(*) Chemical methods:-

In these methods progress of reaction can be followed by withdrawing a definite quantity of sample and analysing it chemically at different intervals of time. There are two ways of withdrawing a sample, depending on nature of reaction being studied. For the reaction taking place at room temp, a sample of reaction mixture is prepared & is kept in Constant temp bath. After sample has attained temp of bath, aliquots are withdrawn at suitable time intervals. The aliquotes can be analysed by a suitable volumetric method after freezing or quenching it.

Example:-

Hydrolysis of ethyl acetate by sodium hydroxide in aqueous medium at room temp by this method. The reaction is

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

A reaction mixture having required conc. of reactants is kept in at a thermostat. The progress of reaction can be followed by withdrawing a known volume of reaction mixture after it attained temp of bath. The aliquotes is added to a known excess of dil. HCl so as to arrest reaction. The excess of acid left can be back titrated by NaOH.

(a) Sealed tube method:-

When reactions use volatile liquid, loss of liquid at higher temp introduces a problem. For such systems "Sealed tube method" is generally employed. This method involves preparing a no. of sealed tubes having reaction mixture.

After having kept them at desired temp, these sealed tubes are removed at suitable intervals, and contents are analysed after "freezing" reaction, by way of direct methods.

e.g:- Study of reaction betⁿ C_2H_5ONa & $n\text{-}C_4H_9Br$ in ethanol at 60°C.

$$n\text{-}C_4H_9Br + NaOC_2H_5 \longrightarrow NaBr + n\text{-}C_4H_9OC_2H_5$$

(b) Decomposition of H_2O_2 by Volumetric method:-

Decomposition of H_2O_2 may be studied by removing samples of reaction solution at different time intervals and titrating with std. $KMnO_4$ solution.

(*) Physical methods:-

These methods involve measurement of some physical property which is related to Conc. But property being measured must be different from reactants to products to an appreciable extent. Moreover it should also vary linearly with Conc. changes of reactant & product.

Main limitation of physical methods is that verification is essential for proportionality between Conc & physical property beforehand.

Measurements of physical properties can be used to follow course of reaction. Samples of reaction mixture can be taken at suitable times, & these samples can be then analysed by measuring some physical property. Following are the methods which are generally used for study of reaction kinetics

Chemical Kinetics

* Experimental methods of following kinetics of a reaction :-

① Physical methods :-

(a) Spectrophotometric method - (Absorbance)

If a beam of light is allowed to make incident on a medium, a part of it gets absorbed by medium but rest gets transmitted, reflected & scattered. The extent of absorption depends on the chemical composition, thickness & conc. of absorbing molecule present in it. This is given by Beer-Lambert's law which can be put as follows:

$$I = I_0 e^{-\epsilon \cdot c \cdot l}$$

$$\ln \frac{I_0}{I} = \epsilon \cdot c \cdot l$$

$$\ln \frac{I_0}{I} = \epsilon \cdot c \cdot l = D \text{ or } A \text{ or } E$$

Here,

I = Intensity of transmitted light,
I_0 = Intensity of incident light,
c = Concentration in mole/litre,
l = thickness of sol^n in cm through which light travelled,
ϵ = molar extinction coefficient or molar absorptivity

I/I_0 = fraction of incident light transmitted by medium

$\log \frac{I_0}{I}$ = optical density (D)/absorbance (A)/extinction (E).

The law is true for monochromatic light & in systems where only one type of light absorbing species is present. The wavelength at which maximum absorption takes place is characteristic of a substance.

In spectrophotometric kinetic study it is possible to follow course of reaction measuring optical density at a particular wavelength as a function of time. If the Beer-Lambert's law is valid, the optical density (D) will be proportional to concentration. This will provide calibration curve, it is possible to determine unknown conc. of a reactant by using calibration curve at diff. or various time intervals.

Example:-

Kinetics of alkaline hydrolysis of methyl acetate can be conveniently followed by this method at 332 nm. The optical density can be measured spectrophotometrically at 332 nm by withdrawing thermostated reaction mixture at suitable time intervals. The specific reaction rate constant can be calculated by using following eq^n:

$$K = \frac{2.303}{t} \log_{10} \frac{D_\infty - D_0}{D_\infty - D_t}$$

where D_0, D_t & D_∞ denote optical density at begining, at time t & at infinity, respectively.

Potentiometric method:- (EMF)

This technique is of much use in study of fast ionic reactions. Potentiometric method is based on the fact that potential of a reversible electrode in a solution having its own ions, has been found to vary with conc. (activity) of ion, acting as reactant or product. The potential of electrochemical cell whose overall reaction is

$$aA + bB \rightarrow cC + dD$$

has been as follows:

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \log_e \left[\frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b}\right]$$

when a chemical change taking place, it is only change in cell emf which is due to change in conc. of species in indicator half cell. In this way it is possible to determine change in conc. of species of interest from change in cell emf.

Example:-

Bromination of N,N dimethyl aniline (ArH) in which indicator electrode (bright pt foil) is immersed into a soln having ArH, bromine and relatively large conc. of bromide ion while reference electrode is SCE. Emf of indicator electrode is given as follows:

$$E = E^{\circ}_{cell} - \frac{RT}{2F} \log_e \frac{[Br_2]}{[Br^-]^2}$$

$$E = E^{\circ}_{cell} - \frac{RT}{2F} \log_e [Br_2] \quad \left(\because [Br^-] \text{ is constant}\right) \quad \text{---(1)}$$

The reaction taking place may be represented as follows

$$ArH + Br_2 \rightarrow ArBr + HBr$$

The rate is given as follows:

$$-\frac{d[Br_2]}{dt} = K[ArH][Br_2]$$

On rearranging terms, we get

$$\frac{1}{[Br_2]} \frac{d[Br_2]}{dt} = K[ArH] \quad \text{---(2)}$$

On rearranging differentiating eq^n (1) & using eq^n (2), we get,

$$\frac{dE}{dt} = \frac{RT}{2F} \frac{d[\log_e [Br_2]]}{dt} = -\frac{RT}{2F}\left\{\frac{1}{[Br_2]} \frac{d[Br_2]}{dt}\right\}$$

$$= K[ArH]\left[\frac{RT}{2F}\right]$$

Thus,

$$K[ArH] = \frac{2F}{RT} \cdot \frac{dE}{dt} \quad \text{or} \quad K' = \left(\frac{2F}{RT}\right)\left(\frac{dE}{dt}\right)$$

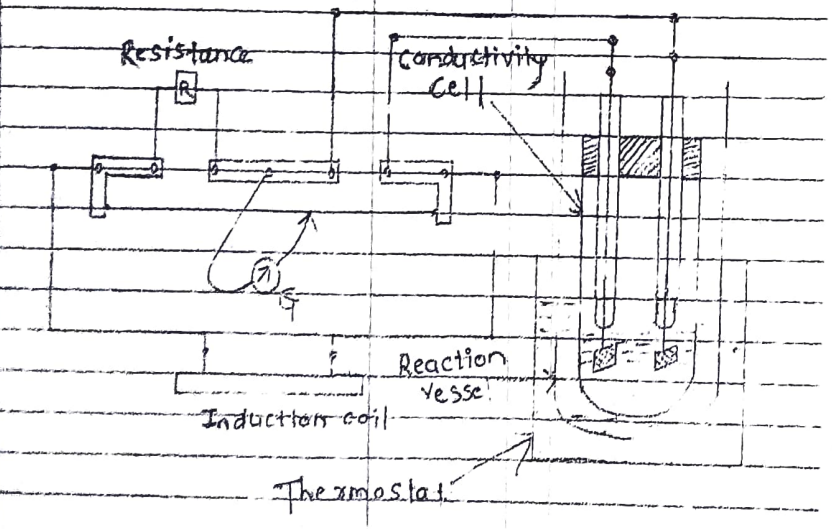
Where K' represents pseudo first order constant. It is possible to determine K' from potential data at various intervals of time. This can also be determined graphically in which dE/dt can be determined as slope of E-time plots.

c. Electrical Conductivity :- (Conductance measurement)

Rate of ionic reactions occuring in ionising solvents such as water can be determined by measuring the conductivity of reaction mixture as a function of time t. In dilute aq. solutions, where ionic conductances are almost constant, conductivity can be regarded as a linear function of conc. of several ions & therefore, to extent of reaction.

For moderately dilute solutions, after measuring conductivity, Onsager eq^n is used to know real conductivity of solutions.

Kinetics of such type of reaction can be readily & accurately studied by measuring electrical conductance of reaction mixture at suitable intervals of time at a desired temp by using a conductivity bridge.



Apparatus for measurement of Conductance of rea mixture

Here, Conductivity should have a linear relationship with Conc., solvent used must have a high dielectric constant. In dilute solutions, change in conductivity can be regarded as proportional to extent of reaction. Thus, if we take Conductivity at time zero, C_0, Conductivity at time t, C_t & Conductivity at infinity, C_∞ then,

$$x \propto (C_0 - C_t)$$

$$(a-x) \propto (C_t - C_\infty)$$

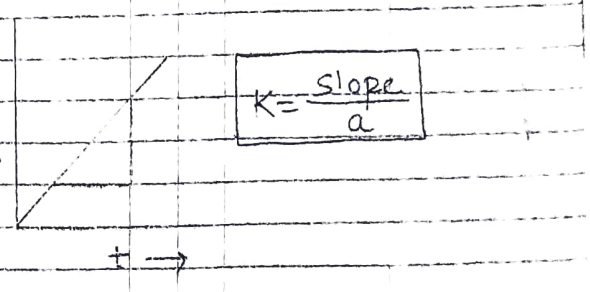
$$a \propto (C_0 - C_\infty)$$

When the reaction has been a second order one, then corresponding values of a & (a-x) can be substituted in fundamental eq^n for 2nd order. Slope of plot of $\frac{C_0 - C_t}{C_t - C_\infty}$ Vs t would be provide value of rate Constant K.

Example:- Saponification of ester by using alkali

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COO^{\ominus}Na^{\oplus} + C_2H_5OH$$

Since mobility of $CH_3COO^{\ominus}$ produced is much less than that of reactant $OH^{\ominus}$, Specific Conductance would decrease with time.



$$K = \frac{\text{Slope}}{a}$$

(4) Gas evolution method — (Pressure/volume)

→ Rate of chemical reaction can be evaluated by determining amount of gas liberated from or absorbed by a liquid reacting system.

→ Old & widely used procedure is applicable whenever one of the reactants or products is a gas.

→ Since reaction occurs in liquid & quantity of matter appearing or disappearing is measured in gas phase, it is essential that distribution eqm betn two phases be maintained.

→ Apparatus consists of a thermostated reaction vessel in which liquid can be agitated, connected to gas burette or manometer. (Device used to measure pressure.)

→ The liquid can be agitated by shaking flask or by means of a rotary stirrer. To avoid errors due to changing ambient temp burette should be calibrated.

(a) Volume of gaseous product or reactant at constant pressure:

When one of reactants or product is a gas, its volume is determined by using a manometer or gas burette. In order to know an exact relation between extent of reaction & observed increase in volume, one has to know volume of liquid mixture & stoichiometry of reaction. Consider a reaction:

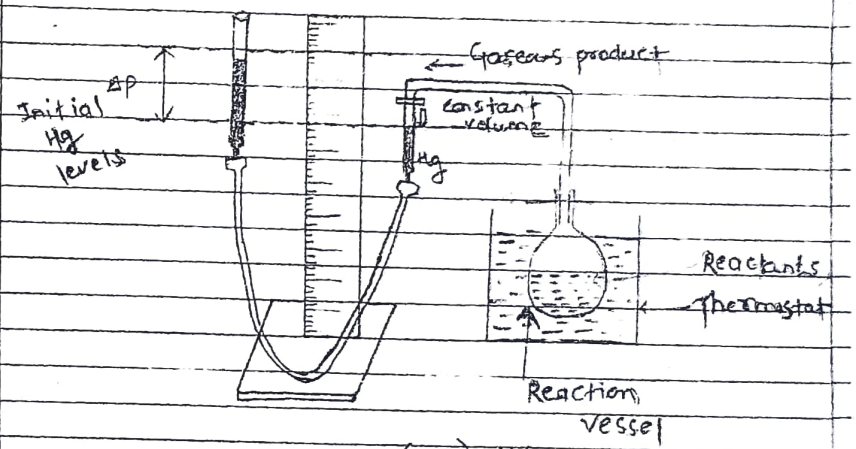
$$A + pB \rightarrow qC + D$$

where only C is gaseous. Conc. of A is given by following relation

$$[A] = [A]_0 - \left(\frac{n_C}{qV}\right)$$

where, n_C = no. of moles of gas C which are formed in certain time & V = volume of liquid

But $n_C = \frac{pV}{RT}$



$$[A] = [A]_0 - \left(\frac{p}{RT}\right)\frac{\Delta V}{qV}$$

Thus, it is possible to ascertain conc. of reactant A from change in gas volume (ΔV) at const. p.

When gas collects in burette, pressure increases. The excess of Hg is run out by opening stop cock so that level of Hg in both limb doesn't change throughout expt. The increase in volume is noted down as shown in figure after different intervals of time.

Example:-

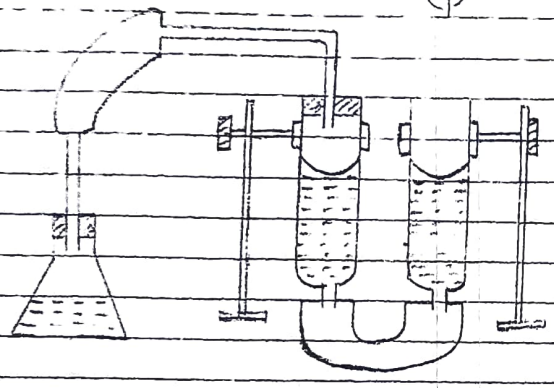
(i) Decomposition of diazonium chloride at const. T:-

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2(g)$$

(ii) Decomposition of N_2O_5 in CCl_4 sol. at const. T:-

$$N_2O_{5(soln)} \longrightarrow N_2O_4 + \tfrac{1}{2}O_{2(g)}$$

(iii) Decomposition of H_2O_2:- $2H_2O_{2(aq)} \rightarrow 2H_2O + O_{2(g)}$



Apparatus involving study of evolution of gases in the reactions

The rate of reaction will be given by,

$$\frac{d[O_2]}{dt} = [H_2O_2]^n \quad \text{——} (1)$$

In order to find rate constant, we should know conc. of H_2O_2 at various time intervals. If mol of O_2 is known, mol of H_2O_2 can be found out. The mol of O_2 is found from gas-volume relationship.

The conc. of H_2O_2 can also be determined in following way. If V_t & V_∞ refer to volumes of oxygen evolved at time t & ∞, then

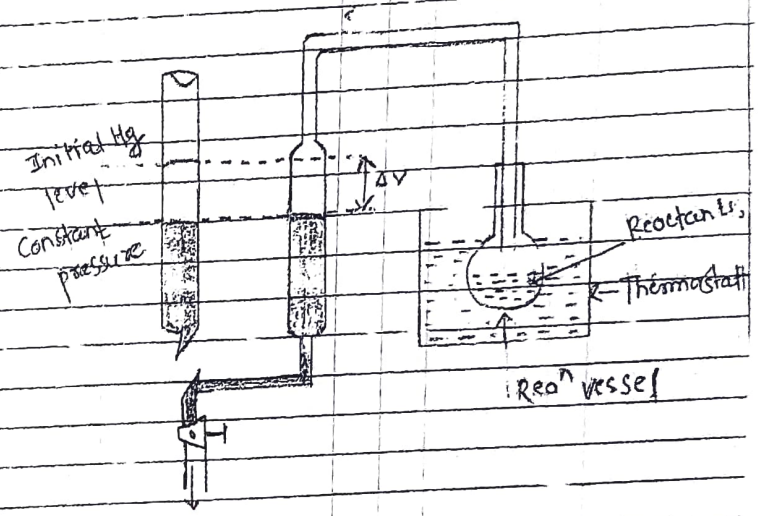
$$(V_\infty - V_t) \propto [H_2O_2]$$

Eq^n (1) becomes,

$$\frac{d[O_2]}{dt} = K(V_\infty - V_t)^n$$

Thus, Kinetics of decomposition of H_2O_2 can be studied.

(b) Change of pressure at constant volume:-



This method is used when one of the reactants or products is a gas. When reaction takes place, gas evolved forces travel of Hg in the shorter closed limb to move down. In order to maintain volume of the gas constant, one has to move the reservoir upwards until Hg in the shorter limb reaches same level as before. The difference in the level of Hg gives increase in pressure.

The increase of pressure developed at different intervals of time is noted from the difference in two Hg levels, as indicated in fig.

The kinetic of homogeneous gas reactions are very commonly studied by measuring the changing pressure of the system at const. T & V. When reaction results in a change in the total no. of gas molecules, its progress can be followed by measuring total pressure

Example :-

Synthesis of hydrogen chloride from its elements can be studied by immersing reaction vessel in liquid oxygen & measuring pressure, which is due to hydrogen only.

e) **Polarography :-** (Diffusion current)

→ It is an interesting & potentially useful technique for study of reaction kinetics.

→ The polarographic apparatus can be readily modified to yield a continuous automatic record of course of reaction.

→ Its kinetic usefulness to data has been in the study of biological processes involving appearance or disappearance of oxygen.

→ Principle underlying polarographic technique is measuring resulting current, when gradually increasing steady voltage is being applied across electrodes (out of which one is dropping Hg electrode) which are immersed into solution of an electro-active substance in a supporting electrolyte. The potential corresponding to point of inflection of curve (fig ⑥) is known as half wave potential ($E_{1/2}$). It is characteristic of nature of the substance and doesn't depend upon its conc. in solution. The eq^n describing potential as a function of current at any point of the polarogram is

$$E = E_{1/2} + \frac{RT}{nF} \log_e \left\{ \frac{i_d - i}{i} \right\}$$

magnitude of diffusion limited current (i_d) which depends upon temp., viscosity of medium & on the conc. of electro-active substance is given by following Ilkovic eq^n

$$i_d = 607 n . D^{1/2} m^{2/3} t^{1/6} C$$

where,

i_d = average diffusion current in μA,

n = no. of e^-s consumed in red^n of one mole of electroactive species,

D = diffusion coefficient of species involved in electrode reaction, expressed in $cm^2 sec^{-1}$,

C = Conc. in mm/lit,

m = flow of mercury (from dropping electrode) in mg/sec,

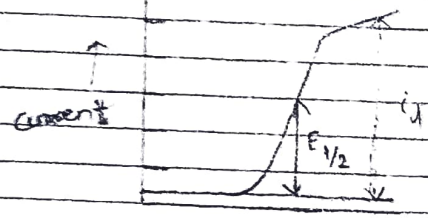
t = drop time in seconds

Thus, it means that if all factors remain constant, i_d varies linearly with conc. of electro-active species. Conc. range for polarographic analysis should be $10^{-3} - 10^{-4}$ molar. An outstanding feature of this technique is, small amounts of solution (a few cm^3) are required for studying the estimations.

It's possible to study kinetic study of the reactions satisfactorily by polarography in which at least one of components of reaction mixture (either reactants, intermediates or products) is electro active. For a systematic polarographic examination we should know before-hand how changes in supporting electrolyte, like pH, buffer type, solvent, temp etc. affect polarographic wave. one should also ascertain whether wave found is independent on conc. of compound under study. Diffusion controlled currents are most frequently used for

kinetic study, but other types of polarographic currents (kinetic or catalytic currents) can be applied for this purpose as well.

In order to measure polarographic currents, this reaction is performed directly in polarographic cells at const. temp as shown in fig (b)



Polarogram

Kinetics of Chain Reactions:-

There are two approaches to problem of mathematical representations of chain reactions

(i) Non-steady treatment:-

This method is followed by Russians. It involves high mathematical equations. These equations are highly complicated.

(ii) Steady-state treatment:-

This method is followed by British and American workers. According to this treatment, conc. of a free radical or intermediate or chain carrier is constant at any instant

$$\text{i.e } \frac{d[R]}{dt} = 0$$

where, R = free radical / intermediate / chain carrier

In all chain reactions, there is an initial slow step which gives rise to active species which carry out subsequent steps. These active species are called chain carriers and initial reaction itself is called chain initiation step.

(i) $M \xrightarrow{K_1} R$ chain initiation step

In the subsequent step or steps, chain carriers, formed in chain initiation steps, react with other reacting substances to form intermediate steps. These are called chain propogation or branching steps.

In some cases new chain carriers are formed or generated these steps are called chain transfer steps

(ii) $M + R^{\cdot} \xrightarrow{K_2} \alpha R + M'$ — Branching chain step

In end when there are not enough molecules of reactants to be converted to reaction products, active chain carriers are converted to non-active molecular species. These steps are termed as chain termination steps.

(iii) $R + M \xrightarrow{K_3}$ product — Final reaction

(iv) $R \xrightarrow{K_4}$ destruction at surface

(v) $R \xrightarrow{K_5}$ destruction in gas phase

Let us now apply steady state treatment to radical R, we get

$$\Rightarrow \frac{d[R]}{dt} = 0$$

$$K_1[M] + K_2(\alpha-1)[R][M] - K_3[R][M] - K_4[R] - K_5[R] = 0$$

or $$R = \frac{K_1[M]}{K_3[M] + (K_4 + K_5) - K_2(\alpha-1)[M]} \quad \text{——(1)}$$

The overall rate of reaction is given by step (iii)

$$V = K_3[R][M] \quad \text{——(2)}$$

Substituting value of [R] from eq^n (1) in eq^n (2), we obtain

$$V = \frac{K_3 \cdot K_1[M]^2}{K_3[M] + (K_4 + K_5) - K_2(\alpha-1)[M]} \quad \text{——(3)}$$

Chain length:-

It is defined as rate of overall reaction divided by rate of initiation reaction

$$\text{Chain length} = \frac{\text{Rate of overall reaction}}{\text{Rate of chain initiation step}}$$

Rate of initiation reaction (i) $= K_1[M]$

Rate of overall reaction $= V$

where $V = \dfrac{K_3 \cdot K_1[M]^2}{K_3[M] + (K_4 + K_5) - K_2(\alpha-1)[M]}$

$$\text{Chain length} = \frac{V}{K_1[M]}$$

$$= \frac{K_3 \cdot K_1[M]^2}{K_3[M] + (K_4 + K_5) - K_2(\alpha-1)[M] \cdot K_1[M]}$$

$$= \frac{K_3[M]}{K_3[M] + (K_4 + K_5) - K_2(\alpha-1)[M]}$$

② Decomposition of ozone:-

Chapman & his co-workers studied decomposition of ozone in presence of excess of oxygen & found the reaction to be of the second-order in ozone.

In 1905 John reinvestigated reaction & reported that rate of reaction was inversely proportional to the oxygen concentration. The mechanism as follows:

(1) $O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O$

(2) $O + O_3 \xrightarrow{k_3} 2O_2$

As decomposition of simple molecules like ozone must be of second order, Benson and Axworthy (1957) postulated following mechanism:

(1) $O_3 + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O + M$

(2) $O + O_3 \xrightarrow{k_3} 2O_2$

On applying steady-state treatment to oxygen atoms, we obtain

$$\frac{d[O]}{dt} = k_1[O_3][M] - k_2[O_2][O][M] - k_3[O][O_3] = 0$$

or $k_2[O_2][O][M] + k_3[O][O_3] = k_1[O_3][M]$

or $[O]\left(k_2[O_2][M] + k_3[O_3]\right) = k_1[O_3][M]$

$$[O] = \frac{k_1[O_3][M]}{k_2[O_2][M] + k_3[O_3]} \quad \text{——— (1)}$$

Overall rate may be put as follows:

$$-\frac{d[O_3]}{dt} = k_1[O_3][M] - k_2[O_2][O][M] + k_3[O][O_3] \quad \text{——— (2)}$$

Combining eq^n (1) & (2), we get

$$= k_1[O_3][M] - \frac{k_2[O_2]k_1[O_3][M][M]}{k_2[O_2][M] + k_3[O_3]} + \frac{k_3 k_1[O_3][M][O_3]}{k_2[O_2][M] + k_3[O_3]}$$

$$= k_1[O_3][M]\left\{k_2[O_2][M] + k_3[O_3]\right\} - k_2[O_2]k_1[O_3][M][M] + k_3 k_1[O_3][M][O_3]$$

$$= \frac{k_2[O_2][M] + k_3[O_3]}{k_1[O_3][M]k_2[O_2][M] + k_1[O_3][M]k_3[O_3] - k_2[O_2]k_1[O_3][M][M] + k_3k_1[O_3][M][O_3]}$$

$$= \frac{k_2[O_2][M] + k_3[O_3]}{2\left(k_1k_3[O_3]^2[M]\right)}$$

$$-\frac{d[O_3]}{dt} = \frac{2\left(k_1k_3[O_3]^2[M]\right)}{k_2[O_2][M] + k_3[O_3]} \quad \text{——— (3)}$$

From eq^n (3), it is evident that the rate is inversely proportional to the oxygen conc. when sufficient oxygen is present, and for the second order behaviour when oxygen is present.

* Reaction between NO_2 & F_2 :-

$$2NO_2 + F_2 \longrightarrow 2NO_2F \quad \text{——— (1)}$$

Stoichiometric eq^n reveals that reaction bet^n NO_2 & F_2 may be third order, but experimental data reveal that reaction has been actually of second order, first order in NO_2 & first order in F_2. The mechanism as follows:

(1) $NO_2 + F_2 \xrightarrow{K_1} NO_2F + F$ (slow)

(2) $F + NO_2 \xrightarrow{K_2} NO_2F$ (fast)

As the first step is slow & is rate determining step, it means that rate law is of second order & can be written as:

$$\text{Rate} = K[NO_2][F_2] \quad \text{——— (2)}$$

By using steady-state approximation for reaction in eq^n (1), same rate law can be found out. Here F is intermediate. On writting differential eq^n & equating it to zero, we get

$$\frac{d[F]}{dt} = K_1[NO_2][F_2] - K_2[F][NO_2] = 0$$

$$[F] = \frac{K_1}{K_2}[F_2] \quad \text{——— (3)}$$

Rate of disappearence of NO_2 may be given as follows:

$$-\frac{d[NO_2]}{dt} = K_1[NO_2][F_2] + K_2[NO_2][F] \quad \text{——— (4)}$$

On substituting [F] from eq^n (4) into eq^n (3), we get

$$\frac{d[NO_2]}{dt} = K_1[NO_2][F_2] + K_2[NO_2]\left(\frac{K_1}{K_2}[F_2]\right)$$

$$= 2\left(K_1[NO_2][F_2]\right)$$

or

$$-\frac{1}{2}\frac{d[NO_2]}{dt} = K_1[NO_2][F_2]$$

* Decomposition of nitrogen pentoxide :- (Ogg)

Ogg suggested it's mechanism as follows:

$$2N_2O_5 \longrightarrow 4NO_2 \text{ (g)} + O_2 \text{ (g)}$$

mechanism:-

$$N_2O_5 \xrightarrow{K_1} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{K_2} N_2O_5$$

$$NO_2 + NO_3 \xrightarrow{K_3} NO_2 + O_2 + NO$$

$$NO + N_2O_5 \xrightarrow{K_4} NO_2 + NO_2 + NO_2$$

The intermediates are [NO], [NO_3] & net rates of change of their conc. are:

$$\frac{d[NO]}{dt} = K_3[NO_2][NO_3] - K_4[NO][N_2O_5] = 0$$

$$\frac{d[NO_3]}{dt} = K_1[N_2O_5] - K_2[NO_2][NO_3] - K_3[NO_2][NO_3] = 0$$

The net rate of change of Conc. of N_2O_5 is,

$$\frac{d[N_2O_5]}{dt} = -k_1[N_2O_5] + k_2[NO_2][NO_3] - k_4[NO][N_2O_5]$$

Replacing Conc. of intermediates by using eqns above,

$$\frac{d[N_2O_5]}{dt} = \frac{-2k_1k_3[N_2O_5]}{k_2 + k_3}$$

(*) Ionic reaction :- Salt effect

Velocity constants of ionic reactions depend upon charges of reacting ions & also ionic strength of solution. Thus effect of electrolytes can be divided into two main types:

(a) Primary salt effect :-
It refers to effect of ionic strength on rate constant.

(b) Secondary salt effect :-
It refers to actual change in conc. of reacting ions by addition of electrolytes.

(a) Primary salt effect :-

This effect was made by Bronsted (1922) & further modified by Bjerrum which more simple than Bronsted theory. According to Bjerrum reacting ions 1st form an activated complex which is in eqm with reactants & then activated complex decomposes to yield products. Thus, rate of reaction is determined by conc. of the activated complex.

$$A^{Z_A} + B^{Z_B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[AB^{Z_A+Z_B}\right]^* \xrightarrow{k_3} \text{products}$$

Where A & B are reacting ions,
Z_A & Z_B = Charges on reacting ions,
AB = Activated Complex,
$Z_A + Z_B$ = Charge on activated complex,
k_1, k_2, k_3 = Velocity constants.

According to law of mass action, eqm Const. is given by,

$$K^* = \frac{a_{AB}}{a_A \cdot a_B} \quad \text{---------- (1)}$$

where $K^* (K_1/K_2)$ is eq^m const for process $A+B \rightleftharpoons AB^*$. a_A, a_B & a_{AB} represent activities of reactants A, B & activated complex AB respectively.

But activity = actual conc. × activity coefficient

$$a = C \times \gamma \quad \text{——— (2)}$$

Value of activity coefficient is less than unity except in infinitely dilute solutions. Replacing activities in eq^n (1), we get

$$K^* = \frac{C_{AB}\gamma_{AB}}{C_A C_B \gamma_A \gamma_B} \quad \text{——— (3)}$$

where C_{AB}, C_A, C_B = actual conc. of A, B & AB,
γ_A, γ_B & γ_{AB} = corresponding activity coefficients

Eq^n (3) may be written as,

$$C_{AB} = K^* \frac{C_A C_B \gamma_A \gamma_B}{\gamma_{AB}} \quad \text{——— (4)}$$

Now the rate of reaction $= k_3 C_{AB}$ ——— (5)
where k_3 is a rate const for reaction,

$$[AB] \xrightarrow{k_3} \text{products}$$

Combining eq^{ns} (4) & (5), we get

$$\text{Rate of reaction} = k_3 K^* \frac{C_A C_B \gamma_A \gamma_B}{\gamma_{AB}} = k_0 \frac{C_A C_B \gamma_A \gamma_B}{\gamma_{AB}} \quad \text{——— (6)}$$

where, $k_0 = k_3 K^*$

The experimental rate of reaction is given by,

$$\text{Rate of reaction} = k C_A C_B \quad \text{——— (7)}$$

Comparing eq^{ns} (7) & (6), we get

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma_{AB}} \quad \text{——— (8)}$$

where k_0 is rate constant at infinite dilution when $\gamma_A = \gamma_B = \gamma_{AB} = 1$. It means that any added substance which alters values of activity coefficients of reactants & activated complex will change experimental rate of reaction.

The logarithm of eq^n (8) is,

$$\log k = \log k_0 + \log \frac{\gamma_A \gamma_B}{\gamma_{AB}} \quad \text{——— (9)}$$

According to Debye-Huckel theory, activity coefficients γ of an ion of charge z is related to ionic strength μ of dilute solution by expression

$$-\log \gamma = 0.509 z^2 \sqrt{(\mu)} \text{ at } 25^\circ C \quad \text{——— (10)}$$

For A, B & AB, eq^n (10) can be written as,

$$-\log \gamma_A = 0.509 z_A^2 \sqrt{(\mu)} \quad \text{——— (11)}$$
$$-\log \gamma_B = 0.509 z_B^2 \sqrt{(\mu)} \quad \text{——— (12)}$$
$$-\log \gamma_{AB} = 0.509 (z_A + z_B)^2 \sqrt{(\mu)} \quad \text{——— (13)}$$

Substituting eq^{ns} (11), (12), (13) in eq^n (9), we get

$$\log k = \log k_0 - \left[0.509 z_A^2 + 0.509 z_B^2 - 0.509 (z_A + z_B)^2\right] \sqrt{(\mu)}$$

$\log k = \log k_0 + 2 \times 0.509\, Z_A Z_B \sqrt{(\mu)}$

$\log k = \log k_0 + 1.018\, Z_A Z_B \sqrt{(\mu)}$

$\log k/k_0 = 1.018\, Z_A Z_B \sqrt{\mu}$

Eq (5) is known as Brønsted–Bjerrum eq? As the variation of specific rate k with ionic strength depends on charges of reacting species, three special cases may arise:

Case I:- First case arises when $Z_A Z_B = 0$. It mean that one of reactant is non-electrolyte. The rate Const would be independent of ionic strength $\sqrt{\mu}$.

e.g.:-

(i) $[Cr(NH_2CONH_2)_6]^{3+} + 6H_2O \rightarrow [Cr(H_2O)_6]^{3+} + 6NH_2CONH_2$

(ii) $CH_2ICOOH + CNS^- \rightarrow CH_2(CNS)COOH + I^-$

In both cases, one reactant is non-electrolyte. Hence $Z_A Z_B = 0$

Case II:- Second case arises when $Z_A Z_B$ is positive. It means that Z_A & Z_B are of same sign. The rate Constant for such reaction would increase with $\sqrt{(\mu)}$.

e.g.:-

II(a) :- $S_2O_8^{2-} + I^- \rightarrow$ product

Reaction betⁿ persulphate & iodide ions, R.D.S is given above. The value for $Z_A Z_B$ is +2 although both ions have negative valency.

II(b) :- Reaction betⁿ mercury ions with Cobalto-ammonium bromide ions, value of $Z_A Z_B$ is 2×2 i.e 4. Hence salt effect is positive.

$[Co(NH_3)_5Br]^{2+} + Hg^{2+} \rightarrow$ products

Case III:- Third case arises when $Z_A Z_B = -1$. It means that Z_A & Z_B are of opposite sign. For such reactions rate Const would decrease with $\sqrt{(\mu)}$.

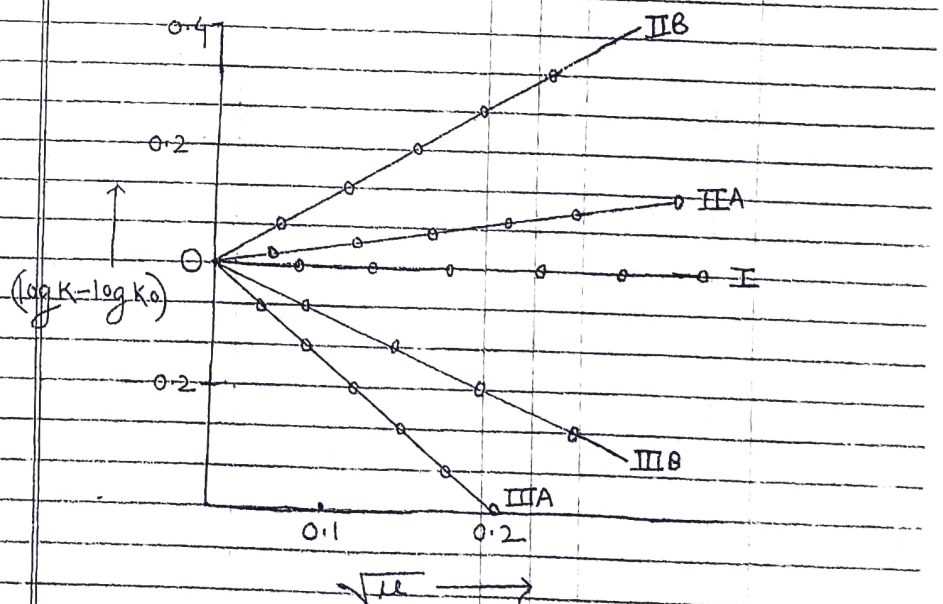
e.g.:-

III(a) $H_2O_2 + H^{\oplus} + Br^{\ominus} \rightarrow$ products

For this reaction $Z_A Z_B = -1$

III(b) Reaction between Cobalto-ammonium bromide & hydroxyl ion, value of $Z_A Z_B = -2$. Hence salt effect is negative.

$[Co(NH_3)_5Br]^{2+} + OH^{\ominus} \rightarrow [Co(NH_3)_5OH]^{2+} + Br^{\ominus}$



Secondary salt effect:-

As secondary salt effect is involved in catalytic reactions. It can be studied by changing actual conc. of catalytically active ions. If these are produced by a strong acid or a strong base, secondary salt effect is negligible. It becomes important when ions are produced by dissociation of weak electrolyte. Consider catalytic effect of hydrogen ions which are produced by a mixture of a weak acid & its salt at a definite conc. the eqⁿ constant K_A for reaction

$$HA + H_2O \rightarrow H_3O^{\oplus} + A^{\ominus}$$

is given by

$$K_A = \frac{(a_{H_3O^{\oplus}})(a_{A^-})}{a_{HA}}$$

$$\therefore K_A = \frac{C_{H_3O^{\oplus}} \cdot C_{A^{\ominus}}}{C_{HA}} \times \frac{\gamma_{H_3O^{\oplus}} \cdot \gamma_{A^{\ominus}}}{\gamma_{HA}} \quad (a = c\gamma) \quad \text{---} (1)$$

As we know that pH of a mixture of a weak acid & its salt is of constant composition. It follows that

$$K_A \frac{C_{HA}}{C_A} = \text{Const.} = K$$

Therefore, eqⁿ (1) can be put as

$$C_{H_3O^{\oplus}} = K \frac{\gamma_{HA}}{\gamma_{H_3O^{\oplus}} \cdot \gamma_{A^{\ominus}}} \quad \text{---} (2)$$

As activity term varies with ionic strength of medium, it follows that hydrogen ion conc. & its catalytic activity will also vary with ionic strength of medium. This is

secondary salt effect.

As velocity of reaction involving hydrogen ions as catalyst is proportional to the conc of ions, it can be written as,

$$K = K_0 \frac{\gamma_{HA}}{\gamma_{A^{\ominus}} \gamma_{H_3O^{\oplus}}}$$

where K_0 = constant & its value becomes equal to experimental rate constant provided values of the $\gamma_{HA}, \gamma_{A^{\ominus}}$ & $\gamma_{H_3O^{\oplus}}$ are unity. By using Debye-Huckel limiting law, eqⁿ (2) can be written as,

$$\log K = \log K_0 + 1.02\sqrt{(\mu)}$$

Thus, rate constant will increase with increasing conc. of electrolyte.

* Catalysis :-

The word catalysis was 1st used by Berzelius (1836)

Def^n :-

Any substance which alters rate of chemical rea^n & remains unaffected during that reaction is known as Catalyst & the phenomenon is known as 'Catalysis'

Classification of Catalysis :-

(a) Homogeneous Catalytic reaction :-

when reactants & Catalyst are present in one phase

e.g. :-

(I) gaseous phase :- lead chamber process

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO_{(g)}} 2SO_{3(g)}$$

Here reactants (SO_2 & O_2) & Catalyst (NO) are in the gaseous phase.

(II) Liquid phase :- Hydrolysis of ester in presence of dil. HCl

$$CH_3COOC_2H_5 + H_2O \xrightarrow{HCl} CH_3COOH + C_2H_5OH$$

(b) Heterogeneous Catalysis :-

when reactants & Catalyst are present in diff. phases

e.g. :-

(I) Liquid phase :- Decomposition of H_2O_2

$$2H_2O_2 \xrightarrow[Au]{Pt \text{ or }} 2H_2O + O_2$$

Here we use Colloidal Sol^n of gold or platinum

(II) Gaseous phase :- Manufacture of ammonia

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe/Mo_{(s)}} 2NH_{3(g)}$$

* Mathematical expression of autocatalytic reactions :-

Autocatalysis :-

The process in which one of the products of rea^n acts as catalyst is known as autocatalysis.

e.g. :-

Hydrolysis of an ester is autocatalysed by acid which is a product of the reaction.

$$R-\overset{O}{\overset{\|}{C}}-OR' + H_2O \rightleftharpoons R'COOH + R'OH$$

Expression :-

Consider hydrolysis of methyl acetate in which product formed (acetic acid) catalyses reaction.

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

a — b — initial

(a−x) — (b+x) — After time t

Suppose a & b are initial amount of ester & acetic acid respectively. Suppose x, extent of reaction, according to law of mass action, is given by,

$$\frac{dx}{dt} = k(a-x)(b+x)$$

or

$$\frac{dx}{(a-x)(b+x)} = k\,dt$$

On Seperating variables, we get

$$\frac{1}{a+b}\left[\frac{1}{a-x}+\frac{1}{b+x}\right]dx = K\,dt$$

On integration, we get

$$\frac{1}{a+b}\left[\ln(b+x)-\ln(a-x)\right] = Kt + C \quad \text{——} (1)$$

Evaluate 'c' by putting $x=0$, $t=0$ then

$$c = \frac{1}{a+b}\ln b/a \quad \text{——} (2)$$

On substituting eq^n (2) in eq^n (1), we get

$$\frac{1}{a+b}\left[\ln(b+x)-\ln(a-x)\right] = Kt + \frac{1}{a+b}\ln b/a$$

or

$$K = \frac{1}{(a+b)t}\ln\frac{a(b+x)}{b(a-x)}$$

This has been experimentally verified.

(*) Enzyme Catalysis:-

Enzymes are complex organic compounds which are produced by living plants & animals. They disperse in water forming colloidal solutions & are very specific catalysts. As enzymes are having dimensions in colloidal range (1000–10000 Å) & their kinetic behaviour is similar to that of heterogeneous process, enzyme catalysis has been referred to as "Microheterogeneous catalysis." Each enzyme can catalyze specific reaction.

e.g:-

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

maltose

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

(*) Mechanism & Kinetics of Enzyme-Catalyzed Reactions:-

Biochemists L. Michaelis & M. Menten proposed, in 1913, a mechanism for kinetics of enzyme-catalyzed reactions which envisages following steps:

(i) Step (1):-

Enzyme combines with reactant (substrate) to form an enzyme substrate complex which remains in eq^m with enzyme & substrate

$$E + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES \quad \text{——} (1)$$

where E = Enzyme, S = Substrate & Es = enzyme substrate complex.

(a) Step ②:

Enzyme substrate Complex (ES) can decompose to form products with simultaneous regeneration of the enzyme.

$$ES \xrightarrow{K_2} E + P \quad \text{——— (2)}$$

where P = product. In overall reaction, $S \longrightarrow P$ the enzyme is consumed in step ① & regenerated in step ②.

According to rate determining step, rate of reaction is given by,

$$r = -\frac{d[S]}{dt} = +\frac{d[P]}{dt} = K_2[ES] \quad \text{——— (3)}$$

using steady-state approximation for ES, we have

$$\frac{d[ES]}{dt} = K_1[E][S] - K_{-1}[ES] - K_2[ES] = 0 \quad \text{——— (4)}$$

Now [E] can't be measured experimentally. The eq^n between free & bound enzyme is given by enzyme conservation eq^n viz,

$$[E]_0 = [E] + [ES] \quad \text{——— (5)}$$

where $[E]_0$ = Total enzyme conc. (which can be measured)
[E] = free enzyme conc.,
[ES] = bound (reacted) enzyme conc.,

$$[E] = [E]_0 - [ES] \quad \text{——— (6)}$$

On substituting for [E] in eq^n ④, we get

$$\frac{d[ES]}{dt} = K_1\{[E]_0 - [ES]\}[S] - K_{-1}[ES] - K_2[ES] = 0 \quad \text{-- (7)}$$

$$K_1[E]_0[S] = \{K_{-1} + K_2 + K_1[S]\}[ES] \quad \text{——— (8)}$$

$$[ES] = \frac{K_1[E]_0[S]}{K_{-1} + K_2 + K_1[S]} \quad \text{——— (9)}$$

On substituting for [ES] in eq^n ③ we get

$$r = \frac{K_1 K_2 [E]_0 [S]}{K_{-1} + K_2 + K_1[S]} \quad \text{——— (10)}$$

On dividing numerator & denominator by K_1, we get

$$r = \frac{K_2[E]_0[S]}{(K_{-1} + K_2)/K_1 + [S]} = \frac{K_2[E]_0[S]}{K_m + [S]} \quad \text{——— (11)}$$

where new constant 'K_m' called Michaelis constant,

$$K_m = (K_{-1} + K_2)/K_1$$

If it is assumed that all the enzyme has reacted with substrate at high conc., the reaction will be going at maximum rate. No free enzyme will remain so that $[E]_0 = [ES]$. Hence from eq^n ③ we get

$$r_{max} = V_{max} = K_2[E]_0 \quad \text{——— (12)}$$

where V_{max} = maximum rate, using notation of enzymology.

The michaelis menten eq^n can be written as,

$$r = V_{max}[S]/(K_m + [S]) \quad \text{——— (13)}$$

Two cases may arise:

(a) If $K_m \gg [S]$, $[S]$ can be neglected in denominator of eq^n (13) giving

$$r = V_{max}[S] / K_m = K'[S] \quad \text{(first order reaction)} \quad \text{——— (14)}$$

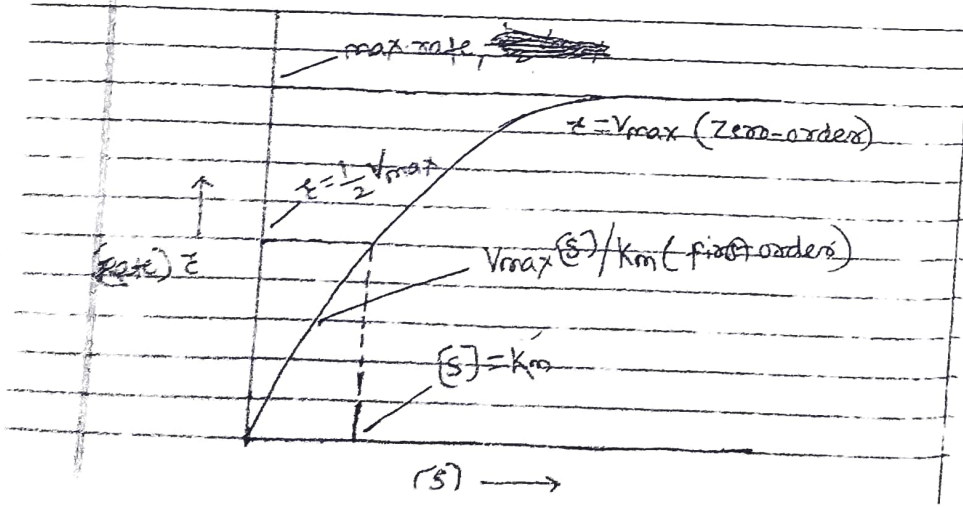
(b) If $[S] \gg K_m$, K_m can be neglected in denominator, giving

$$r = V_{max} = \text{constant} \quad \text{(zero order reaction)} \quad \text{——— (15)}$$

These two cases may be shown diagrammatically in fig. below:

Again, if $K_m = [S]$, $r = \frac{1}{2} V_{max}$

Hence, Michaelis constant may be defined as equal to that conc. of S at which rate of formation of product becomes half maximum rate obtained at high conc. of S.



The const. k_2 in eq^n (12) is termed as turnover number of the enzyme. The turnover number may be defined as no. of molecules converted in unit time by one molecule of enzyme. Typical values of k_2 are 1 to 1,000 per second though they may be as large as 10^5 to 10^6 per second.

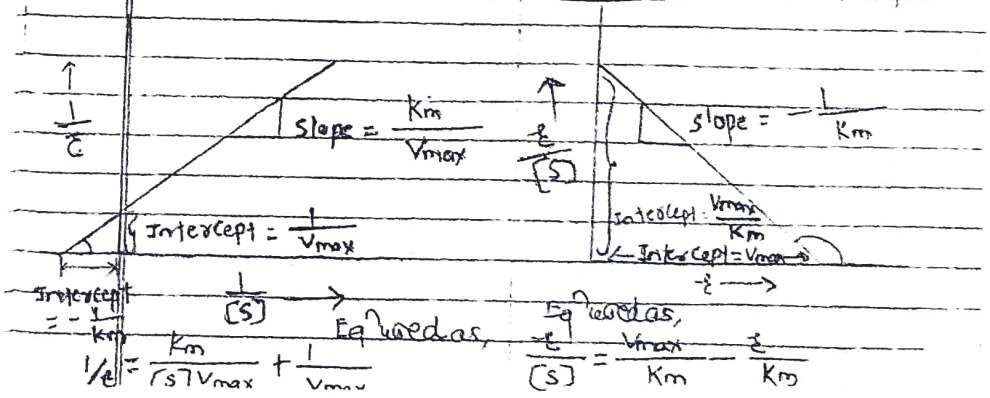
Q.1 Why reaction rate of enzyme catalysed reaⁿ gets changed from 1st order to zero order as [S] gets increased?

→ Enzyme molecule is having one or more 'active sites' at which substrate must be bound in order that catalytic action may take place. At low [S], most of these active sites remain unoccupied at any time. As [S] gets increased, no. of active sites which get occupied increases. Hence reaction rate also gets increased. But at very high (conc) [S], all active sites get occupied at any time. So that further increase in substrate conc. will not further increase in formation of enzyme-substrate complex.

It rather becomes difficult to determine V_{max} (hence K_m) directly from plot of r Vs [S]. However it becomes possible to rearrange eq^n (13) so as to permit some alternative plots for easy determination of V_{max}

Two of the best known methods as follows:

(1) Lineweaver-Burk method (2) Eddie-Hofstee method



(*) Acid-Base Catalysis:-

A very considerable number of homogeneous catalytic reactions are known which are catalysed by acids & bases. These reactions are known as acid-base catalysis.

(A) Types of acid-base catalysis

(I) Specific hydrogen ion catalysis:-

→ These reactions which are catalysed by H^+ ion only

e.g.:- Inversion of cane sugar catalysed by H^+ ions only.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^\oplus} C_6H_{12}O_6 + C_6H_{12}O_6$$

Rate of this reaction is found to be proportional to the conc. of H^+ ions in sol'n of substrate (cane sugar)

$$\frac{dx}{dt} = K[H^+][\text{Cane Sugar}]$$

(II) Specific hydroxyl ion catalysis:-

→ These are the reactions which are catalysed by $OH^\ominus$ ions only.

e.g.:- Conversion of acetone into diacetone is catalysed by $OH^\ominus$ ions only.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{OH^\ominus} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

(III) Hydrogen & hydroxyl ion catalysis:-

→ These are the reactions in which $H^\oplus$ & $OH^\ominus$ ions simultaneously acts as catalysts.

e.g.:- Hydrolysis of ester is catalysed by H^+ as well as by $OH^\ominus$ ions.

$$CH_3-\overset{O}{\overset{\|}{C}}-O-C_2H_5 + H_2O \xrightarrow[OH^\ominus]{H^\oplus \text{ or }} CH_3COOH + C_2H_5OH$$

(*) General acid-base catalysis:-

Taylor, Lowry & others showed that reactions catalysed by $H^\oplus$ ions or $OH^\ominus$ ions seemed to be influenced by substances, undissociated acid or base, cations of weak bases like NH_4^+ ions or anions of weak acids like $CH_3COO^\ominus$ ions. In short, all substances which have a tendency to loose or to gain a proton can function as catalysts.

(A) Types of general acid-base catalysis:-

(I) General acid catalysis:-

→ These are the reactions which are catalysed by hydrogen ions, undissociated acids & cations of weak bases.

→ In short, reactions which are catalysed by any subs. which has a tendency to loose a proton

e.g.:- Iodination of acetone which is catalysed by monochloroacetic acid & its salt.

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$$

(II) General base catalysis:-

→ These are the reactions which are catalysed by hydroxyl ions, undissociated bases, anions of weak acids only.

→ In short, reactions which are catalysed by a substance which has tendency to gain a proton.

e.g.:- Decomposition of nitramide in solution catalysed by hydroxyl ions, acetate ions & H_2O.

$$NH_2NO_2 \longrightarrow N_2O + H_2O$$

(III) General acid-base catalysis:-

These are the reactions which are catalysed by hydrogen ions, hydroxyl ions, weak acids, weak bases, cations of weak acids & bases.

e.g.:- Mutarotation of glucose is an example of this type.

Mechanism of acid-base catalysis

(a) Catalysed transformation of α-glucose in β glucose may be written as

$$H^+(I) + GH \rightarrow (HGH)^+ \xrightarrow{\text{Rearrangement}} HG + H^+(II)$$

where H^+ (I) is a proton supplied by acid catalyst, GH is α-glucose, HGH^+ is intermediate complex which is unstable, HG is β-glucose & H^+ (II) is removed by base catalyst.

(b) Decomposition of nitramide catalysed by $OH^\ominus$ ions

$$NH_2NO_2 + OH^\ominus \longrightarrow H_2O + NHNO_2^\ominus \text{ unstable} \downarrow N_2O + OH^\ominus$$

(*) Kinetics of acid-base catalysis:-

Acid base catalysed reactions take place by transfer of proton from an acid to a substrate molecule (S) or from substrate molecule to base. Hence reaction bet^n an acid HA & substrate (S) may be put as follows:

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

$$SH^+ + H_2O \xrightarrow{K_2} \text{Product}$$

Immediately after start of reaction, SH^+ will attain a steady state conc. Hence

$$\frac{d[SH^+]}{dt} = K_1[S][HA] - K_{-1}[SH^+][A^-] - K_2[SH^+] = 0$$

$$K_1[S][HA] = K_{-1}[SH^+][A^-] + K_2[SH^+]$$

$$[SH^+] = \frac{K_1[S][HA]}{K_{-1}[A^-] + K_2} \quad \text{---(1)}$$

It is of interest to take into consideration the limiting cases.

Case I:- If $K_2 >> K_{-1}[A^-]$, then

$$[SH^+] = \frac{K_1}{K_2}[S][HA]$$

Under these conditions, reaction is subject to general acid catalysis. The overall rate of reaction would be equal to rate of formation of product, then

$$\text{Reaction rate} = K_2[SH^+]$$

or $$\text{reaction rate} = K_1[S][HA]$$

It means that rate of reaction is proportional to conc. of the substrate & acid

Case II:- If $K_2 << K_{-1}[A^-]$, then eq (1) becomes

$$[SH^+] = \frac{K_1[S][HA]}{K_{-1}[A^-]}$$

Now Consider dissociation of HA

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

which is characterized by

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

Overall rate of reaction is given by,

$$\text{Rate} = K_2 \frac{K_1[S][HA]}{K_{-1}[A^-]}$$

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

$$\therefore \text{Rate} = \left(\frac{K_1 \cdot K_2}{K_{-1}}\right)\frac{[H^+]}{K_a}[S]$$

or $$\text{Rate} = K'[H^+][S]$$

Hence reaction rate is proportional to $[H^+]$ even in presence of HA & A^-.

(*) Heterogeneous Catalysis :-

(a) Adsorption of gas on a surface :-

A reaction taking place on a surface is supposed to consist of four consecutive steps.

(i) Diffusion of gases to surface
(ii) Adsorption of gases on surface
(iii) Reaction on the surface
(iv) Desorption & diffusion of product from surface to bulk.

Steps (i), (ii) & (iv) don't take part in overall rate determining process. Thus, it is step (iii) which determines overall rate & it is the conc. of the molecules on surface of which reaction rate would depend. In quantitative treatment of heterogeneous catalysis, Langmuir concept of unimolecular film on surface is fully accepted.

Postulates:-

(1) Adsorbed gas is unimolecular in thickness.
(2) Rate of condensation & rate of adsorption of the molecules will be equal.

Suppose,

θ = fraction of surface area covered by gas,
$(1-\theta)$ = fraction of bare surface available for adsorption,
P = Pressure of the gas

Thus,

Rate of adsorption $= K_1(1-\theta)p$ ——— (1)

Rate of evaporation $= K_2\theta$ ——— (2)

where K_1, K_2 = constants for given system. At eqm, these two rates are equal. Then

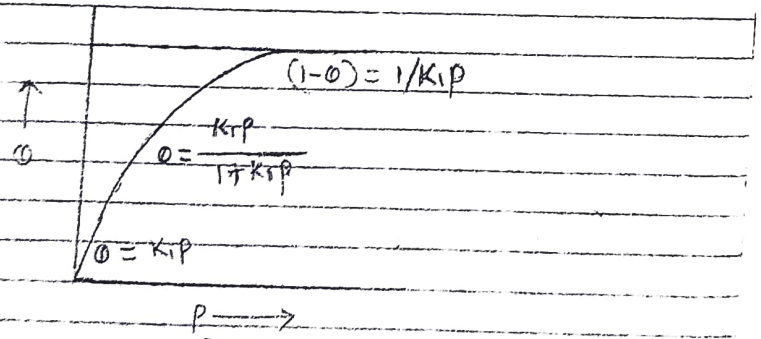
$$K_1(1-\theta)p = K_2\theta$$

or $$\theta = \frac{K_1 p}{K_2 + K_1 p}$$ (∴ Dividing numerator & denominator by K_2)

$$= \frac{bp}{1+bp} \quad \text{——— (3)}$$

where $b = K_1/K_2$ & termed as langmuir adsorption isotherm

Graphical representation :-



Limiting cases of eq^n (3)

(a) When adsorption is slight either due to low p or due to low adsorption capacity of surface, b is small & bp may be neglected compared to unity. Hence eq^n (3) gets reduced

$$\theta = bp$$

i.e extent of adsorption is directly proportional to the pressure & reaction will behave as one of the 1st order.

(b) When adsorption is strong, surface gets covered by a monomolecular thick layer of gas i.e when b or p or both are large, then $bp \gg 1$ & eq^n (3) is transfered into

$$\theta = \frac{bp}{bp} = 1$$

Under these conditions, reaction rate is constant or independent of pressure & rea^n is considered to be kinetically zero order.

(c) Another deduction can be made from eq^n (3)

$$1-\theta = 1 - \left(\frac{bp}{1+bp}\right)$$

$$= \frac{1}{1+bp}$$

If adsorption is strong, $bp \gg 1$, then

$$1-\theta = \frac{1}{bp}$$

i.e fraction of surface still available for adsorption would be inversely proportional to pressure of gas.

Kinetics of Heterogeneous reactions :-

3) Bimolecular Surface Reactions :-

If A is reactant molecule & S the surface atom of solid, then

$$A + S \xrightarrow{K_1} AS \quad \text{— adsorption}$$

$$AS \xrightarrow{K_{-1}} A + S \quad \text{— Desorption}$$

$$AS \xrightarrow{K_2} \text{Products} \quad \text{— Decomposition}$$

where AS – adsorbed molecule.

Suppose θ be the fraction of surface covered by A at any instant t & pressure P. According to the Langmuir–Hinshelwood reaction rate would be,

$$\text{Rate}(r) = K_2\theta \quad \text{——— (1)}$$

Applying Steady state approximation for [AS],

$$\frac{d[AS]}{dt} = K_1[A][S] - K_{-1}[AS] - K_2[AS] = 0$$

$$[AS] = \frac{K_1[A][S]}{K_{-1} + K_2} \quad \text{——— (2)}$$

Now let Conc. of vacant sites, $[S] = C_S(1-\theta)$ & Conc. of occupied sites, $[AS] = C_S\theta$

where, C_S – Total Conc. of active sites on surface. On substituting values of [S], [AS] in eq^n (2) we get,

$$C_S\theta = \frac{K_1[A]C_S(1-\theta)}{K_{-1} + K_2}$$

$$\theta = \frac{K_1[A](1-\theta)}{K_{-1} + K_2}$$

$$\frac{1}{\theta} = \frac{K_{-1} + K_2}{K_1[A](1-\theta)}$$

$$\frac{1-\theta}{\theta} = \frac{K_{-1} + K_2}{K_1[A]}$$

$$\text{or } \frac{1}{\theta} - 1 = \frac{K_{-1} + K_2}{K_1[A]}$$

$$\frac{1}{\theta} = \frac{K_{-1} + K_2}{K_1[A]} + 1$$

$$\therefore \frac{1}{\theta} = \frac{K_{-1} + K_2 + K_1[A]}{K_1[A]}$$

$$\therefore \theta = \frac{K_1[A]}{K_1[A] + K_{-1} + K_2} \quad \text{——— (3)}$$

Substitute value of θ in eq^n (1), we get

$$r = \frac{K_2K_1[A]}{K_1[A] + K_{-1} + K_2} \quad \text{——— (4)}$$

Eq^n (4) may be written in the form

$$\frac{1}{r} = \frac{1}{K_2} + \frac{K_{-1} + K_2}{K_2K_1[A]} \quad \text{——— (5)}$$

$$\left(\therefore \frac{1}{r} = \frac{K_1[A] + K_{-1} + K_2}{K_2 \cdot K_1[A]} = \frac{K_{-1}[A]}{K_1 \cdot K_2[A]} + \frac{K_{-1} + K_2}{K_2 \cdot K_1[A]}\right)$$