

★ Calculation for order of the reaction.

there are following methods to calculate order of reaction.

1) Method of integration (hit and trial)

We have experimental data \rightarrow time & concentration.

Time	t_0	t_1	t_2	t_3	t_n
concentration.	c_0	c_1	c_2	c_3	c_n

a) let

$$\text{zero order : } K = \frac{c_0 - c_t}{\Delta t}$$

\Rightarrow If K is constant from data
it is zero order

\Rightarrow If K is not constant then go for first order.

b) let

$$\text{First order : } K = \frac{2.303}{t} \log \left(\frac{c_0}{c_t} \right)$$

\Rightarrow If K is constant from data then
it is first order

\Rightarrow if K is not constant then go
for second order ...

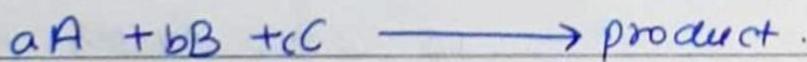
and so on.

2. Graphical Method.

Time	0	t_1	t_2	t_3	t_n
Conc.	c_0	c_1	c_2	c_3	c_n

make graph of concentration Vs time from given data. and compare with standard and to concentration Vs time curves.

3. Experimental method. (initial rate law method)



$$\text{rate} = k (c_A)^x (c_B)^y (c_C)^z$$

$$[A_0] \quad [B_0] \quad [C_0] \quad \text{initial rate.}$$

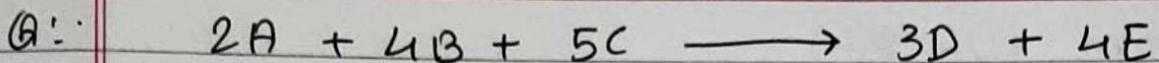
$$\text{Ex. 1} \quad a_1 \quad b_1 \quad c_1 \quad r_1 = k a_1^x b_1^y c_1^z$$

$$\text{Ex. 2} \quad a_2 \quad b_2 \quad c_2 \quad r_2 = k a_2^x b_2^y c_2^z$$

$$\text{Ex. 3} \quad a_3 \quad b_3 \quad c_3 \quad r_3 = k a_3^x b_3^y c_3^z$$

$$\text{Ex. 4} \quad a_4 \quad b_4 \quad c_4 \quad r_4 = k a_4^x b_4^y c_4^z$$

we have four eqⁿ and four unknown we can solve for x, y, z & k.



From following experimental data.

	$[\text{A}]_0$ (M)	$[\text{B}]_0$ (M)	$[\text{C}]_0$ (M)	initial rate (M sec $^{-1}$)
Ex. 1	0.02	0.02	0.02	$4 \times 10^{-3} = k a_1^x b_1^y c_1^z$
Ex. 2	0.01	0.02	0.02	$4 \times 10^{-3} = k a_2^x b_2^y c_2^z$
Ex. 3	0.02	0.04	0.02	$16 \times 10^{-3} = k a_3^x b_3^y c_3^z$
Ex. 4	0.02	0.02	0.04	$2 \times 10^{-3} = k a_4^x b_4^y c_4^z$

Calculate:

- 1) Order of the reaction w.r.t A, B, C as well as overall order of the reaction.
- 2) Specific reaction rate.
- 3) initial rate when ^{initial} concentration of each reactant was 0.01 M.
- 4) Calculate rate of disappearance of A, B, C and rate of appearance of D & E for 3rd question.

Soln: 1) from ①/② ③

$$\frac{4 \times 10^{-3}}{4 \times 10^{-3}} = \frac{k (0.02)^x \cdot (0.02)^y \cdot (0.02)^z}{k (0.01)^x \cdot (0.02)^y \cdot (0.02)^z}$$

$$\therefore \left(\frac{0.02}{0.01}\right)^x = 1$$

$$\Rightarrow x = 0$$

From ① & ③

$$y = 2$$

from ① & ④

$$z = -1$$

$$\begin{aligned}\text{∴ overall order} &= x + y + z \\ &= 0 + 2 - 1 \\ &= 1\end{aligned}$$

2) Specific reaction rate = k .

$$\therefore 4 \times 10^{-3} = k(0.02)^0 \cdot (0.02)^2 \cdot (0.02)^{-1}$$

$$\therefore 4 \times 10^{-3} = k(0.02)$$

$$\frac{4}{2} \times 10^{-1} = k$$

$$\therefore [k = 0.2 \text{ sec}^{-1}]$$

$$\therefore [k = 0.2 \text{ sec}^{-1}]$$

3) $\gamma = k (0.01)^0 (0.01)^2 (0.01)^{-1}$

$$\gamma = 0.2 \times 0.01$$

$$\gamma = 2 \times 10^{-3} \text{ M} \cdot \text{sec}^{-1}$$

4) $\frac{\gamma_A}{2} = \frac{\gamma_B}{4} = \frac{\gamma_C}{5} = \frac{\gamma_D}{3} = \frac{\gamma_E}{4} = 2 \times 10^{-3}$

4. Half life method.

$$t_{1/2} \propto C_0^{1-n}$$

$$\frac{(t_{1/2})_I}{(t_{1/2})_{II}} = \left[\frac{(C_0)_I}{(C_0)_{II}} \right]^{1-n}$$

From this method we can calculate overall order of the reaction.

a: Student have following experimental data.

initial concentration	10 M	5 M	2.5 M	20 M
half life	20 min	19.9 min	20.1 min	20 min.

$$\textcircled{1} \cdot \frac{20}{20} = \left(\frac{10}{20} \right)^{1-n}$$

$$\Rightarrow \boxed{n=1}$$

b: calculate order of the reaction from following data.

conc.	10 M	5 M
Half life	2 min	4 min.

~~$$\left(\frac{10}{5} \right) = \left(\frac{\cancel{2}10}{\cancel{2}5} \right)^{1-n}$$~~

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

~~$$\Rightarrow \boxed{n=2}$$~~

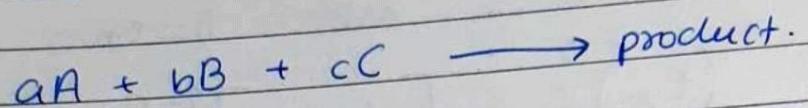
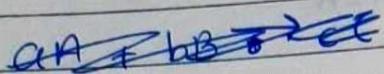
$$\frac{2}{4} = \left(\frac{10}{5} \right)^{1-n}$$

$$2^{-1} = 2^{(1-n)}$$

$$\Rightarrow n = 2.$$

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5. Ostwald isolation method.



rate :- $K (C_A)^x (C_B)^y (C_C)^z$

Note for the calculation of order w.r.t to
any reactant.
make other reactant in excess amount.

Note:

$$\log \theta = \frac{E_a}{2.303 R} \times \frac{10}{T(T+10)}$$

Q:

$$\# \boxed{\frac{K_2}{K_1} = \theta^{\frac{(T_2 - T_1)}{10}}}$$

if concentration
is kept same.

★ Temperature effect :-

Temperature coefficient (θ)

it is the ratio of ratio of rate constants at different temperature where Temperature difference is 10°C .

$$\theta = \frac{K_{T+10}}{K_T} \quad T \text{ in } {}^\circ\text{C.}$$

e.g.: $\frac{K_{35}}{K_{25}} = \theta$

$\therefore K_2 = K_1 (\theta)^{\frac{(T_2 - T_1)}{10}}$

$$\frac{K_{35}}{K_{28}} \neq \theta$$

temperature coefficient can take values from $\theta \in [2, 3]$

- a: For a reaction rate constant at 25°C was $4 \times 10^{-3} \text{ sec}^{-1}$ calculate rate constant at 55°C . if temperature coefficient (θ) = 2.

$$\frac{K_{55}}{K_{25}} = (\theta)^3$$

~~$4 \times 10^{-3} \times 2^3 = 32 \times 10^{-3}$~~

$$\boxed{K_{55} = 8 \times 4 \times 10^{-3}}$$

$$\boxed{K_{55} = 32 \times 10^{-3} \text{ sec}^{-1}}$$

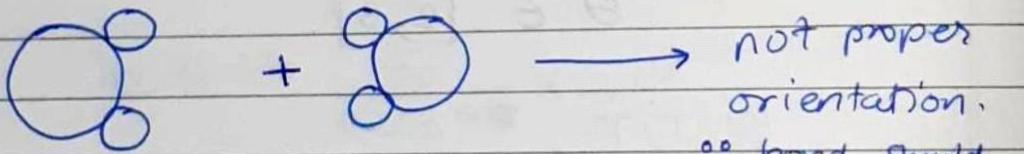
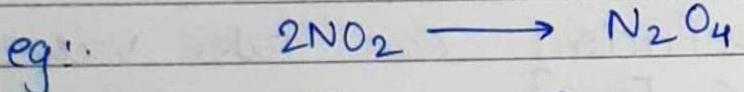
★ Arrehenius theory :-

during any chemical reaction there will be ~~as~~ collision b/w reactant molecules and product molecules. during collisions bonds will break between reactant molecules and bonds will form for product molecules.

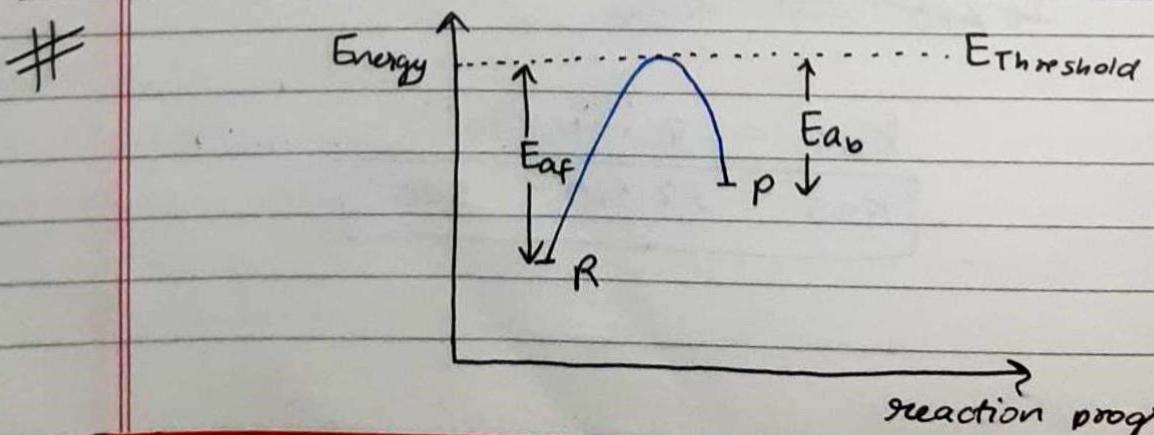
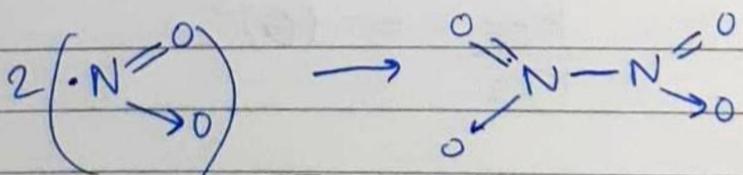
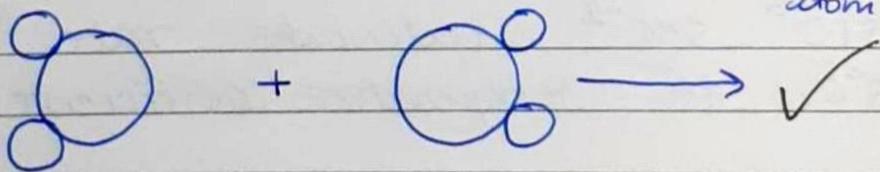
All the collisions are not effective collisions.

For effective collision it should have proper orientation and a fixed amount of energy or more.

activation energy.



∴ bond should form b/w N-N atom.



Note:- In some free radical reactions
the activation energy is zero.

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$E_{af} \rightarrow$ activation energy in forward direction.

$E_{ab} \rightarrow$ activation energy in backward direction.

$E_{th} \rightarrow$ threshold energy

From Maxwell distribution curve, $e^{-\frac{E_a}{RT}}$ are fraction of molecules having effective collision.

∴ rate $\propto e^{-\frac{E_a}{RT}}$

rate $\propto (\text{concentration})^n$

rate $\propto A$ (orientation)

∴ $K = A e^{-\frac{E_a}{RT}}$

$K \rightarrow$ rate constant.

$A \rightarrow$ pre-exponential factor/
frequency factor (will provide
information about orientation)

$E_a \rightarrow$ activation energy.

$T \rightarrow$ Temp. (in K)

$R \rightarrow 8.31 \text{ J/mol K}$.

$n \rightarrow$ overall order of reaction

$$\text{rate} = A e^{-\frac{E_a}{RT}} (\text{concentration})^n$$

$$\begin{aligned} T_1 \longrightarrow K_1 &= A e^{-\frac{E_a}{RT_1}} \\ T_2 \longrightarrow K_2 &= A e^{-\frac{E_a}{RT_2}} \end{aligned}$$

$\therefore \#$

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

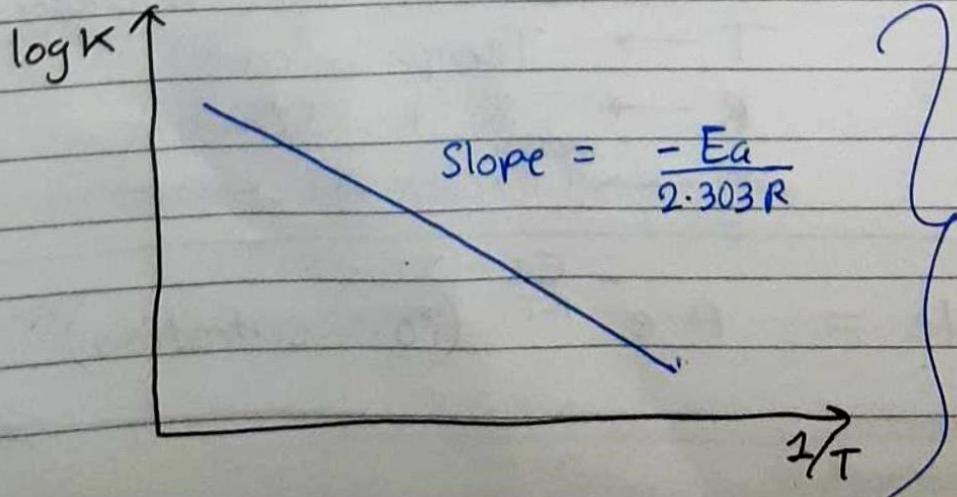
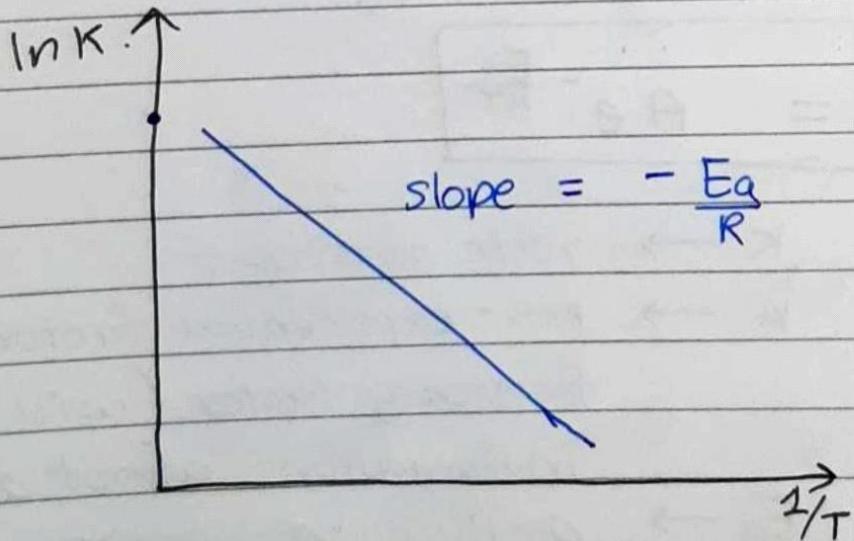
$$K = A e^{-\frac{E_a}{RT}}$$

$\therefore \#$

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

$\therefore \#$

$$\log K = \log A - \frac{E_a}{2.303 RT}$$



Q: for a reaction temperature coefficient was 3 for reaction at 27°C to 37°C what will be activation energy for the reaction.

$$\log\left(\frac{K_{37}}{K_{27}}\right) = \frac{E_a}{2.303 R} \left[\frac{1}{27} - \frac{1}{37} \right]$$

$$\log(3) = \frac{E_a}{2.303 R} \frac{10}{27 \times 37}$$

$$\begin{aligned} \therefore E_a &= \frac{\log(3) \times 2.303 \times 8.31 \times 27 \times 37}{10} \\ &= \frac{0.48 \times 2.3 \times 8.31 \times 999}{10} \\ &= 48 \times 2.3 \times 8.31 \\ &= \frac{0.48 \times 19.113 \times 999}{10} \\ &= \frac{9.168 \times 999}{10} \\ &= 915.8832 \text{ J} \end{aligned}$$

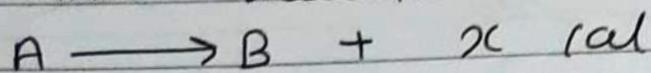
wrong

$\because T$ is in $^{\circ}\text{C}$
it should be in ' K '.

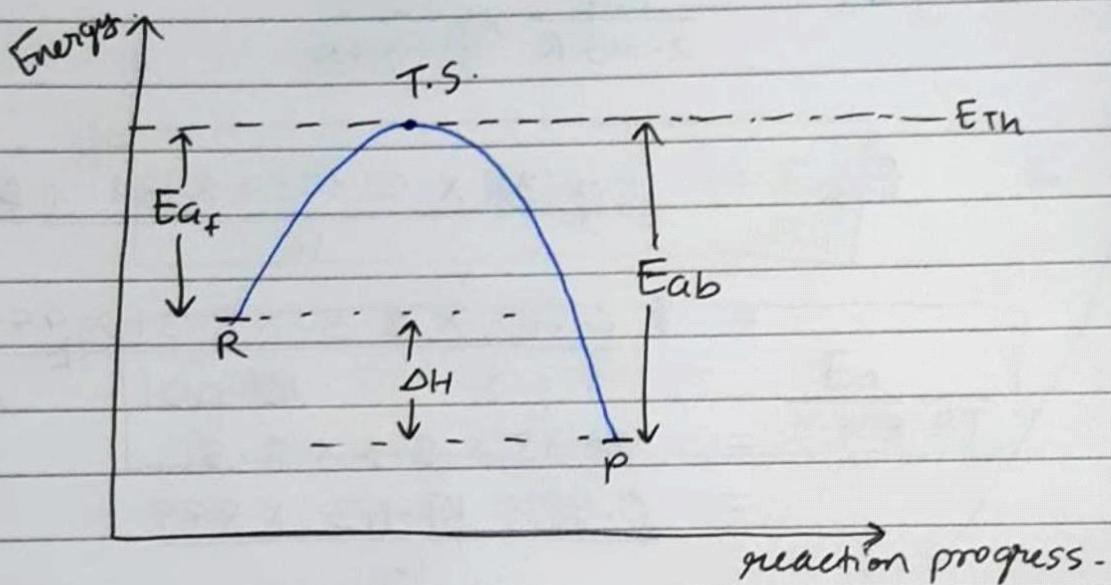
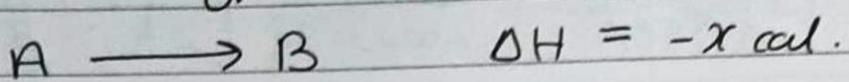
$$\therefore E_a = \log 3 \times 2.303 \times 8.31 \times$$

There are two type of chemical reaction.

1) exothermic reaction.

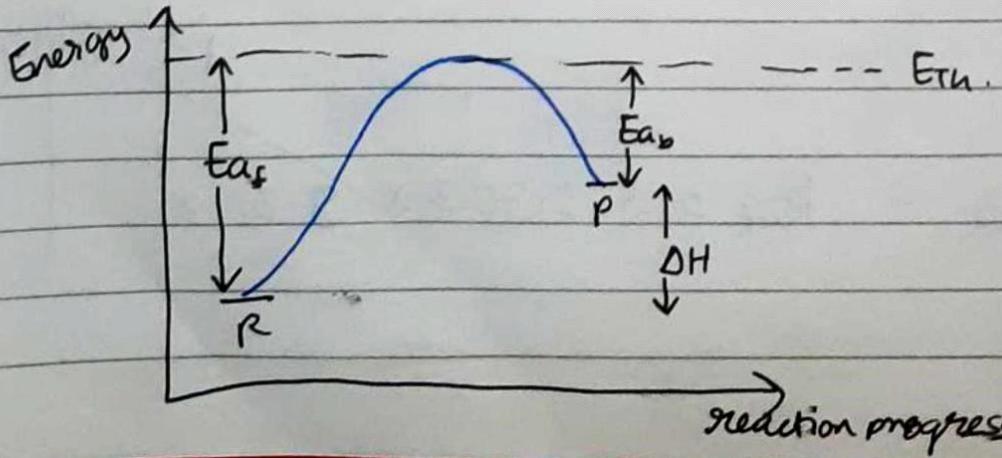
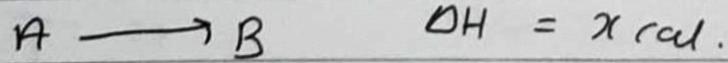
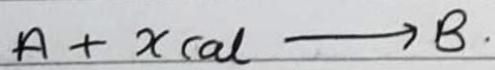


or



$$\therefore E_{a,b} = E_{a,f} + |\Delta H|$$

2) Endothermic reaction.



molecularity $\in \{1, 2, 3\}$
 ↓
 no. of reacting particle colliding
 at a time.

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$$\therefore E_{af} = E_{ab} + |\Delta H|$$

Q8. For a reaction $A \rightarrow B$ $\Delta H = -60 \text{ Kcal}$
 if $E_{af} = 200 \text{ Kcal}$. what will be E_{ab} ?

$$\begin{aligned} E_{ab} &= E_{af} + |\Delta H| \\ &= 200 + 60 \\ &= \underline{\underline{260}} \text{ Kcal.} \end{aligned}$$

★ There are two types of chemical reaction.

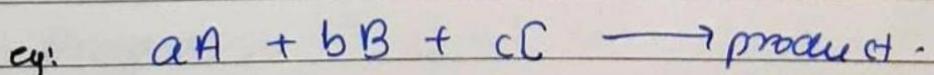
I Single step or simple reaction or elementary reaction.

→ it will occur in single step.

→ there will be no intermediate formed.

Molecularity :- it is sum of stoichiometric coefficients of reactant for any reaction.
 it can't be ~~fraction~~ negative or zero.

$$\therefore \text{molecularity } \in I^+ = \{1, 2, 3\}$$



molecularity or $a+b+c$

molecularity of reaction can't be more than 3 because molecularity is number of reacting

molecules colliding at a time.

For single step reaction molecularity and order will be same.

For ex 1 $A + B \longrightarrow$ product is

single step reaction
then what is the order of reaction.

$$\text{order} = \text{molecularity} = 1+1 = 2$$

$$\therefore \text{rate} = K(C_A)^1(C_B)^1$$

ex. 2. $2A \longrightarrow$ product.

$$\text{order} = \text{molecularity} = 2$$

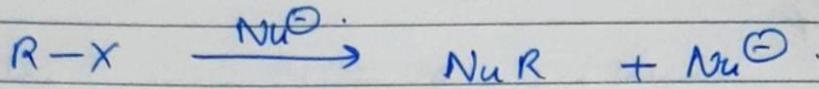
$$\therefore \text{rate} = K(C_A)^2$$

eg. 3. $2A + 3B \longrightarrow$ product } by multiplying
2 in eg 2.

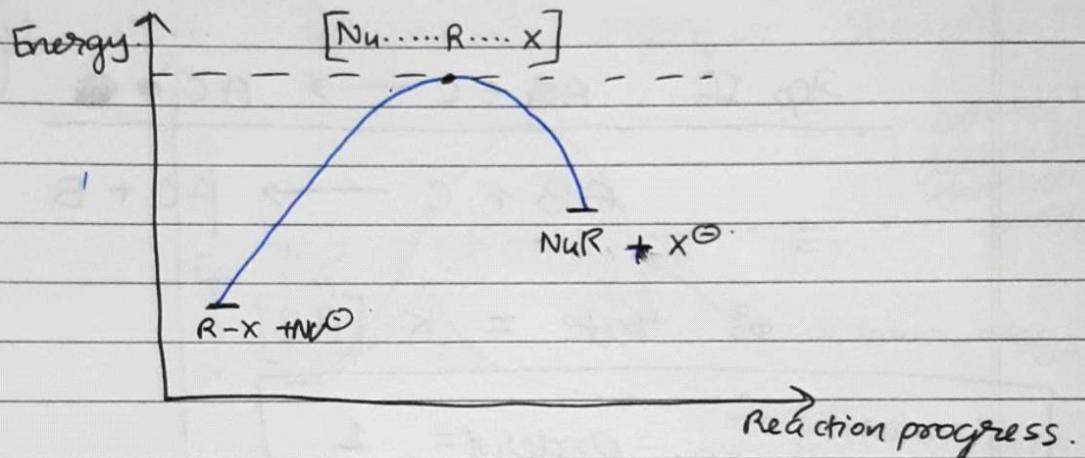
$$\text{order} = \text{molecularity} \neq 2+2 = 4$$

Note: → ∵ we can't multiply or divide any single step reaction by any number.

• eg: SN^2 .



$$\text{rate} = k [Rx] [Nu^-]$$



here molecularity = ~~order~~ = 2

\therefore it is single step / elementary reaction / simple reaction.

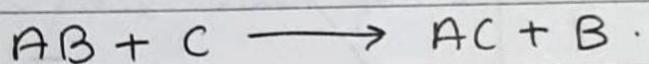
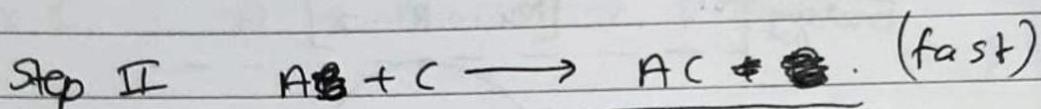
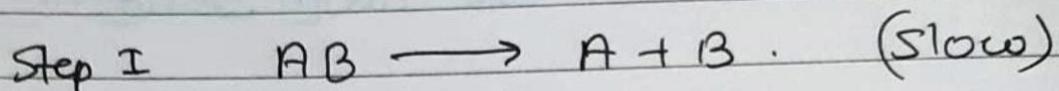
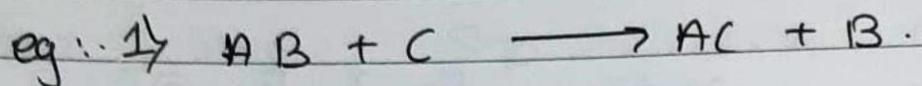
II Multip~~e~~ step reaction / complex reaction.

The reaction will occur in multiple steps.

Intermediate will form during reaction progress.

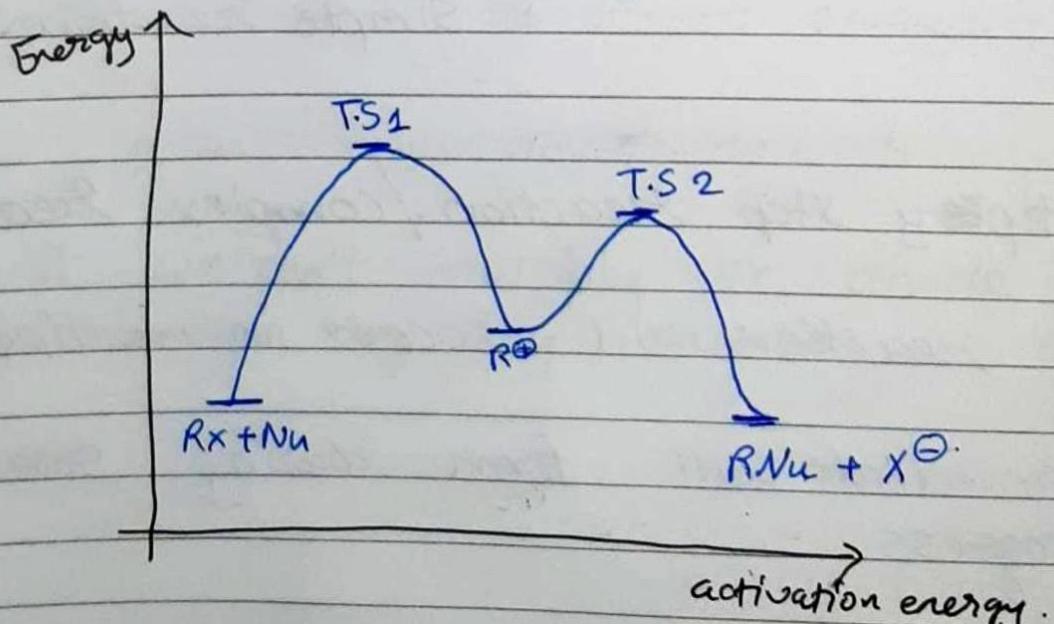
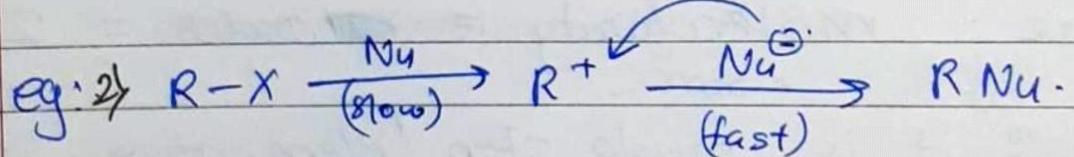
Note: we can't define molecularity of reaction but for steps we can define it in multiply step reaction.

Rate determining step will be slowest step.



$\therefore \text{rate} = k[\text{AB}]$

molecularity of slowest step. = order of reaction.



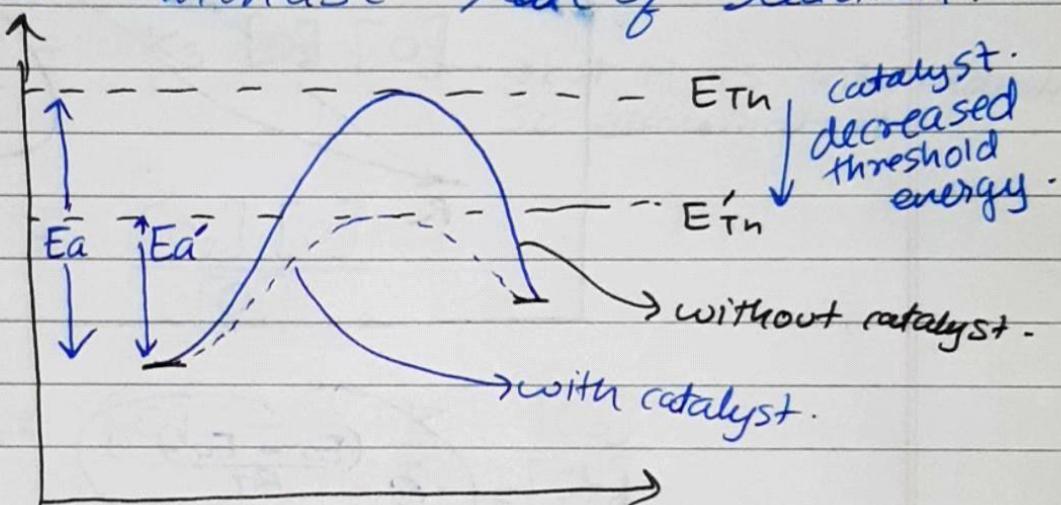
Note: the step having more activation energy will be slow.

★ Effect of catalyst.

There are two type of catalyst

1) Positive catalyst

it will increase rate of reaction.



$$K \propto = A e^{-\frac{E_a}{RT}}$$

$$K' = A e^{-\frac{E_a'}{RT}}$$

$$\frac{K'}{K} = e^{\left(\frac{(E_a - E_a')}{RT}\right)}$$

positive greater than one.

$$\therefore \frac{K'}{K} > 1$$

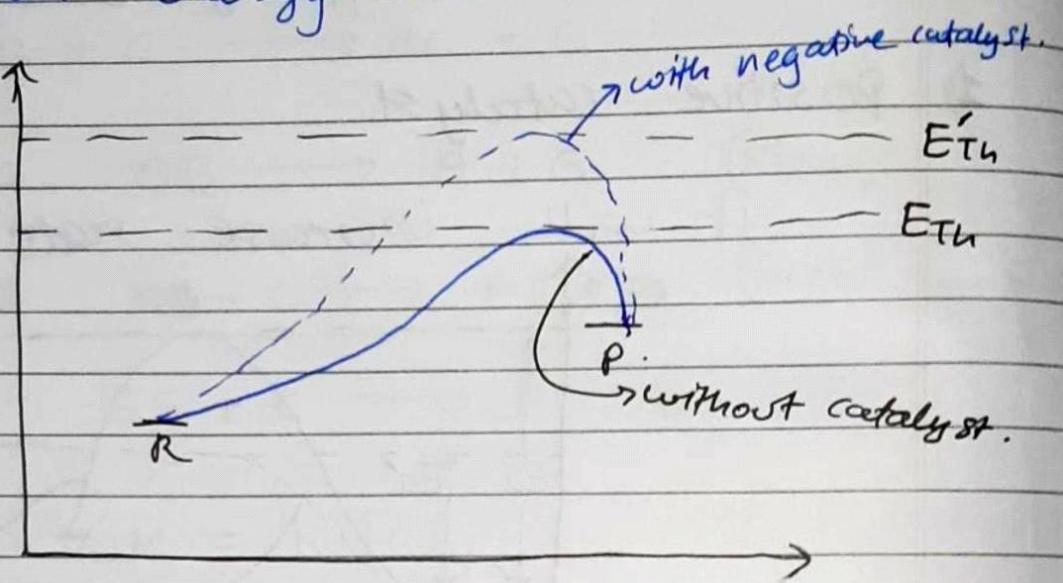
$$\therefore K' > K.$$

$$\Rightarrow \gamma' > \gamma$$

↓ without catalyst.
with catalyst-

2) Negative catalyst.

activation energy will increase.



$$\frac{k'}{k} = e^{\frac{(E_A - E'_A)}{RT}}$$

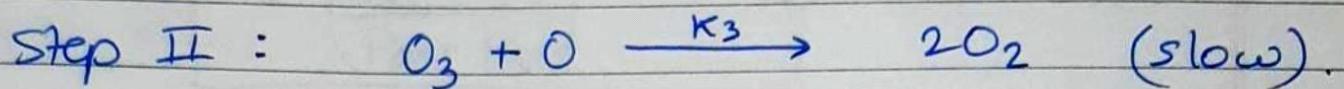
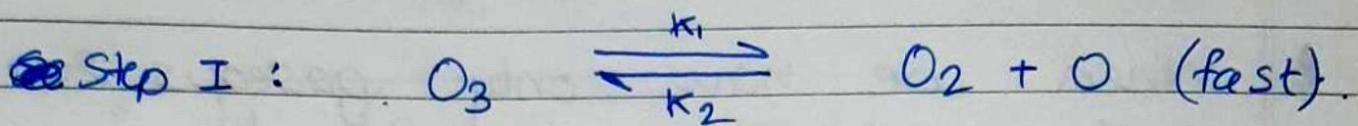
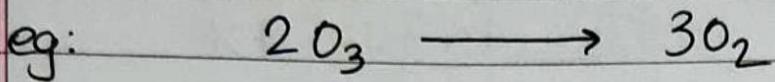
~~mag.~~ less than one.

$\therefore k' < k.$

$\therefore \gamma' < \gamma.$

↓ ↓ without
with catalyst.
(-ve) catalyst.

Note: For multi-step reaction R.D.S will be slowest step. But in rate law expression there shouldn't be any intermediate if any ~~int~~ intermediate is present then eliminate with supporting equilibrium reaction.



$$\text{rate} = k_3 [O_3] [O]$$

but it is intermediate
so eliminate it.

$$\frac{k_1}{k_2} = \frac{[O_2] [O]}{[O_3]}$$

$$\therefore [O] = \frac{k_1}{k_2} \frac{[O_3]}{[O_2]}$$

$$\therefore \text{rate} = \frac{k_3 k_1}{k_2} [O_3]^2 [O_2]^{-1}$$

\therefore order of reaction = 1

order w.r.t to $[O_3] = 2$.

order w.r.t to $[O_2] = -1$.