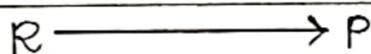# Chemical Kinetics

The branch of chemistry which deals with the study of speed or rate of chemical reactions , the factor affecting the rate of reaction and the mechanism by which the reaction proceed is known as chemical kinetics.

Rate of Reaction :-

The rate of reaction is the change in the concentration of any one of the reactants or product per unit time .

$$R \longrightarrow P$$

$$\text{Rate of reaction} = \frac{-\Delta[R]}{\Delta t} = \frac{+\Delta[P]}{\Delta t}$$

Significance of negative and positive sign :-

- The rate of reaction is always positive.
- The minus sign along with first term is used to show that the concentration of reactant is decreasing.
- The plus sign along with second term is used to show that the concentration of product is increasing .

Unit $M\ time^{-1}$ or $atm\ time^{-1}$

$\hookrightarrow mol\ L^{-1} sec^{-1}$

Rate - Average and Instantaneous :-

Average rate of reaction is change in concentration of any of the reactant or any of product per unit time over a specified interval of time.
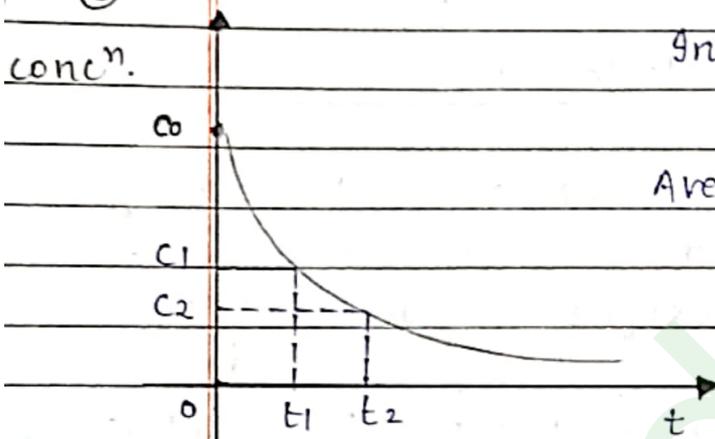
$$\text{rate}_{avg.} = \frac{-\Delta[R]}{\Delta t} = \frac{+\Delta[P]}{\Delta t}$$

Instantaneous rate of reaction .i.e. rate of reaction at any instant of time is rate of change of conc. of any one of reactant or product at particular instant of time

$$\text{rate}_{inst.} = \frac{-d[R]}{dt} = +\frac{d[P]}{dt} \quad, \text{ as } \Delta t \to 0.$$
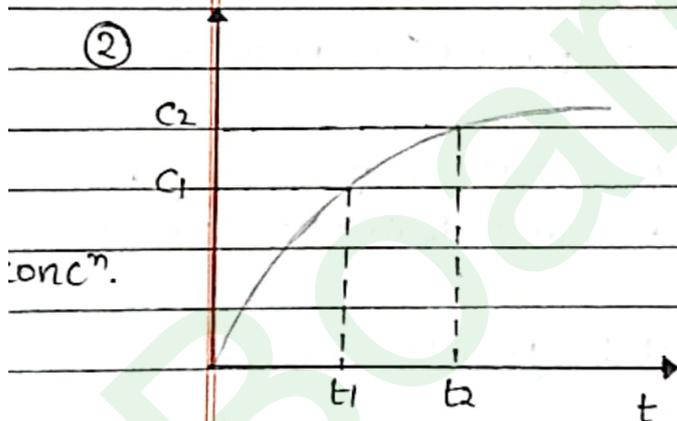
Graphically :-

①

conc.

$$\text{Inst.rate} = \frac{-d[R]}{dt} = \text{slope of tangent.}$$

$$\text{Average rate} = \frac{-\Delta[R]}{\Delta t} = \frac{-(C_2 - C_1)}{t_2 - t_1}$$
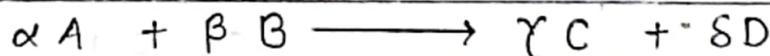
$$\boxed{C_1 > C_2}$$

②

conc.

$$\text{Inst.rate} = \frac{d[P]}{dt} = \text{slope of tangent}$$

$$\text{Average rate} = \frac{\Delta[P]}{\Delta t} = \frac{C_2 - C_1}{t_2 - t_1}$$

$$\boxed{C_2 > C_1}$$

in general ,
$$\alpha A + \beta B \longrightarrow \gamma C + \delta D$$

$$\text{Rate of reaction} = \frac{-d[A]}{\alpha \, dt} = \frac{-d[B]}{\beta \, dt} = \frac{d[C]}{\gamma \, dt} = \frac{d[D]}{\delta \, dt}$$

• equation must be balance.
• coefficient is multiplies for rate of reaction.

also, we can write as :

Rate of disappearance of A $= -\dfrac{d[A]}{dt}$

Rate of disappearance of B $= -\dfrac{d[B]}{dt}$

Rate of appearance of C $= +\dfrac{d[C]}{dt}$

Rate of appearance of D $= +\dfrac{d[D]}{dt}$

Factors Influencing Rate of reaction :-

1. Nature of reactant : different amount of energies are required for breaking of different bond & different amount of energies are released in formation of bond.

2. Concentration :- Greater the reactant's concentration, faster the reaction.

3. Temperature :- the rate of reaction increases on increasing of temperature.

4. Presence of catalyst :- A catalyst generally Increase the speed of a reaction without being consumed in reaction.

5. Surface area of reactant :- greater the surface area, faster the reaction.

6. Presence of radiation :-
   some reaction's rate increases with increase in intensity of light.

Rate law :-

It states that rate of chemical reaction is directly proportional to product of concentration of reactant to the some

$$\alpha A + \beta B \longrightarrow \gamma C + SD$$

power, which may or may not be equal to respective Stoichiometric coefficient.

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

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

where, K = rate constant or specific reaction rate

x = order with respect to A

y = order with respect to B.

$x + y$ = overall order of of reaction.

Rate Constant (K) :-

It may be defined as the rate of reaction when the molar concentration of each reactant is taken as unity. That is why rate constant is also called specific reaction rate.

Characterstics of rate constant :-

(i) . Rate constant is measure of rate of reaction.

(ii). Each reaction has definite value of K at a particular temperature.

(iii) . Value of rate constant for same reaction changes with temperature.

(iv). value of K does not depend upon concentration of reactant.

(v) The unit of rate constant depend upon order of rn^{n}?

Unit of K : $\text{rate} = K [A]^{n} [B]^{y}$

$$M \sec^{-1} = K (M)^{n+y}$$

$$M \sec^{-1} = K \cdot (M)^{n}$$

$$\therefore K = \frac{M \sec^{-1}}{M^{n}} = \boxed{M^{1-n} \sec^{-1} = K}$$

Order of reaction :-

The sum of exponent to which molar concentrations in rate law equation are raised to express the observed rate of reaction is called order of reaction.

$$rate = K[A]^n [B]^y$$

then , overall order of reaction $= n+y$.

Difference between rate of reaction and reaction rate constant :-

|	Rate of reaction	Reaction rate constant
1.	It is change in concent of a reactant or product per unit time	1. It is a constant of proportionality in the rate law equation and equal to rate of reaction when M of each reactant is unity.
2.	Rate of reaction at any instant of time depends upon the molar conc. of reactants at that time	2. It does not depend upon the concentration of reactants.
3.	unit is always, $M s^{-1}$	3. unit depends on the order of reaction.

MOLECULARITY OF A REACTION :-

The number of reacting species (atoms , ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

On the basis of molecularity chemical reaction i's of following type :-

1). Unimolecular Reaction :

when one reacting species i's involved.
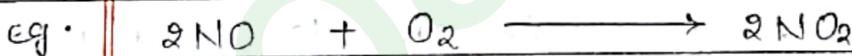
eg. decomposition of ammonium nitrate

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$
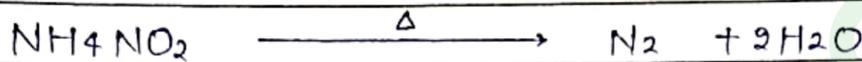
2). Bimolecular Reaction :

when reaction involve simultaneous collision between two species.

eg. dissociation of Hydrogen Iodide.

$$2HI \longrightarrow H_2 + I_2$$

3). Trimolecular or termolecular reaction :

Reaction involve simult. collision between three reacting species.

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

Note : The probability of reacting more than three molecule is very small and hence molecularity more than three i's very rare.

★ the overall rate of reaction i's controlled by the slowest step in a reaction called the rate determining step.

eg. $2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$
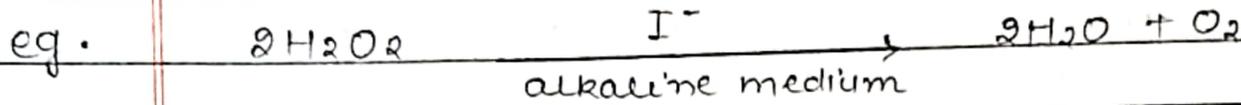
$$\text{rate} = \frac{-d[H_2O_2]}{dt} = K[H_2O_2][I^-]$$

The reaction is first order w.r.to both H_2O_2 and I^-.

1) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow)
2) $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ (fast)
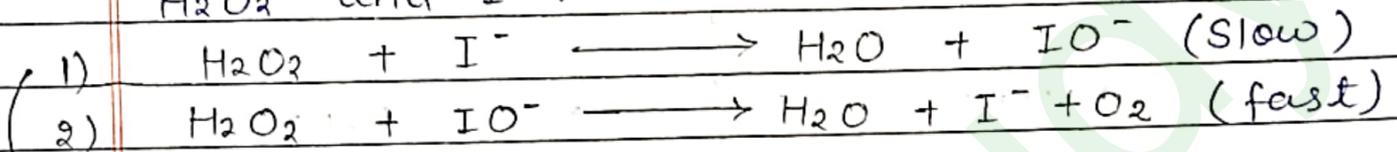
Step (1) (slow) is rate determining step.
Both steps are bimolecular elementary reaction.
IO^- is Hypoiodite ion and is intermediate.
Molecularity = 2
Order = 2nd order reaction.

ORDER of reaction	Molecularity of reaction.
• Sum of power of concen-tration of reactant in rate equation.	• Sum of number of species participating in an elementary reaction.
• Based on experimental value.	• Theoretical concept.
• It can be positive, negative, zero and fractional.	• It can only be whole number like 1, 2, 3 etc.
• applicable for both elementary and complex reaction,	• applicable for element-ary reaction only.

• order of reaction i's given by the slowest step .	• molecularity of slowest step i's same as the order of overall reaction.
• It have effect of temperature and pressure.	• No effect of order pressure and temperature .

Integrated Rate Equation :-

1) <u>Zero order reaction :</u>

$$R \rightarrow P$$

rate $= \dfrac{-d[R]}{dt} = K[R]^0$ rate of reaction is independent of conc. of reaction

$$\dfrac{d[R]}{dt} = -K$$

$$d[R] = -K \, dt \quad —①$$

integrating eq-① both side-

$$\int dR = \int -K \, dt$$

$$[R] = -Kt + C \quad —②$$

initially , t = 0 , R_0 (initial conc?.)

$$[R_0] = C \quad —③$$

Putting the value of eq ③ in ②-

$$[R] = -Kt + [R_0]$$

$$Kt = [R_0] - [R]$$

$$\boxed{K = \frac{[R_0] - [R]}{t}}$$
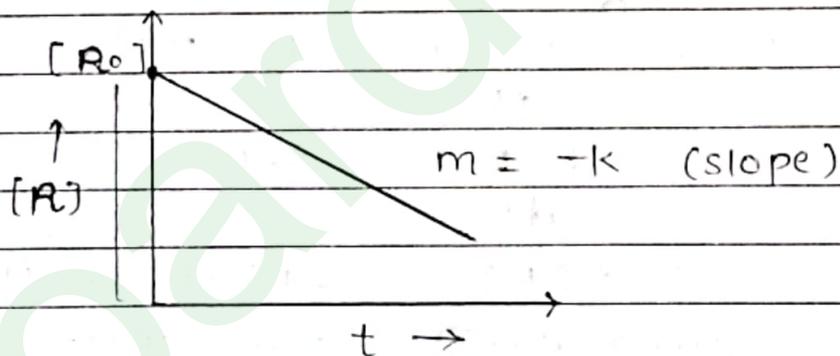
where R is concentration of reactant at any time.

→ In zero order reaction, rate of reaction is independent of concentration of the reactant.

from above;

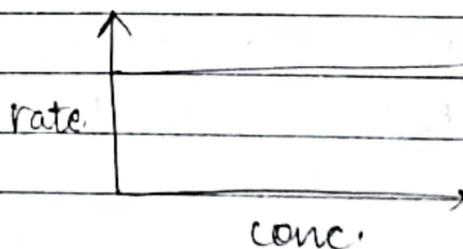$$[R] = [R_0] - kt$$

$$y = mn + c$$

Graph:

$m = -k$ (slope)

$$Rate = k[A]^0$$
$$Rate = k$$
$$Rate \propto k$$

∵ rate is independent of concentration of reactant.

Half life of a reaction :-

It is the time period when the chemical rxn is half completed or finished.

for zero order reaction;
$$R \rightarrow P$$
$t = 0 \quad [R_0]$

$t = t_{\frac{1}{2}} \quad \dfrac{[R_0]}{2}$

$$Kt = [R_0] - [R]$$
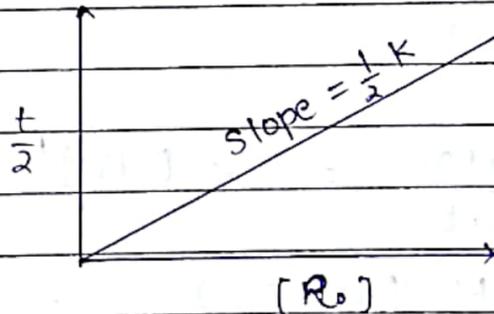
$$t = \dfrac{[R_0] - [R]}{K}$$

$$t_{\frac{1}{2}} = \dfrac{[R_0] - [R_0]/2}{K}$$

$$\boxed{t_{\frac{1}{2}} = \dfrac{[R_0]}{2K}}$$
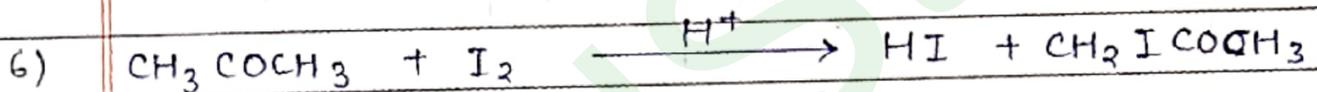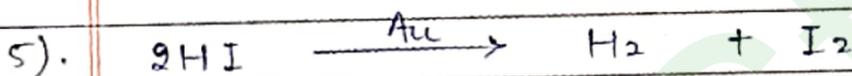
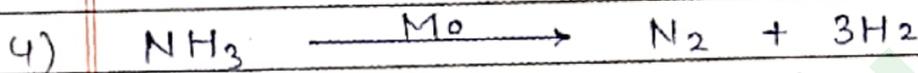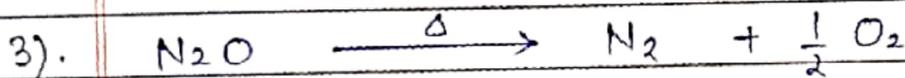where, R_0 is initial concentration.

on comparing,
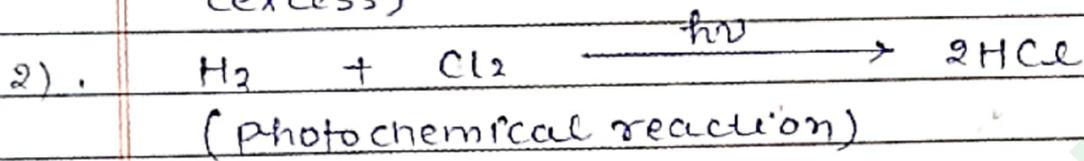$$t_{\frac{1}{2}} \propto [A_0]$$

Examples :—   (Zero order reaction)

1). Those reaction in which a reactant is in excess.

Substrate   enzyme →   Product
(excess)

2). H_2 + Cl_2 $\xrightarrow{h\nu}$ 2HCl
(Photo chemical reaction)

3). N_2O $\xrightarrow{\Delta}$ N_2 + $\frac{1}{2} O_2$

4) NH_3 $\xrightarrow{Mo}$ N_2 + $3H_2$

5). $2HI$ $\xrightarrow{Au}$ H_2 + I_2

6) CH_3COCH_3 + I_2 $\xrightarrow{H^+}$ HI + CH_2ICOCH_3

2). <u>First Order Reaction</u> :

Those reaction in which rate of reaction is dependent on concentr. of any of the reactant (only one).

$$A \longrightarrow P$$

$t = 0$ (a)
$t = t$ $(a-n)$

$$rate = -\frac{dn}{dt} = k[A]^1$$

$$-\frac{dn}{dt} = k(a-n) \quad —①$$

$$\int \frac{dn}{(a-n)} = \int -kdt$$

integrating equation on both side we get,

$$\ln(a-x) = -Kt + C \quad -②$$

initially, $t = 0$, $x = 0$

$$\ln(a) = C \quad -③$$

$$\ln(a-x) = -Kt + \ln a \quad -④$$

$$Kt = \ln(a) - \ln(a-x)$$

$$Kt = \ln\frac{[a]}{[a-x]}$$

also, $\ln = 2.303 \log_{10}$
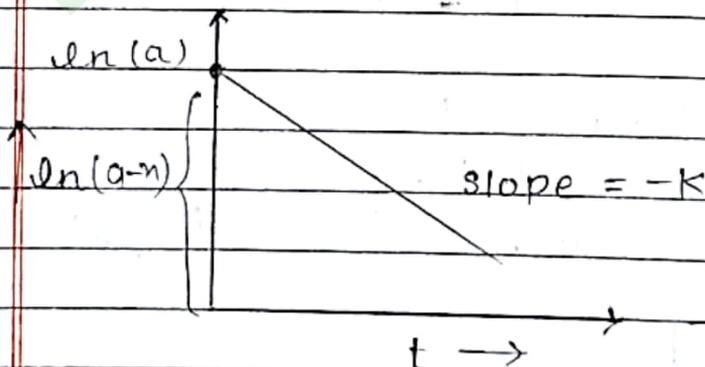
$$Kt = 2.303 \log_{10}\frac{[a]}{[a-x]}$$

$$\boxed{K = \frac{2.303}{t} \log_{10}\frac{[a]}{[a-x]}}$$

where $[a]$ and $[a-x]$ i's initial and final concentration respectively.
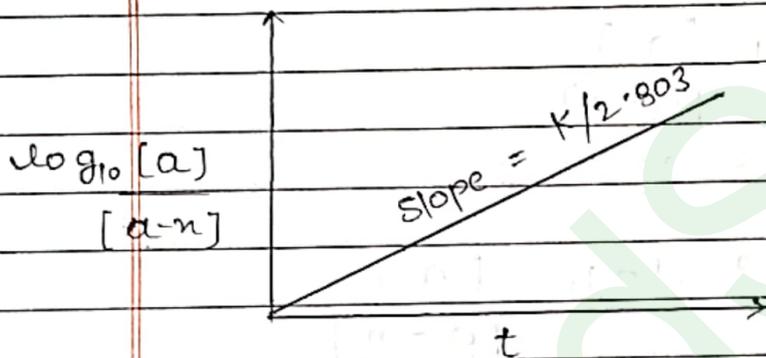
on comparing, the equation ④

$$y = mx + c.$$

graph

$$\log_{10} \frac{[a]}{[a-n]} = \frac{Kt}{2.303} + \log_{10}[a]$$

$$K = \frac{2.303}{t} \log_{10} \frac{[a]}{[a-x]}$$

$$\underbrace{\log_{10} \frac{[a]}{[a-n]}}_{y} = \underbrace{\frac{K \times t}{2.303}}_{mn}$$

Half Life of first order reaction —

$$A \longrightarrow P$$

$t=0 \quad a$

$t = t_{\frac{1}{2}} \quad a - \dfrac{a}{2} \quad (n = a/2)$
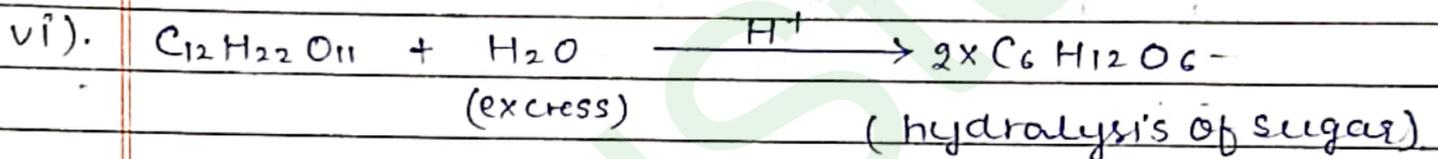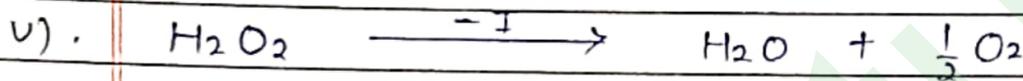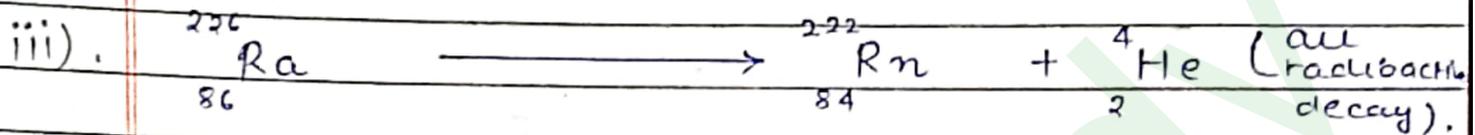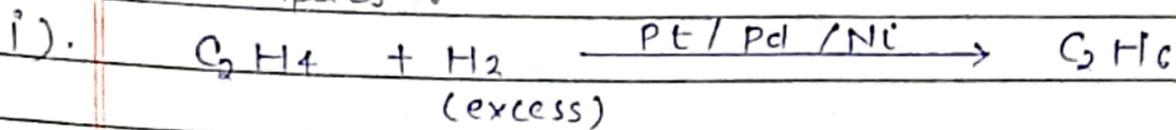
$$t = \frac{2.303}{K} \log_{10} \frac{[a]}{[a-n]}$$

$$t_{\frac{1}{2}} = \frac{2.303}{K} \log_{10} \frac{[a]}{[a/2]}$$

$$t_{\frac{1}{2}} = \frac{2.303}{K} \log_{10} 2 \qquad (\log 2 = 0.301)$$

$$\boxed{t_{\frac{1}{2}} = \frac{0.693}{K}}$$

Examples :-

i). $C_2H_4 + H_2 \xrightarrow{\text{Pt/Pd/Ni}} C_2H_6$
(excess)

ii). $N_2O_5 \xrightarrow{\Delta} 2NO_2 + \frac{1}{2}O_2$

iii). $^{226}_{86}Ra \longrightarrow {}^{222}_{84}Rn + {}^{4}_{2}He$ (α radioactive decay).

iv). $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

v). $H_2O_2 \xrightarrow{-I} H_2O + \frac{1}{2}O_2$

vi). $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} 2 \times C_6H_{12}O_6 -$
(excess)   (hydralysis of sugar)

vii). $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
(ester)   (excess)

viii). $SO_2Cl_2 \xrightarrow{\Delta} SO_2 + Cl_2$
Thionyl chloride
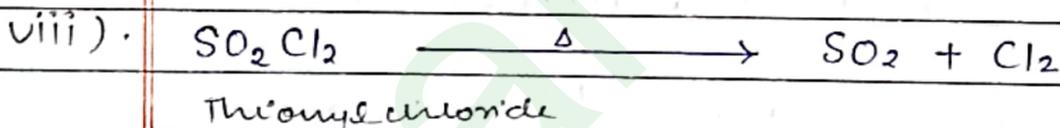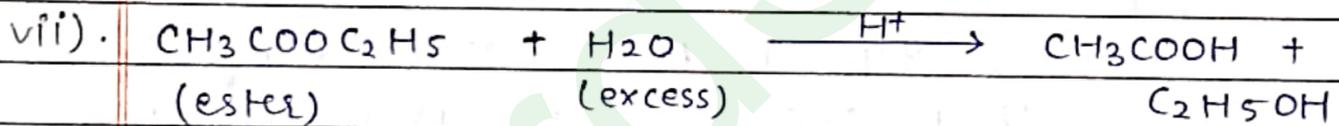
FIRST ORDER REACTION IN TERMS OF PRESSURE

$A(g) \longrightarrow B(g) + C(g)$
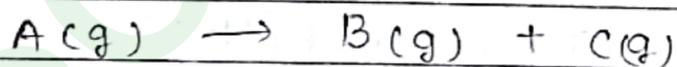
	$A(g)$	$B(g)$	$C(g)$
t = 0	P_i	0	0
t = t	$(P_i - n)$	x	x

at time t :-

$P_t = P_i - n + n + n$
$P_t = P_i - n$
(total pressure)

$$P_t = P_i - x \implies x = P_t - P_i$$

at time t ; P_A (Pressure of gas A at t)

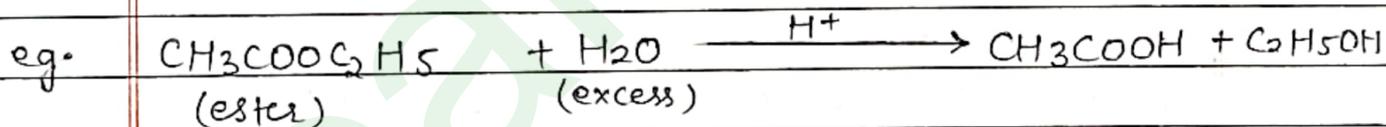$$P_A = P_i - x \implies P_i - P_t + P_i = 2P_i - P_t$$

$$\boxed{K = \frac{2 \cdot 303}{t} \log_{10} \frac{[P_i]}{[2P_i - P_t]}}$$

→ initial pressure

→ Final pressure

Pseudao - Unimolecular or Pseudo first order reaction :-

Sometimes, in a reaction or in an inter-mediate step or rate determining step more than one reacting species is observed but the order of reaction remains one.

eg.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{\;\;H^+\;\;} CH_3COOH + C_2H_5OH$$
(ester) (excess)

$$\text{rate} = K' [CH_3COOC_2H_5][H_2O]$$
$$K'[H_2O] = K$$
$$\therefore \text{rate} = K [CH_3COOC_2H_5]^1$$

here molecularity $= 2$ but order $= 1$

eg.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\;\;H^+\;\;} C_6H_{12}O_6 + C_6H_{12}O_6$$
(cane sugar) (excess) (glucose) (fructose)
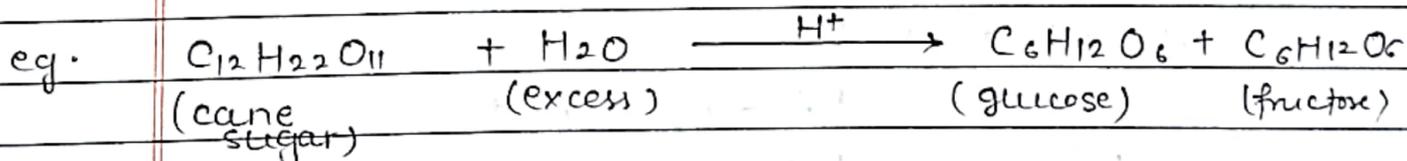
rate $= K' [C_{12}H_{22}O_{11}][H_2O]$

$K'[H_2O] = K$

rate $= K[C_{12}H_{22}O_{11}]'$

molecularity $= 2$, but order $= 1$.

eg.

$$CH_3 - \overset{O}{\overset{||}{C}} - O - \overset{O}{\overset{||}{C}} - CH_3 + 2 C_2H_5OH \rightarrow 2CH_3COOC_2H_5 + H_2O$$

(excess)
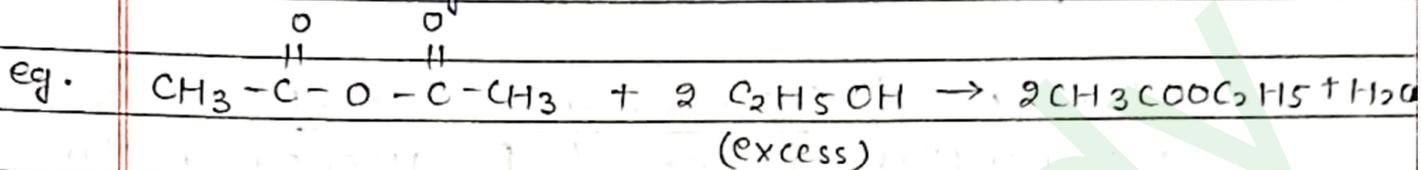
rate $= K' [(CH_3CO)_2O][C_2H_5OH][C_2H_5OH]$

$K = K'[C_2H_5OH][C_2H_5OH]$

rate $= K[(CH_3CO)_2O]$

molecularity $= 3$ but order $= 1$. pseudo

So, there are all example of first order reaction.

Temperature dependence of rate of reaction :-

Consider an enample,

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

at

0°C	→	10 days
25°C	→	5 hours
50°C	→	12 min

the rate of chemical reaction is temperature dependent and generally it increases with increase in temp

✱ 'with increase in temperature by 10°C - the rate of reaction doubles.

Arrhenius Equation-

Arrhenius explained the effect of temperature on rate of reaction.

$$k = A e^{-Ea/RT}$$

where A is Arrhenius constant or free exponential factor / Frequency factor.((because it gives the frequency of binary collision of reacting molecule per second per liter).

Ea is the energy of activation,
R is gas constant and
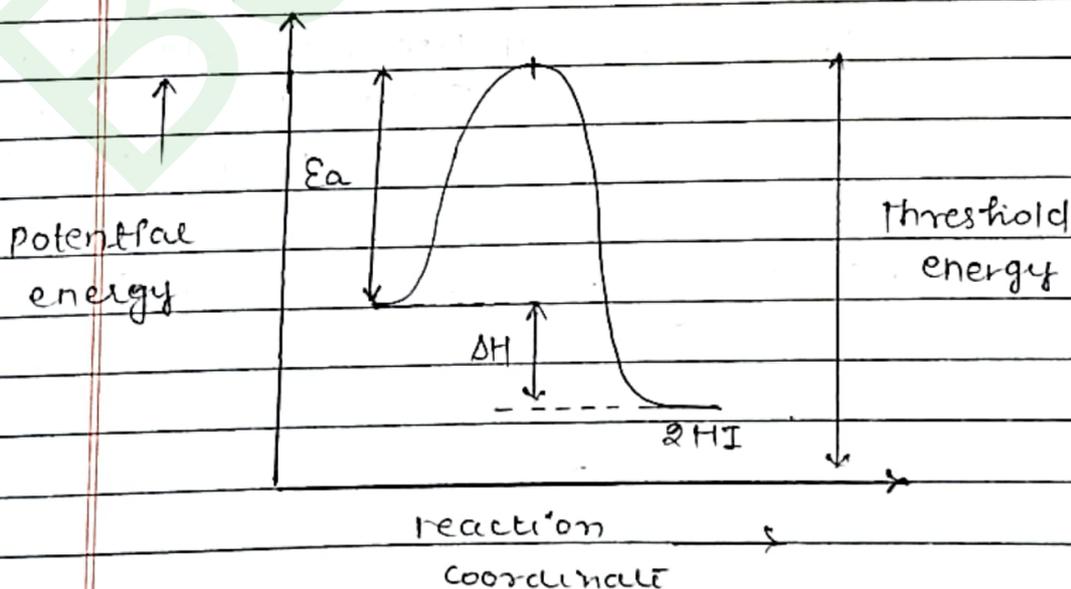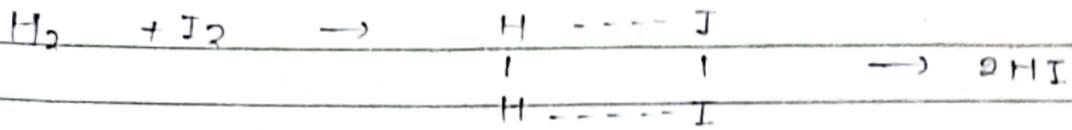T is absolute temperature.

'A' and 'Ea' are collectively called Arrhenius parameters.

The factor $e^{-Ea/RT}$, gives fraction of molecule N_E / N_T having energy equal to or greater than activation energy.
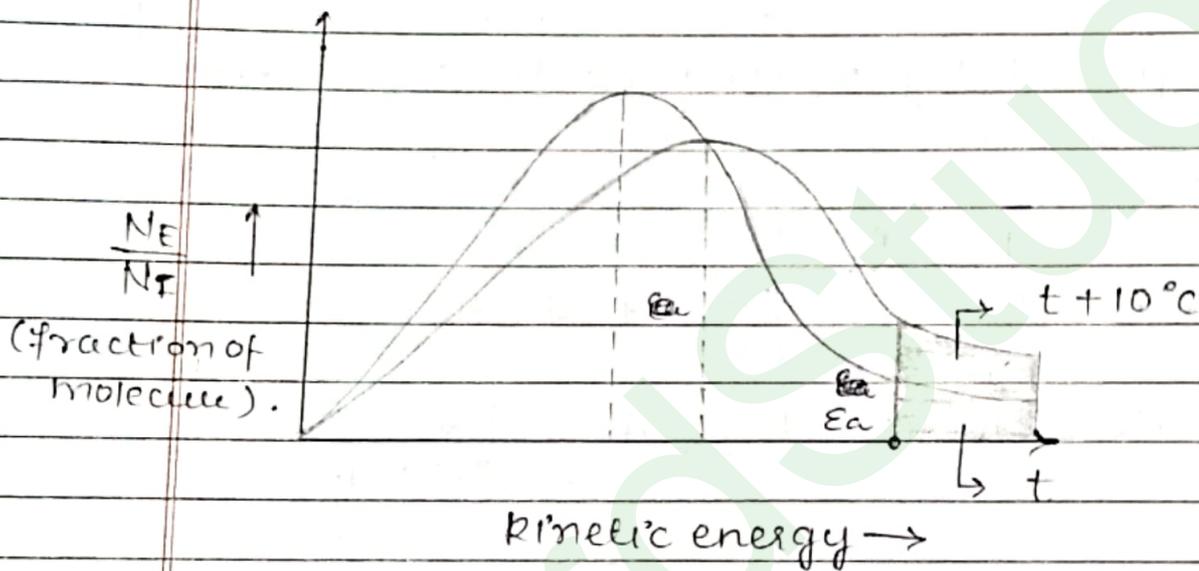
N_T is total number of molecule and
N_E is molecule that have kinetic energy.

potential energy ↑

Ea

ΔH

2HI

Threshold energy

reaction coordinate →

$$H_2 + I_2 \longrightarrow \begin{array}{c} H \cdots I \\ | \quad\quad | \\ H \cdots I \end{array} \longrightarrow 2HI$$

(intermediate)
which is
highly unstable
high energy.

Threshold energy = Activation Energy + Energy possesed
by reaction.

$\dfrac{N_E}{N_T}$

(fraction of molecule).

Ea

Ea

Ea
Ea

t + 10°C

t

kinetic energy →

Initially at temperature t the gas have a
lower most probable value of kinetic energy
and lesser number of gas posses activation
energy to carry the reaction and form product.

When t + 10°C, the most probable kinetic
energy gases increases comparatively and
large no. of gases occupy Ea.
∴ larger no. of product are formed.
∴ Rate of reaction increases on increasing
the temperature by 10°C.
the peak of curve corresponds to the most
probable kinetic energy.

Activation Energy :-

Activation energy is the energy given or required by reactant to reach the threshold point so that the intermediate can be formed and product formation takes place.

Threshold Energy :-

Is the minimum energy required by reactants to cause effective collision.

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

$$\ln K = -\frac{Ea}{RT} + \ln A$$

$$\log_{10} K = \log_{10} A - \frac{Ea}{2.303 RT}$$

$$\log_{10} K_1 = \log_{10} A - \frac{Ea}{2.303 \, R \, T_1} \qquad -①$$

$$\log_{10} K_2 = \log_{10} A - \frac{Ea}{2.303 \, R \, T_2} \qquad -②$$

Subtract & ① from ② -

$$\log_{10} K_2 - \log_{10} K_1 = \frac{Ea}{2.303 \, R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log_{10} \frac{K_2}{K_1} = \frac{Ea}{2.303 \, R} \left[\frac{T_2 - T_1}{T_1 \, T_2} \right]$$

$$\log_{10} \frac{K_2}{K_1} = \frac{E_a}{2 \cdot 303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Collision Theory :-

Reactant are considered as hard sphere, when the hard sphere collide with eachother with suitable kinetic energy they form an intermediate followed by product.

* The number of particles that collide per second in a given molecule volume is called as collision frequency (Z).

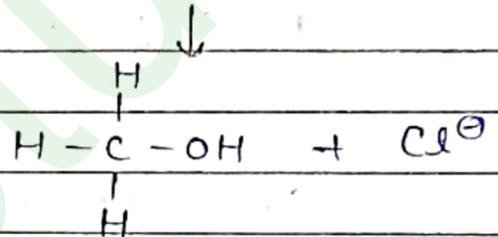* In gaseous phase, for binary collision /system the Z is in range of $10^{25} - 10^{28}$.

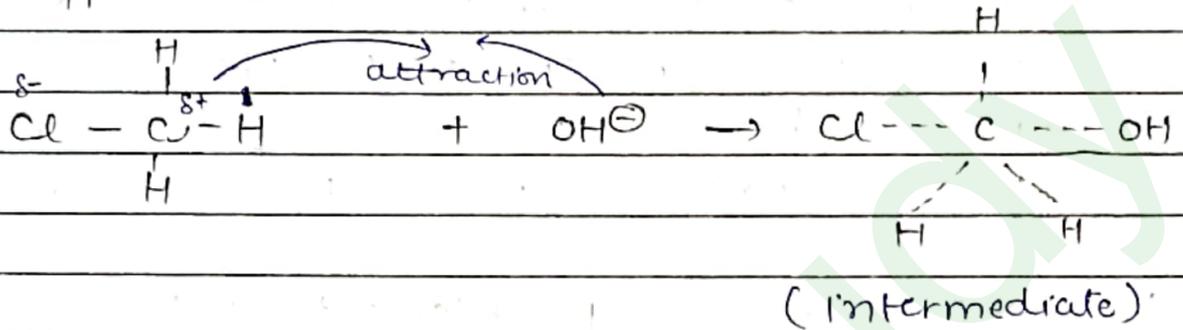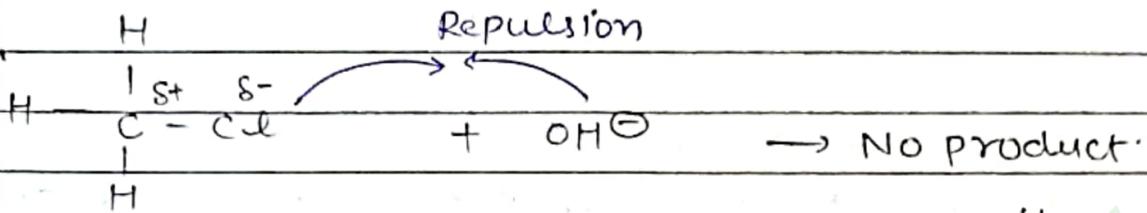* If after collision they are able to form product then collision is effective.

∵ reaction will take a very short time and vice-versa

Factors affecting the effective collision:-

① Energy barrier: for an effective collision the reactants must have threshold energy.

Energy < Threshold < Energy
(no effective   energy
collision)   (effective collision)

②   Orientation barrier .

$$H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{\underset{\delta^+}{C}}} - \underset{\delta^-}{Cl} \quad + \quad OH^{\ominus} \quad \xrightarrow{\quad} \quad No \ product.$$

Repulsion

$$\underset{\delta^-}{Cl} - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{\underset{\delta^+}{C}}} - H \quad + \quad OH^{\ominus} \quad \longrightarrow \quad Cl \ - - - \overset{H}{\overset{|}{C}} \ - - - OH$$

attraction

$$\underset{H \quad\quad H}{}$$

(Intermediate)

$$\downarrow$$

$$H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - OH \quad + \quad Cl^{\ominus}$$

collision factor .

$$Rate \quad = \quad Z_{AB} \ e^{-Ea/RT}$$

$$Rate \quad = \quad P \ Z_{AB} \ e^{-Ea/RT}$$

$$\hookrightarrow probability \\ factor$$

Effect on catalyst on rate of reaction :-

Catalyst :

       Those substance that decreases or increases the rate of reaction without participating chemically in a reaction.
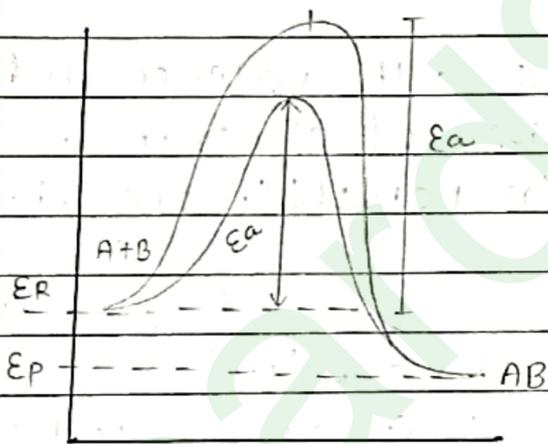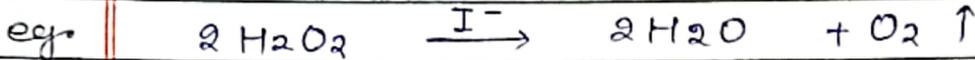
→   Catalyst never interfere with ΔG of a reaction (it will not start or stop the reaction).
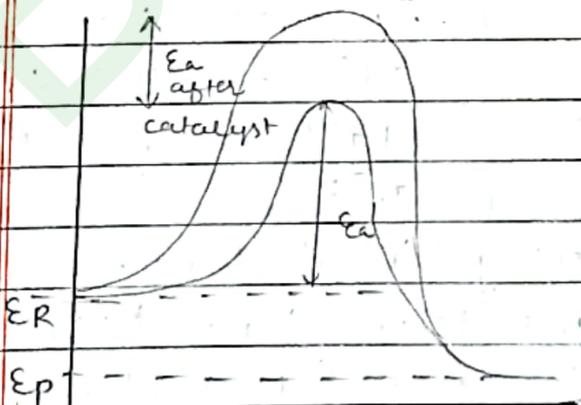
$\Delta G = 0$: no reaction

$\Delta G = +ve$: non - spontaneous reaction

$\Delta G = -ve$: spontaneous reaction.

$$\Delta G = \Delta H - T \Delta S$$

eg. $2 H_2O_2 \xrightarrow{I^-} 2H_2O + O_2 \uparrow$

Step ① $H_2O_2 + I^- \longrightarrow H_2O + OI^{\ominus}$

Step ② $H_2O_2 + IO^- \longrightarrow H_2O + O_2 + I^{\ominus}$

$2H_2O_2 \longrightarrow 2H_2O + O_2 .$

Positive catalyst:
are those that decrease
the Ea of reactant
∴ rate of reaction
increases because lower
activation energy can
be achieved earlier
and faster.

Negative catalyst: those
catalyst that increases
Ea of reaction ∴ rate of
reaction decrease because
higher Ea can be
achieved slower and
R.O.R decreases.

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Thank you!

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