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Chemical Kinetics

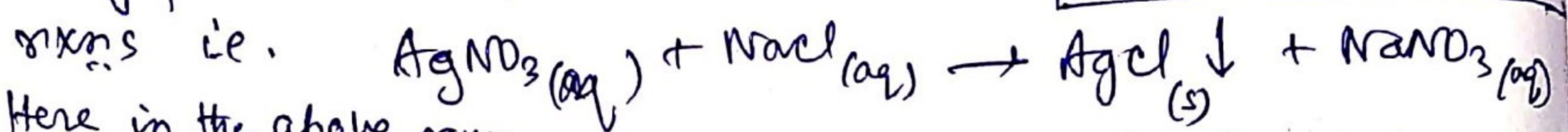
Chemical kinetics deals with

- Study of the rates of chemical rxns
- factors affecting the rates of the rxns
- Mechanism by which the rxns proceed.

Classification of Rxns on the basis of Rates

Very fast Reactions:

Some rxns such as — ionic rxns occur very fast. For example, precipitation type



Here in the above rxn,

Precipitation of AgCl occurs instantaneously by mixing of aqueous solution of AgNO_3 & NaCl .

Very slow Reactions

Some rxns are very slow. For example rusting of iron in the presence of air and moisture.

Moderate rxns

Rxns which are neither very slow nor very fast but take place at moderate speeds. Rxns like — inversion of cane sugar and hydrolysis of starch, which proceed with a moderate speed.

Rate of Rxn

$$\text{Rate} = \frac{\text{Moles of reactants used}}{\text{Time required for this change}} = \frac{x}{t}$$

$$\text{or } \text{Rate} = \frac{\text{Change in concentration}}{\text{Time taken for Change}} = \frac{dx}{dt}$$

Its unit is mole L^{-1} .

For a rxn, $A \rightarrow B$, the rate may be expressed in two ways:

$$\text{Rate} = \frac{\text{Decrease in concentration of A}}{\text{Time taken}}$$

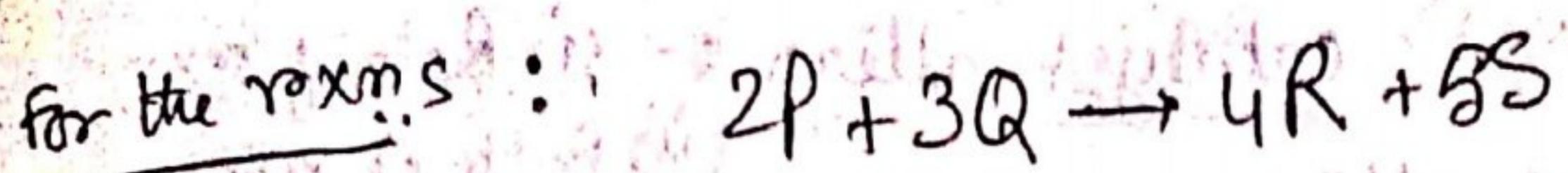
$$= -\frac{[A]_2 - [A]_1}{t_2 - t_1} = (-) \frac{\Delta [A]}{\Delta t}$$

$[A]_1 > [A]_2$

where $[A]_2$ & $[A]_1$ are molar concn. of A at a time t_2 and t_1 respectively

• Rate = $\frac{\text{Increase in concentration of } B}{\text{Time taken}} = \frac{[B]_2 - [B]_1}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$

where $[B]_2$ and $[B]_1$ are the molar concentrations of B at time t_2 & t_1 respectively.



$$\text{Rate} = -\frac{1}{2} \frac{d[P]}{dt} = -\frac{1}{3} \frac{d[Q]}{dt} = +\frac{1}{4} \frac{d[R]}{dt} = +\frac{1}{5} \frac{d[S]}{dt}$$

■ Average rate of Rxn \Rightarrow It is the rate measured over a long time interval i.e.

$$\text{Avg. rate of rxn.} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$

$$r_{\text{avg.}} = \frac{\Delta x}{\Delta t} = (-) \frac{\Delta[R]}{\Delta t} = + \frac{\Delta[P]}{\Delta t}$$

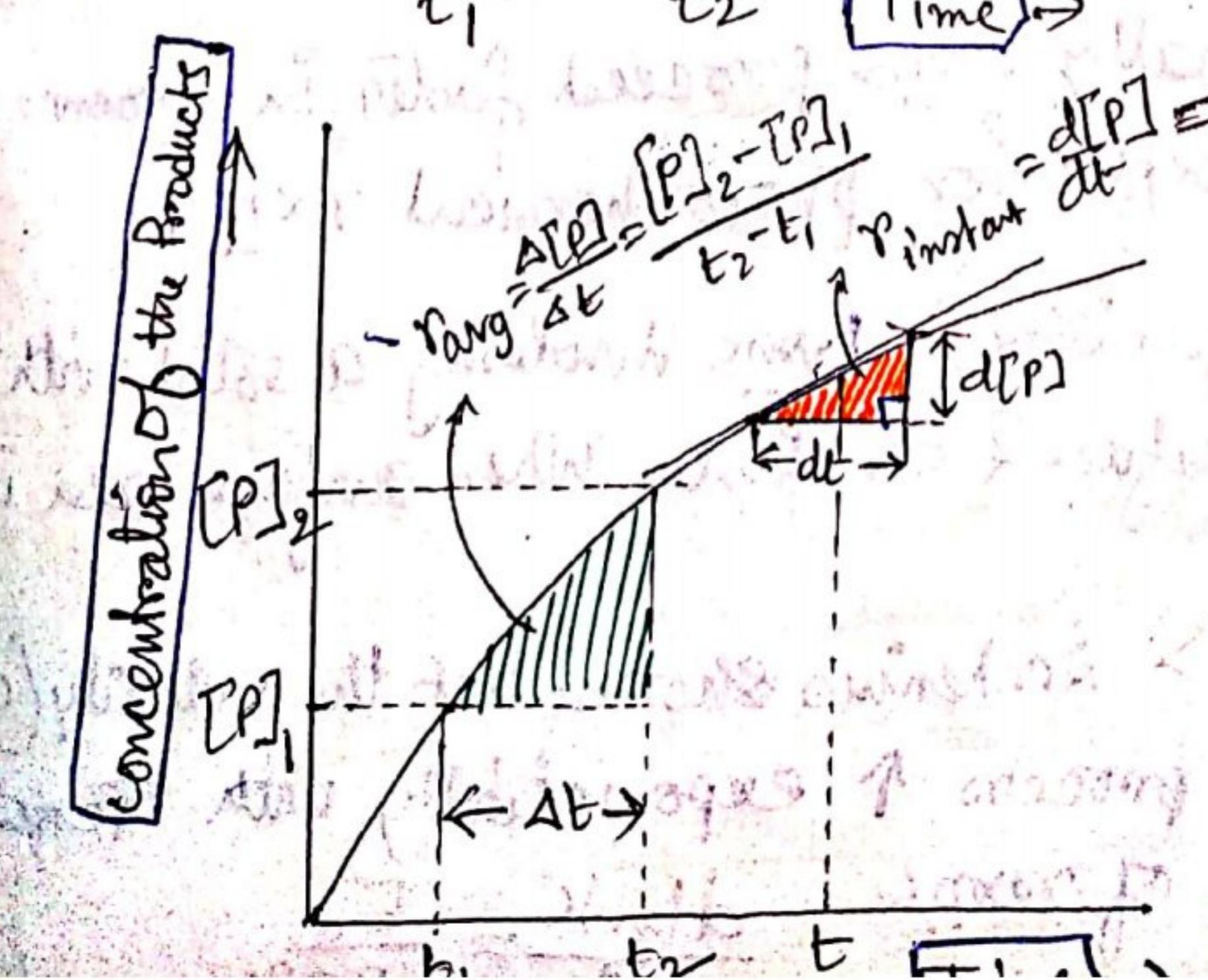
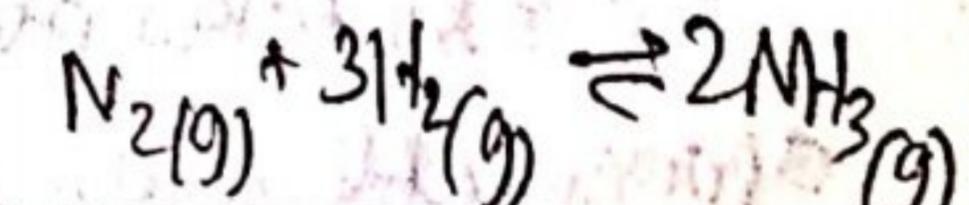
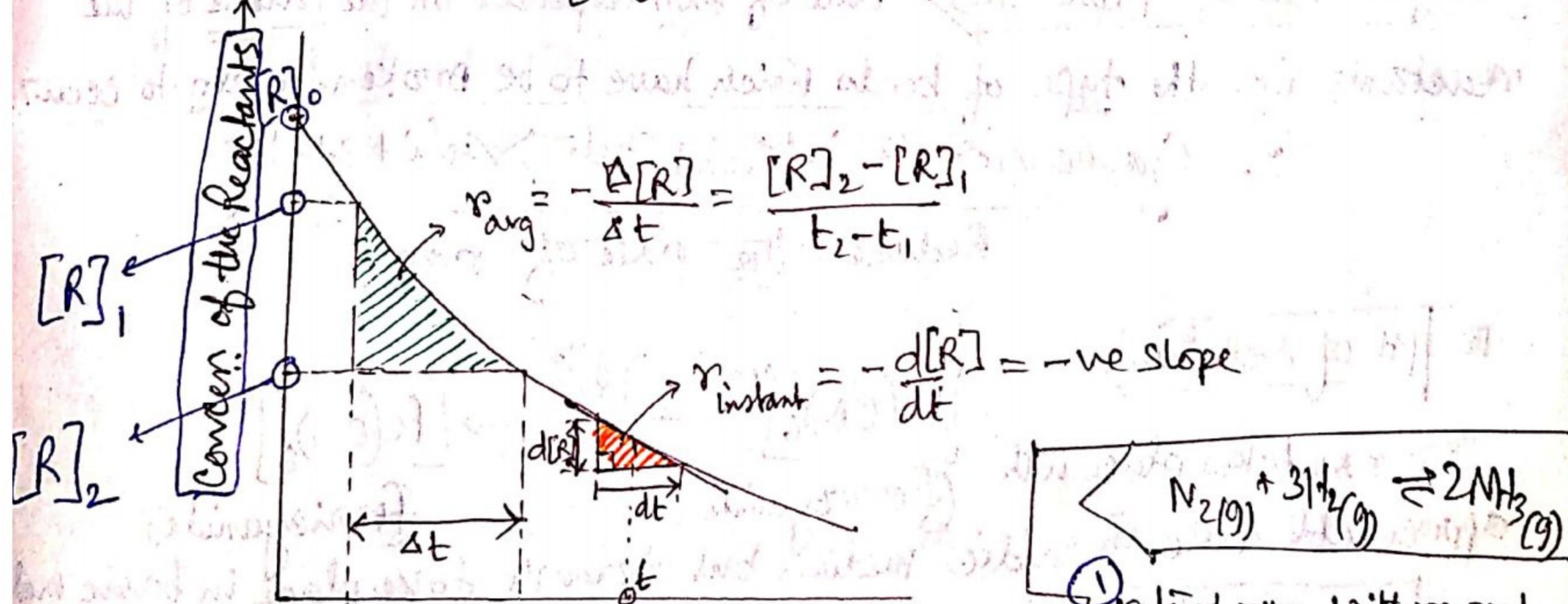
■ Instantaneous rate of rxn \Rightarrow It is rate at any moment, i.e. when time interval is very small i.e. rate of rxn. at a particular instant.

$[R]$ = Active mass of reactants

$[P]$ = Active mass of products

i.e. Instantaneous rate of rxn. $= \frac{dx}{dt}$

$$\text{or, } r_{\text{instantaneous}} = \lim_{t \rightarrow 0} \left[\frac{\Delta x}{\Delta t} \right] = \frac{dx}{dt} = - \frac{d[R]}{dt} = + \frac{d[P]}{dt}$$



① rate of rxn. with respect to (w.r.t) N_2 $= - \frac{d[N_2]}{dt}$

② rate of rxn. w.r.t H_2 $= - \frac{1}{3} \frac{d[H_2]}{dt}$

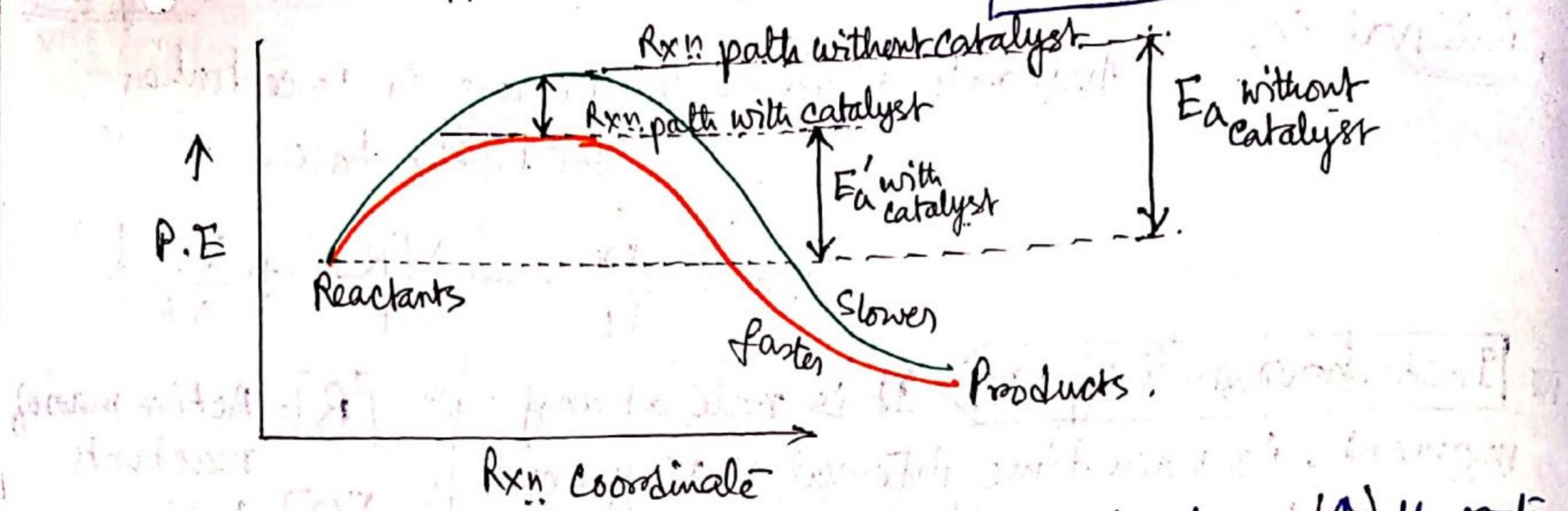
③ rate of rxn. w.r.t NH_3 $= + \frac{1}{2} \frac{d[NH_3]}{dt}$

Rate of rxn. $= - \frac{d[N_2]}{dt} = - \frac{1}{3} \frac{d[H_2]}{dt} = + \frac{1}{2} \frac{d[NH_3]}{dt}$

Factors Affecting Rate of Res.

- Concentration of the reactants

- Presence of a catalyst \rightarrow catalyst alters :-
- * But catalyst doesn't alter the following parameters given as, :- : ΔG , ΔH , ΔS of a rxn.
- ① Rate of rxn.
- (ii) Path of rxn.
- (iii) Activation Energy (E_a)
- (iv) Threshold Energy (E_{Th})
- (v) Rate constant (k)



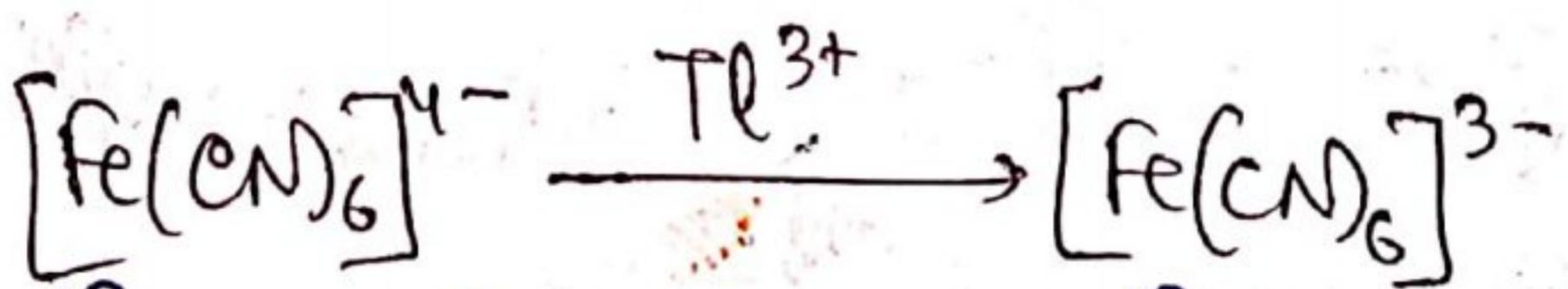
- Kinetic Coordinate

{ o Presence of the catalyst lowers down the E_a' , hence (\uparrow) the rate of rxn.

o Presence of -ve catalyst (\uparrow) the E_a hence ~~(\downarrow)~~ the rate of rxn.

■ **Nature of Reactants** Rate of rxn depends on the nature of the reactants i.e. the type of bonds which have to be broken for rxn to occur.

Pt of Solution



This rxn takes place with (Ferrocyanide) (Ferricyanide)
appreciable rate in acidic medium but doesn't take place in basic medium

■ Exposure to Light

Exposure to light \rightarrow Normally rxns proceed faster in presence of light. Radiations are useful for photochemical rxn.

- Surface Area of Solid reactants → Reactions involving a solid with liquid or a gas occur on surface & are faster when surface area is more.

more.

Temperature of the rxn. \rightarrow Arrhenius showed that the velocity (or rate) constant K of a chem. process \uparrow exponentially with Temp. for a large number of rxns.

$$\frac{d\ln K}{dT} = \frac{E_a}{RT^2}$$

$$\frac{d\ln K}{dt} = \frac{E_a}{RT^2}$$

$$\text{or } d\ln K = \frac{E_a}{RT^2} dt \rightarrow \int d\ln K = \frac{E_a}{R} \int \frac{dt}{T^2} \rightarrow \ln K = -\frac{E_a}{RT} + \ln A$$

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



Usually rxns are faster at higher temp.s.

- The term $e^{-E_a/RT}$ is called Boltzmann's factor, which represents the fraction of molecules having energy in excess of activation energy.
- A = the constant. Known as Arrhenius frequency factor or pre-exponential factor, represents the number of effective collisions occurring per unit time.

- E_a = the activation energy of a rxn, this is the minimum amount of energy required by reactant molecules to participate in a rxn. is called activation energy (E_a^*)

- At two different temp.s T_1 & T_2 if we measure the rate constants K_1 & K_2 then

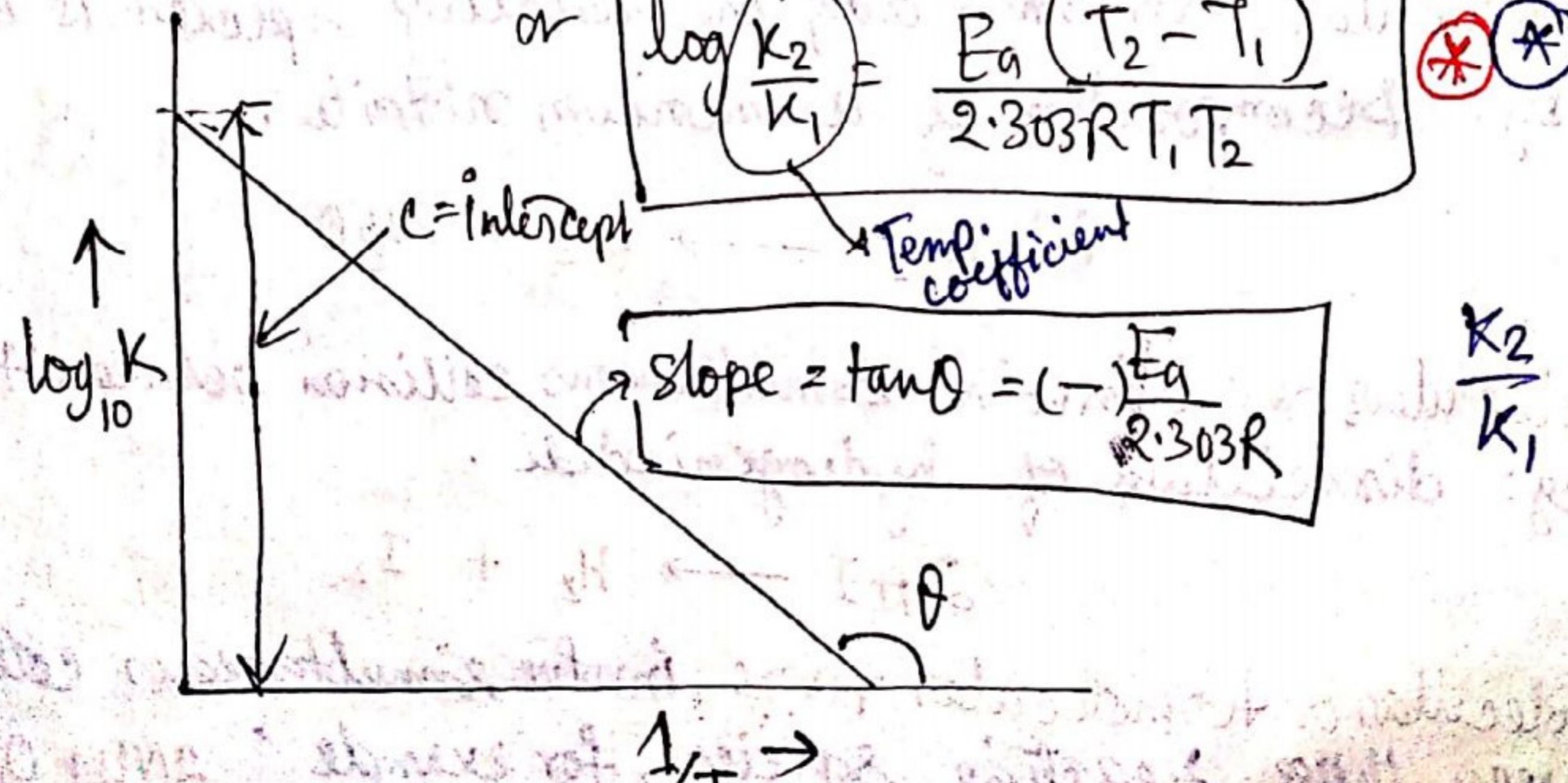
$$\log_{10} K_1 = \log_{10} A - \frac{E_a}{2.303 RT_1} \quad (i)$$

$$\log_{10} K_2 = \log_{10} A - \frac{E_a}{2.303 RT_2} \quad (ii)$$

On division, eqn (ii) by eqn. (i) we get

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

or $\log \frac{K_2}{K_1} = \frac{E_a (T_2 - T_1)}{2.303 R T_1 T_2}$



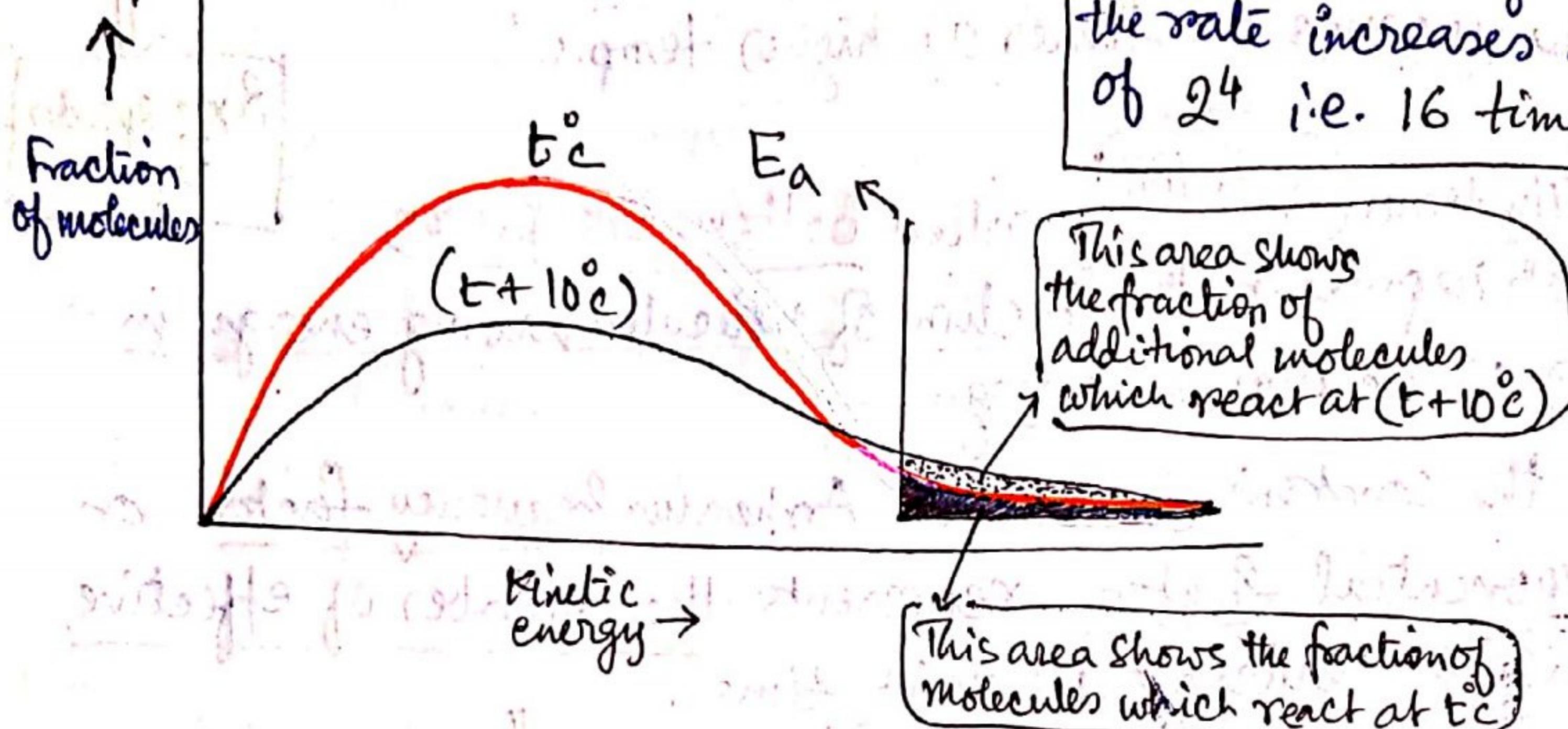
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What's Temperature Coefficient?

- The ratio of 2 specific rates measured at temps. that differ by 10°C is called the temp. coefficient. $\mu = \frac{k_t + 10}{k_t} = 2 \text{ or } 3$

- The rates of many reactions are approximately doubled or tripled for every 10°C rise in temp.

For a rxn whose μ is 2, if the temp. is raised from 25°C to 65°C the rate increases by a factor of 24 i.e. 16 times.



- In Arrhenius eqn. $k = A e^{-E_a/RT}$, collectively A and E_a are called as the Arrhenius parameters of the reaction. When $T \rightarrow \infty$ (infinity)

$$\text{then } k = A e^0 = A$$

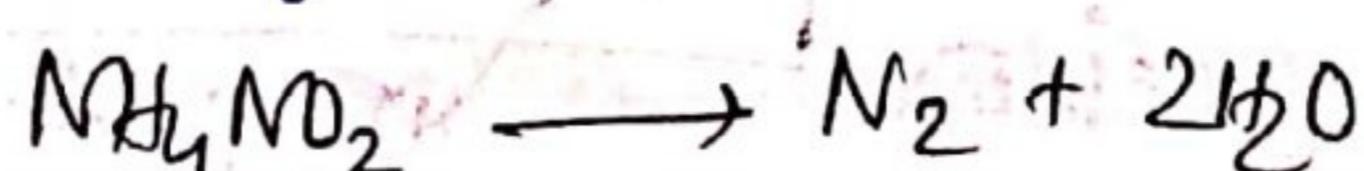
$$\text{when } E_a \rightarrow 0$$

$$\text{then also } k = A e^0 = A$$

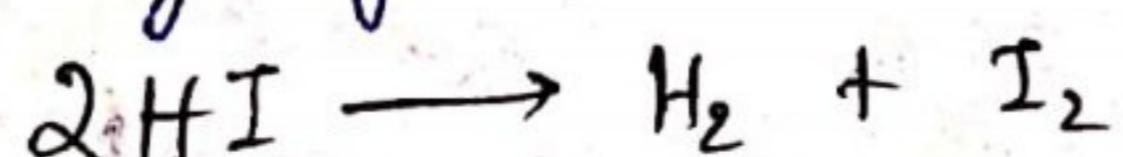
- Molecularity: The number of reacting species (atoms, ions or molecules) taking part in an elementary rxn, which must collide simultaneously in order to bring about a chemical rxn, which is indicated by the sum of the stoichiometric coefficients of the reactants in the chemical equation, is known as molecularity.

- Depending on the number of reacting molecules, rxn can be unimolecular, bimolecular, or tri(ter)-molecular.

- Unimolecular rxn: when only one reacting species is involved.
eg: decomposition of ammonium nitrite.

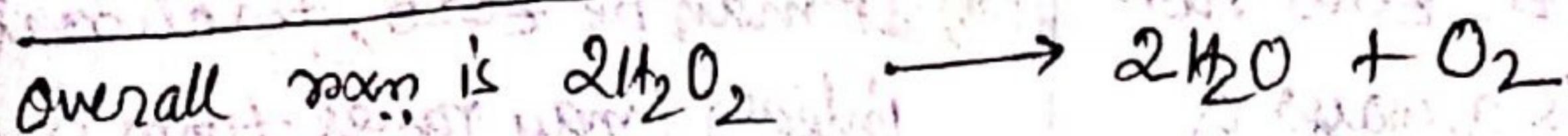
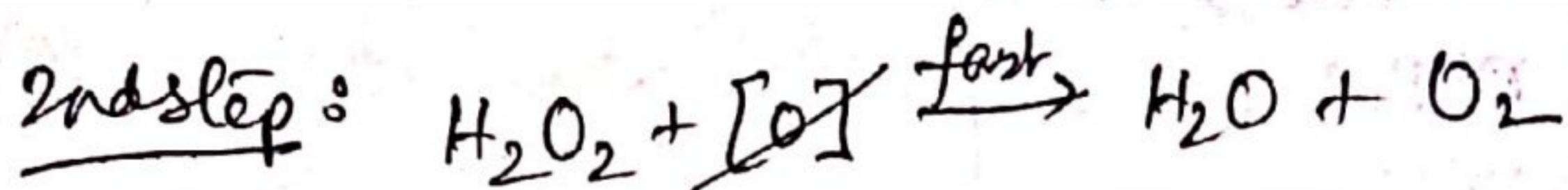
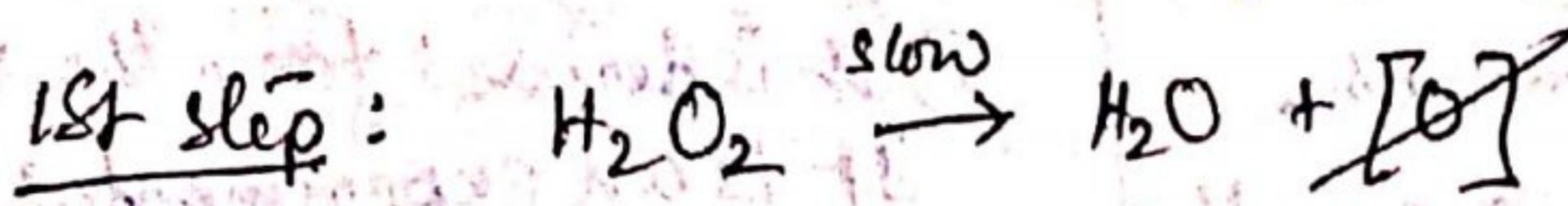


- Bimolecular rxns involve simultaneous collision between two species
eg: dissociation of hydrogen iodide.



- Trinolecular or termolecular rxns involve simultaneous collision between three reacting species, for example $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

- Molecularity above three is not usually seen.
- The overall molarity of a complex rxn is equal to the molarity of the slowest (or rate determining) step.
For example, decomposition of Hydrogenperoxide occurs in 2 steps



$$\therefore \text{Rate} = k[\text{H}_2\text{O}_2]^1, \text{Molecularity} = 1.$$

Order It is defined as the number of molecules of reactants whose concentration determines the rate law expression or it is the sum of the exponents to which the concentration terms must be raised to express the rate of rxn from experimental data.

Rxns

Rate law

Order

- $\text{N}_2\text{O}_5(g) \rightarrow 2\text{NO}_2(g) + \frac{1}{2}\text{O}_2(g); r = k[\text{N}_2\text{O}_5]^1 \rightarrow 1$
- $5\text{Br}^- + \text{BrO}_3^-(aq) + 6\text{H}^+ \rightarrow 3\text{Br}_2(l) + 3\text{H}_2\text{O}(l); r = k[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^{1.5} \rightarrow (1+1+2)=4$
- $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g); r = k[\text{NO}_2]^2 \rightarrow 2$
- $\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g); r = k[\text{NO}_2][\text{CO}] \rightarrow 2$
- $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g); r = k[\text{NO}]^2[\text{O}_2] \rightarrow 3$
- $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3 + \text{CO}; r = k[\text{CH}_3\text{CHO}]^{3/2} \rightarrow 1.5$
- $2\text{NH}_3(g) \xrightarrow{\text{Fe(s)}} \text{N}_2(g) + 3\text{H}_2(g); r = k[\text{NH}_3]^0 \rightarrow 0$
- $2\text{O}_3(g) \rightarrow 3\text{O}_2(g); r = k[\text{O}_3]^2[\text{O}_2]^{-1} \rightarrow (2-1)=1$
- $\text{H}_2(\text{para}) \rightarrow \text{H}_2(\text{ortho}); R = k[\text{H}_2(\text{para})]^{3/2} \rightarrow 1.5$
- $\text{H}_2(g) + \text{Cl}_2(g) \xrightarrow{\text{h}\nu} 2\text{HCl}; R = k[\text{H}_2]^0[\text{Cl}_2]^0 \rightarrow 0$

Molecularity

- ① It's the total number of species taking part in an elementary step of chemical rxn.
- ② It's a theoretical concept.
- ③ It is derived from R.D.S in the mechanism of rxn.
- ④ It can neither be zero nor fractional. It is always a whole number.

Rxns with molarity ≥ 4 are rare.

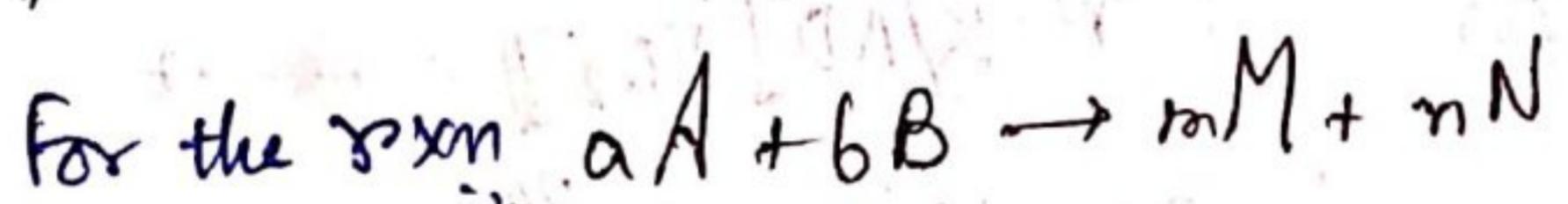
Order

- ① It's the sum of the powers raised on the concentration terms of the reacting species in rate law.
- ② It is derived from the rate expression. It is an experimental quantity.
- ③ It may be zero, fractional or an integer (may range from 0 to 3)
- ④ It depends upon pressure and temperature.

Rxns with order > 4 are also rare.

Law of Mass action

This law was given by Guldberg and Waage, 1864. According to this law, "At a given temp., the rate at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to the powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the rxn."



$$\text{Rate, } r \propto [A]^a [B]^b$$

$$\text{or rate} = \frac{dx}{dt} = r = K [A]^a [B]^b$$

The proportionality constant named as velocity or rate constant:

When $[A] = [B] = 1$ then

$$(\frac{dx}{dt})_{\text{rate}} = K$$

Thus at a given temp. the rate constant of a rxn is equal to the rate of the rxn when the concentration of each of the reactants is unity.

Rate law :- It is the experimentally observed expression in which rate is related to molar concentration of reactants with each term raised to some power which may or may not be the stoichiometric coefficient of the reacting species in the balanced chemical equation.

Thus rate law can be given as:

$$\text{rate} = K [A]^x [B]^y$$

(Experimental interpretation instead of $\text{rate} = K [A]^a [B]^b$)

(Theoretical interpretation according to Law of mass action) where

x may or may not equal to a or y major may not equal to b .

Unit determination of the rate constant (k)

$$\text{Rate} = k [\text{concentrations}]^n \quad \text{where } n = \text{order of the rxn}$$

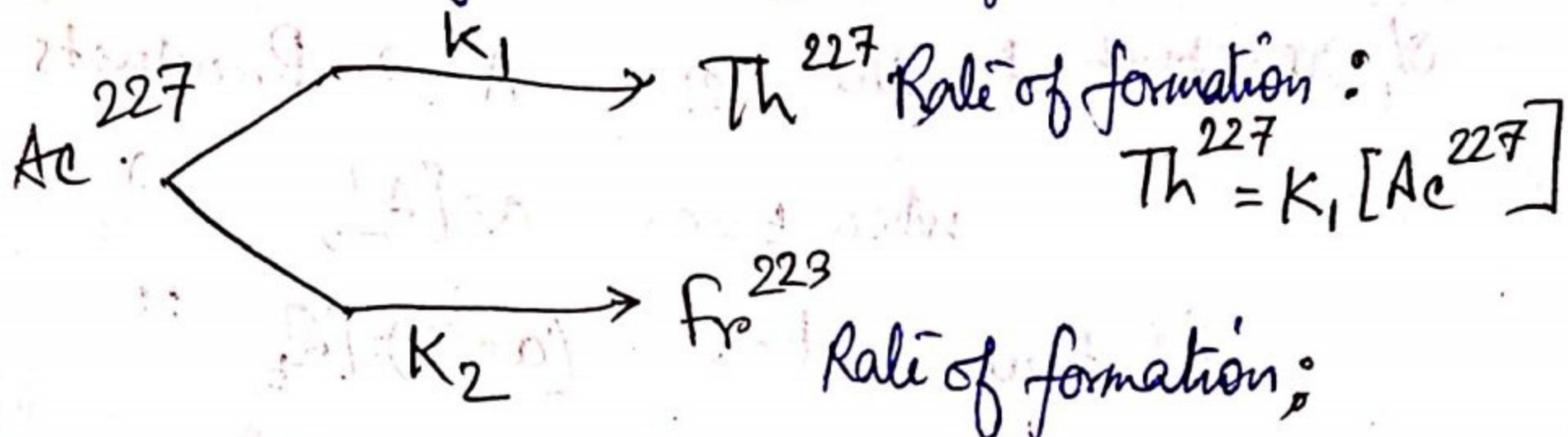
$$\frac{\text{Concentration}}{\text{Second}} = k [\text{concentration}]^n$$

$$\text{unit of } k = (\text{concentration})^{1-n} \text{ second}^{-1}$$

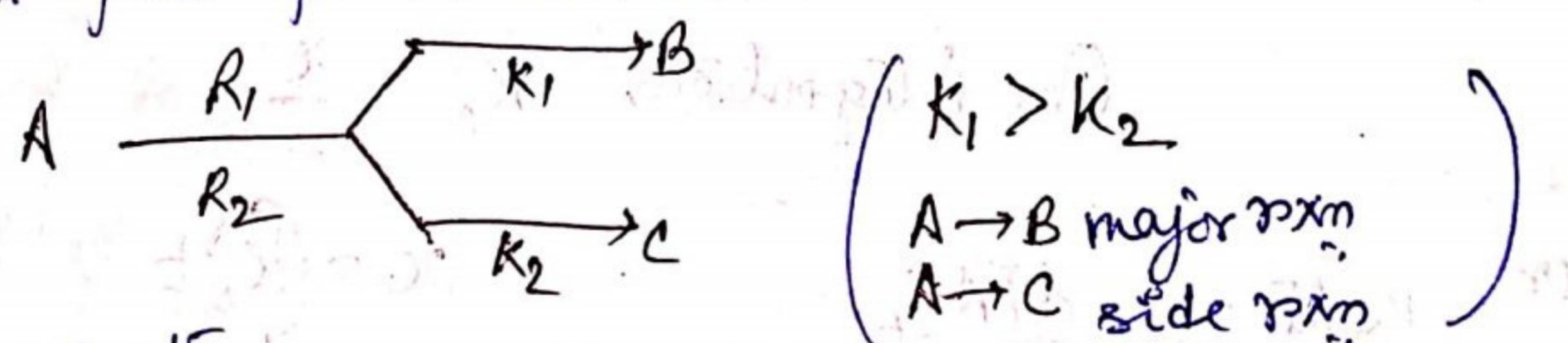
for $n=0$, i.e. for zero order rxn unit of k is

x and y may or may not be equal to a and b .

* Rate law equation involving side rxns or parallel rxns eg:



consider a parallel rxn in which elementary rxns follow first order kinetics



Let the concentration of A at time t is $[A]$ and thus rate

$$R_1 = k_1 [A]_t \quad \text{and} \quad R_2 = k_2 [A]_t$$

and overall rate at which A reacts is $R = -\frac{d[A]}{dt} = R_1 + R_2$
 $= k_1 [A]_t + k_2 [A]_t$

$$R = (k_1 + k_2) [A]_t$$

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

Here k_a = overall rate constant and is equal to sum of rate constants of side rxns (i.e. $k_1 + k_2 + \dots$)

On integration, $\ln \frac{[A]_0}{[A]_t} = k_a \text{arg } t$

$$k_a \text{arg } t = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

$$\text{also } \frac{R_1}{R_2} = \frac{k_1}{k_2}$$

$$\text{and } \frac{d[B]_t}{dt} = k_1[A]_t \text{ and } \frac{d[C]_t}{dt} = k_2[A]_t$$

$$\text{or } \frac{[B]_t}{[C]_t} = \frac{k_1}{k_2}$$

Also $k_1 = \text{Kang} \times \text{fractional yield of } B$

$k_2 = \text{Kang} \times \text{fractional yield of } C.$

Types of Order Rxns :- Zero Order Rxns :-

In a zero order rxn, rate is independent of the concentration of reactant. for the rxn. $A \rightarrow \text{Products.}$

$$\text{when } t=0 \quad a=[A]_0$$

$$\text{At time } t=t \quad (a-x)=[A]_t$$

$$\text{Rate} = \frac{dx}{dt} = K_0 [A]^0 = K_0 (a-x)^0$$

$$\text{On integration, } K_0 = \frac{x}{t}$$

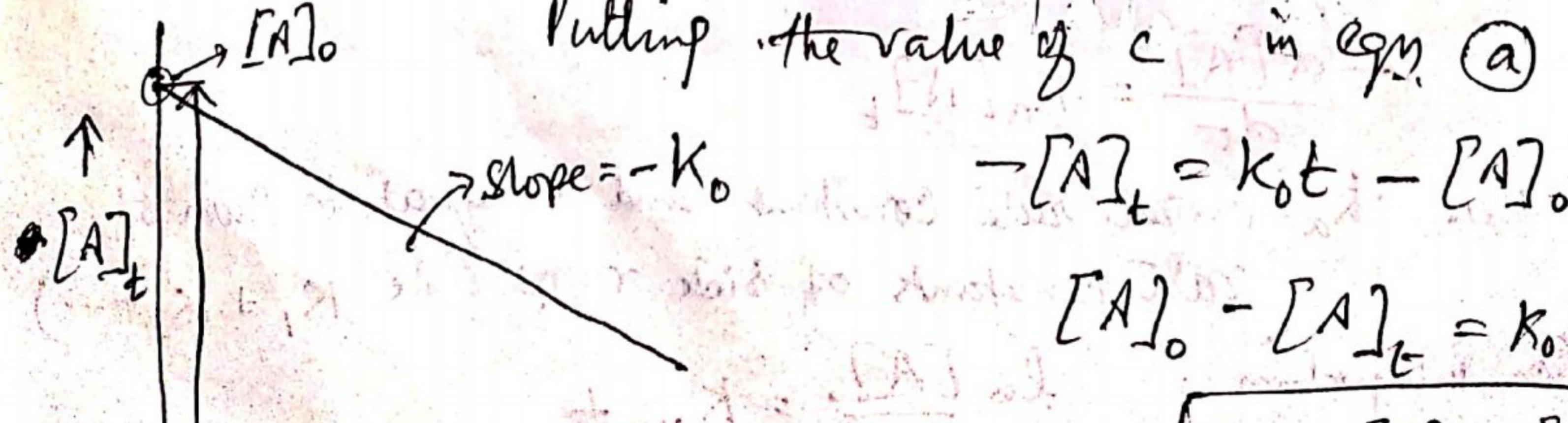
$$\text{or Rate} = -\frac{d[A]_t}{dt} \quad x = K_0 t$$

$$\text{or, } -\frac{d[A]_t}{dt} = K_0 [A]_t \quad \text{has unit concn. time}^{-1}$$

$$\text{On integration, } -[A]_t = k_0 t + C \quad \text{integration constant}$$

$$\text{At } t=0, [A]_t = [A]_0 \text{ then } C = -[A]_0$$

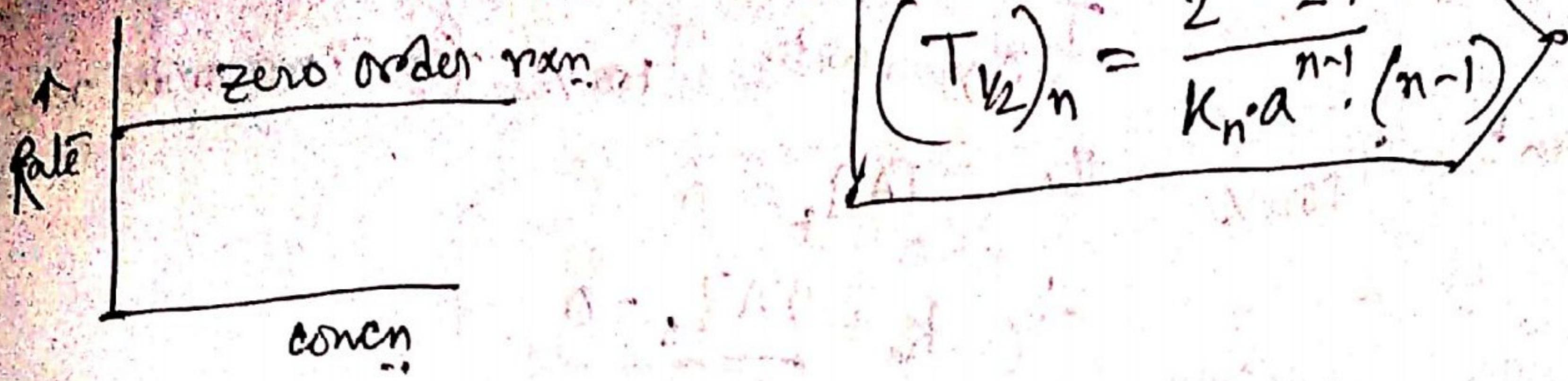
Putting the value of C in eqn. (a) we get



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

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

$$\therefore k_0 = \frac{[A]_0 - [A]_t}{t}$$



Half-life period for zero order rxn

It is the time in which the concentration of a reactant is reduced to one half of its initial concn i.e.

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

n = order of the rxn

$$\text{when } t = t_{1/2}, K_0 = \frac{[A]_0 - \frac{[A]_0}{2}}{t_{1/2}}$$

$$\text{then } [A]_t = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{[A]_0}{2K_0}$$

\therefore half-life period for zero order rxn

dep is directly proportional to the initial concentration of the reactant.

Relation between $T_{50\%}$ (or $t_{1/2}$) = $t_{75\%}$ for a zero order rxn

$$T_{75\%} = \frac{[A]_0 - \frac{[A]_0}{4}}{K_0}$$

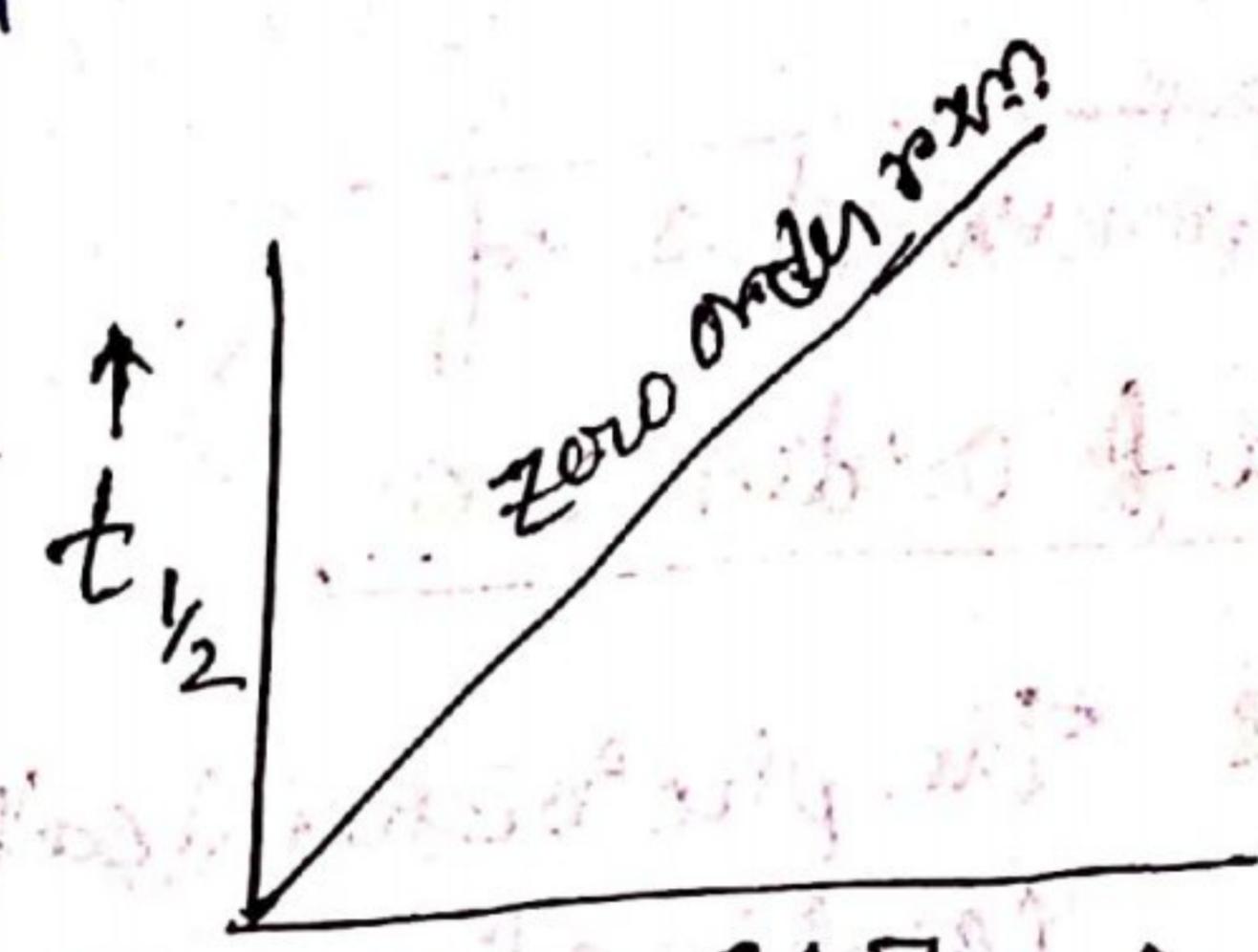
$$\text{when } t = 75\%, [A]_t = \frac{[A]_0}{4}$$

$$T_{75\%} = \frac{3[A]_0}{4K_0}$$

$$\text{Similarly } T_{50\%} = \frac{[A]_0}{2K_0}$$

$$\frac{T_{75\%}}{T_{50\%}} = \frac{\frac{3[A]_0}{4K_0}}{\frac{[A]_0}{2K_0}} = \frac{3}{2}$$

$$\therefore T_{75\%} = 1.5 \times T_{50\%}$$



Relation between $T_{50\%}$ with $T_{100\%}$ for zero order rxn.

When $t = T_{100\%}$, then $[A]_t = 0$

$$\therefore k_0 = \frac{[A]_0 - 0}{t_{100\%}}$$

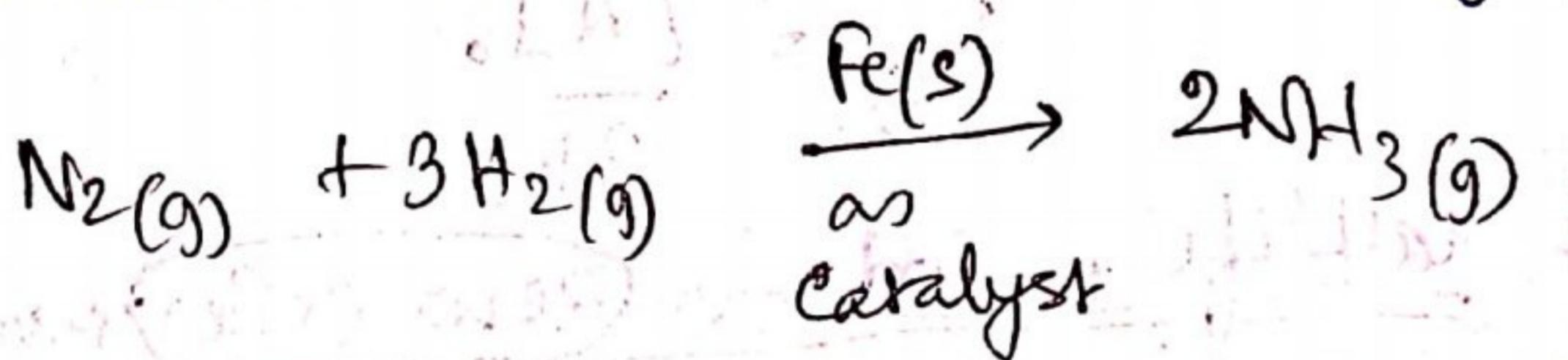
$$t_{100\%} = \frac{[A]_0}{k_0} \quad t_{50\%} = \frac{[A]_0}{2k_0}$$

$$\frac{t_{100\%}}{t_{50\%}} = \frac{\frac{[A]_0}{k_0}}{\frac{[A]_0}{2k_0}} = 2$$

$$\therefore t_{100\%} = 2 \times t_{50\%}$$

Few examples of zero order rxn.

- The photochemical combination of H_2 & Cl_2 i.e. $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$
- Decomposition of ammonia on a hot platinum surface at high pressure.



$$\text{Rate} = \frac{K_1[NH_3]}{1 + K_2[NH_3]} \quad \text{or } K_1 \text{ & } K_2 \text{ are constants}$$

When $[NH_3]$ is very low, $K_2[NH_3]$ can be neglected compared to unity i.e. $1 + K_2[NH_3] \approx 1$

$$\text{then Rate} = K_1[NH_3] \quad \text{i.e. the}$$

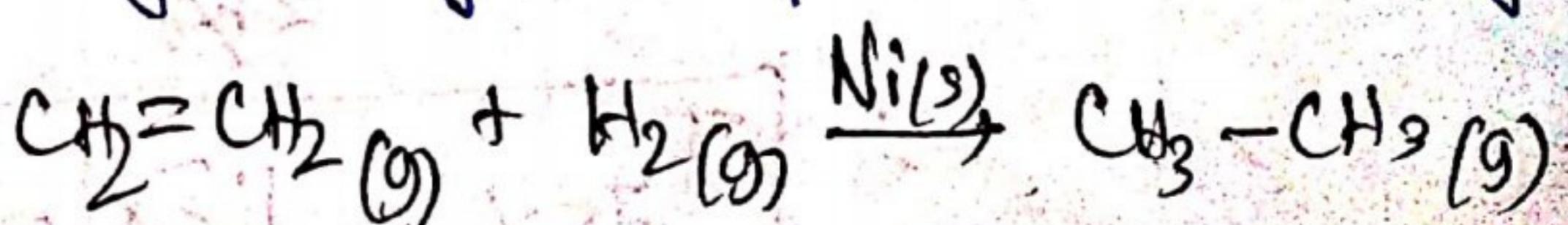
rxn. is first order in ammonia,

At higher concentration of ammonia, $K_2[NH_3] \gg 1$

$$\text{Thus Rate} = \frac{K_1[NH_3]}{K_2[NH_3]} = \frac{K_1}{K_2} = K \text{ (at constant)}$$

i.e. the rxn. is zero order w.r.t. NH_3 .

- Zeroth order rxns generally take place in a heterogeneous system.



1st order Rxn: In the first order rxn, rate is determined by the change of one concentration term only.

for the rxn, $A \rightarrow \text{products}$

At $t=0$, initial concn $a = C_0 = N_0$

At time $t=t$, $(a-x)$

At time $t=t_1$, $(a-x_1)$

At time $t=t_2$, $(a-x_2)$

$$\text{rate} = \left(\frac{dx}{dt} \right) = k_1 [A]_t$$

$$\text{or}, \frac{dx}{dt} = k_1 (a-x)$$

$$\frac{dx}{(a-x)} = k_1 dt$$

On integration

$$\rightarrow \ln(a-x) = k_1 t + C \quad (a)$$

integration constant

When $t=0$,

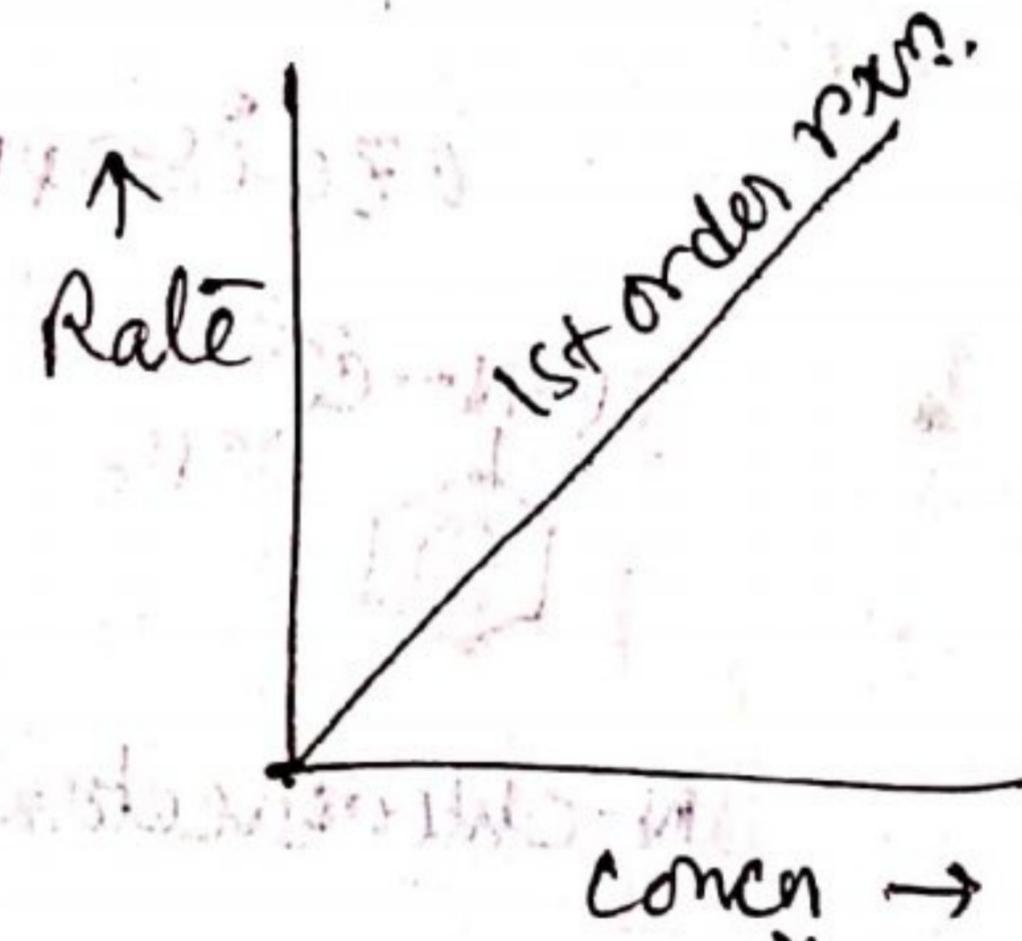
then $\ln(a-x) = 0 \therefore C = \ln a$, putting the value

of C in eqn (a) we get

$$\rightarrow \ln(a-x) = k_1 t - \ln a$$

$$\ln a - \ln(a-x) = k_1 t$$

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



in an alternative way

$$K_1 = \frac{1}{t} \ln \frac{a}{a-x}$$

$$K_1 = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

This is the integral form of 1st order rate constant expression

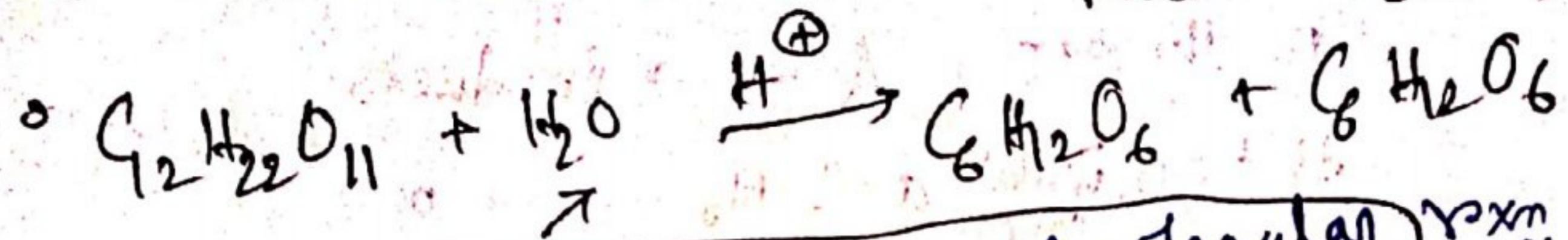
$$-\ln C_0 + \ln C_t = -k_1 t$$

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

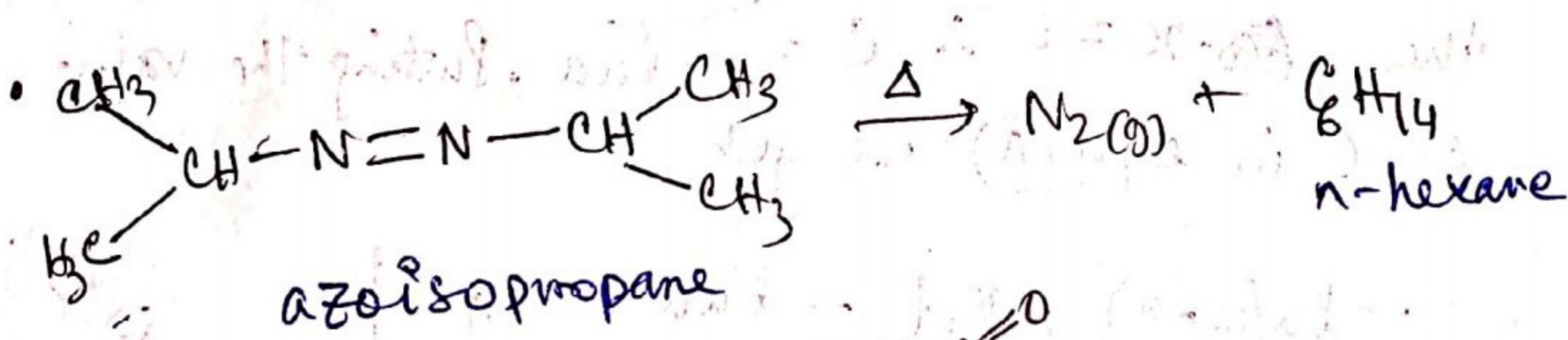
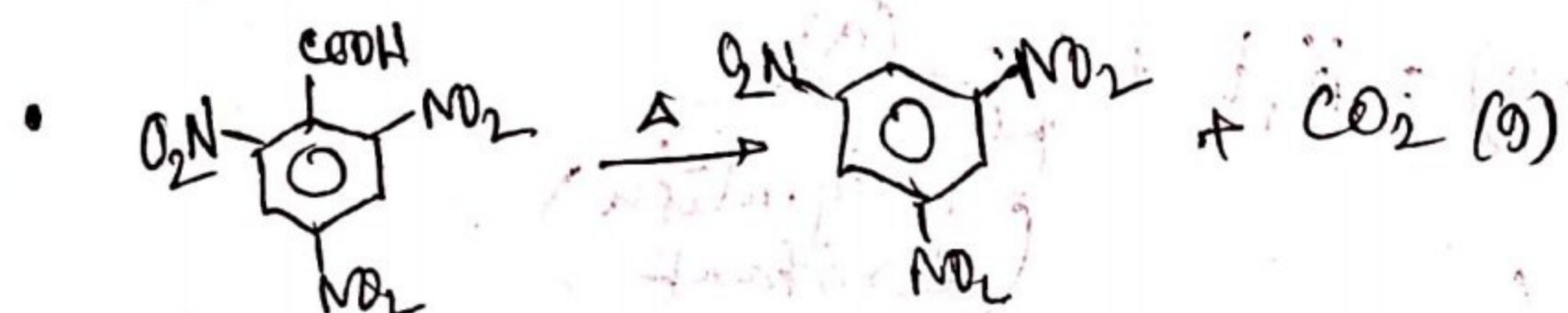
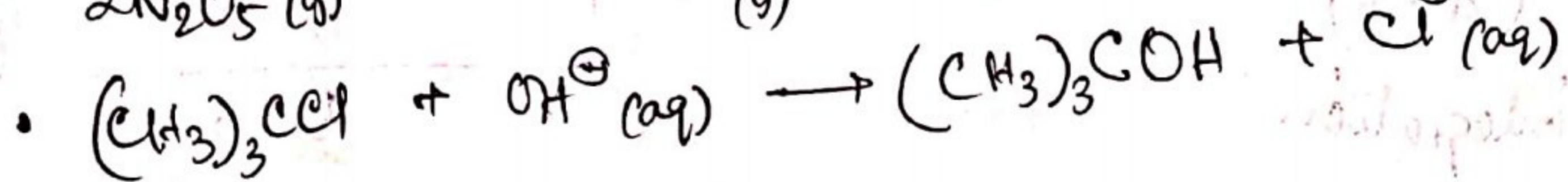
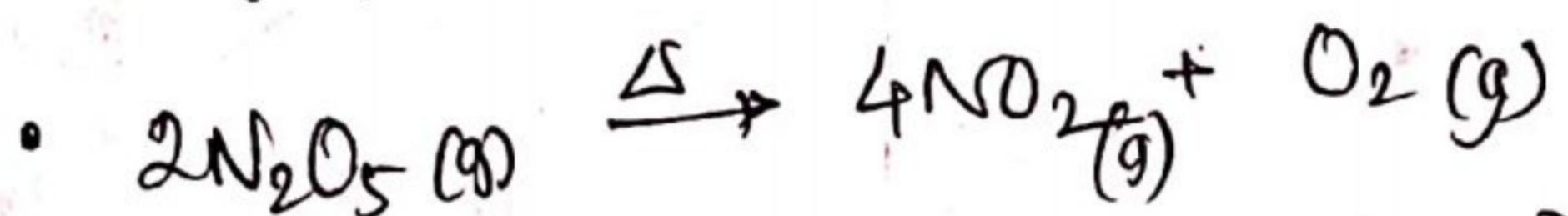
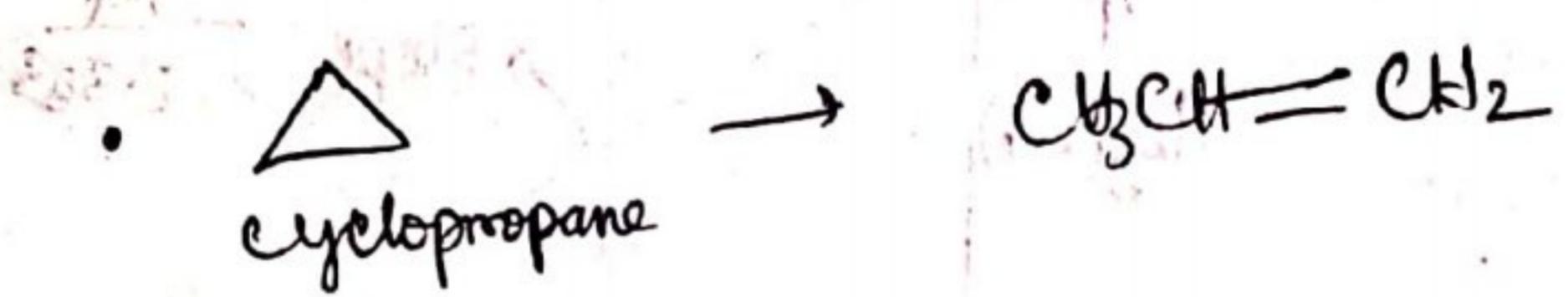
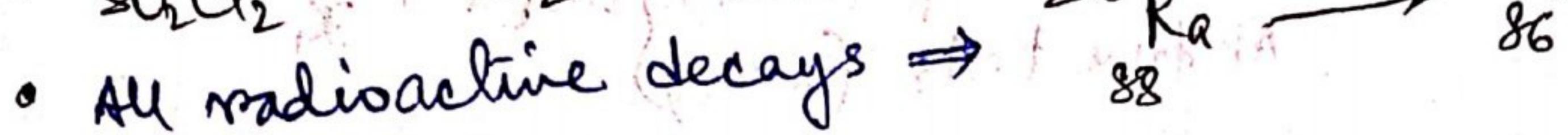
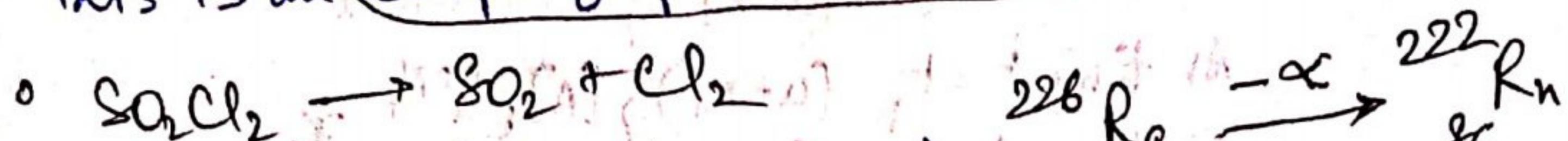
$$C_t = C_0 e^{-k_1 t}$$

$$N_t = N_0 e^{-k_1 t}$$

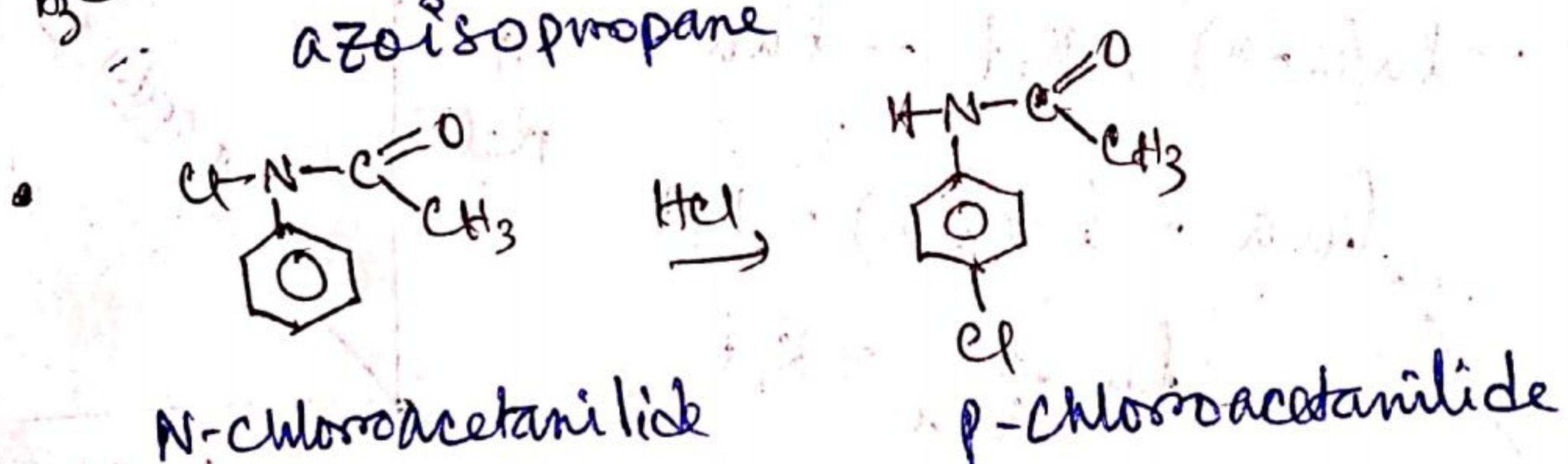
Few Examples of 1st order rxn: $C_2H_6(g) + H_2O \rightarrow C_2H_6(g)$
 Rate = $K[C_2H_6]$



This is an example of pseudounimolecular rxn.

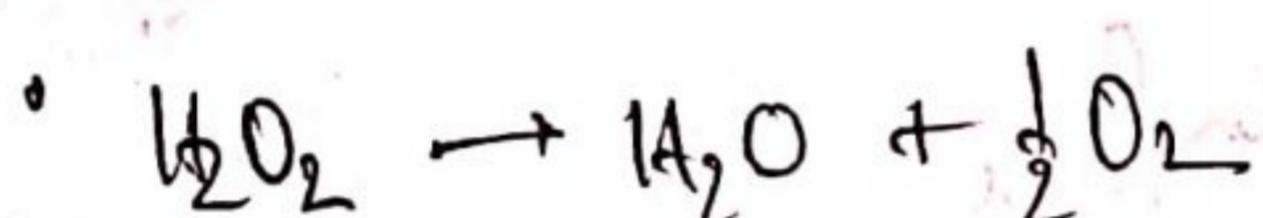


Azoisopropane



N-chloroacetanilide

p-chloroacetanilide



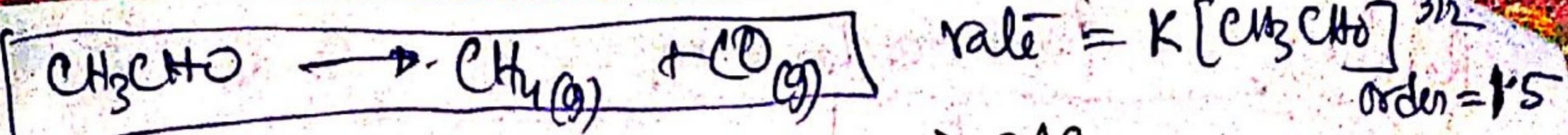
Average T_{avg} = $\frac{1}{k_1}$ of a 1st order rxn,
 life

T_{avg} = $\frac{T_{50\%}}{0.693} = 1.44 T_{50\%}$

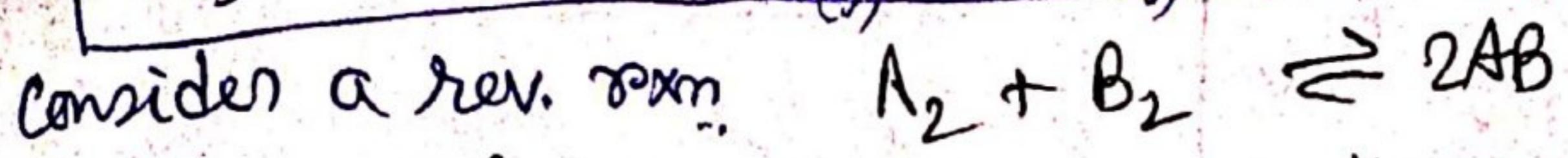
is sometimes referred to as the natural life time of the reactant A decreases to $\frac{1}{2}$ of the original value (say C_0).

$$C_t = C_0 e^{-k_1 t_{avg}} = C_0 e^{-k_1 / k_1}$$

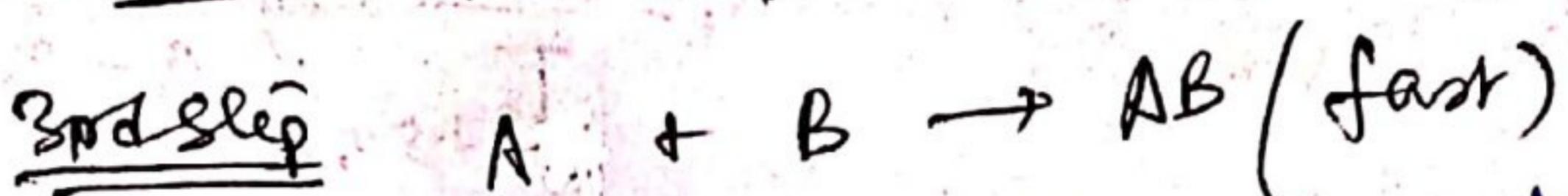
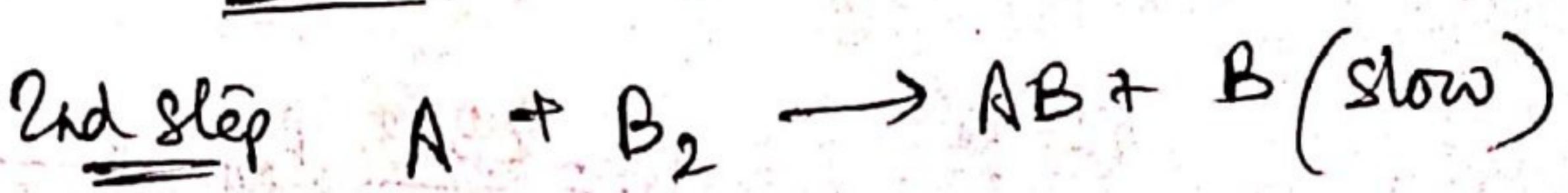
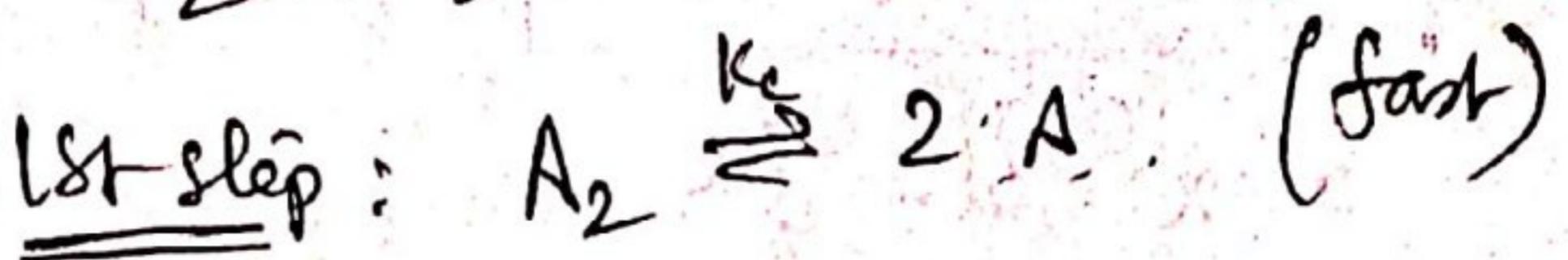
$$C_t = \frac{C_0}{e^{k_1 t}}$$



order = 1.5



Mechanism



Rate law is determined as follows: slowest step is the rate determining

$$\text{step (RDS) thus Rate} = K[A][B_2]$$

Here [A] should be eliminated since it is not the original reactant.

$$K_c = \frac{[A]^{1/2}}{[A_2]} \Rightarrow \text{from the first step,}$$

$$\text{Thus } [A] = K_c^{1/2} [A_2]^{1/2}$$

$$\text{From 2nd step: Rate} = K[A][B_2]$$

$$\text{is a new constant} = (K \cdot K_c)^{1/2} [A_2]^{1/2} \cdot [B_2]$$

$$\text{Rate} = K \cdot [A_2]^{1/2} \cdot [B_2]$$

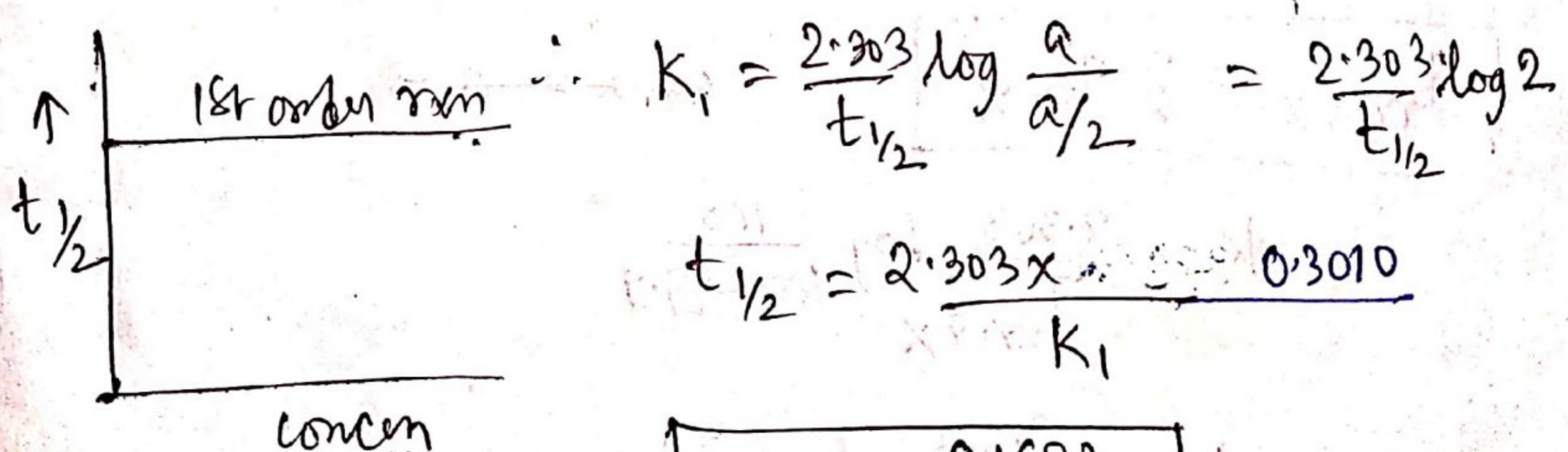
$$\underline{\text{Order}} = 3/2 = 1.5$$

Half life for 1st order

When $t = t_{1/2}$ or T_{50} or $T_{0.5}$ then

$$a - x = a - a/2$$

$$= a/2$$



$$t_{1/2} = \frac{0.693}{K_1}$$

∴ Half life for 1st order rxn is independent of the ~~time~~ Concentration of the reactant.

2nd order Rxns are of 2 types

When $t=0$, initial no. of moles $a \ a \ 0$

After time t , final concn $(a-x) \ (a-x) \ 2x$

$$\frac{dx}{dt} = K_2(a-x)^2$$

$$\int_0^x \frac{da}{(a-x)^2} = \int_0^t k dt$$

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

$$k_2 = \frac{1}{t} \left[\frac{1}{a-x} - \frac{1}{a} \right]$$

$$\text{Also, } k_2 = \frac{1}{(t_2-t_1)} \left[\left(\frac{1}{a-x_2} - \frac{1}{a-x_1} \right) \right]$$

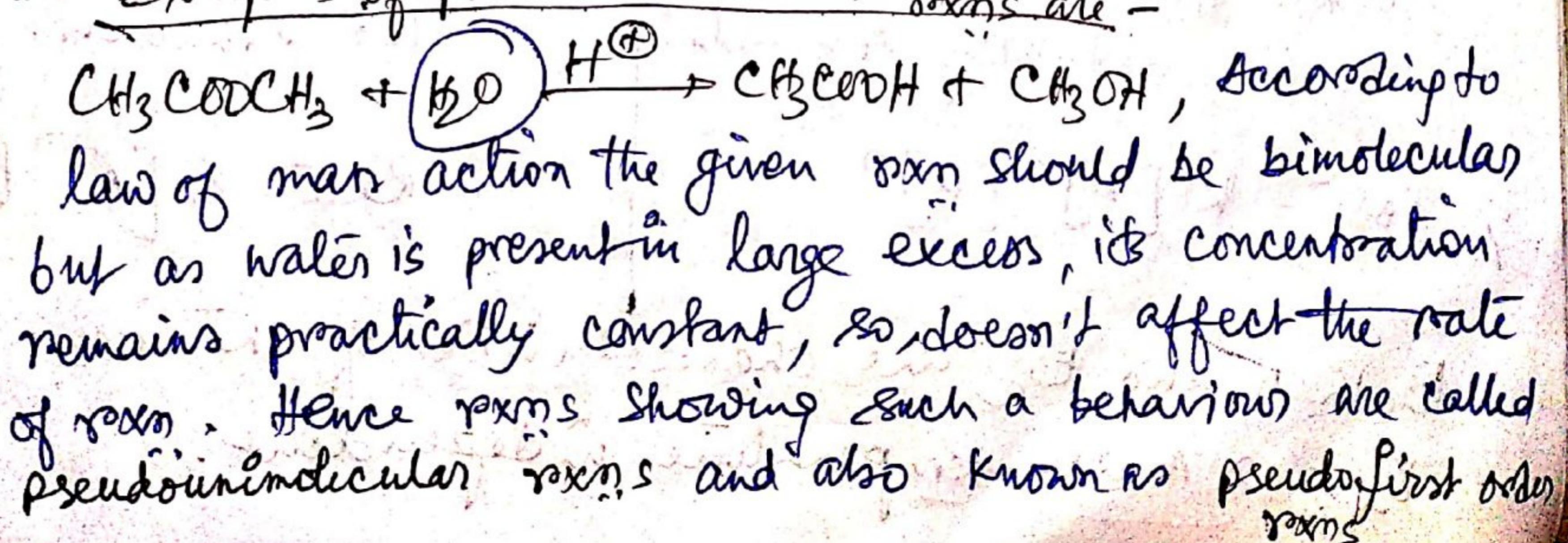
$$\text{or } k_2 = \frac{1}{(t_2-t_1)} \left[\frac{x_2 - x_1}{(a-x_1)(a-x_2)} \right]$$

where $(a-x_1)$ and $(a-x_2)$ are the concn of the reactant A at time t_1 & t_2 respectively.

k' is pseudo 1st order rate constant.

k' will have units of 1st order and K will have units of 2nd order.

■ Examples of pseudounimolecular rxns are -



A + B \rightarrow Products

$a \ b \ 0$

$(a-x) \ (b-x) \ 2x$

$$\text{Rate law is } \left(\frac{da}{dt} \right) = K[A][B] \\ = k(a-x)(b-x)$$

$$\int_0^x \frac{da}{(a-x)(b-x)} = \int_0^t k dt$$

If reactant A and B have different concentration, a and b respectively then

$$K = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

If reactant A is in excess, i.e.

$a \gg b$ then

$$(a-b) \approx a, \\ (a-x) \approx a, \text{ so}$$

that the above eqn reduces to

$$K = \frac{2.303}{at} \log_{10} \frac{b}{(b-x)}$$

$\text{or, } k' = kxa = \frac{2.303}{t} \log_{10} \frac{b}{(b-x)}$

This is the rate constant of the first order rxn. This is an example of pseudo-unimolecular rxn.

Difference between Rate of Rxn & Rate constant of Rxn

Rate of Rxn.

- It is the speed at which the reactants are converted into the products at any moment of time.
- It depends upon the concentration of reactant species at that moment of time.
- It generally decreases with the progress of rxn.

Rate constant of Rxn.

- It is the constant of proportionality in the rate law expression.
- It refers to the rate of the rxn. at the specific point when concentration of every reacting species is unity.
- It is constant and does not depend on the progress of the rxn.

Difference between Rate Law and Law of Mass Action.

Rate Law

- It is an experimentally observed law.
- Depends on the concentration terms on which the rate of reaction actually depends.

$$\text{Rate} = k [A]^a [B]^b$$

Law of Mass Action

- It is a theoretical law.
- Based upon the stoichiometry of the equation.

$$\text{Rate} \propto k [A]^a [B]^b$$

Both A and E_a are characteristics of the rxn.
 E_a and A are temperature independent.

Since rate constant k is inversely proportional to T_{50} at a given concentration, hence —

$$E_a = \frac{2.303 RT T'}{(T' - T)} \log \frac{(T_{50})_T}{(T_{50})_{T'}}$$

The rate of chemical reaction generally increases on increasing the temperature.

Based on K. E. theory of gases, Arrhenius proposed that —

- A chemical reaction takes place due to the collision among reactant molecules. The number of collisions taking place per unit volume of the expn. mixture is known as collision frequency (Z)

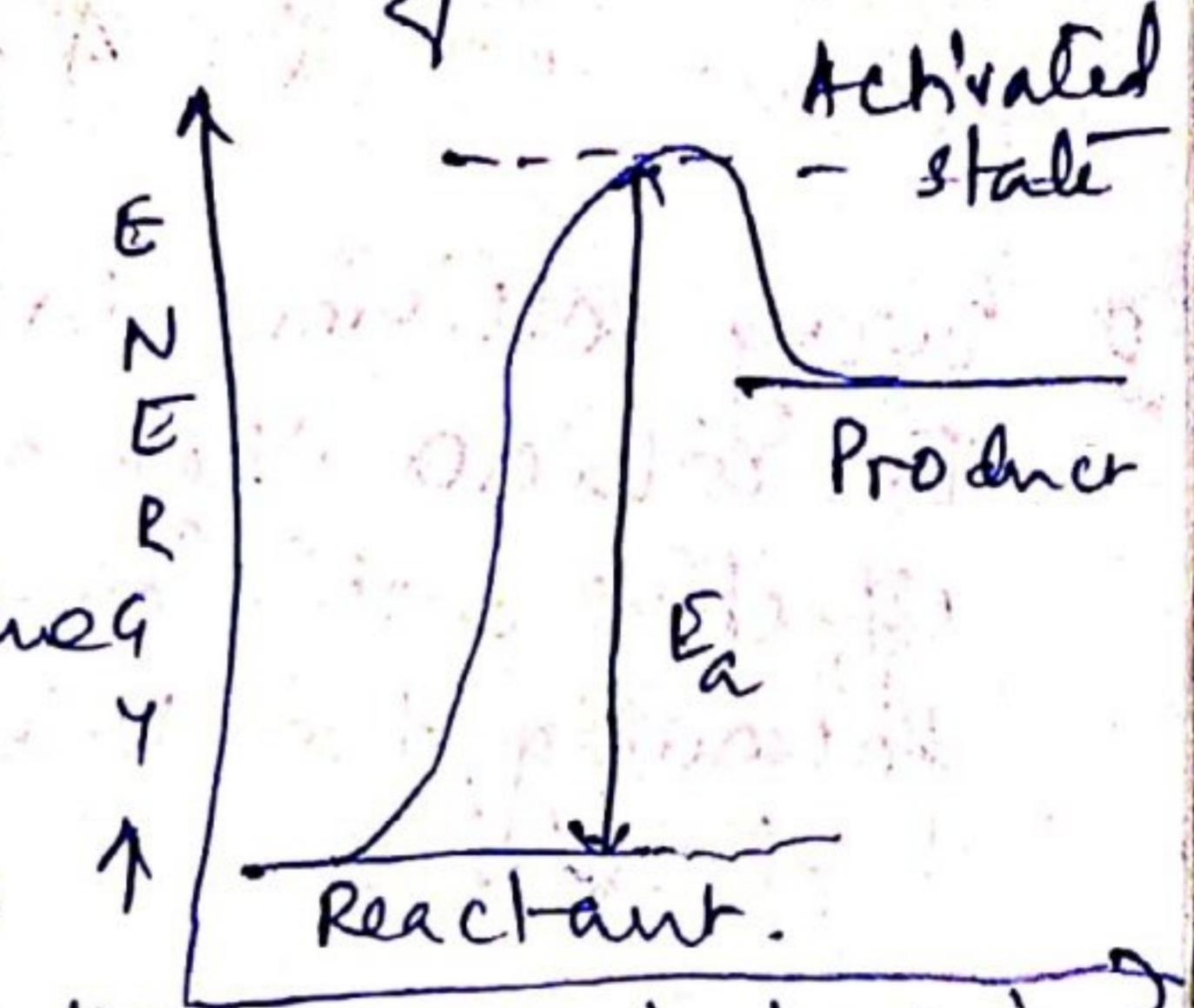
- The fraction of collisions with an energy equal to or greater than the activation energy E_a is represented by f and when E_a is large compared to RT .

$$f = e^{-E_a/RT}$$

The fraction of collisions having proper orientation for conversion of reactants to products is called the steric factor, P .

For the expn. $A + BC \rightarrow AB + C$, the value of P is expected to be about 0.5 because A has a nearly 50:50 probability of colliding with each of the B. and C and of BC. For trans of complex molecules, P is a fraction considerably less than 0.5. For bimolecular expn.

Collision rate = $Z [A][B]$ where, Z is a constant related to collision frequency (in the unit of $M^{-1} s^{-1}$)



Reaction rate $\propto p \times f \times \text{collision rate}$

$$= Pf^2 [A][B]$$

$$\text{Thus, rate constant } K_r = Pf^2 = P^2 e^{-E_a/RT}$$

where $P^2 = A$

$$\therefore K_r = A e^{-E_a/RT}$$

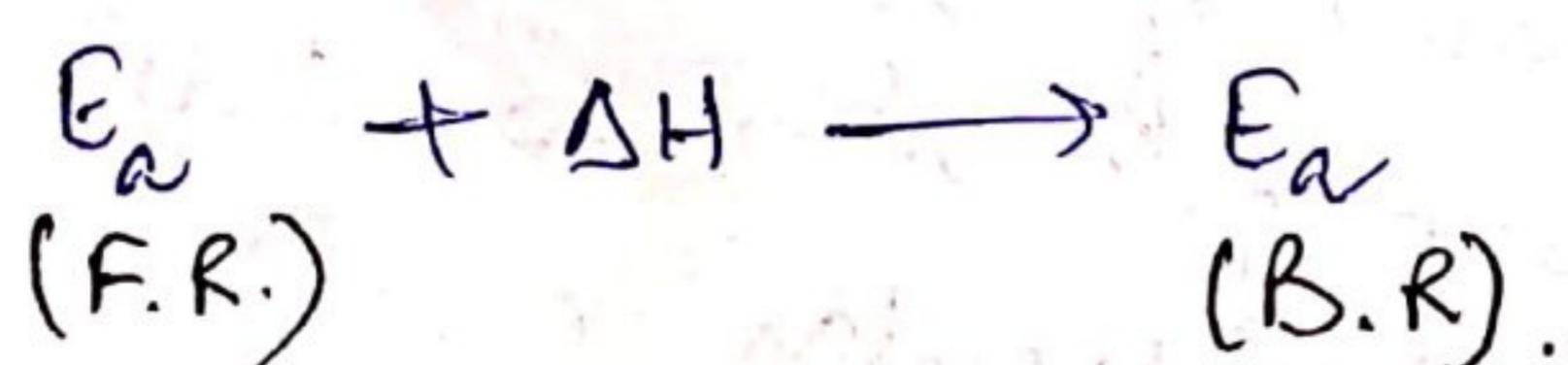
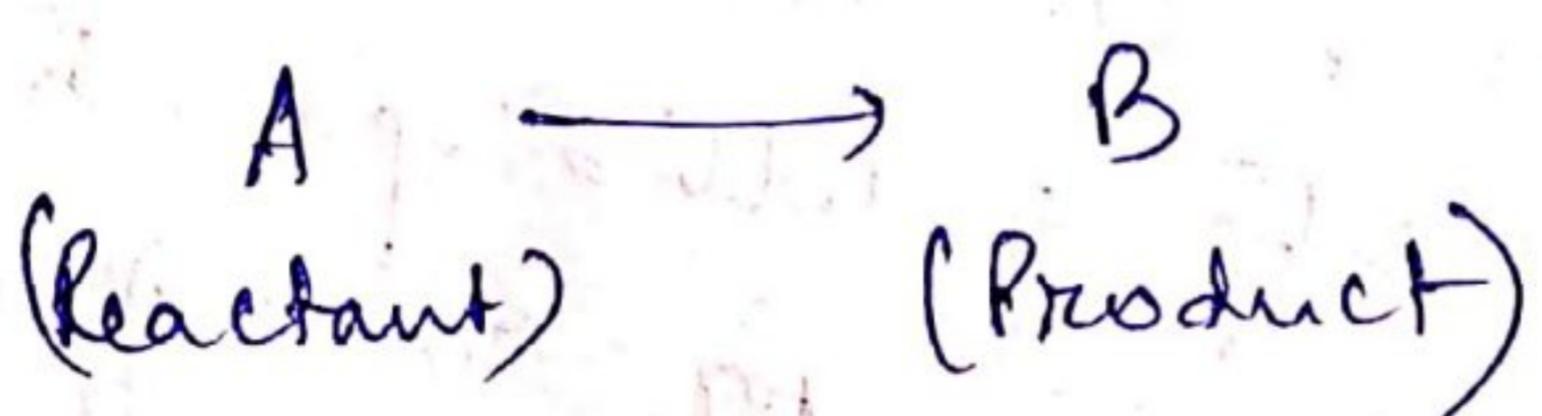
Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be effective to be cleared:

→ Energy barriers: The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur is known as Threshold energy.

The minimum amount of energy required by the reactant molecules to participate in a reaction is called Activation energy (E_a).

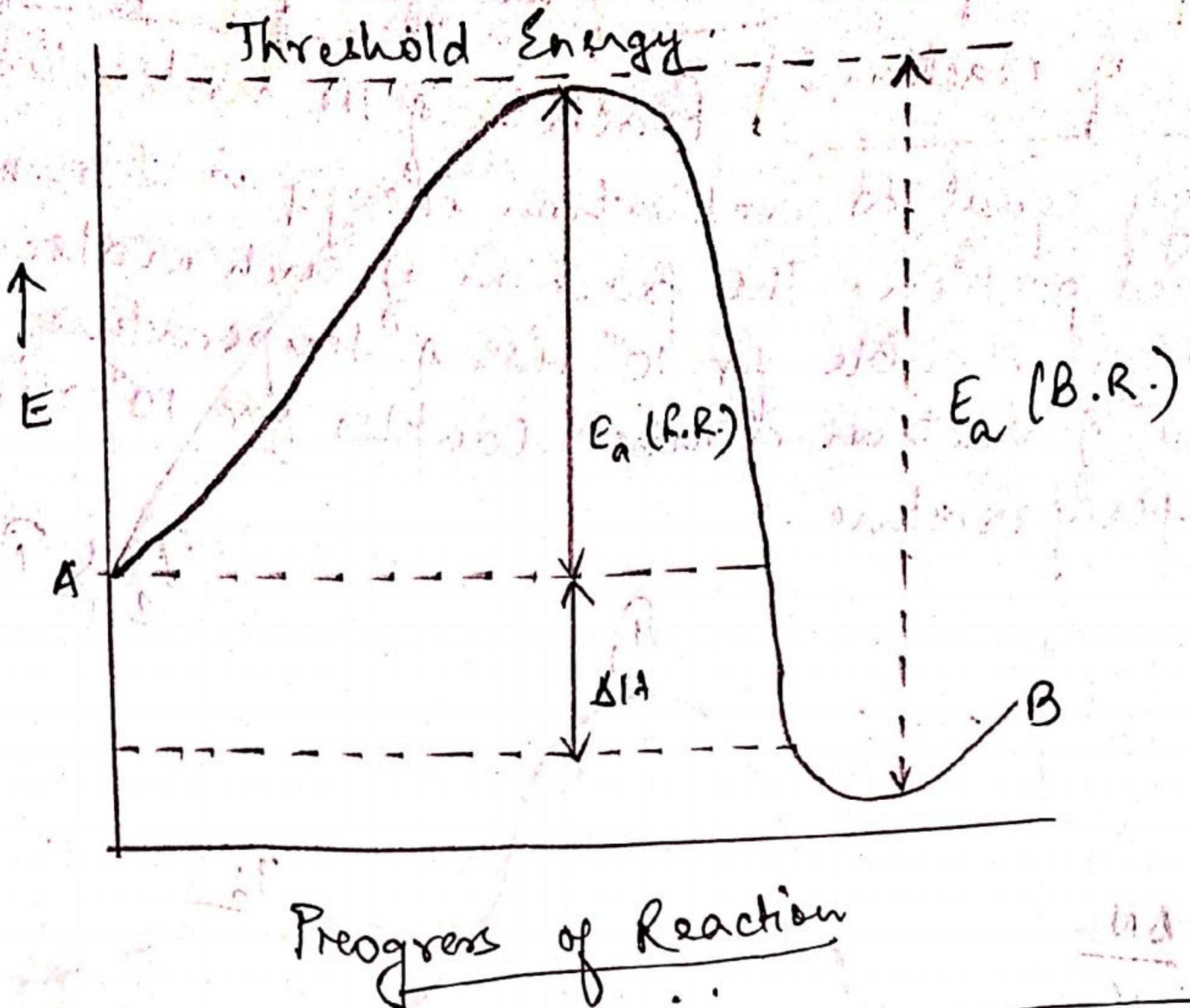
Orientation barriers: Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make a collision effective.

Graphical Representation of Exothermic Rxn:

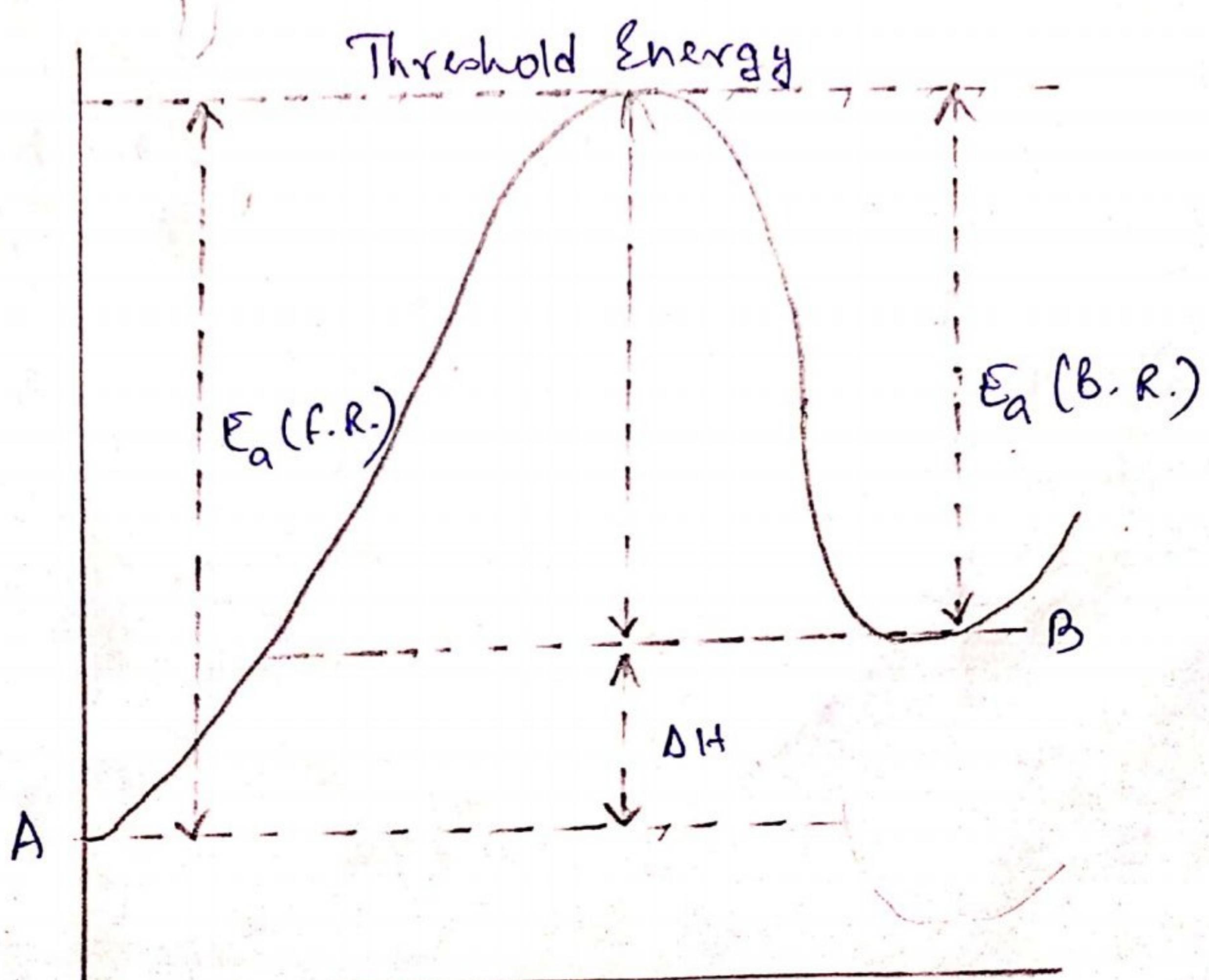
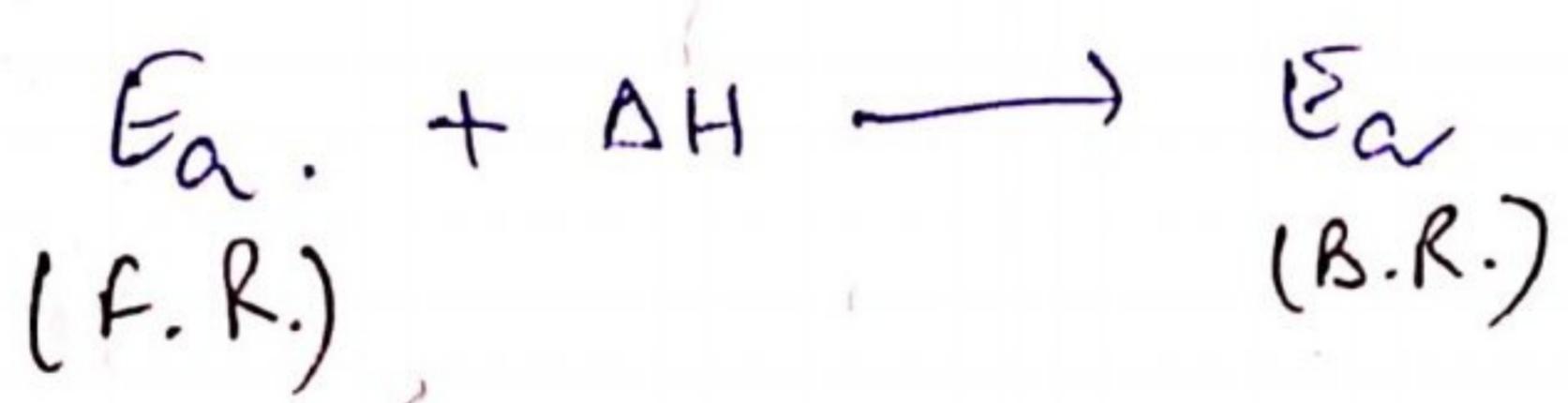
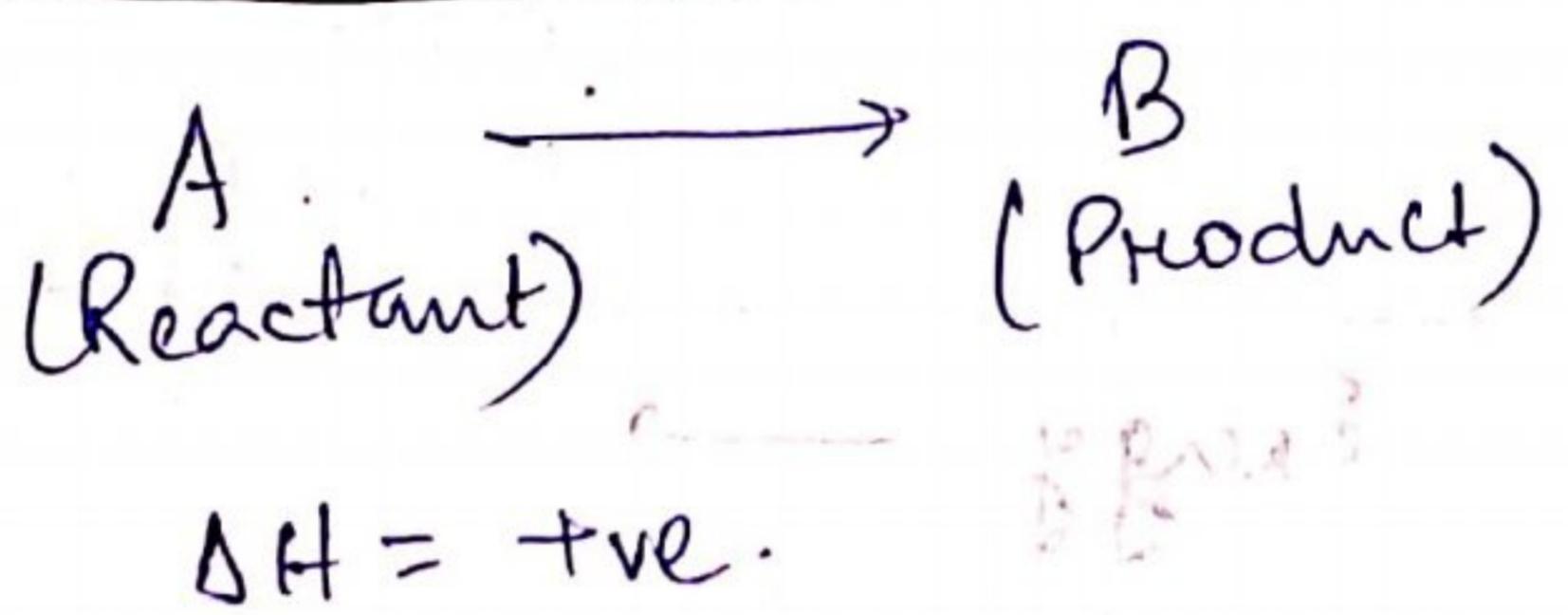


where F.R. is forward Reaction, &
B.R. is backward Reaction.

$$\Delta H = -ve$$



Graphical Representation of Endothermic Reactions



Progress of Reaction.

Graphical representation of the effect of temperature on rate of reaction:

Fraction of the molecules having energy equal to activation energy is shown by the shaded portion. The fraction of such molecules become almost double for 10° rise of temperature and the rate of reaction almost doubles for 10° rise of temperature.

$$T_2 > T_1$$

