Classical Collision Theory of Reaction Rates

According to classical collision Theory, molecule must colide to react and the rate of chemical reaction is proportional to the number of reacting molecules, i.e,

Rate $\propto$ No. of colliding Molecules liter/per Second.

The collision theory accounts for the dependence of the rate of the product of concentration terms. Let us consider that molecule A combines directly with a molecule of B to form AB. i.e, $A + B \longrightarrow AB$

Visualise four molecules each of A and B in a box. In how many ways can collision b/w A and B occur?

One A molecule can collide with any of four B molecules; Hence it has four opportunites for collision. The same is true four each of four A molecules, making 16 possible collisions in all. collision per Second. Thus, the rate of the is proportional product of the concn.

$$\text{Rate} \propto [A][B]$$

Mathematical Treatment:-

The rate of the reaction b/w two identical molecules is given by,

$$\frac{dx}{dt} = Ze^{-E/RT} \quad \text{— (1)}$$

Where

Z → No. of binary collisions

E → Activation Energy.

According to the kinetic theory of gases, the velocity is related to conc. by the relation.

$$\frac{dx}{dt} \propto n^2 \text{ or } \frac{dx}{dt} = kn^2 \quad \text{—— (2)}$$

Where k → specific Rate constant

n → conc. of the reactent

From the reaction equation (1) and equation (2), We have

$$k = \frac{Z}{n^2} e^{-E/RT} \quad \text{— (3)}$$

From the simple kinetic theory of gases, the value of z is given by,

$$Z = 4n^2\sigma^2\left(\frac{\pi RT}{M}\right)^{1/2} \quad \text{— (4)}$$

Where σ → collision diameter, substituting the value of z is given by

$$k = 4\sigma^2\left(\frac{\pi RT}{M}\right)^{1/2} e^{-E/RT} \quad \text{— (5)}$$

Where $Z = 4\sigma^2\left(\frac{\pi RT}{M}\right)^{1/2}$ is collision no. and is defined as → The number of collisions per second when there is only one reactent molecule per ml of the gas.

On taking logarithm of eqⁿ (5), We get

$$\log k = \log\left[4\sigma^2\left(\frac{\pi RT}{M}\right)^{1/2}\right] - \frac{E}{RT} \quad \text{—(6)}$$

Differentiating the expression with respect to T.

$$\frac{d\log k}{dT} = \frac{1}{2T} + \frac{E}{RT^2} \quad \text{— (7)}$$

The expression $1/2T$ can be neglected in comparison with E/RT^2. Therefore the eqⁿ (7) becomes as,

$$\frac{d\log K}{dT} = \frac{E}{RT^2} \quad -(8)$$

Eqⁿ (8) is identical with Arrhenius equation. If the reaction nvolves two different molecules, then the value of collision umber (z) is given by

$$z = \sigma^2 \left[8\pi RT \left(\frac{M_1 + M_2}{M_1 M_2} \right) \right]^{1/2} \quad -(9)$$

Where

M_1 & M_2 → Molecular Weight

σ → Mean of the molecular collisions diameter of two Reactents.

Failures of Collision Theory:-

Thus, theory fails in a number of cases such as

1) The bimolecular polymerisation of ethylene occurs at a rate which is slower by a factor of 5×10^{-4} than the theoretical value calculated from simple collision theory

2) The polymerisation of 1:3 butadiene proceeds at a rate which is slower by a factor of 10^{-4} than the value calculated from ~~cal~~ from eqⁿ (5).

3. The chain reaction proceed at a very fast rate which is much higher than the value obtained from eqⁿ (5)

Modification of collision Theory:-

Steric Factor:- A sufficient no. of slow reactions are known which show that the phenomenon is limited to few instances and the equation $k = Ze^{-E/RT}$ reduces to,

$$k = PZe^{-E/RT}$$

Where P= probability factor or steric factor.

Which makes allowances for effect causing deviations from the ideal behaviour. The value of P varies from unity to 10^{-8} depending upon the nature of the reacti

Theorie's of Unimolecular Reactions:-

Lindemann's theory:-

1) Reactant molecule are activated by collision with one another. Some of molecules may posses suffici energy of pass into the final product without receiving additional energy. Such molecules are usuall termed as activated molecules.

) If the rate of activated molecules to convert int product is slow as compared with * which activate molecules are deactivated by collision, a stationar concentration of activated complex may be forme

(3) At low, pressure, the collision cannot maintain a supply of activated molecules. Therefore the rate of the reaction will depends upon the rate of activation and hence is porportional to the squre of concⁿ of reacting molecules. Thus the reaction becomes of the second order at low pressure

Mathematical Explanation:-

(i) **Activation by collisions:-** The process of energisation by collisions is represented by

$$A + A \longrightarrow A^* + A$$

Where A is a normal molecule and A^* is an activated molecule which possesses sufficient energy to pass into the products.

$$\therefore \quad \text{Rate of Activation} = k_1 [A]^*$$

Where k_1 is the specific rate constant for the Second order reaction,

(ii) **Deactivation by collision:-** The process of deactivation may be reprented as

$$A^* + A \xrightarrow{k_2} A + A$$

$$\therefore \text{Rate of decomposition} = k_2 [A^*][A]$$

When the rate of decomposition is slow as compared with the rate of activation, III). Decomposition:- The de-composition of activated molecules may be reprented as,

$$A^* \xrightarrow{k_3} \text{Product} \quad , \; k_3 \to \text{first order const.}$$

As the concn of $[A]^*$ is so small that is not changing with time, it means that according to steady state treatment $\frac{d[A^*]}{dt} = 0$ i.e, —(1)

But the rate of formation of A* is given by

$$\frac{d[A^*]}{dt} = k_1 [A]^2 - k_2 [A][A^*] - k_3 [A^*] \quad -(2)$$

Applying condition of equation (1) to equation (2), We get

$$k_1 [A] - k_2 [A][A^*] - k_3 [A^*] = 0$$

$$k_1 [A]^2 = k_3 [A^*] + k_2 [A][A^*]$$

$$= [A^*] [k_3 + k_2 [A]]$$

$$[A]^* = \frac{k_1 [A]^2}{k_2 [A] + k_3} \quad -(3)$$

But the rate of reaction will be proportional to the concn of activated molecule, one may write,

$$\text{rate} = k_3 [A^*] \quad -(4)$$

Substituting eqn(3) in eqn (4), We get

$$\boxed{\text{rate} = \frac{k_3 k_1 [A]^2}{k_2 [A] + k_3}} \quad -(5)$$

i, At High pressure:-

——x——x——x——

At High pressure k_2 [A] is far greater than k_3, It means that k_3 can be neglected in comparison with k_2 [A].

$$\text{rate} = \frac{k_3 k_1 [A]^{\cancel{2}}}{k_2 \cancel{[A]}}$$

$$\text{rate} = \frac{k_3 k_1}{k_2}[A]$$

$$\boxed{\text{rate} = k'[A]}$$ (First order kineti

(ii) At low pressure:- At low pressure k_3 is great

——x——x——

than k_2, It follows that k_3

be neglected in comparison with k_3.

$$\text{rate} = \frac{k_1 \cancel{k_3}}{\cancel{k_3}}[A]^2$$

$$\boxed{\text{rate} = k_1 [A]^2}$$ (Second order Ki

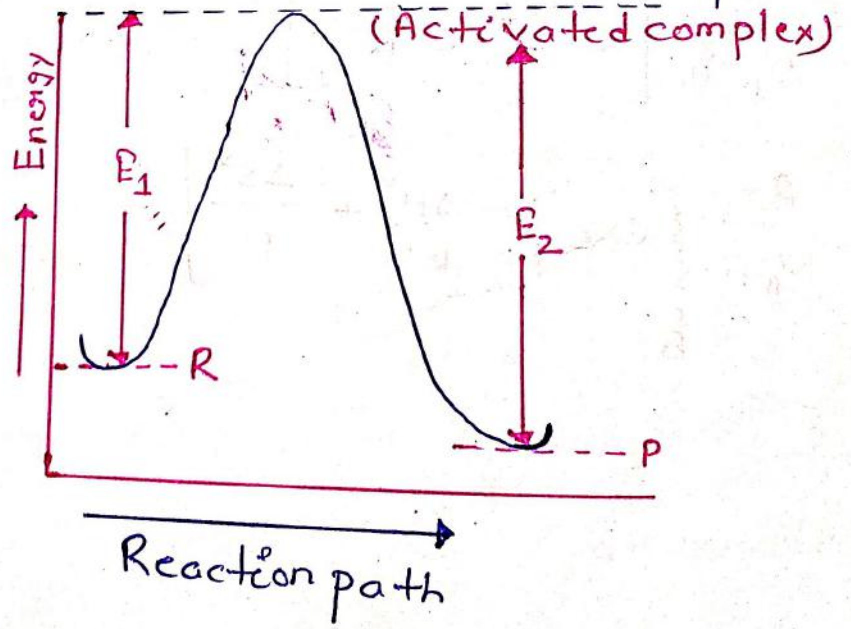
Transition state theory:-

This theory was first given by Marcelin (1915) and then developed by Eyring (1935), so this theory is called Eyring Theory. According to this theory, the reactent molecules are first transformed into intermediate transition state (also known as activated complex). The activated complex is note in a stabte of stable equilibrium, since it lies at a maximum potential energy.

Postulates of transition state theory:-

(i) As the reacting molecules approach each other, there is a continuous series of changes in bond distance These changes are accomponied by energy changes.

(ii) The reactant molecules are changed into an energy rich intermediate called activated complex or transition state.



Where

E_1 = Activation energy of reactent

E_2 = " " " Product

(iii) The activated complex may be formed by some loose association or bonding of reactent molecules with necessary arrangement of valence bonds and energy. If it is a unimolecular reaction, the reactant molecule may produce activated complex by rearrangement of atoms and redistribution of energy.

V) The activated complex, though unstable, has transient
(जब एक situation stable time में जाती हो)
extstence. It is treated formally as a ~~treated~~ with an independent enity. The activated complex remains in equilibrium with the reactents and its potential energy is maximum. Finally activated complex decompse its energy

) The energy of transition state greather than the energy of Reactent and product.

Thermodyanamic treatment of T.S.T. :-

—x——x——x——x——x—

onsider a bimolecular reaction b/w A and B. According
o T.S.T. :-

$$A + B \rightleftharpoons [X^*] \longrightarrow \text{Product}$$

The equilibrium constant of activated complex is,

$$k^* = \frac{[X^*]}{[A][B]} \quad \text{or} \quad [X^*] = k^*[A][B] \qquad —①$$

According to the transition state theory,

$$\frac{dx}{dt} = [X^*] \times \text{Rate (or frequency) of dissociation of activated complex}$$

from eqn (1) and eqn (2)

$$\frac{dx}{dt} = k^*[A][B] \times \text{Rate (or frequency) of dissociation of activated complex} \quad —③$$

One vibrational degree of freedom of activated complex is quite unstable and reponsible for disrupting the activa complex into the product. The frequency of such vibration will be low and average energy will be order to k_BT, i.e,

$$E_{vib} = k_BT = \hbar\nu$$

$$\nu = \frac{k_BT}{\hbar} \quad —④$$

Where k_B → Boltzman constant

$\hbar$ → Plank's constant.

Now from the equation (3)

$$\frac{dx}{dt} = k^*[A][B] \times \frac{k_BT}{\hbar} \quad —⑤$$

for conversion of reactent into products,

$$\frac{dx}{dt} = k[A][B] \quad —⑥$$

Now from eqn (5) and eqn (6)

$$k[\cancel{A}][\cancel{B}] = k^*[\cancel{A}][\cancel{B}] \times \frac{k_BT}{h}$$

$$\boxed{k = k^* \frac{k_BT}{\hbar} \quad —⑦}$$

This eqn represents mathematical statement of T.S.T.

According to the thermodynamics, k^* and ΔG can be related from the following relation,

$$\Delta G^* = -RT \ln k^* \quad \text{— ⑧}$$

Where ΔG^* = Standard free energy change.

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

$$-RT \ln k^* = \Delta H^* - T\Delta S^* \quad (\text{From eq}^n \text{ ⑧})$$

$$\ln k^* = \frac{-(\Delta H^* - T\Delta S^*)}{RT}$$

$$k^* = e^{-(\Delta H^* - T\Delta S^*)/RT} \quad \text{— ⑨}$$

From eq^n ⑦ and ⑨,

$$k = \frac{k_B T}{h} \times e^{-(\Delta H^* - T\Delta S^*)/RT}$$

$$\boxed{k = \frac{k_B T}{h} \times e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/RT}}$$

— ⑨

Equation (9) is known as the Eyring Equation.

Where, ΔH^* = Standard enthaly change

ΔS^* = " entropy "

Eq^n (9) can be applied not only to bimolecular process but also unimolecular and trimolecular process.

Eq^n (9) can also be expressed in different from involvin experimental energy of E_a instead of the heat of activatio ΔH^*. The change of equilibrium constant K^* with temp. is given by,

$$\frac{d \ln k}{dT} = \frac{\Delta E^*}{RT^2} \quad \text{—— (10)}$$

Where ΔE^* = increase in the energy of activation when the reactents go from the initial to the activated state.

According to eq^n (9),

$$k = K^* \frac{RT}{Nh} = K^* \frac{k_B T}{h}$$

$$\ln k = \ln K^* + \ln T + \ln\left(\frac{R}{Nh}\right)$$

Diff. above eq^n w. r. to t,

$$\frac{d \ln k}{dT} = \frac{d \ln K^*}{dT} + \frac{1}{T} = 0 \quad \text{—— (11)}$$

combining eq^n (10) and eq (11),

$$\frac{d \ln k}{dT} = \frac{\Delta E^*}{RT^2} + \frac{1}{T}$$

$$\frac{d \ln k}{dT} = \frac{\Delta E^* + RT}{RT^2} \quad \text{—— (12)}$$

According to the Arrhenius Equation,

$$k = A \cdot e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

Diff. above eqn w. r to T,

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad \text{—— (13)}$$

rom eqn (12) and eqn (13)

$$\frac{E_a}{RT^2} = \frac{\Delta E^* + RT}{RT^2}$$

$$E_a = \Delta E^* + RT \quad \text{—— (14)}$$

Now, $H^* = E^* + PV^*$

For a change at constant P

$$\Delta H^* = \Delta E^* + P\Delta V^*$$

$$\Delta E^* = \Delta H^* - P\Delta V^* \quad \text{—— (15)}$$

ombining eqn (14) and eqn (15)

$$E_a^* = \Delta H^* - P\Delta V^* + RT \quad \text{—— (16)}$$

for an ideal gas,

$$PV = nRT$$

$$P\Delta V^* = \Delta n^* RT$$

$$E_a^* = \Delta H^* - P\Delta V^* + RT$$

$$= \Delta H^* + RT - \Delta n^* RT \quad \text{—— (17)}$$

Where

Δn^* = change in no of moles in passing from intial to the activated state

$\Delta V^* =$ change in volume when the reactents pass from intial to activated state.

Case I :- Unimolecular Reactions

$$\Delta n^* = 0 \text{ and } \Delta V^* = 0$$

From eqn (17)

$$E_a = \Delta H^* + RT$$

Now from eqn (9), We get

$$k = \frac{RT}{Nh} e^{-(E_a - RT)/RT} \cdot e^{\Delta S^*/R}$$

$$\boxed{k = \frac{RT}{Nh} e^{1} e^{-E_a/RT} \cdot e^{\Delta S^*/R}} \quad \text{—(18)}$$

Case II :- Bimolecular Reactions :-

$$\Delta n^* = 1$$

$$E_a = \Delta H^* + 2RT$$

Now from eqn (17)

$$k = \frac{RT}{Nh} e^{-(E_a - 2RT)/RT} \cdot e^{\Delta S^*/RT}$$

$$\boxed{k = \frac{RT}{Nh} e^{2} \cdot e^{-E_a/RT} \cdot e^{\Delta S^*/R}} \quad \text{—(19)}$$

Now comparing eqn (18) and (19) with Arrhenius Equation ($k = A e^{-E_a/RT}$), We get

$$\boxed{A = \frac{RT}{Nh} e^{\Delta S^*/R}}$$

Frequency factor is related to the entropy of Activation (ΔS^*)

Kinetic Salt Effect :- An important feature of reaction b/w ions is the way in which the ddition of an inert electrolyte, i.e, one whose ions do not nter in the chemical reaction taking place can alter he rate of the reaction proceeding in the system. This henomenon is known as **Kinetic Salt Effects.**

The effect of electrolytes is two types:-

Primary Salt Effect 2. **Secondary Salt Effect**

Primary Salt Effect

The influence of electrolytic concentration on the activity coefficient and rate of reaction.

It is involved in non-catalytic reactions.

Let us consider a reaction,

$$A + B \underset{}{\overset{K^*}{\rightleftharpoons}} X^* \xrightarrow{k} \text{Product}$$

hree, K^* → Equilibrium constant for activation process and is given by-

$$K^* = \frac{a^*}{a_A\, a_B} = \frac{[X^*]}{[A][B]} \frac{y^*}{y_A \cdot y_B}$$

$$[X^*] = K^* [A][B] \frac{y_A \cdot y_B}{y^*} \quad \text{---} (1)$$

Rate of reaction is given by, (Acc. to T.S.T.)

$$\text{Rate} = \frac{-d[A]}{dt} = [X^*]\,\frac{k_bT}{h} \quad \text{— ②}$$

$$\text{Rate} = \frac{K_bT}{h}\,K^*\,[A]\,[B]\,\frac{\gamma_A\gamma_B}{\gamma^*} \quad \text{— ③}$$

But experimentally rate of reacn is given by,

$$\text{Rate} = k\,[A]\,[B] \quad \text{— ④}$$

From eq ③ and eqn ④

$$k\,\cancel{[A]}\,\cancel{[B]} = k^*\,\cancel{[A]}\,\cancel{[B]}\,\frac{\gamma_A\gamma_B}{\gamma^*}\cdot\frac{K_bT}{h}$$

$$k = \frac{K_bT}{h}\cdot k^*\,\frac{\gamma_A\,\gamma_B}{\gamma^*} \quad \text{— ⑤}$$

$$k = k_o\,\frac{\gamma_A\cdot\gamma_B}{\gamma^*} \quad \text{— ⑥}$$

Where k_o = Rate constant when all activity cofficent are unity.

Taking log on the both sides,

$$\log k = \log k_o + \log\gamma_A + \log\gamma_B - \log\gamma^* \quad \text{— ⑦}$$

([illegible])

We know that activity coifficient vary with concn, Acc. to Debye - Huckel limiting law,

$$\log y_{\pm} = - A z^2 \sqrt{I} \quad \text{—} \quad ⑧$$

Where

Z = valency of the ion

I = Ionic strength of the solution.

$y_{\pm}$ = Activity coefficients.

It is given by

$$I = \frac{1}{2} \Sigma m_i Z_i^2 = \frac{1}{2}(m_1 z_1^2 + m_2 z_2^2 + ----)$$

since the change of Activated complex $\mp Z_A + Z_B$

$$\log k = \log k_0 \cancel{+} A \sqrt{I} \left[(Z_A^2 + Z_B^2 - (Z_A + Z_B)^2 \right]$$

$$\log k = \log k_0 + 2A \, Z_A \cdot Z_B \sqrt{I} \quad \text{—} \quad ⑨$$

For eqn soln At 25°, A = 0.509

$$\log k = \log k_0 + 1.02 \, Z_A \cdot Z_B \sqrt{I}$$

The equation is valid for fairly dilute soln as it has been derived applying Bebye- Huckel limiting Law for dilute soln. The above eqn is known as Brownste Relationship.

If the values of log k - log k₀ are against √I, then it should be straight line with a slope 1.02 $Z_A Z_B$.

According to Equation variation of the rate const. with incresing ionic strength depend on the magnitude and sign Z_A and Z_B, Whe have three types of curve-

1. When $Z_A \cdot Z_B$ is positive :-

In such case, the reacting ions must have same charge either positive or Negative. so the reaction velocity increase with increase ionic strength. This type of phenomenon is called positive solt Catalysis.

(i) $[Co(NH_3)_5 Br]^{2+} + Hg^{2+} \longrightarrow P$ $(Z_A \cdot Z_B = 4)$

(ii) $I^- + S_2O_8^{2-} \longrightarrow P$

$(Z_A \cdot Z_B = 2)$

2. When $Z_A \cdot Z_B$ is Negative:- The reacting ions must have the opposite charges. The reaction velocity will then dec. with inc. Ionic strength or vice versa.

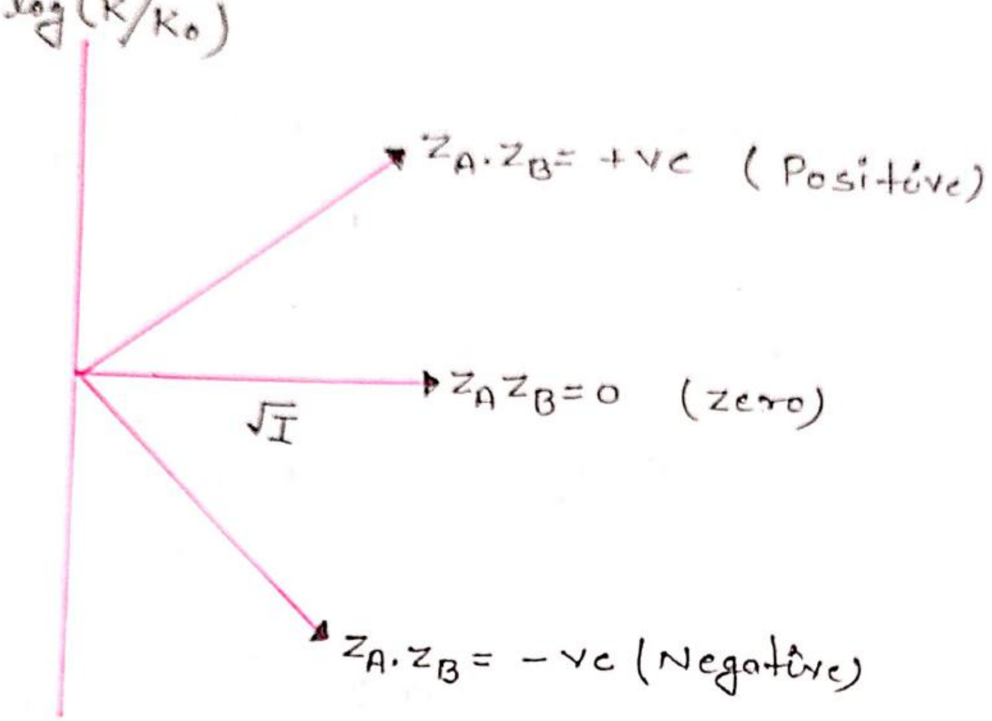
(i) $H^+ + Br^- + H_2O_2 \longrightarrow P$

(ii) $[Co(NH_3)_5 Br]^{2+} + OH^- \rightarrow P$ $(Z_A \cdot Z_B = -1)$

$(Z_A \cdot Z_B = -2)$

3. When $Z_A \cdot Z_B$ is Zero:-

In dilute sol^n, the ionic $conc^n$ has little or no effect on the rate of reaction or velocity const. In the inversion of cone sugar by acids. It is assumed that the complex is formed by a union of $C_{12}H_{22}O_{11}$ and H^+ (or H_3O^+). We find that $Z_A = 0$, $Z_B = 1$, so that $Z_A \cdot Z_B = 0$



Secondary Salt Effect:-

In primary salt effect addition of electrolyte (salt) or variation f ionic strength affect activity coefficient and ence rate.

But in the recⁿ where H^+ and OH^- ion (produced from weak acid or weak salt) act as a catalysing agent, he addition of salt influence the conc. of H^+ and OH^- ons. Since the rate of reaction depends on conc. f H^+ and OH^- ions. It is effected by the salt Concⁿ. This is called secondary salt effect.

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \cdot \frac{\gamma_A \gamma_B}{\gamma_{HA}}$$ [K_a = dissociation const. of weak acid]

$$[H^+] = \frac{K_a[HA]}{[A^-]} \frac{y_{HA}}{y_{A} \cdot y_{H^+}}$$

$$[H^+] = K \frac{y_{HA}}{y_A \, y_{H^+}}$$

Where $K =$ Const. as $\frac{K_a[HA]}{[A^-]}$ remains const. for a given acid – salt mix.

Since the Rate $\propto [H^+]$

The rate constant for a given acid – salt ratio

$$K = K_0 \frac{y_{HA}}{y_A \cdot y_{H^+}}$$

Where, $K_0 =$ Rate const. in the absence of sec. salt effect and includes primary salt effect.

But At 25°C

$$\log K = \log K_0 + 1.018 \sqrt{I}$$

When I is increased, conc. of H^+ increase, so rate of recn of (acid – catalysed recn inc.)

(The ionic strength must be kept const during acid/base catalysed)

Q4. Discuss Homogenous catalysis?

The phenomenon of increase in the reaction with the help of catalyst is known as catalysis.

Types of catalysis

Homogenous catalysis

In which the reactants and the catalyst form a single phase.

Hetrogenous catalysis

In which the reactents form one phase but the catalyst forms a diff. phase, usually solid.

Homogenous Catalysis

Acid - Base catalysts

Enzyme catalysts

(i) Acid - Base catalysis :- The mechanism of acid cat. reactions in which there occur a transfer of proton form an acid to a substrate S. The protonated substrate then reacts with water to form the product P, as shown below

$$S + HA \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} SH^+ + A^{-1}$$

$$SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+$$

The rate of appearance of product is given by

$$\frac{d[P]}{dt} = k_2[SH^+] \quad — ①$$

S.S.A. approximation to SH^+:

$$[S][HA] - k_{-1}[SH^+][A^-] - k_2[SH^+] = 0$$

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

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

ing eqn (1) and eqn (2) - - -

$$= k_2[SH^+] = \frac{k_1 k_2 [S][HA]}{k_{-1}[A] + k_2} \quad -(3)$$

$[A]$, then $\frac{d[P]}{dt} = k_1[S][AH^+] \quad -(4)$

y say that the reaction is general acid

f However, $k_2 << k_{-1}[A]$, then

$$\frac{[P]}{t} = \frac{k_1 k_2 [S][HA]}{k_{-1}[A]} = \left(\frac{k_1 k_2}{k_1 K}\right)[S][H^+]$$

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

Second Mechanism:— Here we assume that in the second step, the acid form of the substance reacts with a base A instead of water molecule.

$$S + AH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A$$

$$SH^+ + A \xrightarrow{k_2} P + AH^+$$

Applying S.S.A for $[SH^+]$, as before We have

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

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

Making use of Eq(2), the rate formation of the product is given by

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

This is an example of acid catalysis.

Enzyme catalysis:—

A very important type of Homogenous catalysis includ Reactions catalyzed by certain complex substances Known as Enzymes. Enzymes are proteins with high relativ molar mass of the specific reaction.

For instance, the enzyme diatase produced in the germinated barely seeds converts starch into maltos -sugar

Mechanism:– In 1913, bochchemist L. Michaelis and Miss maud Menten: proposed a mechanism for the kinetics of enzyme – catalysed reaction which envisages the following step.

Step I:– Formation of Enzyme – substrate complex

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES$$

Step II:– Decomposition of the complex

$$ES \xrightarrow{k_3} E + P$$

Where E is the (free) enzyme, S is the substrate (i.e the reactent); ES is the enzyme-Substrate comple
P is the product.

In the overall reaction $S \longrightarrow P$, the enzyme is consumed in step 1 and regenerated in step 2.

According to the slow R.D.S., The rate of reaction is given by

$$r = -\frac{[dS]}{dt} = +\frac{d[P]}{dt} = k_3[ES] \quad \text{—(1)}$$

Using steady - state Approximation for ES, We have

$$k_1[E][S] - k_2[ES] - k_3[ES] = 0 \quad \text{—(2)}$$

Now, [E] can not be measured experimentally, The Equilibrium b/w the free and the bound enzyme is given by the enzyme conservation equation,

$$[E]_0 = [E] + [ES]$$

$$[E] = [E]_0 - [ES] \quad \text{—(3)}$$

$[E]_0 \rightarrow$ Total Enzyme Concn

$[E] \rightarrow$ free Enzyme Concn

$[ES] \rightarrow$ bound enzyme concn.

substituting for [E] in eqn (2)

$$k_1 [[E]_0 - [ES]] [S] - k_2 [ES] - k_3 [ES] = 0$$

$$k_1 [E]_0 [S] - k_1 [ES][S] - k_2 [ES] - k_3 [ES] = 0$$

$$k_1 [E]_0 [S] = (k_1 [S] + k_2 + k_3) [ES]$$

$$[ES] = \frac{k_1 [E]_0 [S]}{k_1 [S] + k_2 + k_3} \quad — (4)$$

Now from eqn (1),

$$r = \frac{k_3 [E_0] [S] k_1}{k_1 [S] + k_2 + k_3}$$

$$r = \frac{k_3 [E]_0 [S]}{\frac{k_2 + k_3}{k_1} + [S]}$$

The quantity $(k_2 + k_3)/k_1$ is known as Michaelis constant and may be denoted by Km, Therefore

$$\boxed{r = \frac{k_3 [E]_0 [S]}{K_m + [S]}}$$

The above eqn is known as Michaelis- Menton equation.

S-(P-92)

Q4 Explain of general feature of fast reaction?

Reation that take place in times shorter than the time required to mix the reactents cannot be investigated by conventional methods. such reactions are termed fast reactions. Powerful experimental technique for studying the kinetics of fast reaction have been developed by the German chemist Manfred Eigen since 1950.

Eigen and his coworkers used relaxtion methods to investigate fast reaction in solution.

In this method, the reacting system in equilibrium is subjected to a sudden variation in some physical parameter on which the equilibrium const. of the reaction dependns. The system changes to new state of chemical equilibrium. The rate of this change, called relaxation, is then investigated. Relaxtion studies are carried out with such parameters as temp, poressure and electric field.

Factor Effecting Reaction Rate:-

1. Nature of the reactents:- The reaction rate varies depending upon what substances are reacting. Acid/base reactions, the formation of salts, and ion exchange are usually fast reactions. When covalent bond formation takes place b/w the molecules and when large moleculers are formed, the reactions tend to be slower.

The nature and strength of bonds in reactant molecules greatly influence the rate of their transformation into products.

Physical state:- The physical state (solid, liquid or gas) of a reactent is also an important factor of the rate of change, When reactents are in same phase, as in aqueous solⁿ, thermalmotion brings them into contonct. However when they are in seprate phase the reaction is limited to the interface b/w the reactents.

concentration:- The reactions are due to collisions of reactant species. The frequency with which the molecules or ions collide depends upon their concentrations. The more crowded molecule are, the more likely they are to collide and react with one another. Thus, on increase in the concⁿ of the reactents will usually results in the corresponding increase in the reaction rate, while a decrease in concentrations will usually reverse effect, For example combustion will occur more rapidly in pure oxygen than in air (21% oxygen)