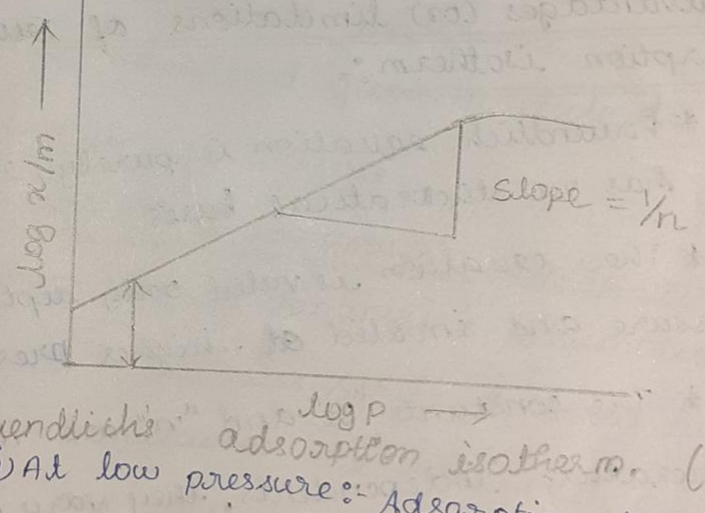
FRUENDLICH'S ADSORPTION ISOTHERM:-

The relationship between the magnitude of adsorption (x/m) and Pressure (P) can be expressed mathematically by an emprical. equation known as Freundlich adsorption isotherm.

i.e., $\frac{x}{m} = k p^{1/n}$.

Derivation of Fruendlich's Adsorption isotherm:-

The equation for fruendlich's adsorption isotherm may be derived. from the result observed from the grap (Fig a). Thus.



Fruendlich's adsorption isotherm. (fig .a)

i) At low pressure:- Adsorption increases with pressure.

$$\frac{x}{m} \propto P \text{ (or) } \frac{x}{m} = kP.$$

ii) At high pressure:- Adsorption is almost constant.

$$\frac{x}{m} = \text{constant (or) } \frac{x}{m} = k.$$

(iii) At intermediate (normal) pressure :- Adsorption depends on 0 to 1 power of pressure (i.e., fraction a power of pressure).

$$\frac{x}{m} \propto P^{1/n} \quad (\text{or}) \quad \frac{x}{m} = K P^{1/n} \longrightarrow ①$$

when, n = whole number.

This equation ① is called Freundlich's adsorption isotherm.

Taking logarithm on both sides, the above equation becomes,

$$\log x/m = \log K + 1/n \log P$$

On plotting $\log x/m$ Vs $\log P$, a straight line is obtained with a slope of $1/n$ and intercept $\log K$.

Disadvantages (or) limitations of Freundlich's adsorption isotherm :-

* Freundlich equation is purely empirical and has no theoratical basis.

* The equation is valid only upto a certain pressure and invalid at higher pressure.

* The constants "K" and "n" are not temperature independents, they vary with temperature.

* Freundlich's adsorption isotherm fails when the concentration of adsorbate is very high.

LANGMUIR'S ADSORPTION ISOTHERM :-

Langmuirs derived an equation based on some theoratical considerations. The postulates (or) Assumptions of Langmuir's theory are.

Assumptions (or) Postulates :-

* Valencies at the surface of adsorbent are not fully satisfied.

* The adsorbed gas layer on the solid surface is only one molecule thick.

* The surface of the solid is homogeneous so the adsorbed layer is uniform all over the adsorbent.

* There is no interaction between the adjacent adsorbed molecules.

* The adsorbed gas molecule do not move around on the surface.

Derivation of Langmuir's isotherm :-

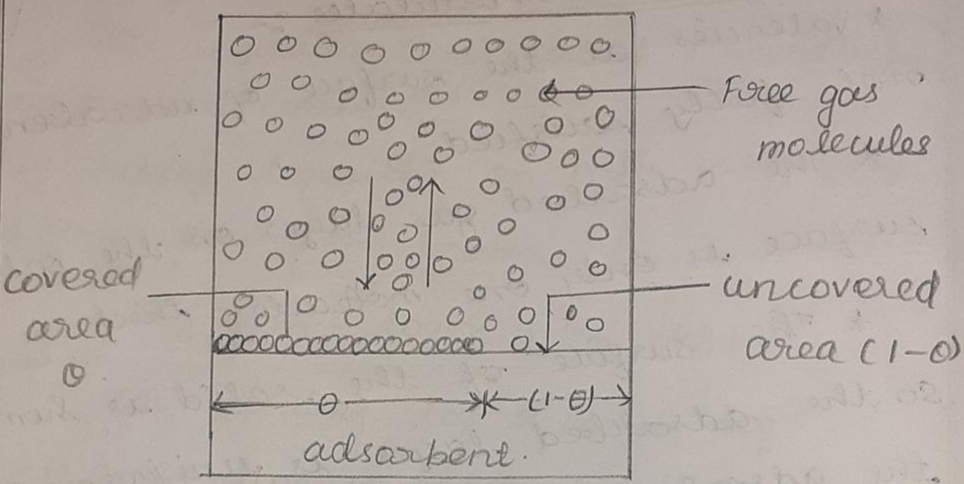
According to Langmuir's assumptions, when the gas molecules strike a solid surface, some of the molecules are adsorbed and some of these are desorbed. Thereby dynamic equilibrium is established between adsorption and desorption. If A is gas molecule and M is surface then.

$$A_{(g)} + M_{(surface)} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} AM.$$

Let,

Fraction of the total surface covered by the adsorbed molecule } = θ

Fraction of uncovered area (vacant area) } = $(1-\theta)$



Equilibrium between free molecule and adsorbed molecules.

Fig (a)

∴ The rate of desorption is proportional to number of adsorbed molecules } = $R_d = K_d\ \theta$

where, K_d = Rate constant for desorption.

Thus, the rate of adsorption is proportional to available uncovered area } = $R_a = K_a (1-\theta) p$

where, K_a = Rate constant for adsorption.

At equilibrium.

Rate of desorption ≡ Rate of adsorption.

$\therefore K_d\ \theta = K_a (1-\theta) p$

$= K_a P - K_a \theta P$

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

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

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

Dividing the equation ① by K_d it becomes

$$\theta = \frac{(K_a / K_d) P}{1 + (K_a / K_d) P} \cancel{\longrightarrow} ②$$

$$\theta = \frac{KP}{1 + KP} \longrightarrow ②$$

Where, $K_a / K_d = K$ = equilibrium constant, called adsorption coefficient.

But, the amount of gas adsorbed per gram of the adsorbent, x, is proportional to θ.

$$x \propto \theta \longrightarrow ③$$

On comparing equation ② and ③, it becomes.

$$x \propto \frac{KP}{1 + KP}$$

$$x = K' \frac{KP}{1 + KP} \longrightarrow ④$$

where K' = New constant.

The equation ④ gives the relation between the amount of gas adsorbed to the pressure of the gas at constant temperature is known as Langmuir's Adsorption isotherm.

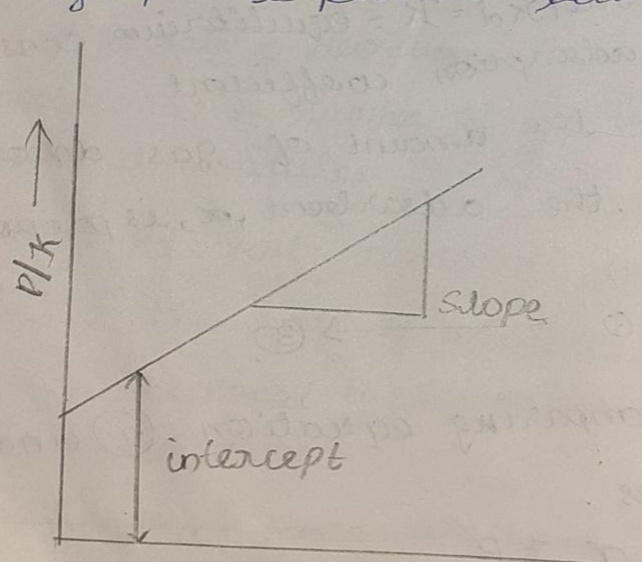
The above equation ④ may be written as.

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

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

$$\frac{1}{K'K} + \frac{K}{K'K}P = \frac{P}{x} \longrightarrow ⑤$$

The equation ⑤ is similar to an equation for a straight line (i.e, $y = c+mx$). If the graph is plotted between, P/x Vs P, we should get a straight line with slope $K/K'K$ and intercept $\frac{1}{K'K}$.



Fig(b). Plot of P/x vs P.

This equation is found valid in all cases.

case (i) :- At low temperature pressure.

If the pressure (P) is very low. $\frac{K}{K'K}$ term is negligible,

$$\text{i.e.,}\ \frac{1}{K'K} >> \frac{K}{K'K}.P,$$

hence, equation ⑤ becomes.

$$\frac{1}{K'K} = \frac{P}{x} \ (\text{or})\ x = PK'K \longrightarrow ⑥$$

$$(\text{or})\ x \propto P.$$

i.e., amount of adsorption per unit weight of adsorbent is directly proportional to the "P" at low P.

case (ii) : At high pressure.

If the pressure (P) is high $\frac{1}{K'K}$ is negligible,

$$\text{i.e.,}\ \frac{K}{K'K}P. >> \frac{1}{K'K}$$

hence equation ⑤ becomes

$$\frac{K}{K'K}P = \frac{P}{x} \ (\text{or})\ x = K' \ [\text{constant}]$$

$$(\text{or})\ x = K'P^0 \longrightarrow ⑦$$

i.e., extent of adsorption is independent of pressure of the gas, because the surface becomes completely covered at high pressure.

Case (iii) :- At normal pressure

If the pressure (P) is normal (intermediate) the equation ④ becomes

$$x = K' p^n \longrightarrow ⑧$$

where, n lies between 0 and 1

Equation ⑧ is Freundlichs adsorption isotherm.

Limitations (or) Merits and demerits :-

* Langmuirs adsorption isotherm is applicable only at low pressure, but fails at higher pressure.

* According to Langmuir's adsorption theory, the adsorption is monolayer, but multi layer adsorption is also possible.

P

APPLICATIONS OF ADSORPTION:-

* Activated charcol:-

(a) It is used in gas-masks, which adsorb all undesirable (toxic) gases, while purified air passes through its pores.

(b) It is also used for removing colouring matter from the sugar solution and the decoloration in vinegar.

* Silica and alumina gels:-

These are used as adsorbent for removing moisture and for controlling humidities of room.

* In heterogeneous catalyst:-

In heterogeneous catalyst, the molecules are adsorbed on the surface of catalyst which form "adsorption complex". Then it decomposes to form product.

Example:-

(i) Manufacture of SO_3 by contact process

(ii) hydrogenation of oils.

* Fuller's earth:-

It is used in large quantities for refining petroleum and vegetable oils, which adsorb unwanted materials.

*** Ion - exchange resins :-**

Softening of hard water can be done based on the principle of completing adsorption using Ion-exchange resins

*** Froth Flotation process**

The sulphide ores (PbS, ZnS, Cu_2S) are freed from silica and other earthy matter by forth flotation process. (oil adsorbs sulphide portion and is removed from ores only, but not others)

*** Arsenic poisioning:-**

colloidial ferric hydroxide is administered, which adsorbs arsenic poision and is removed from the body by vomiting.

*** Lake test for Al^{3+}:-**

It is based on the adsorption of litmus colour by $Al(OH)_3$ precipitate.

*** Mordants:-**

These are used in dying industry, which adsorb the colouring matter without attaching to the fabrics.

*** Production of High Vacua:-**

If the partially evacuated vessel is connected to a container of activated charcol (or) silica gel cooled with liquid air, it will adsorb all the gas molecules in the vessel. This results in a very high vaccum.

* Chromatographic analysis:-

Selective adsorption by alumina, megnesia, etc., can be used for separating different pigments and also mixtures of small quantities of organic substances with the help of adsorption chromatography.

* Measurement of surface area:-

Surface area of powders and rough surfaces can be measured using adsorption measurements.

*Evaporation of water is minimised:-

Due to the scarcity of water during summer layer of stearic acid is spread over water lakes and reservoirs. The adsorbed stearic acid on the surface of water minimises evaporation of water.

BET Equation :-

The BET equation (named after Brunauer Emmentt, and Teller who developed the theory) was first published in 1938 (Brauner 1938) and continues to be the most widely used method to determine the number of molecules/atoms of a gas needed to form a monolayer, X_m of adsorbed gas on a solid surface.

The BET Equation (Equation 1) describes the relationship between the number of gas molecules adsorbed (X) at a given relative pressure (P/P_0), where c is a second parameter related to the heat of adsorption.

$$\frac{1}{X[(P_0/P)-1]} = \frac{1}{X_m C} + \frac{C-1}{X_m C}\left(\frac{P}{P_0}\right)$$

Equation 1 :- Equation for surface area measurement.

The BET equation strictly describes a linear plot of $1/[X(P_0/P)-1]$. Vs. P/P_0 which for most solids, using nitrogen as the adsorbate is restricted to a limited region of the adsorption isotherm, usually in the P/P_0 range of 0.05 to 0.35.

The surface area, SA, is calculated from the slope and intercept according to Equation 2.

$$SA = \frac{1}{\text{slope} + \text{intercept}} \cdot CSA.$$

where CSA is the cross-sectional area of the adsorbate.

BET Adsorption:-

Techniques to determine the adsorbed gas molecules:-

The gas adsorption method is based on the gas adsorption theory on solid surfaces.

The changing curve of equilibrium adsorption capacity with pressure is called the adsorption isotherm.

The specific surface area and pore distribution of the porous sample can be obtained from the measurement and ~~analy-~~ analysis of the adsorption isotherm. The gases are always physically adsorbed on the solid surface at low temperatures in the atmosphere of adsorptive gases.

$$\frac{1}{X[(P_0/P)-1]} = \frac{1}{X_mC} + \frac{C-1}{X_mC}\left(\frac{P}{P_0}\right)$$

According to the BET multilayer adsorption model, the adsorption capacity has the following relationship with the gas partial pressure (BET equation): Where p is the gas pressure at the measurement (Pa), P_0 is the saturated vapor pressure of gas at the adsorption temperature (Pa), P/P_0 is the relative pressure, X is the adsorption capacity for the monolayer adsorption (kg or m3), and C is the BET constant.

The letter is related to the energy of the first layer of adsorption and represents the interaction strength between the gas and the solid. X_m can be calculated from the adsorption isotherm. A line is obtained by plotting the $P/[X(P_0-P)]$ versus P/P_0, and the gas adsorption capasity $X_m = 1/(a+b)$ can be obtained from the slope a $[a = (C-1)/(X_m C)]$ and intercept b $[b = 1/(X_m C)]$. Generally, C is big enough, and the intercept can be taken as 0. The total surface area can be calculated from the monolayer adsorption capacity as follows: Where X_m is the saturated adsorption capacity of the monolayer.

Role of adsorbents in Ion-Exchange Adsorption:-

Synthetic resins are used mainly as ion-exchange resins (or) ion-exchangers. These ion-exchangers possess one adsorbed ion on it. which can be released and adsorbs another like ion. This process is called ion-exchange adsorption.

Definition:-

Ion exchange adsorption is defined as, "the process of releasing the ion and adsorbing another like ion".

Classification of ion-exchangers:-

Ion-exchangers are classified into two types.

1. cation exchanger
2. Anion exchanger.

1. Cation exchanger:-

Resins containing acidic functional groups ($-COOH$, $-SO_3H$) are capable of exchanging their H^+ ions with other cations cation exchange resin is represented as RH_2.

Examples:-

i) Sulphonated coals
ii) Sulphonated polystyrene.

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2. Anion exchanger :-

Resins containing basic functional groups ($-NH_2$, $-OH$) are capable of exchanging their anions with other anions. Anion exchange resin is represented as $R'(OH_2)$.

Examples:-

i) Cross linked ~~quaronto~~ quaternary ammonium salts.

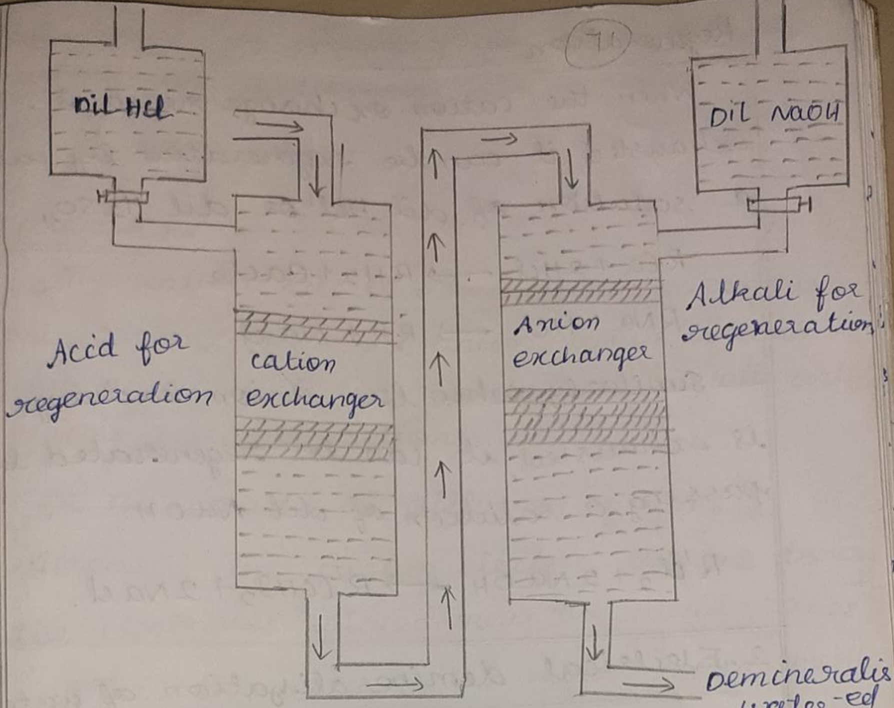
ii) Urea - formaldihide resin

Applications of ion-exchange adsorption

Ion-exchange adsorption has many useful applications in industry and medicine.

1. Water softening (Dimineralisation process) :-

The hard water first passed through a cation exchange column (Fig a), which adsorbs all the cations like Ca^{2+}, Mg^{2+}, Na^+, K^+, etc., present in the hard water.



Dimineralisation process

$$RH_2 + CaCl_2 \rightarrow RCa + 2HCl.$$

$$RH_2 + MgSO_4 \rightarrow RMg + H_2SO_4.$$

$$RH + NaCl \rightarrow RNa + HCl.$$

The cation free water is then passed through a anion exchange column, which adsorbes all the anions like Cl^-; SO_4^{2-}, HCO_3^-; etc., present in the water.

$$R'(OH)_2 + 2HCl \rightarrow R'Cl_2 + 2H_2O.$$

$$R'(OH)_2 + H_2SO_4 \rightarrow R'SO_4 + 2H_2O.$$

The water coming out of the anion exchanger is completely free from cations and anions. This water is known as demineralised water or deionised water.

Regeneration

When the cation exchange resin is exhausted, it can be regenerated by passing a solution of dil HCl or dil H_2SO_4.

$$RCa + 2HCl \longrightarrow RH_2 + CaCl_2$$

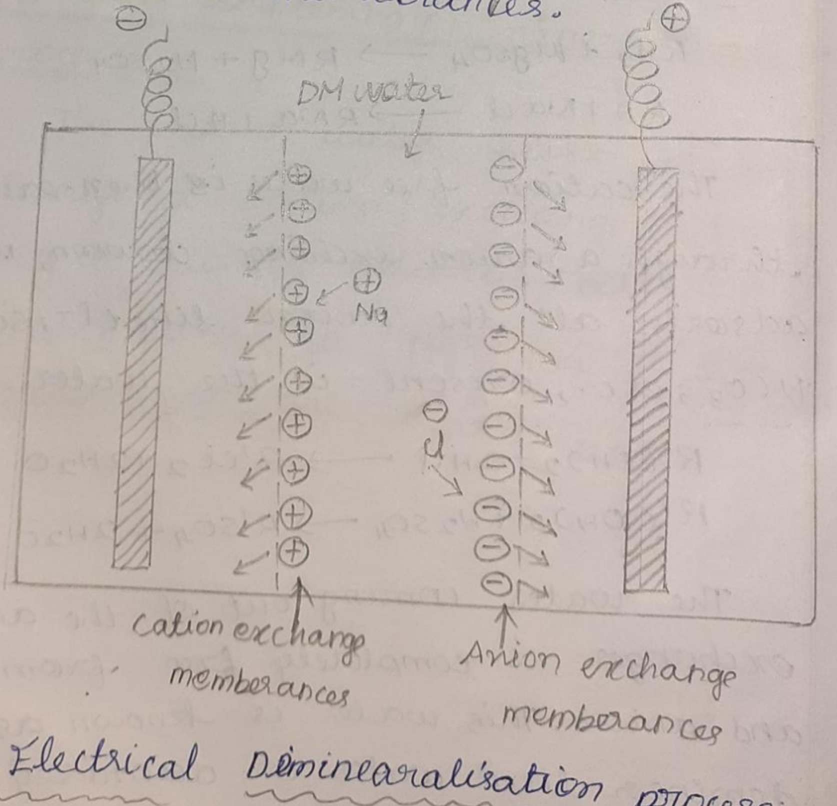
$$RNa + HCl \longrightarrow RH + NaCl.$$

Similarly, when the anion exchange resin is exhausted, it can be regenerated by passing a solution of dil NaOH.

$$R'Cl_2 + 2NaOH \longrightarrow R'(OH)_2 + 2NaCl.$$

2. Electrical demineralization of water :-

Ion-exchange resins supported on paper or fibre can be used as membrance, called ion-selective memberances.



Electrical Demineararalisation process

~~treatment of polluted air (or) water~~, of ~~which the followings are~~ important.

1. ~~Down flow~~

Process :-

* The cation selective memberanes permits only cations but not anions, while anions, while anion selective memberanes permit only anions but not cations.

* The rate of diffusion of ions is increased by passing electric current through the electrodes placed near the memberanes.

* Thus the water in the middle compartment is free from all the ions.

3. Medical uses :-

(a) Excess Sodium salts from the body fluids can be removed by giving a patient a suitable ion-exchanger to eat.

(b) weakly basic anion-exchanger are used to remove excess acid (or) "acidity" in the stomach

UNIT-III

catalysis:-

A substance that alters the rate of chemical reaction without itself undergoing any change is known as a catalyst and the phenomenon is known as catalyst.

General charactaristics of a catalyst:-

1). The catalyst does not initiate a reaction. It alters a speed of the reaction only. A possitive catalyst alters the speed of the reaction by changing the route of the reaction, which changes the energy requirements of the reactants suitably.

2) The catalyst does not chang the position of the equilibrium. It hastens the attainment of equilibrium.

② 3) The catalyst cannot change the nature of the product.

(a) nature (b)

4) Only a small quantity of the catalyst is required.

(c) (d)

5) The catalyst remains unchanged in amount and in chemical composition at the end of the reaction. However, it may undergo some physical change.

6) They are specific in action. i.e., a catalyst is effective for a paticular reaction only.

A catalyst may either increase the rate of a reaction. If the rate of the reaction is increased, the catalysis is called positive catalysis. If the rate of the reaction is decreased, the catalysis is called negative catalysis. There are two main types of catalysis namely, ①.

i. Homogeneous catalysis and

ii. Heterogeneous catalysis.

I Homogeneous catalysis :-

In this type of catalytic reaction, catalyst, reactants and products remain in the same phase and the reacting system as a whole remains homogeneous throughout.

i. Gas phase homogeneous catalysis :-

There are a few known cases of this type of catalysis. Nitric oxide gas catalyses the combination of sulphur dioxide and oxygen in the lead chamber process of the manufacture of sulphuric acid.

$$2SO_2 + O_2 \xrightarrow{NO} 2SO_3.$$

The nitric oxide gas also acts as a catalyst in the oxidation of carbon monoxide with oxygen,

$$2CO + O_2 \xrightarrow{NO} 2CO_2.$$

ii. Liquid phase homogeneous catalysis :-

Hydrolysis of cane sugar in aqueous solution in the presence of a mineral acid as catalyst is an example for liquid phase homogeneous catalysis.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Hydrolysis of methyl acetate in the presence of an acid is another example.

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

II. Heterogeneous catalysis:-

In this type of catalysis, the catalysis and the reactants are in the different phase. This type of industrial importance and has been studied in detail than homogeneous catalysis. The catalyst which are generally used in this type are : Pt, Ni, Cu and Fe. Usually in a state of fine powder, oxides of Zn, Cr, Bi and Mo are also used as catalysis.

a. Heterogeneous Catalyst having gaseous reactants and solid catalysis:-

There are a large number of gaseous reactions, which are examples for heterogeneous catalysis. A few of them are as follows.

i. Oxidation of sulphur dioxide to sulphur trioxide in the contact process of the manufacture of sulphuric acid with V_2O_5.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

ii. Combination of hydrogen and oxygen to give water in the presence of Pt as catalyst

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O.$$

iii. Formation of amonia from hydrogen and nitrogen in the presence of Fe_2O_3 as catalyst.

$$N_2 + 3H_2 \xrightarrow{Fe_2O_3} 2NH_3.$$

b. Hetrogeneous catalyst having liquid reactants and solid catalyst:

i. Decomposition of hydrogen peroxide in presence of colloidal platinum.

$$2H_2O_2 \xrightarrow{P.t} 2H_2O + O_2$$

ii. Decomposition of aqueous solution of a hypochloride in presence of oxides of Nickel.

$$Ca(ClO)_2 \xrightarrow{NiO} CaCl_2 + O_2$$

Catalysis.

Catalysis, It is a wellknown laboratory observation that the decomposition of potassium chlorate takes place much more rapidly and at a much lower temperature if a little manganese dioxide is added to it. The reaction is written as :-

$$2KClO_3 \xrightarrow{MnO_3} 2KCl + 3O_2.$$

Manganese dioxide is not used up at all and can be recoverded unchanged.

A substance that can influence the rate of a chemical reactions but which itself is not consumed and remains unchanged is known as a catalyst and the phenomenon is called catalysis.

There are several other examples of catalytic reactions and catalyts. For example, the oxidation of hydrochloric acid gas by oxygen takes place more quickly if the gases are passed over cupric chloride.

$$4HCl + O_2 \xrightarrow{CuCl_3} 2H_2O + 2Cl_2$$

The combination of hydrogen and oxygen to form water which is slow at ordinary temperatures proceeds more rapidly in the presence of platinum.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O.$$

Auto catalysis :- In certain reaction, one of the products acts as a catalyst. For example, the oxidation of oxalic acid by acidified potassium permanganate, represented by the following equations. ⑲

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$$

$$5(O) + 5\begin{array}{c}COOH\\|\\COOH\end{array} \longrightarrow 10CO_2 + 5H_2O.$$

increases in velocity as the reaction progress. This acceleration is to the presence of manganese (II) ions which are formed in the reaction.

This type of phenomenon in which one of the products itself acts as a known as auto-catalyst.

Promoters :- It has been observed in a number of cases that the activity of a catalyst is considerably increased by the addition of a passed substance which by itself has no catalytic property.

- Such a substance, which (though not a catalyst by itself) promotes the activity of a catalyst, is called a promoter

Thus, molybdenum promotes the catalytic activity of iron in the Haber process for the manufacture of ammonia :

$$N_2 + 3H_2 \underset{\text{molybdenum}}{\overset{\text{iron.}}{\rightleftharpoons}} 2NH_3$$

Oxides of aluminium, thorium and Uranium also promotes catalytic activity of iron for the above reaction. copper and tellurium promote the catalytic activity of nickel in hydrogenation of oils.

Acid - base catalysis :-

There are a number of homogeneous catalytic reactions which are brought about by acids and bases. The subject of acid - base catalysis, therefore, has assumed a special importance.

The catalytic effect of dilute mineral acids on the inversion of sucrose has been well-known for a long time.

$$\underset{\substack{\text{Sucrose}\\ \text{(dextro-rotatory)}}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\substack{\text{Glucose}\\ \text{(dextro-rotatory)}}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose.}\\ \text{(leavo-rotatory)}}}{C_6H_{12}O_6.}$$

Hydrolysis of a nitrile, first to amide and then to ammonium salt the corresponding fatty acid, is catalysed by acids as well as

ii) $RCONH_2 + H_2O \longrightarrow RCOONH_4$
Amide. Amm. Salt

Similarly, hydrolysis of an ester to give the corresponding acid and alcohol is accelerated in the presence of acids.

$$RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH$$

It has been known for a long time that in acid-base catalysis, if in fact, the hydrogen ion or hydroxyl ion which acts as the catalyst~~is~~. Thus, Arrhenius showsed that the inversion of cane-sugar or hydrolysis of an ester or nitrile was accelerated by the hydrogen ion irrespective source from which it was derived. Similarly, the mutarotation of Glucose, the conversion of acetone into diacetone alocohol and the hydrolysis of nitriles, are catalysed by hydroxyl ions.

The recent work has shown that in the reaction catalysed by acids not only hydrogen ions but also undissociated acid and even cations of weak bases (such as NH_4^+), in short, all substances which have a tendency to give up a proton, can show catalytic activity. Similarly, ~~if~~ in the reactions catalysed by alkalies, not only hydroxyl ions but also undissociated bases and even anions of weak acids (such as CH_3COO^-) can function as catalysts. It is this discovery which has led to the development of the modern concept of acid and bases. According to this concept, a reaction which is catalysed by an acid is also catalysed by any substance which has a tendency to lose a proton. This is known as general acid catalysis and an acid is defined as a substance which has a tendency to lose a proton. Similarly, a reaction which is catalysed by a base is catalysed by all substances ~~by~~ which have a tendency to gain a proton. This is known as general base catalysis and, a base is defined as a substance which has a tendency to gain a proton.

Some reactions such as mutarotation of glucose, hydrolysis of nitriles and esters and enolisation of acetone, are catalysed by both acids and bases.

Theory of acid-base catalysis:-

Further careful experiments have shown that catalytic activity of an acid (or a base) for a given reactions depend upon its readiness to lose (or gain) a proton. Therefore, the mechanism of acid-base catalysis appears to involve losing or gaining of proton. It is belived that a complex is formed first by the transfer of a proton (from the acid catalyst) to the reactant molecule (say, glucose or ethyl acetate or acetone). This process, which is slow and determine the rate of the reaction, is followed by a rapid internal rearrangement is removed by the basic catalyst.

A few examples may be considered to illustrate the mechanism of acid-base catalysis.

i) Mutarotation of Glucose:- Let GH represent α-glucose and HG its isomer, β-Glucose. The catalysed transformation of α-Glucose into β-Glucose may be represented as below:

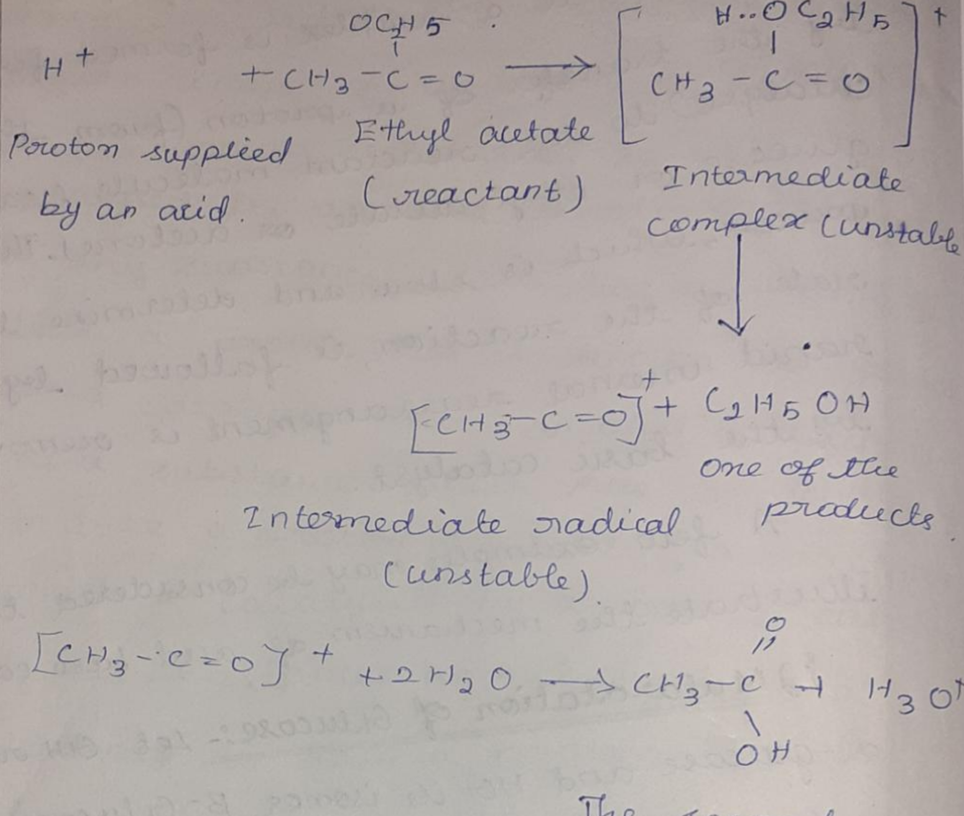
$$H^+ + GH \longrightarrow H.GH^+ \longrightarrow HG + H^+$$

H^+	GH	$H.GH^+$	HG	H^+
Proton applied by acid catalyst	α-Glucose (reactant)	The inter-mediate complex	β-Glucose (Product	Proton removed by base-catalyst

The rate of mutarotation of glucose is extremely small in pyridine, a base and also in cresol, an acid, but is appreciably high in a mixture of the two solvents.

(ii) Hydrolysis of Ethyl acetate :-

This may be representated as below:



$$H^+ + CH_3-\overset{OC_2H_5}{\overset{|}{C}}=O \longrightarrow \left[CH_3-\overset{H\cdot\cdot OC_2H_5}{\overset{|}{C}}=O \right]^+$$

Proton supplied by an acid.

Ethyl acetate (reactant)

Intermediate complex (unstable

$$\downarrow$$

$$[CH_3-C=O]^+ + C_2H_5OH$$

Intermediate radical (unstable).

One of the products.

$$[CH_3-C=O]^+ + 2H_2O \longrightarrow CH_3-\underset{OH}{\underset{\backslash}{\overset{O}{\overset{\|}{C}}}} + H_3O^+$$

The second product.

Evediently, one out of the two molecules of water acts as a base as it takes up the proton.

Enzyme catalysis :-

A very important type of catalysis includes reactions catalysed by certain complex organic substances known as Enzymes. Enzymes are proteins with high molecular weights of the order of 10,000 or even more and are derived from living organisms. Each enzyme can catalyse a specific reaction. For instance, the enzyme diaistase produced in the germinated barely seeds converts starch into maltose sugar.

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{Diatase} nC_{12}H_{22}O_{11}$$

Starch. Maltose sugar

Another enzyme known as maltase converts maltose into Glucose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Maltase} 2C_6H_{12}O_6$$

Maltose Glucose.

The enzyme known as zymase, produced by living yeast cells, converts glucose into ethyl alcohol.

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_6OH + 2CO_2$$

Glucose. Ethyl alcohol

The enzyme urease present in Soyabeans brings about quantitative, hydrolytic decomposition of urea into ammonia and carbon dioxide.

$$NH_2CONH_2 + H_2O \xrightarrow{Urease} 2NH_3 + CO_2$$

The enzyme reactions are sensitive to temperature. Generally, the Optimum temperature for maximum enzyme activity varies between 15°C and 25°C. The catalyti activity of enzymes is due to their capacity to lower the activation energy for a particular reaction.

Mechanism of enzyme-catalysed reactions:-

Michaelis and Menten suggested the following mechanism for enzyme-catalysed reactions:-

Let E represent the enzyme and S, the substance, generally referred to as the substrate, with which the enzyme reacts. The first stage is the formation of an intermediate complex represented as X:

$$\underset{\text{Enzyme}}{E} + \underset{\text{Substrate}}{S} \xrightarrow{k_1} \underset{\text{intermediate complex}}{X} \longrightarrow ①$$

The complex may either dissociate back into E and S or may give rise to the final product represented as P. These two posibilities are represented by the following equations:

$$X \xrightarrow{k_2} E + S \longrightarrow ②$$

$$X \xrightarrow{k_3} P \longrightarrow ③$$

k_1, k_2 and k_3 are the rate contacts for the respective reactions.

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

$$\frac{d(X)}{dt} = k_1[E][S] - k_2[X] - k_3[X]$$

$$= k_1[E][S] - (k_2+k_3)[X] \longrightarrow ④$$

Where [E], [S] and [X] represent molar concentrations of the enzyme, the substrate and the complex, respectively.

The rate of formation of the product P, as represented by equation (3), is given by the following equation:

$$\frac{d(P)}{dt} = k_3[X] \longrightarrow ⑤$$

Equation ④ may also be written as:

$$\frac{d[X]}{dt} = k_1\{[E]_0 - [X]\}[S] - (k_2+k_3)[X] \downarrow ⑥$$

where $[E]_0 = [E]+[X]$. It may be noted that since [E] represents molar concentration of the unreacted enzyme and [X] represents the concentration of the enzyme which has entered into complex formation, $[E]_0$ stands for the total concentration of

Enzyme.

As the reaction proceeds, the intermediate complex formed in accordance with equation ①, decomposes instantaneously in accordance with equations ⑤ and ⑥. In other words,

$$\frac{d[X]}{dt} = 0 \longrightarrow \text{⑦}$$

This state is termed as the stationary state.

At the stationary state, equation ⑥ may be written as:

$$k_1\{[E]_0-[X]\}[S] = (k_2+k_3)[X] \longrightarrow \text{⑧}$$

or $k_1[E]_0[S] = \{(k_2+k_3)+k_1[S]\}[X]$

or $$[X] = \frac{k[E]_0[S]}{k_2+k_3+k_1[S]}$$

$$= \frac{[E]_0}{1+\frac{k_2+k_3}{k_1[S]}} \longrightarrow \text{⑨}$$

Substituting this value of [X] in equation (5), we get.

$$\frac{d(P)}{dt} = \frac{k_3[E]_0}{1+\frac{k_2+k_3}{k_1[S]}} \longrightarrow \text{⑩}$$

The quantity $\frac{k_2+k_3}{k_1}$ is known as Michaelis constant and may be denoted by K. Thus,

$$\frac{d(P)}{dt} = \frac{k_3[E]_0}{1+K/[S]} \longrightarrow \text{⑪}$$

If $\frac{d(P)}{dt} = \frac{k_3[E]_0}{2}$, i.e, if the rate of formation of the product is equal to half of the maximum rate at which the reaction proceeds at high concentration of S, then

$$K = [S] \longrightarrow \text{⑫}$$

Thus, Michaelis constant is equal to that concentration of S at which the rate of formation of the product is half the maximum rate obtained at high concentration of S.

It is evident from equation ⑪ that

(i) if [S] is very small as compared to K, the factor K/[S] will be negligible as compared to unity and hence the rate of formation of P will be ~~independent of the concentration [S]. In other words, the reaction will be of zero order with respect to S.~~

~~(ii) If [S] is very~~ lo directly proportional to [S], i.e., the reaction will be of the First order

(ii) If [S] is very large as compared to k, the factor k/[S] will be negligible as compared to unity and hence the rate of formation of P will be independent of the concentration [S]. In other words, the reaction will be of Zero order with respect to S.

(iii) In both the above cases, the reaction remains of the first order with respect to the total concentration $[E]_0$ of the enzyme.

The above conclusions have been confirmed by experiment