- **Rate of rxn**: change in conc. of any of reactants or product per unit time.

$$\text{Rxn rate} = -\frac{\Delta[\text{Reactant}]}{(\text{St. coeff.})\,\Delta t} = -\frac{\Delta[\text{Reactant}]}{(\text{St. coefficient})\,\Delta t}$$

- **Rate law**: An expression which shows how the rxn rate is related to concs of the reactant

$$\text{for ex} \rightarrow \quad 2A + B \rightarrow \text{product} \qquad \text{rate} = k[A]^m[B]^n$$

- **Order**: Sum of powers of conc terms in the rate law

  Methods for determination of order — 1) Using integrated rate equations (devised by Vant Hoff)
  2) Graphical method
  3) Using half life period (Ostwald)
  4) The differential method $(r = k_n c^n)$
  5) Ostwald's isolation method.

  > unit of rate constant
  > $k = (\text{mol } l^{-1})^{n-1} s^{-1}$
  > n is order

- **Molecularity**: for elementary rxn — number of reactant molecules involved in a rxn.
  for complex rxn — number of molecules or atoms taking part in rate determining step (ie slowest step)

Order	Molecularity
1. Sum of powers of conc in rate law expression	1. number of reacting species undergoing simultaneous collision
2. experimentally determined value	2. Theoretical concept
3. can have fractional value	3. always a whole number
4. can assume zero value	4. cannot have zero value
5. can change with physical conditions.	5. is invariant for a chemical eqn

- **Factors influencing rate**: 1) Nature of reactants (defines Ea)
  2) concs of reactants (increases no of collisions)
  3) temperature (increase in energy, hence increase in no of collision)
  generally temp ↑ rate ↑
  As a result, an increase of temp by $10°c$ doubles the rxn rate.
  Ratio of rate constants of rxn at 2 diff temps differing by $10°$ is called Temperature coefficient $= \dfrac{k_{35°}}{k_{25°}}$
  4) Catalyst (lowers Ea)
  5) Pressure (increase in collisions, hence prob. of to get proffered orientation increases)
  6) Surface area of solid reactants (lowers Ea)

- **Zero order rxn**: reactant A decomposes

	Differential rate law	Integral rate law
Zero order	$-\dfrac{d[A]}{dt} = k[A]^0$	$[A] = [A]_0 - kt$
First order	$-\dfrac{d[A]}{dt} = k[A]$	$[A] = [A_0]e^{-kt}$
Second order	$-\dfrac{d[A]}{dt} = k[A]^2$	$\dfrac{1}{[A]} - \dfrac{1}{[A_0]} = kt$

- **Pseudo order rxn**: one of the reactants is in excess. hence it shows an order different from the actual order. ex→ hydrolysis of ester.
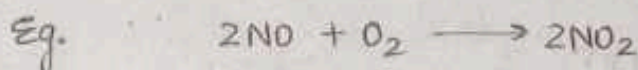
Unit-2

Chemical Kinetics

- Second order reactions
- Fast and slow rxns
- Temperature effect
- concept of Activated state - Energy

- Determination of order
- Steady state approx
- Temperature effect
- Potential Energy surface
- Theories of rxn rate

Rate of a Reaction -

Rate of rxn is defined as the rate of change of concentration of any of the products or reactants.

Eg. $2NO + O_2 \longrightarrow 2NO_2$

$$\text{rate of reaction} = -\frac{d[NO]}{2 \cdot dt} = -\frac{d[O_2]}{1 \cdot dt} = +\frac{d[NO_2]}{2 \cdot dt}$$
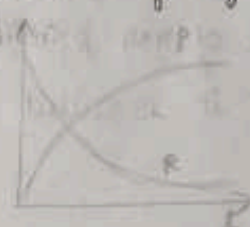
Rate law

Rate law is an expression which shows how the reaction rate is related to the concentration of reactants. is called

$$2A + B \longrightarrow \text{Products}$$

$$r = k[A]^x [B]^y$$

Order of a rxn

Sum of the powers of concentration terms in rate law.

$$r = k[A]^x [B]^y$$

$$\text{order of rxn} = (x+y)$$

Methods for determination of order of a rxn

① By using integrated rate eq.
② Graphical method
③ using Half life period
④ Ostwald's isolation method

① Integrated rate equations

In a reaction in which one of the reactant is present in large concentration (in excess), the rxn shows a different order of rxn practically from the one calculated theoritically. Hence it is called pseudo-order reactions.
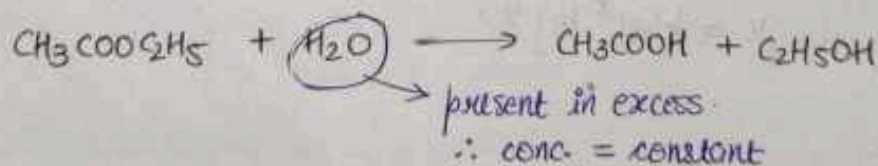
$$r = k[A][B]$$

If B is present in large conc., the practically it's conc. remains constant –

$$\therefore \quad r = k'[A] \quad \leftarrow$$

Pseudo Fist Order Rxn.

Example –

Hydrolysis of Ester –

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

present in excess
$$\therefore conc. = constant$$

$$r = k[CH_3COOC_2H_5][H_2O]$$

$$r = k'[CH_3COOC_2H_5]$$

Second Order Reactions
One reactant
Reaction —

$$A \longrightarrow \text{Products}$$
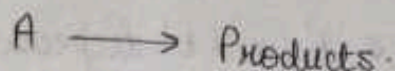
$t = 0$	a	0
$t = t$	$a-x$	x

a = initial concentration (mol $\bar{L}^1$).

x mols have reacted in time 't'

$$r = k[A]^2$$

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

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

$$(x_2=)$$
$$(a-x)$$
$$(t)$$

$$\int_{(x_1=0)} \frac{dx}{(a-x)^2} = \int_{(0)} k\,dt$$

$$\left[\frac{1}{a-x}\right]_0^x = kt$$

$$\left(\frac{1}{a-x} - \frac{1}{a}\right) = kt$$

$$\boxed{k = \frac{1}{t} \frac{x}{a(a-x)}}$$ Integrated rate eq.
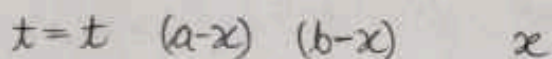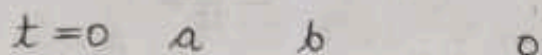
Ex. $\longrightarrow$ Hydrolysis of Ester by NaOH.

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

⇒ Integrated rate equation when two different reactants are present.

$$x = k[A][B] \quad ; \quad A + B \longrightarrow P$$

Initial concentration of A and B are 'a' & 'b' mol L⁻¹ respectively.

$$x = -\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

$$
\begin{array}{ccccc}
 & A & + & B & \longrightarrow P \\
t=0 & a & & b & 0 \\
t=t & (a-x) & & (b-x) & x
\end{array}
$$

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

$$\int_{0}^{x} \frac{dx}{(a-x)(b-x)} = \int_{0}^{t} k\,dt$$

$$\int_{0}^{x} \frac{dx}{(b-a)(a-x)} + \int_{0}^{x} \frac{dx}{(a-b)(b-x)} = kt$$

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

$$\boxed{\left(\frac{1}{a-b}\right) \ln\left[\frac{(b-x)\,a}{(a-x)\,b}\right] = kt}$$

Derive an expression for half-life of nth order reaction.

$$A \longrightarrow \text{Products}$$

$$r = R[A]^n$$

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

$$-\frac{d[A]}{dt} = k[A]^n$$

$$\int_{A_0}^{A_0/2} \frac{d[A]}{[A]^n} = \int_0^t -k\,dt$$

$$\left[\frac{A^{-n+1}}{-n+1}\right]_{A_0}^{A_0/2} = -kt$$

$$\left(\frac{1}{n-1}\right)\left[\frac{1}{A^{n-1}}\right]_{A_0}^{A_0/2} = kt$$

$$\left(\frac{1}{n-1}\right) \frac{(2)^{n-1}}{(A_0)^{n-1}} - \frac{1}{(A_0)^{n-1}} = kt$$

$$\frac{1}{(n-1)t}\left(\frac{(2)^{n-1}-1}{(A_0)^{n-1}}\right) = k$$

$$\boxed{T_{1/2} = \frac{1}{(n-1)k}\left(\frac{(2)^{n-1}-1}{(A_0)^{n-1}}\right)}$$

② Graphical Method.

First order —

$$t = \frac{1}{k} \ln\left(\frac{C_0}{C_t}\right) \quad \Big/ \quad t = \frac{1}{k} \ln\left(\frac{a}{a-x}\right)$$

$\Big(\begin{array}{l} C_0 = \text{initial conc} \\ C_t = \text{conc. at} \\ \quad \text{time } t \end{array}\Big)$

$$\ln C_0 - \ln C_t = kt$$

$$\boxed{\ln C_t} = \ln C_0 - \underbrace{kt}_{\longrightarrow x}$$
$\underset{y}{\uparrow}$

$$y = -mx + c \qquad \Big(\begin{array}{l} m = k \\ c = \ln C_0 \end{array}\Big)$$
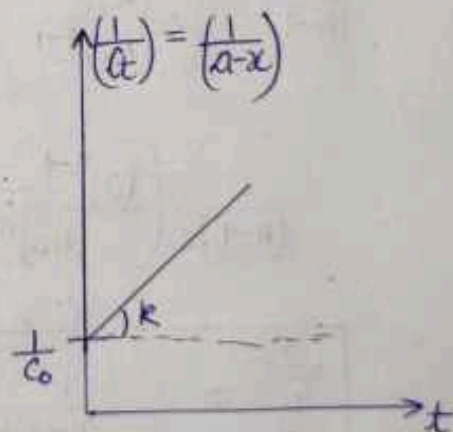
$\ln(C_t) = \ln(a-x)$

$$\text{slope} = -k$$
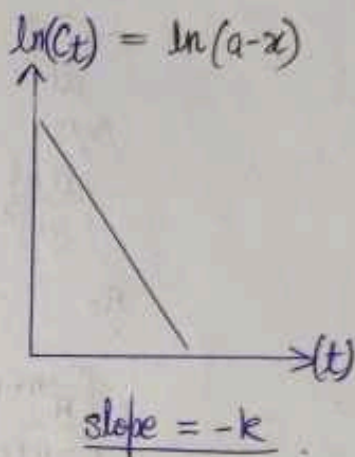
Second order

$$t = \frac{1}{k}\left[\frac{1}{C_t} - \frac{1}{C_0}\right] \quad \Big/ \quad t = \frac{1}{k}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$$

$$\underset{\underset{\downarrow_y}{x}}{\underset{\uparrow}{kt}} = \left(\frac{1}{C_t}\right) - \frac{1}{C_0}$$

$$y = mx + c \qquad \begin{array}{l} m = k \\ c = \frac{1}{C_0} \end{array}$$

$\left(\frac{1}{C_t}\right) = \left(\frac{1}{a-x}\right)$

③ <u>Half life period method</u>.

$$T_{1/2} \propto \frac{1}{[A]} \qquad 2^{nd} \text{ order } rxn$$

$$\left(A = \text{initial concentration} \right)$$

$$T_{1/2} \propto \frac{1}{[A]^2} \qquad 3^{rd} \text{ order } rxn.$$

$$T_{1/2} \propto \frac{1}{[A]^{n-1}} \qquad n^{th} \text{ order } rxn.$$

$$t_1 \propto \frac{1}{[A_1]^{n-1}} \quad ; \quad t_2 = \frac{1}{[A_2]^{n-1}}$$

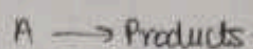$$\frac{t_1}{t_2} = \frac{[A_2]^{n-1}}{[A_1]^{n-1}}$$

simlifying,

$$\boxed{n = 1 + \frac{\log\left[t_1/t_2\right]}{\log\left[A_2/A_1\right]}}$$

Formulas -:

First Order -

$$R = \frac{2\cdot303}{t} \log_{10}\left(\frac{C_0}{C_t}\right)$$ (single reactant) $A \longrightarrow$ Products

$$T_{1/2} = \frac{0\cdot693}{R}$$

$$\begin{bmatrix} C_0 = \text{Initial conc.} \\ C_t = \text{conc. of A after} \\ \text{some time 't'} \end{bmatrix}$$

Second order -

$$R = \frac{1}{t}\left[\frac{1}{C_t} - \frac{1}{C_0}\right]$$ (single reactant) $A \longrightarrow$ Pro.

$$R = \left(\frac{1}{A_0 - B_0}\right) \log\left[\frac{(B_0 t)(A_0)}{(A t)(B_0)}\right]$$ (two reactants) $A + B \longrightarrow$ Pro.

$$t=0. \quad A_0 \quad B_0 \quad 0$$
$$t=t \quad A_t \quad B_t \quad x$$

$$\begin{pmatrix} A_t = A_0 - x \\ B_t = B_0 - x \end{pmatrix}$$

$$T_{1/2} = \frac{1}{R C_0}.$$

Zero Order

$$R = \frac{C_0 - C_t}{t}$$ (single reactant)

$$T_{1/2} = \frac{2C_0}{2R}$$

④ Ostwald's Isolation Method

$$A + B + C \longrightarrow \text{Products}$$

$\longrightarrow$ Order with respect to A, B and C are found out individually.

$\longrightarrow$ For determining order wrt A, B and C are taken in large amounts, so that their conc. remains constant.

$\longrightarrow$ Same is done for B and C.

$$n = \text{order of rxn} = n_A + n_B + n_C$$

order wrt   order   order
A   wrt B   wrt C.

SOLVED PROBLEM. From the following data for the decomposition of N_2O_5 in CCl_4 solution at 48°C, show that the reaction is of the first order

t (mts)	10	15	20	∞
Vol of O_2 evolved	6.30	8.95	11.40	34.75

SOLUTION

For a first order reaction the integrated rate equation is

$$\frac{1}{t} \log \frac{V_\infty}{V_\infty - V_t} = k$$

In this example, $V_\infty = 34.75$

t	$V_\infty - V_t$	$\frac{1}{t} \log \frac{V_\infty}{V_\infty - V_t}$	=	k
10	28.45	$\frac{1}{10} \log \frac{34.75}{28.45}$	=	0.00868
15	25.80	$\frac{1}{15} \log \frac{34.75}{25.80}$	=	0.00862
20	23.35	$\frac{1}{20} \log \frac{34.75}{23.35}$	=	0.00863

Since the value of k is fairly constant, it is a **first order reaction**.

7

SOLVED PROBLEM. The following data was obtained on hydrolysis of methyl acetate at 25°C in 0.35N hydrochloric acid. Establish that it is a first order reaction.

t (secs)	0	4500	7140	∞
ml alkali used	24.36	29.32	31.72	47.15

SOLUTION

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

At any time, the volume of alkali used is needed for the acid present as catalyst and the acid produced by hydrolysis.

The volume of alkali used for total change from t_0 to t_∞ gives the initial concentration of ester. Thus,

$$a = 47.15 - 24.36 = 22.79 \, \text{ml}$$
$$(a-x) \text{ after } 4500 \text{ sec} = 47.15 - 29.32 = 17.83 \, \text{ml}$$
$$(a-x) \text{ after } 7140 \text{ sec} = 47.15 - 31.72 = 15.43 \, \text{ml}$$

Substituting values in the rate equation above, we have

$$k = \frac{2.303}{4500} \log \frac{22.79}{17.83} = 0.00005455$$

$$k = \frac{2.303}{7140} \log \frac{22.79}{15.43} = 0.0000546$$

Since the values of k in the two experiments are fairly constant, the reaction is of the first order.

8

Theories of Reaction -

① Collision Theory -

rate constand $= k$

$$k = Zpf$$

$$f \propto e^{-Ea/RT}$$

$$\underline{k = Ae^{-Ea/RT}}$$

Arrhenius equation.

z = collision frequency

p = the fraction of molecules with proper orientation.

f = the fraction of molecules with sufficient Energy.

Theory -

says that

A chemical reaction will take place between the reactants only if -

① The molecules of reactants collide in a proper orientation.

② The molecules must collide with sufficient Kinetic Energy, to over come the activation Energy barrier and rxn can take place

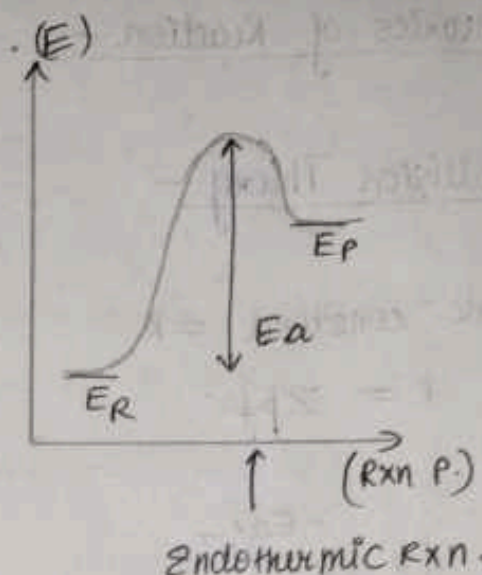correct orientation = ensure direct contact b/w atoms for bond formation and bond breaking.

E_a = Activation Energy

E_R (Reactants)

E_P (Products)

Energy

Rxn Progress

↑
Exothermic rxn
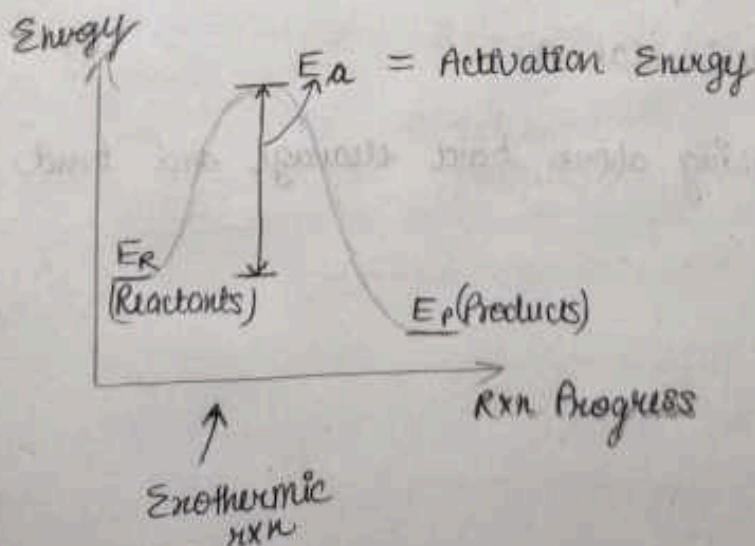
Arrhenius Equation

$$k = Ae^{-Ea/RT}$$

$$\log k = \log A + \left(\frac{-Ea}{RT}\right) \times \frac{1}{2 \cdot 303}$$

$$\log k_1 = \log A + \frac{(-Ea)}{2 \cdot 303 RT_1}$$

$$\log k_2 = \log A + \frac{(-Ea)}{2 \cdot 303 RT_2}$$

$$\log \frac{k_2}{k_1} = \frac{Ea}{2 \cdot 303 R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$


Endothermic Rxn.

Limitations of Collision Theory.

① ~~They~~ This theory applies to only simple gaseous rxns, or rxn in which reactants are simple molecules.

② This theory assumes that only Kinetic Energy contributes for overcoming Energy barrier, ignoring Rotational and vibrational Energy.

③ No method to determine steric effect.

④ In case of complex rxn, the theoritical rate constants are different from the experimental one.

⑤ They theory says nothing about bond cleavage and bond formation.

② Transition state theory

This theory states that, direct collision of reactant molecules does not yield product, during the rxn a transition state or activated complex is formed which decomposes to yield product.

$$A + B-C \longrightarrow ABC^{\neq} \longrightarrow A-B + C$$
$$\text{(Activated state)}$$
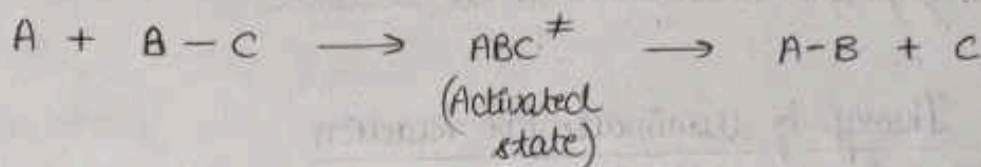
As

① The colliding molecules approach each other, they are slowed down due to repulsion caused by their electron clouds. In this process the kinetic energy is converted to Potential Energy.

② As the molecules come close ⟶ electron clouds interpenetrate ⟶ causing rearrangement * of valence electrons.

③ A partial bond is formed b/w A & B, with simultaneous weaking of bonds b/w B & C. This state is called Transition State.

$$A + B-C \longrightarrow A---B-\cancel{}-C \longrightarrow A+B + C.$$
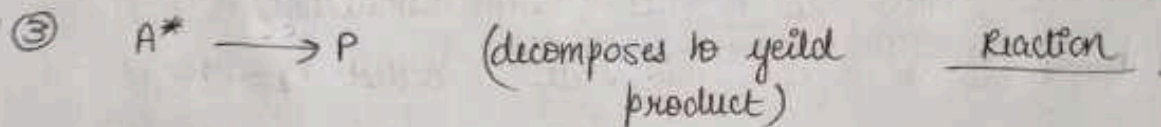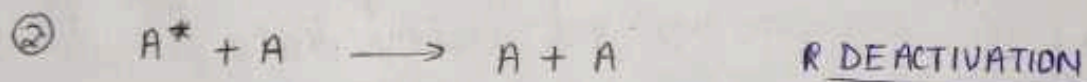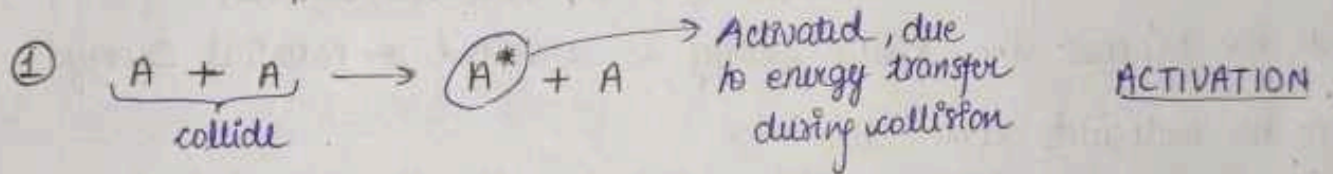
weakening of bond

↑ Partial bond formation
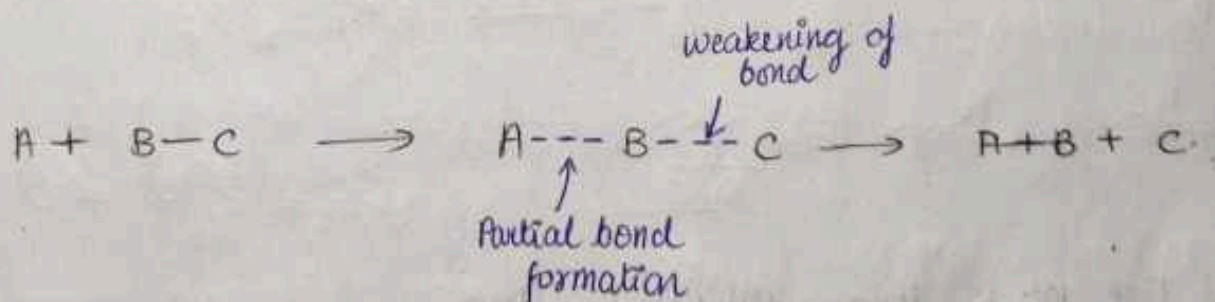
→ Role of catalyst —:

① It provides on alternative pathway of reaction, with lower activation Energy.

② It provides a surface area to the substrate, and the substrate forms weak vander wall forces with catalyst.

Hence.
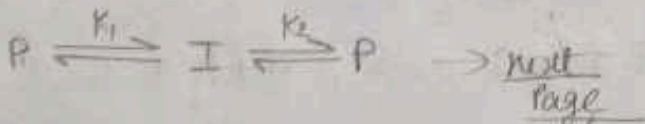③ ~~His~~ providing proper orientation to the reactants.

Lindeman's Theory of Unimolecular Reaction.

⇒ There existed a time lag b/w activation and rxn of molecules. In case of unimolecular rxn —:

there are three possibilities —

① $\underline{A + A} \longrightarrow \boxed{A^*} + A$ → Activated, due to energy transfer during collision   ACTIVATION.
     collide

② $A^* + A \longrightarrow A + A$ R DEACTIVATION

③ $A^* \longrightarrow P$ (decomposes to yeild product)   Reaction

$\dfrac{d[A^*]}{dt} = 0$

$A + A \longrightarrow \boxed{A^*} \longrightarrow P$
                     ↘ short lived

$P \underset{}{\overset{K_1}{\rightleftharpoons}} I \underset{}{\overset{K_2}{\rightleftharpoons}} P$ → next page

by $\boxed{S.S.a.} \dfrac{d[A^*]}{dt} = 0$ → next page.
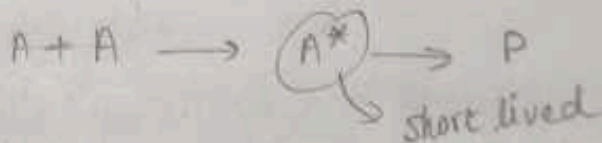
* If time gap is long, step ③ is slow, the rxn should follow FIRST ORDER kinetics.

* If A reacts as soon as formed, step ② is slow then rxn should be second order.

The equilibrium Approximation –

Suppose a reaction occurs with formation of a series of intermediates

$$R \xrightarrow{k_1} I_1 \xrightarrow{k_2} I_2 \xrightarrow{k_3} \cdots \cdots \xrightarrow{k_{n-1}} I_{n-1} \xrightarrow{k_n} I_n \longrightarrow P$$

To find the rate equation, we assume that a rate-determining step exists.

Rate determining step $\longrightarrow$ Slowest

It is further assumed that all the steps preceding the r d s are in equilibrium.

$$R \underset{}{\overset{k_1}{\rightleftharpoons}} I_1 \underset{}{\overset{k_2}{\rightleftharpoons}} I_2 \underset{}{\overset{k_3}{\rightleftharpoons}} \cdots \cdots \underset{}{\overset{k_{n-1}}{\rightleftharpoons}} I_{n-1} \underset{}{\overset{k_n}{\rightleftharpoons}} I_n \rightleftharpoons P$$

The Steady – state Approximation

In rxns where rate determining step (slowest) does not exist, SSA is assumed for transition state

$\hookrightarrow$ short lived.

$$\frac{d[I_1]}{dt} = \frac{d[I_2]}{dt} = \frac{d[I_n]}{dt} = 0.$$

rate of formation = rate of decomposition $\left.\right\} \longrightarrow$ For transition state
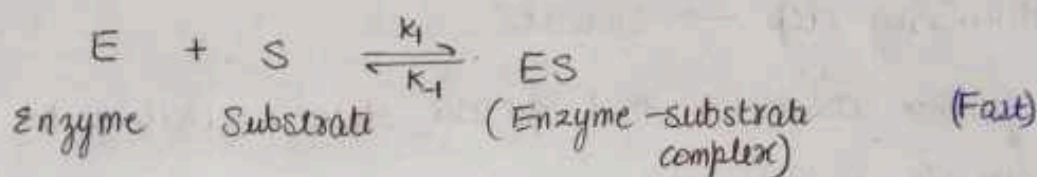
Enzyme Catalysis

complex organic substances = enzymes.

⟶ Proteins with high molar masses.

Mechanism and Kinetics of Enzyme catalyzed Rxn —

Step 1

$$E + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES$$

Enzyme   Substrate   (Enzyme-substrate   (Fast)
                        complex)

Step 2

$$ES \xrightarrow{K_2} P + E \qquad\qquad (slow)$$

                   Prod
                  (Product)
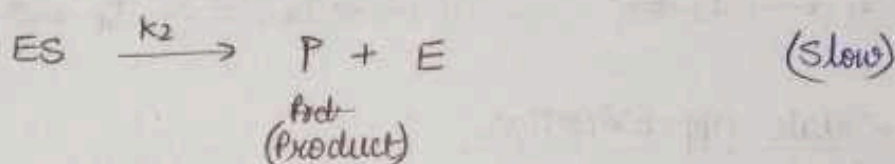
⟹ A true equilibrium can't established in fast step because the subsequent slow rxn is continuously removing the intermediate complex (ES).

⟹ concentration ⟶ $[E] <<< [S]$

             ∴ $[ES] <<< [S]$ ⟶ (steady state approx. can be used)

$$r = -\cancel{\frac{ds}{}} -\frac{d[S]}{dt} = \frac{d[P]}{dt} = K_2[ES]$$

                                                 ⟶ decomposition

$$0 = \frac{d[ES]}{dt} = \underbrace{K_1[E][S]}_{formation} - \underbrace{K_{-1}[ES] - K_2[ES]}$$

Rate of Formation of intermediate = Rate of decomposition of intermediate

$[E]$ ~~so~~ can't be measured experimentally.

Enzyme conservation equation —

$$[E_\bullet]_0 = [ES] + [E]$$

↗ Total enzyme concentration

↓ reacted/ bound enzyme conc.

→ free enzyme conc.

$$[\bar{E}] = [\bar{E_\bullet}]_0 - [ES]$$

substituting —

$$\frac{d[ES]}{dt} = k_1\Big\{[E]_0 - [ES]\Big\}[S] - k_{-1}[ES] - k_2[ES] = 0.$$

$$k_1[E]_0[S] = \Big\{k_1[S] + k_{-1} + k_2\Big\}[ES]$$

$$[ES] = \frac{k_1[E_0][S]}{k_{-1} + k_2 + [S]k_1}$$

$$\Rightarrow \quad \mathcal{H} = \frac{k_1 k_2 [E_\bullet]_0 [S]}{k_{-1} + k_2 + [S]k_1}$$

$$[ES] = \frac{r}{k_2}$$

dividing num. & denom. by k_1 —

Michael-Menten equation → $$[E\!\!\!/S] = \frac{[E_0][S]\,k_2}{\left(\frac{k_{-1}+k_2}{k_1}\right) + [S]} = \frac{[E_0][S]\,k_2}{K_m + [S]}$$

$$K_m = \text{Michaelis constant}$$

$$K_m = \left(\frac{k_{-1} + k_2}{k_1}\right)$$

$\Rightarrow$ when all the enzyme has reacted with substrate, the reaction will be going at __max. rate__.

$$[E] = [ES]$$

$$\mu_{(max)} = k_2 [E]_0 = V_{(max)}$$

$$\uparrow$$

maximum rate, in notation of Enzymology.

Now Michaulis - Menten eq. becomes —:

$$\Rightarrow \quad \mu = V_{max} \; \times \frac{[S]}{k_m + [S]}$$

Case I.

(a) when $\quad k_m \gg [S]$ $\qquad\qquad\qquad$ $k_m + [S] \approx k_m$

$$\mu = V_{max} \cdot \frac{[S]}{k_m}$$

$$\mu = k' [S] \qquad\qquad\qquad \text{(FIRST- ORDER RXN)}$$

Case II

(b) when $[S] \gg k_m$

$$\mu = V_{max} \frac{[S]}{[S]} = V_{max} = \text{constant} \quad \text{[ZERO ORDER]}$$

SOLVED PROBLEM. In the reduction of nitric oxide, 50% of reaction was completed in 108 seconds when initial pressure was 336 mm Hg and in 147 seconds initial pressure was 288 mm Hg. Find the order of the reaction.

SOLUTION

We know that

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2}\right]^{n-1} \qquad \qquad ...(1)$$

where t_1 and t_2 are half-life periods and $[A_1]$ and $[A_2]$ are the corresponding initial concentrations, while n is the order of the reaction.

Taking logs of the expression (1), we have

$$n = 1 + \frac{\log [t_2 / t_1]}{\log [A_1 / A_2]} \qquad \qquad ...(2)$$

Substituting values in expression (2),

$$n = 1 + \frac{\log 108/147}{\log 288/336}$$

$$= 1 + \frac{0.1339}{0.0669} = 1 + 2 = 3$$

Therefore, the reaction is of the **third order**.

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SOLVED PROBLEM. The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation

$$CH_4 (g) + 2S_2 (g) \longrightarrow CS_2 (g) + 2H_2S (g)$$

At 550°C the rate constant for this reaction is 1.1 $l\,mol^{-1}$ sec and at 625°C the rate constant is 6.4 $l\,mol^{-1}$ sec. Calculate E_a for this reaction.

SOLUTION

Here

$$k_1 = 1.1 \text{ litre mol}^{-1}\text{sec.} \quad T_1 = 550 + 273 = 823 \text{ K}$$
$$k_2 = 6.4 \text{ litre mol}^{-1}\text{sec.} \quad T_2 = 625 + 273 = 898 \text{ K}$$

Substituting the values in the equation

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145\,JK^{-1}\,mol^{-1}}\left(\frac{1}{823\,K} - \frac{1}{898\,K}\right)$$

Solving for E_a, gives

$$E_a = \frac{(8.3145\,JK^{-1}\,mol^{-1})\ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823\,K} - \frac{1}{898\,K}\right)}$$

$$= 1.4 \times 10^5 \text{ J/mol}$$

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