

# ★ Chemical Kinetics Phy

Ques-1 Discuss the factors affecting the rate of reaction in details.

Ans - There are six factors affecting the rate of reaction.

- |     |                            |   |   |
|-----|----------------------------|---|---|
| (1) | Nature of reactants        | ↑ | ↑ |
| (2) | Temperature                | ↑ | ↑ |
| (3) | Concentration of reactants | ↑ | ↑ |
| (4) | State of subdivision       | ↑ | ↑ |
| (5) | Catalyst                   | ↑ | ↑ |
| (6) | Radiation                  | ↑ | ↑ |

(1) Nature of reactant : It is a fact that the rate of a chemical rxn depends upon the reactivity or the nature of the reacting species. If there is less reagent the rate of reaction increases.

(2) Effect of temperature :-

The rate of chemical reactions increase with increase in temperature.

$$\log k = a - \frac{b}{T}$$

(3) Concentration of reactants :-

→ The rate of rxn depends upon the concentration of reactants.

→ The rate of reaction increases with increase in concentration of reactants.

(4) Effect of the catalyst :-

- The rate of certain chemical reactions increase in the presence of suitable catalyst.

(5) Reaction medium :-

→ Reaction in gaseous or liquid medium may occur at different rate.

(6) Surface area

→ Larger surface areas of solid reactants and catalyst tend to enhance the rate of reaction.

(7) Effect of heat energy or radiation :-

→ The rate of certain chemical rxns may be enhanced by heat or radiant energy.

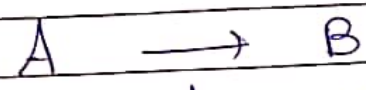


Ques (2)

Write a note on units of rate constant.

Ans

The units of rate constant for a given reaction can be determined by starting with the appropriate rate equation for the reaction.



Conc. are expressed in molar units and time in sec.

(a) A zero order reaction :-

$$\text{Rate, } r = -\frac{d[A]}{dt} = k_0$$

$$\text{units of } k_0 = \frac{\text{unit of } [A]}{\text{units of } t}$$

$$= \frac{\text{mol dm}^{-3}}{\text{s}}$$

$$= \boxed{\text{mol l}^{-1} \text{s}^{-1}}$$

(b) first order reaction :-

$$\text{Rate, } r = -\frac{d[A]}{dt} = k_1[A] = \frac{-d[A]}{dt \times [A]}$$

$$= \frac{\text{mol. lit}^{-1}}{\text{s. mol lit}^{-1}}$$

$$= \boxed{\text{s}^{-1}}$$

(c) Second order reaction :-

$$\text{Rate, } r = -\frac{d[A]}{dt} = k_2[A]^2 \quad \Rightarrow \quad -\frac{d[A]}{dt \times [A]^2}$$

$$\text{unit of } k_2 = \frac{\text{mol lit}^{-1}}{\text{s} \cdot (\text{mol lit}^{-1})^2}$$

$$= \boxed{\text{lit mol}^{-1} \text{s}^{-1}}$$

(d) Third order reaction :-

$$\text{Rate, } r = -\frac{d[A]}{dt} = k_3[A]^3 \quad \Rightarrow \quad -\frac{d[A]}{dt \times [A]^3}$$

$$\text{units of } k_3 = \frac{\text{mol lit}^{-1}}{\text{s} \times (\text{mol lit}^{-1})^3}$$

$$= \boxed{\text{lit}^2 \text{mol}^{-2} \text{s}^{-1}}$$

(e) A half order reaction :-

$$\text{Rate, } r = -\frac{d[A]}{dt} = k_{1/2}[A]^{1/2} \quad \Rightarrow \quad -\frac{d[A]}{dt \times [A]^{1/2}}$$

$$\text{units of } k_{1/2} = \frac{\text{mol lit}^{-1}}{\text{s} \times (\text{mol lit}^{-1})^{1/2}}$$

$$= \boxed{\text{mol}^{1/2} \text{lit}^{-1/2} \text{s}^{-1}}$$

⇒ In general, for an  $n^{\text{th}}$  order reaction,  
the units of  $k_n$  are  $\boxed{(\text{lit})^{n-1} \text{mol}^{1-n} \text{s}^{-1}}$



Ques 3 Derive the integrated form of rate equation for first order / second order reaction / zero order reaction.

Ans :- Integration of rate equation for first order reaction :-

→ The differential rate expression for the 1<sup>st</sup> order reaction,



$$\text{rate} = -\frac{d[A]}{dt} = k_1[A] \quad \text{--- (1)}$$

$$-dCA = k_1 CA \quad \text{--- (2)}$$

→ Bringing concentration terms on one side and the time on the other side, we get,

$$-\frac{dCA}{CA} = k_1 dt \quad \text{--- (2)}$$

→ Let the initial concentration at initial time  $t=0$ , be  $C_0$  subsequently, at any other time,  $t$ , the concentration will be  $C$ .

means  $t = 0$   
 $C = C_0$  (initial)

at,  $t = t$   
 $C = C$  (final at time  $t$ )

$$\int_{C_0}^C \frac{-dC_A}{C_A} = k_1 \int_0^t dt$$

$$[-\ln C_A]_{C_0}^C = k_1 [t]_0^t$$

$$-\ln \left( \frac{C}{C_0} \right) = k_1 [t - 0]$$

$$-\ln \left( \frac{C}{C_0} \right) = k_1 t$$

$$\ln \left( \frac{C}{C_0} \right) = -k_1 t$$

$$\frac{C}{C_0} = e^{-k_1 t}$$

$$C = C_0 e^{-k_1 t}$$

$$k_1 = \frac{1}{t} \ln \frac{C_0}{C}$$

(8)

→ If initial concentration of the reactant is  $a$  and  $x$  moles of it react in time  $t$ , then conc. of the reactant left behind at time  $t$  will be  $a-x$ .

$$k_1 = \frac{1}{t} \ln \frac{a}{a-x}$$

(9)

→ for 1<sup>st</sup> order reaction, the concentration of the reactant decreases and that of the product increases with time.



(ii) Integration of Rate expressions for second order reactions

Ans Case I, when the reactants are different.



where the initial conc. of A is  $a \text{ mol lit}^{-1}$   
B is  $b \text{ mol lit}^{-1}$ .

After time  $t$   $A = x \text{ mol lit}^{-1}$ .

$$A = (a - x)$$

$$B = (b - x)$$

Case - I,  $a > b \rightarrow$

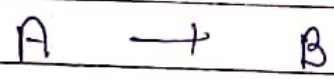
$$k_2 = \frac{1}{(a-b)t} \ln \frac{b(a-x)}{a(b-x)}$$

Case - II,  $b > a$ ,

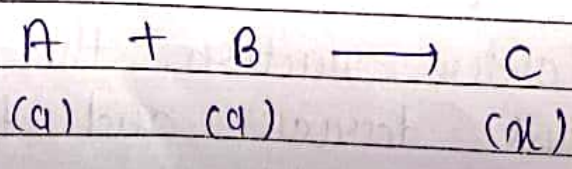
$$k_2 = \frac{1}{(b-a)t} \ln \frac{a(b-x)}{b(a-x)}$$

$\Rightarrow$  Case - II, when both the reactants are the same.

$\rightarrow$  Two molecules of the same reactant are involved in the chemical reaction.



$$\text{rate} = k_2 [A]^2$$



$$\begin{aligned} \text{rate} &= k_2 [A][B] \\ &= k_2 [a][a] \\ &= k_2 [a]^2 \end{aligned}$$

$$\frac{dx}{dt} = k_2 (a-x)^2 \quad \text{--- (1)}$$

where  $a$  = initial concentration of A,  
 $x$  = conc.<sup>n</sup> of the product formed after  
 time  $t$

$(a-x)$  = conc.<sup>n</sup> of A remaining at time  $t$

→ Separating the variables and integrating,

$$\int \frac{dx}{(a-x)^2} = k_2 \int dt$$

$$\int \frac{1}{(a-x)^2} dx = k_2 t + C$$

$$\int (a-x)^{-2} dx = k_2 t + C$$

$$\left( \frac{(a-x)^{-2+1}}{-2+1} \right) (-1) = k_2 t + C$$

$$(a-x)^{-1} = k_2 t + C$$

$$\frac{1}{(a-x)} = k_2 t + C$$

$$t = 0, x = 0, \text{ so, } C = 1/a$$

$$\frac{1}{(a-x)} = k_2 t + \frac{1}{a}$$



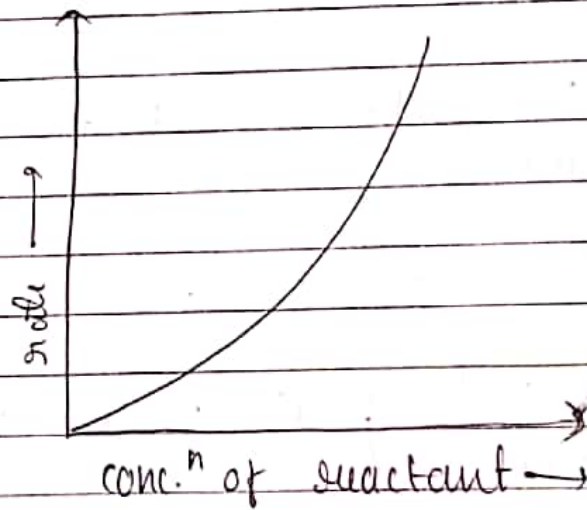
$$\frac{1}{(a-x)} - \frac{1}{a} = k_2 t$$

$$k_2 = \frac{a - (a-x)}{t \cdot a \cdot (a-x)}$$

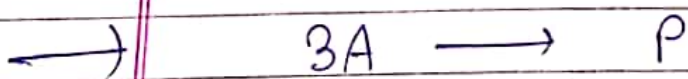
$$k_2 = \frac{1}{t} \left[ \frac{x}{a(a-x)} \right] \quad \text{--- (2)}$$

which is the required integrated expression for the rate constant of 2<sup>nd</sup> order

The plot of  $\frac{x}{a(a-x)}$  versus reactant conc.<sup>n</sup> is



(III) Integration of rate eq<sup>n</sup> for 3<sup>rd</sup> order reaction.



Let  $a$  be the initial conc. of  $A$  and  $x$  the amount of  $A$  that has reacted at time  $t$  so that the amount of  $A$  remaining at time  $t$  is  $a-x$ .

$$\frac{dx}{dt} = k_3 (a-x)^3 \quad \text{--- (1)}$$

$$\int dx$$

→ Separating the variable and integrating.

$$\int \frac{dx}{(a-x)^3} = k_3 \int dt$$

$$\int \frac{1}{(a-x)^3} dx = k_3 t + C$$

$$\int (a-x)^{-3} dx = k_3 t + C$$

$$\frac{(a-x)^{-3+1}}{-3+1} (-1) = k_3 t + C$$

$$\frac{1}{2(a-x)^2} = k_3 t + C$$

→ at  $t=0$ ,  $x=0$ , then  $C = \frac{1}{2a^2}$

$$\frac{1}{2(a-x)^2} = k_3 t + \frac{1}{2a^2}$$

$$k_3 t = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

$$k_3 t = \frac{1}{2t} \left[ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$

$$k_3 = \frac{1}{2t} \left[ \frac{a^2 - (a-x)^2}{a^2(a-x)^2} \right]$$



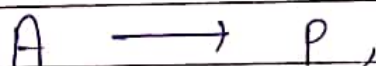
$$K_3 = \frac{1}{2t} \left[ \frac{a^2 - a^2 + 2ax - x^2}{a^2(a-x)^2} \right]$$

$$K_3 = \frac{1}{2t} \left[ \frac{2ax - x^2}{a^2(a-x)^2} \right]$$

$$K_3 = \frac{1}{2t} \left[ \frac{x(2a-x)}{a^2(a-x)^2} \right]$$

(iv) Zero order reaction :-

Ans Reaction rate is not affected by changes in conc<sup>n</sup> of one or more reactants. Then it is known as zero order reaction.



$$r = -\frac{d[A]}{dt} = k_0$$

$$-d[A] = k_0 dt$$

→  $\int_{[A]_0}^{[A]}$  at,  $t=0$ , the conc.<sup>n</sup> is  $[A]_0$ ,  
conc. at  $t=t$ , is  $[A]$

$$-\int_{[A]_0}^{[A]} d[A] = k_0 \int_0^t dt$$

$$[A]_0 - [A] = k_0 t$$

$$k_0 = \frac{1}{t} ([A]_0 - [A])$$

(IV) Half life time :-

$$\rightarrow \text{for } 1^{\text{st}} \text{ O.R.} = t_{1/2} = \frac{0.693}{k_1}$$

$$2^{\text{nd}} \text{ OR} = t_{1/2} = \frac{1}{k_2 a}$$

$$3^{\text{rd}} \text{ OR} = t_{1/2} = \frac{3}{2k_3 a^2}$$

$$\text{zero OR} = t_{1/2} = \frac{[A]_0}{2k_0}$$

Ques 4 What is half life time of reaction?  
Derive its equation for zero / 1<sup>st</sup> / 2<sup>nd</sup> order reaction.

Ans For zero order reaction :-

$$x = a/2, \quad t = t$$

$\rightarrow$  In order to characterize the rate at which a chemical reaction may proceed. It is customary to introduce a convenient parameter called the half life time of the reaction.

$\rightarrow$  The time required for the reaction to be half completed and is called half life time.



→  $t$  is denoted by  $t_{1/2}$ .

⇒  $t_{1/2}$  for zero order reaction :-

$$k_0 t = a x = a/2, \quad t = t_{1/2}$$

$$k_0 = \frac{1}{t_{1/2}} ([A]_0 - [A])$$

$$t_{1/2} = \frac{1}{k_0} ([A]_0 - [A])$$

⇒  $t_{1/2}$  for 1<sup>st</sup> order reaction :-

$$x = a/2, \quad t = t_{1/2}$$

$$k_1 = \frac{1}{t_{1/2}} \ln \frac{a}{a - (a/2)}$$

$$= \frac{1}{t_{1/2}} \ln 2$$

$$k_1 = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = \frac{0.693}{k_1}$$

⇒  $t_{1/2}$  for 2<sup>nd</sup> order reaction :

$$k_2 = \frac{1}{t_{1/2}} \left[ \frac{a/2}{a(a - a/2)} \right]$$

$$k_2 = \frac{1}{t_{1/2}} \left[ \frac{1}{a} \right]$$

$$\boxed{t_{1/2} = \frac{1}{k_2 a}}$$

⇒  $t_{1/2}$  for 3<sup>rd</sup> order reaction :

$$k_3 = \frac{1}{2k_3} \left( \frac{a/2 (2a - a/2)}{a^2 (a - a/2)^2} \right)$$

$$= \frac{1}{2k_3} \left( \frac{a/2 \left(\frac{3a}{2}\right)}{a^2 \left(\frac{a}{2}\right)^2} \right)$$

$$= \frac{1}{2k_3} \left[ \frac{3}{a^2} \right]$$

$$\boxed{t_{1/2} = \frac{3}{2k_3 a^2}}$$

⇒  $n^{\text{th}}$  order reaction :

$$t_{1/2} = \frac{2^{n-1} - 1}{k_n (n-1) a_0^{n-1}}$$



Ques (5)

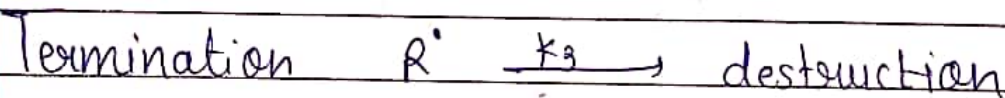
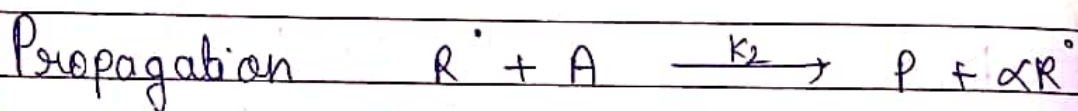
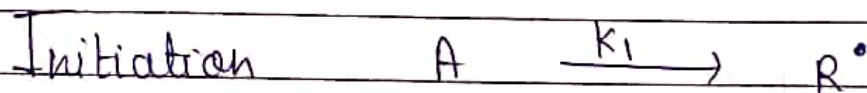
Discuss the kinetics of chain reactions.

Ans

A chain reaction may be classified into two categories -

- (1) Stationary (non branched)
- (2) non stationary (branched)

→ Chain reaction depending on one or more than one radical produced in chain propagation step respectively. A chain reaction may be represented as follows.



where, A = reactant, R = radical, P = product

If  $\alpha = 1$ , then stationary chain radical  
If  $\alpha > 1$ , then chain rxn is a non-stationary

→ The destruction of radical may result at the walls of the vessel or by direct collision with other radical within the gaseous phase.

→ The conc<sup>n</sup> of radical can be determined by applying steady-state approximation

to the radical.

$$\frac{d[R^\cdot]}{dt} = 0 = k_1[A] + k_2(\alpha-1)[R^\cdot][A] - k_3[R^\cdot] \quad \text{--- (1)}$$

$$[R^\cdot] = \frac{k_1[A]}{k_2(1-\alpha)[A] + k_3}$$

$$k_3 = k_w + k_g,$$

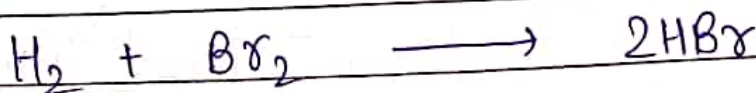
$$[R^\cdot] = \frac{k_1[A]}{k_2(1-\alpha)[A] + k_w + k_g} \quad \text{--- (2)}$$

⇒ Stationary Chain reaction.

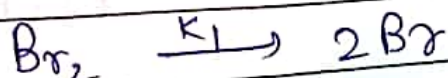
$\alpha = 1$ , in eq<sup>n</sup> (2).

$$[R^\cdot] = \frac{k_1[A]}{k_2 + k_g}$$

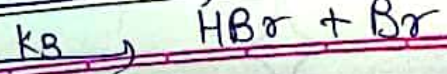
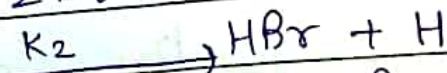
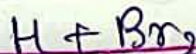
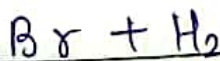
Concentration of radical is simply equal to the ratio of rate of formation of radical in the chain initiation step and rate of destruction of radical in the chain termination step.



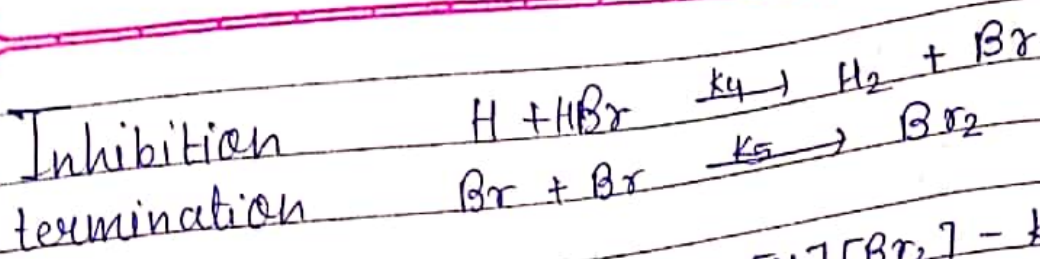
Initiation



Propagation







$$\frac{d[HBr]}{dt} = k_2 [Br][H_2] + k_3 [H][Br_2] - k_4 [H][HBr] \quad \text{--- (1)}$$

$$\frac{d[H]}{dt} = 0 = k_2 [Br][H_2] - k_3 [H][Br_2] - k_4 [H][HBr] \quad \text{--- (2)}$$

$$\frac{d[Br]}{dt} = 0 = 2k_1 [Br_2] - k_2 [Br][H_2] + k_3 [H][Br_2] + k_4 [H][HBr] - 2k_5 [Br]^2 \quad \text{--- (3)}$$

by eq<sup>n</sup> (2) and (3)

$$2k_1 [Br_2] - 2k_5 [Br]^2 = 0$$

$$[Br] = \left( \frac{k_1 [Br_2]}{k_5} \right)^{1/2} \quad \text{--- (4)}$$

from eq<sup>n</sup> (2)

$$[H] = \frac{k_2 [Br][H_2]}{k_3 [Br_2] + k_4 [HBr]}$$

Substituting [Br] from eq<sup>n</sup> (4) in

$$[H] = \frac{k_2 (k_1/k_5)^{1/2} [Br_2]^{1/2} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \quad \text{--- (5)}$$

By eq<sup>n</sup> (1) and (2)

$$\frac{d[\text{HBr}]}{dt} = 2k_3 [\text{H}][\text{Br}_2]$$

Substituting  $[\text{H}]$  from eq<sup>n</sup> ⑤ in the above eq<sup>n</sup>

$$\frac{d[\text{HBr}]}{dt} = 2k_3 \left( \frac{k_2 (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2} [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \right) [\text{Br}_2]$$

$$= \frac{2k_2 (k_1/k_5)^{1/2} [\text{H}_2]}{1 + (k_4/k_3) [\text{HBr}]/[\text{Br}_2]} = \frac{k' [\text{Br}_2]^{1/2} [\text{H}_2]}{1 + k'' [\text{HBr}]/[\text{Br}_2]}$$

$$k' = 2k_2 (k_1/k_5)^{1/2} \text{ and } k'' = k_4/k_3$$

$$1 + k'' [\text{HBr}]/[\text{Br}_2]_0 = 1$$

$$\left( \frac{d[\text{HBr}]}{dt} \right)_0 = k' [\text{Br}_2]_0^{1/2} [\text{H}_2]_0$$



Ques 6

Write a detail note on effect of temperature on rate of rxn with activation energy.

Ans - It is a common experience that increase of temperature has a marked effect on the rate of a chemical reaction.

→ The ratio of the rate constant of a reaction at two temperatures differing by  $10^\circ\text{C}$  is known as the temperature coefficient of the reaction. The temperatures usually selected for this purpose are  $25^\circ$  and  $35^\circ\text{C}$ .

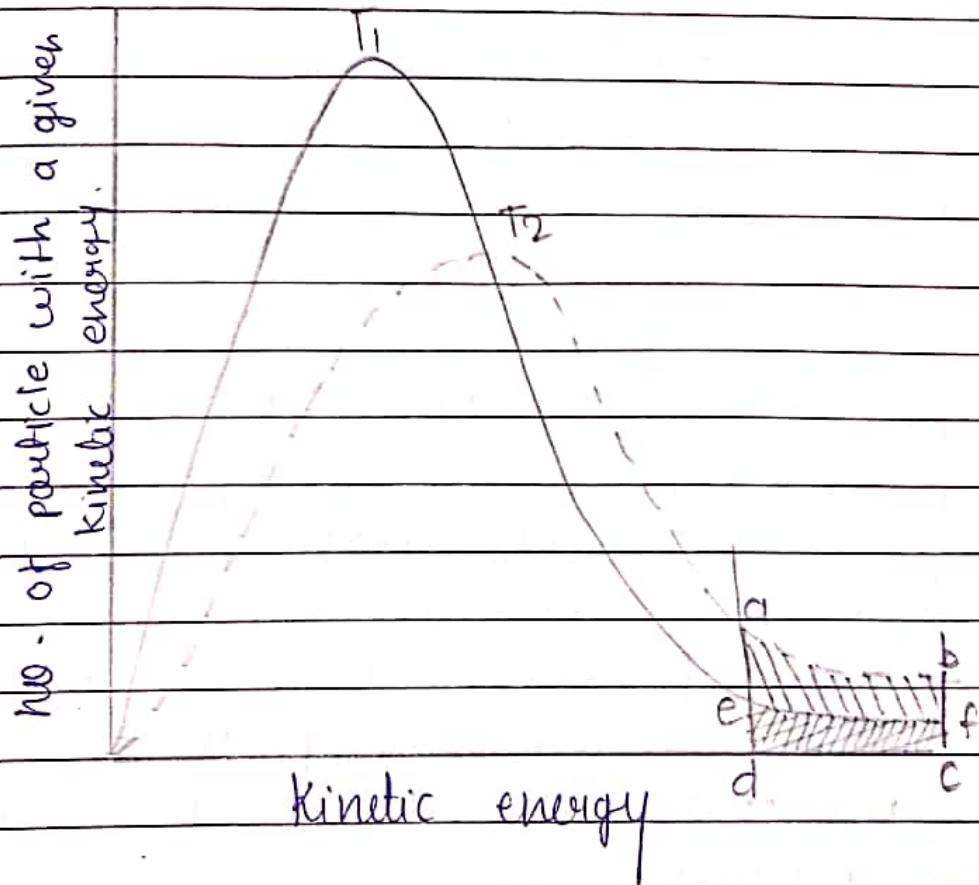
$$\text{Temp. coefficient} = \frac{\text{Rate constant at } 35^\circ\text{C} = K_{35}}{\text{Rate constant at } 25^\circ\text{C} = K_{25}}$$

→ Arrhenius used the Maxwell's distribution of molecular energies to explain the temp. dependence of reaction rates.

→ As the temp. increases from  $T_1$  to  $T_2$ , the energy distribution undergoes a change. As shown in figure there are more molecules on the high side of kinetic energy. The no. of molecules whose energies are equal to or greater than the threshold energy  $E$  at temp.  $T_1$  is represented by shaded area  $efcd$  and at  $T_2$ , area  $abcd$ .

→ The shaded area  $abcd$  is nearly twice the shaded area  $efcd$ . means the

no. of molecules having energy equal or greater than the threshold energy. becomes nearly double even with a small increase of temp. from  $T_1$  to  $T_2$ .

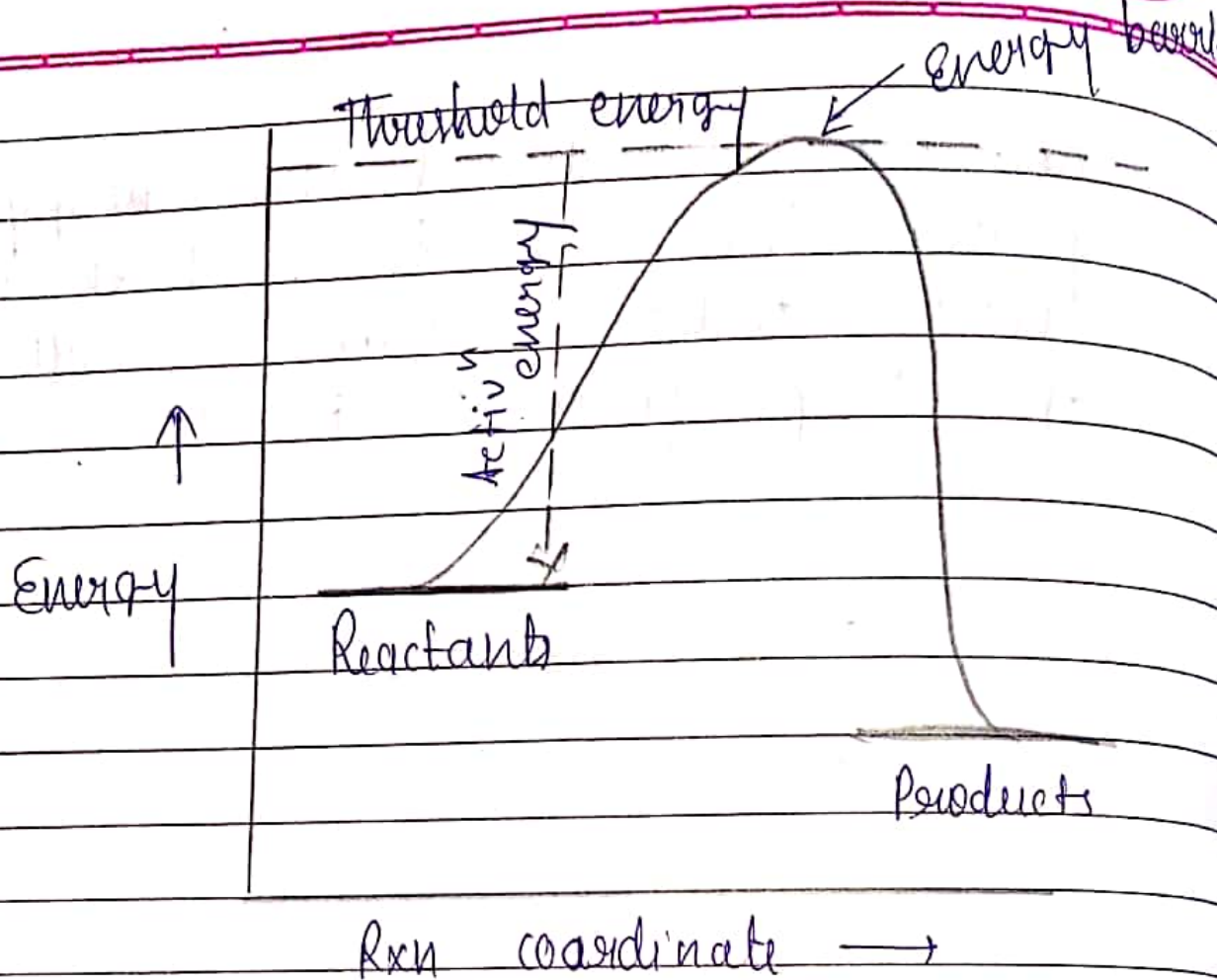


→ Activation energy

→ The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to yield products is known as activation energy.

Activation energy = Threshold energy - Energy actually possessed by molecules





- There is an energy barrier placed bet<sup>n</sup> reactants and products
- This barrier determines the magnitude of threshold energy which reactant molecules must acquire before they can yield products.

Ques (A) Derive Michaelis - Menton equation for enzyme catalyzed reaction.

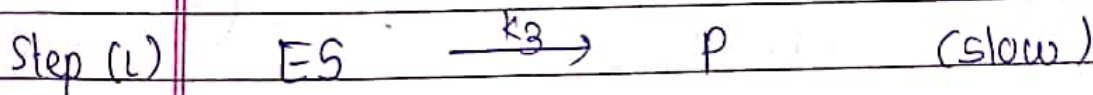
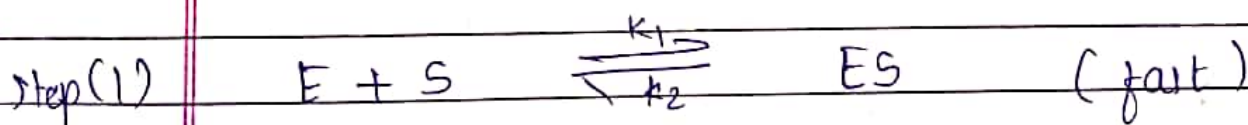
Ans: Enzymes are homogeneous biological catalysts.

→  $[E]_0$  and  $[S]_0$  are initial concentration of enzyme and substrate respectively.

→ The main two features of enzyme catalyzed reaction are as follows.

- (1) The initial rate of product formation is proportional to the total conc. of enzyme  $[E]_0$  for the given amount of substrate  $[S]_0$ .
- (2) For a given  $[E]_0$  and high value of substrate  $[S]_0$ . The rate of product formation become independent of  $[S]_0$  reaching a maximum value known as maximum velocity  $V_{max}$ .

★ Mechanism :-



$$\text{rate } r_1, \quad -\frac{d[S]}{dt} = +\frac{d[P]}{dt} = k_3[ES]$$

Using steady state approximation for ES,

$$k_1[E][S] = k_2[ES] + k_3[ES]$$

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



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

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

$$[E] = [E]_0 - [ES] \quad \text{--- (2)}$$

Putting the value of  $[E]$  is eq<sup>n</sup> (1)

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

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

→ Dividing by  $[ES]$ ,

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

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

$$[ES] = \frac{k_1 [S] [E]_0}{k_2 + k_3 + k_1 [S]} \quad \text{--- (3)}$$

$$\text{rate} = k_3 [ES]$$

$$r_1 = \frac{k_3 \cdot k_1 [S] [E]_0}{k_2 + k_3 + k_1 [S]}$$

dividing numerator and denominator by  $k_1$

$$r_1 = \frac{k_3 [S] [E]_0}{k_2 + k_3 + [S]} \cdot \frac{1}{k_1}$$

$$= \frac{k_3 [E]_0 [S]}{k_m + [S]}$$

( $\because k_m = \frac{k_2 + k_3}{k_1}$ )  
↓  
Michaelis constant

→ for max. velocity :-

$$[E]_0 = [S]$$

$$r_1 = \frac{k_3 [E]_0 [S]}{[S] + k_m} = \frac{k_3 [E]_0}{2} = V_{max}$$

$$r_{1max} = \frac{V_{max} [S]}{[S] + k_m}$$

→  $k_m \gg [S]$

$$\text{rate} = \frac{V_{max} [S]}{k_m} \quad (\text{first order})$$

→  $[S] \gg k_m$

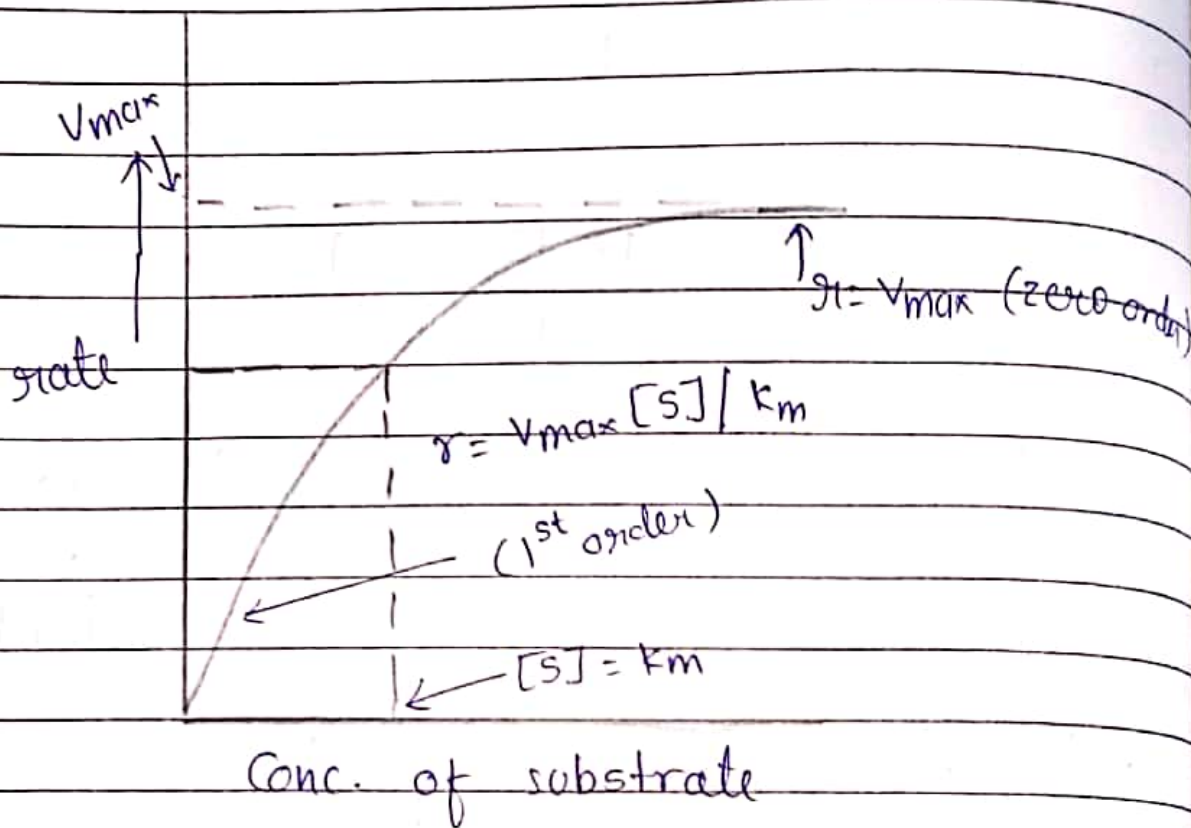
$$\text{rate} = \frac{V_{max} [S]}{[S]}$$

$$\text{rate} = V_{max} \quad (\text{zero order})$$



$$[S] = k_m$$

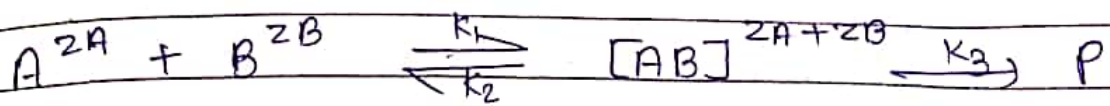
$$\text{rate} = \frac{1}{2} V_{\max}$$



Q8 Explain primary / secondary salt effect on rate of reaction and derive its equation.

Ans Primary Salt effect :-

→ Effect of ionic strength on rate constant is known as primary salt effect.



Equilibrium constant  $K^{\#} = \frac{a_{AB}}{a_A a_B}$

$$K^{\#} = \frac{C_{AB} \gamma_{AB}}{C_A \gamma_A C_B \gamma_B}$$

$$C_{AB} = \frac{K^{\#} C_A \gamma_A C_B \gamma_B}{\gamma_{AB}}$$

rate of reaction =  $k_3 [AB]^{z_A+z_B}$

$$= \frac{k_3 K^{\#} C_A \gamma_A C_B \gamma_B}{\gamma_{AB}}$$

$$= \frac{k_0 C_A \gamma_A C_B \gamma_B}{\gamma_{AB}}$$

$$(\because k_3 K^{\#} = k_0)$$

for the 2<sup>nd</sup> reaction, the rate is given by

$$\text{rate} = k_1 C_A C_B$$

$$k_1 C_A C_B = \frac{k_0 C_A \gamma_A C_B \gamma_B}{\gamma_{AB}}$$

$$k_1 = \frac{k_0 \gamma_A \gamma_B}{\gamma_{AB}}$$



Taking logarithm.

$$\log k_1 = \log k_0 + \log f_A + \log f_B - \log f$$

Acc. to Debye-Huckel limiting law,

$$\log f = -Az^2\sqrt{I}$$

$$\Rightarrow \log k_1 = \log k_0 - Az_A^2\sqrt{I} - Az_B^2\sqrt{I} - A(z_{AB} + z_B)^2\sqrt{I}$$

$$\Rightarrow \log k_1 = \log k_0 - A\sqrt{I} (z_A^2 + z_B^2 - (z_A + z_B)^2)$$

$$\log k_1 = \log k_0 - A\sqrt{I} (z_A^2 + z_B^2 - z_A^2 - 2z_A z_B - z_B^2)$$

$$\log k_1 = \log k_0 + 2A\sqrt{I} z_A z_B$$

at 25°C,  $A = 0.509$

$$\log \frac{k_1}{k_0} = 2(0.509) z_A z_B \sqrt{I}$$

$$\log \frac{k_1}{k_0} = 1.018 z_A z_B \sqrt{I}$$

There are three cases:

- (i) case - I,  
when  $z_A z_B$  are of the same sign  
rate constant would increase  
with increase in ionic strength

② Case - II :-

→ If  $z_A, z_B$  are of the opposite sign rate constant decreases with increasing in ionic strength.

(3) Case - III :-

→ When one of the reactant is uncharged rate constant is independent of ionic strength.

★ Secondary Salt effect :-



Equilibrium constant  $K^{\#} = \frac{[H_3O^+][A^-]}{[HA]}$

$$K^{\#} = \frac{a_{H_3O^+} a_{A^-}}{a_{HA}}$$

$$= \frac{c_{H_3O^+} \gamma_{H_3O^+} c_{A^-} \gamma_{A^-}}{c_{HA} \gamma_{HA}}$$



$$k^{\#} \frac{C_{HA}}{C_{A^{-}}} = \frac{C_{H_3O^{+}} \gamma_{H_3O^{+}} \gamma_{A^{-}}}{\gamma_{HA}}$$

$$k = \frac{C_{H_3O^{+}} \gamma_{H_3O^{+}} \gamma_{A^{-}}}{\gamma_{HA}}$$

$$\left( \therefore k = \frac{k^{\#} C_{HA}}{C_{A^{-}}} \right)$$

$$C_{H_3O^{+}} = \frac{k \gamma_{HA}}{\gamma_{H_3O^{+}} \gamma_{A^{-}}}$$

$$k = \frac{k_0 \gamma_{HA}}{\gamma_{H_3O^{+}} \gamma_{A^{-}}}$$

$$\log k = \log k_0 - A z_{HA}^2 \sqrt{I} + A z_{H_3O^{+}}^2 \sqrt{I} + A z_{A^{-}}^2 \sqrt{I}$$

$$\log \frac{k}{k_0} = 1.018 \sqrt{I}$$