

Chemical Kinetics

Camlin	Date	Page

- ① Rate of a chemical reaction: The rate of a chemical reaction is defined as change in conc. of reactant or product w.r.t time.

5
Rate = change in conc.
time.

consider a reaction $R \rightarrow P$

Rate = decrease in conc. of reactant
change in time.

$$= \frac{(R_2 - R_1)}{t_2 - t_1}$$

$$R_{avg} = \frac{-\Delta R}{\Delta t}$$

15 similarly for product:

Rate = Increase in conc. of product
change in time

$$= \frac{P_2 - P_1}{t_2 - t_1}$$

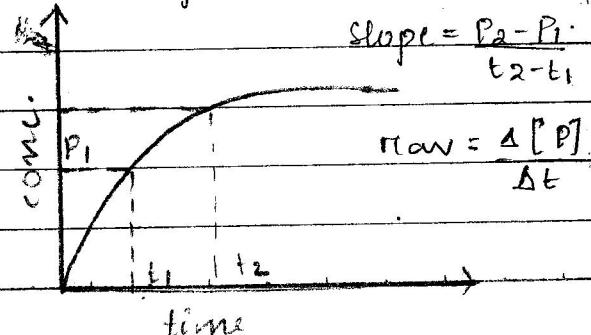
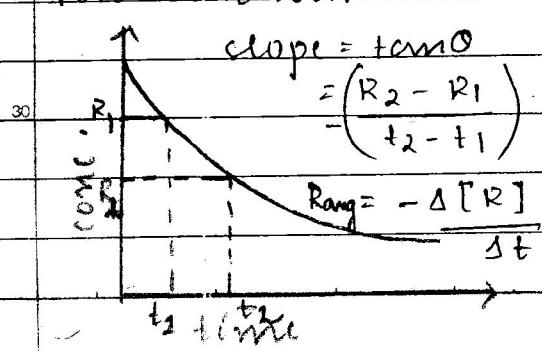
$$R_{avg} = \frac{\Delta P}{\Delta t}$$

- ② unit of rate of reaction:

Rate = change in conc. = $\frac{\text{mol l}^{-1}}{\text{sec}}$

= $\text{mol l}^{-1} \text{ sec}^{-1}$ or M sec^{-1}

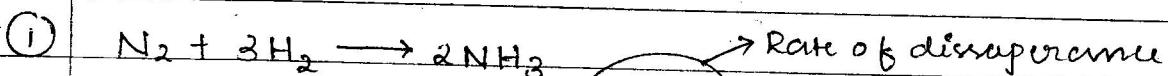
- ③ Graphical representation of average rate of reactions:
→ For reactant:



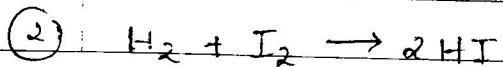
① Instantaneous rate of reaction: It is defined as the rate of a reaction at any instant to time ($t \rightarrow 0$)

$$R_{\text{inst.}} = \lim_{\Delta t \rightarrow 0} -\frac{\Delta [R]}{\Delta t} = -\frac{d[R]}{dt}$$

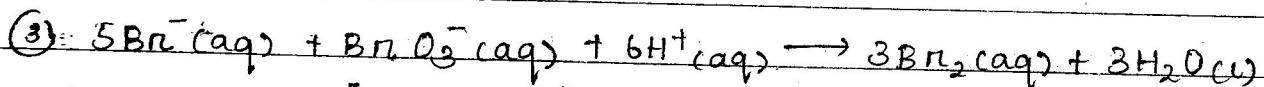
② Expression of average rate of reaction:



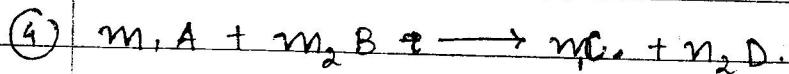
$$\text{r}_{\text{av}} = -\frac{\Delta [N_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta [H_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [NH_3]}{\Delta t} \rightarrow \text{Rate of appearance}$$



$$\text{r}_{\text{av}} = -\frac{\Delta [H_2]}{\Delta t} = -\frac{\Delta [I_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta [HI]}{\Delta t}$$



$$\text{r}_{\text{av}} = -\frac{1}{5} \frac{\Delta [Br^-]}{\Delta t} = -\frac{\Delta [BrO_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta [H^+]}{\Delta t} = \frac{1}{3} \frac{\Delta [Br_2]}{\Delta t} = \frac{1}{3} \frac{\Delta [H_2O]}{\Delta t}$$



$$\text{r}_{\text{av}} = -\frac{1}{m_1} \frac{\Delta [A]}{\Delta t} = -\frac{1}{m_2} \frac{\Delta [B]}{\Delta t} = +\frac{1}{n_1} \frac{\Delta [C]}{\Delta t} = \frac{1}{n_2} \frac{\Delta [D]}{\Delta t}$$

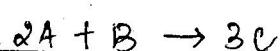
① For an elementary reaction $2A + B \rightarrow 3C$, the rate of appearance of C at time t is $1.3 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$. calculate

(i) Rate of the reaction

(ii) Rate of disappearance of A

(iii) Rate of disappearance of B

Ans.



$$\text{r}_{\text{avg}} = -\frac{1}{2} \frac{\Delta [A]}{\Delta t} = -\frac{\Delta [B]}{\Delta t} = \frac{1}{3} \frac{\Delta C}{\Delta t}$$

$$(i) \text{r}_{\text{avg}} = \frac{1}{3} \times 1.3 \times 10^{-4}$$

$$= 0.433 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$(ii) \text{r}_{\text{avg}} = \frac{1}{2} \frac{\Delta [A]}{\Delta t}$$

$$\Rightarrow 0.433 \times 10^{-4} \times 2 = \frac{\Delta [A]}{\Delta t}$$

$$\Rightarrow 0.866 \times 10^{-4} = \frac{\Delta [A]}{\Delta t}$$

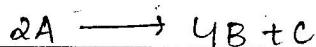
$$(iii) \text{r}_{\text{avg}} = \frac{\Delta [B]}{\Delta t}$$

$$\Rightarrow \frac{\Delta [B]}{\Delta t} = 0.433 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

(25) A gaseous reaction $2A \rightarrow 4B + C$ is carried out in a closed vessel. The $[B]$ is found to increase by $5 \times 10^{-3} \text{ mol L}^{-1}$ in 10 sec. calculate

- (i) Rate of reaction
- (ii) Rate of disappearance of A
- (iii) Rate of appearance of B.

Avg



$$\text{r}_{\text{avg}} = -\frac{1}{2} \frac{\Delta [A]}{\Delta t} = \frac{1}{4} \frac{\Delta [B]}{\Delta t} = \frac{\Delta [C]}{\Delta t}$$

$$(i) \text{r}_{\text{avg}} = \frac{1}{4} \times \frac{5 \times 10^{-3}}{10} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\text{r}_{\text{avg}} = 1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$(ii) 2 \text{r}_{\text{avg}} = \frac{\Delta [A]}{\Delta t}$$

$$\Rightarrow 2.5 \times 10^{-4} = \frac{\Delta [A]}{\Delta t}$$

$$(iii) \frac{\Delta B}{\Delta t} = 4 \times 1.25 \times 10^{-4}$$

$$= 5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

① Factor affecting rate of a chemical reaction:

- The rate of a chemical reaction is influenced by a no. of factors.

- (i) conc. of the reactant
- (ii) temperature
- (iii) Nature of the reactant
- (iv) presence of catalyst
- (v) surface area
- (vi) Effect of radiation

(i) conc. of reactant: Increase in the conc. of reactant, rate of reaction increases

(ii) Temperature: The rate of reaction increases with increase in temp.

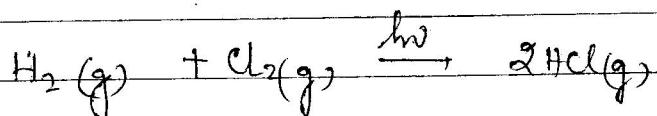
(iii) Nature of the reactant: Normally the rate of reaction is faster when the reactant is in gaseous state.

gas > liquid > solid.

(iv) Presence of catalyst: A catalyst generally alters the rate of a chemical reaction without itself being consumed in the reaction.

(v) Surface area: with increase in surface area rate of reaction increases

(vi) Effect of radiation: some reaction do not take place in the dark condition but can take place in the presence of light.



- ① Rate law and rate expression (law of mass action):
 This law was proposed by Guldberg and Waage in 1864
 the law states that at a particular temp. the rate of a
 such chemical reaction is \propto the product of molar conc. of
 each reactant raised to the power of its stoichiometric
 coefficient from the balanced chemical equation (which
 may or may not be equal from the balanced chemical
 equation).

10 consider a reaction: $aA + bB \rightarrow \text{product}$

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

$$\text{Rate} = K \cdot [A]^a [B]^b \quad [\because K = \text{Rate Velocity constant}]$$

$$\Rightarrow K = \frac{\text{Rate}}{[A]^a [B]^b}$$

$$\text{when } [A] = [B] = 1 \text{ mol l}^{-1} \text{ sec}^{-1}$$

$$\text{then } K = \text{Rate.}$$

Hence rate constant can be defined as the rate of a
 chemical reaction when the conc. of each reactant
 is taken as unity

- ② Characteristics of Rate constant:

- Greater is the value of rate constant, faster is the reaction and vice versa
- Each reaction has a definite value of rate constant at a particular temp.
- The value of rate constant changes with change in temp.
- The value of rate constant does not depend upon the conc. of the reactant but depends on the nature of the reactant.
- The units of rate constant depends upon the order of the reaction.

→ Note: Rate constant is also known as specific reaction rate.

Ques. 5 (3) Difference between rate of reaction and rate constant.

Ans. 5 Rate of reaction

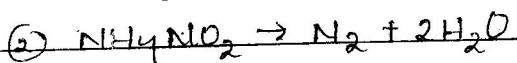
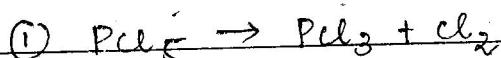
Rate of constant

- It is the speed with which reactant are converted into product.
- It depends upon initial conc. of reactant.
- Its unit is always $\text{mol L}^{-1} \text{ sec}^{-1}$
- It is a proportionality constant.
- It is independent of the initial conc. of reactant.
- Its unit depends upon the order of reaction.

Q) Order and molecularity of the reaction:

- Molecularity: It is defined as the no. of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
- The reaction which can proceed in one step is called elementary reaction.
- The reaction which can proceed more than one step is called complex reaction.
- Each step of a complex reaction is called elementary step of reaction.

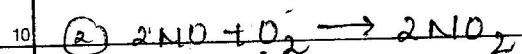
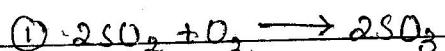
④ unimolecular reaction (1):



⑤ Bimolecular reaction (2):



⑥ Trimolecular reaction (3):



⑦ order of the reaction: It is defined as the sum of the power of conc. in rate law expression.



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

hence order = $a+b$.

Note:

① In elementary reaction both order and molecularity are same.

② A reaction having coefficient 2 or 3 can be behave as a complex reaction.

Example: ① $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$ [It is a complex reaction]

Mechanism = ① $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$ (slow)

② $\text{NO}_2 + \text{F} \rightarrow \text{NO}_2\text{F}$ (fast)

The slowest step is always rate determining step hence

$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$

hence it is a bimolecular second order reaction.

② $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ [It is a complex reaction]

Mechanism = ① $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + [\text{O}]$ (slow)

② $[\text{O}] + [\text{O}] \rightarrow \text{O}_2$ (fast)

Hence order of the reaction is 1.

Q. Difference between order and molecularity.

Ans.

order

molecularity.

→ It is the sum of the powers in rate law expression.

→ It is the total no. of reacting species which bring the chemical change.

→ It may be +ve, -ve, zero and fraction.

→ It is always a whole no. (1, 2, 3, ...)

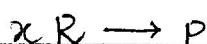
→ It is an experimental concept.

→ It is an theoretical concept.

→ It is meant for both elementary as well as complex reaction.

→ It is only meaningful for elementary reaction.

(b) units of rate constant:



$$\text{Rate} = K [R]^x$$

(i) For zero order reaction

$$\text{Rate} = K [R]^0$$

$$\text{Rate} = K,$$

$$K = \text{mol l}^{-1} \text{ sec}^{-1}$$

(ii) for 1st order reaction

$$\text{Rate} = K [R]$$

$$K = \frac{\text{Rate}}{[R]}$$

$$K = \text{sec}^{-1}$$

(iii) for second order reaction

$$\text{Rate} = K [R]^2$$

$$K = \frac{\text{Rate}}{[R]^2}$$

$$= \text{mol}^{-1} \text{ l sec}^{-1}$$

(iv) G.F

$$\text{mol}^{1-n} \text{ lit}^{n-1} \text{ sec}^{-1}$$

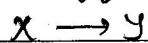
$n \rightarrow$ order of the reaction

25

30

Q) The conversion of molecule $x \rightarrow y$ follows second order kinetics if the conc. of x is increased to three times, how will it affect the rate of formation of y .

Ans.



$$\text{Rate} = K [x]^2 \rightarrow \text{(1)}$$

$$\text{A/q } [x] = 3x$$

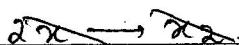
$$\text{Rate}' = K [3x]^2$$

$$\text{Rate}' = 9K[x]^2$$

$$\Rightarrow \text{Rate}' = 9 \text{ Rate}$$

Q) for the reaction $2x \rightarrow x_2$, the rate becomes 3 times when the conc. is increased 27 times. what is the order of the reaction

Ans.



$$\text{Rate} = K [2x]^a$$

$$27 \times \text{Rate}' = K [27x]^a$$



$$\text{Rate} = \frac{1}{2} K [x]^a$$

$$3 \times \text{Rate}' = \frac{1}{2} K [27x]^a$$

$$3 \times \text{Rate}' = \frac{1}{2} \times (27)^a K [x]^a$$

$$3 \times \text{Rate}' = (27)^a \text{ Rate}$$

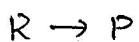
$$\Rightarrow (3)^1 = (3)^{3a}$$

$$\Rightarrow 1 = 3a$$

$$\Rightarrow a = \frac{1}{3}$$

① Integrated rate equation:

- For zero order reaction: A reaction is said to be zero order if its rate is independent of the conc. of the reactant consider a reaction:



$$\text{Rate} = k[R]^0$$

$$\Rightarrow \text{Rate} = k$$

$$\Rightarrow -\frac{dR}{dt} = k$$

$$\Rightarrow dR = -k dt$$

Integrating both side.

$$\Rightarrow \int dR = -k \int dt$$

$$\Rightarrow R = -kt + I \quad \rightarrow (i)$$

Let $R_0 \rightarrow$ initial conc. and $R \rightarrow$ conc. at t

when $t = 0$, $R = R_0$; $I = R_0$

$$\Rightarrow R = -kt + R_0 \quad \rightarrow (ii)$$

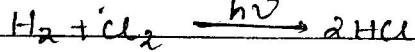
$$\Rightarrow R - R_0 = -kt$$

$$\Rightarrow R_0 - R = kt$$

$$\Rightarrow \frac{k}{R_0} = \frac{R_0 - R}{t} \quad \rightarrow (iii)$$

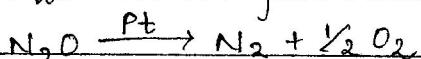
Example of zero order reaction:

- (i) Photchemical reaction between hydrogen and chlorine

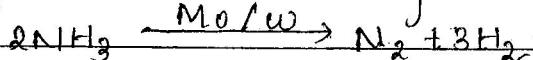


$$\text{Rate} = k[H_2]^0 [Cl_2]^0$$

- (ii) Decomposition of N_2O on hot platinum surface



- (iii) Decomposition of ammonia in the presence of Mo/W



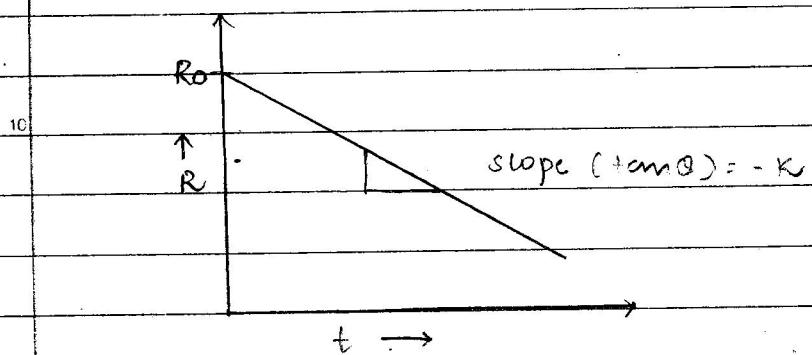
$$\text{Rate} = k[NH_3]^0$$

(iv) some enzyme catalysed reactions are zeroorder reaction

(v) decomposition of HI on gold surface

① characteristic of zeroorder reaction:

① The conc. of the reactant decreases linearly with time
From eqn (i)



② The time required for the reaction to be complete ($R=0$)

$$K = \frac{R_0}{t}$$

③ The unit of rate constant is $\text{mol L}^{-1} \text{sec}^{-1}$

④ Half life time period ($t_{1/2}$): It is the time required to reduce the initial conc. of the reactant to half of the initial value.

$$\text{when } t = t_{1/2}, R = R_0/2$$

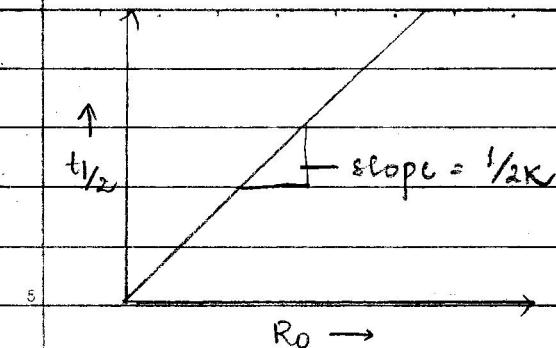
Putting in eqn (3)

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

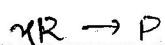
$$t_{1/2} = \frac{R_0}{2K} \rightarrow (4)$$

$$t_{1/2} \propto R_0$$

Hence half life time period \propto initial conc.



- (ii) For First order reaction: A reaction is said to be 1st order if its rate is \propto conc. of the reactant
consider a reaction



$$\text{Rate} = k[R]^x$$

$$-\frac{dR}{dt} = k[R]$$

$$\frac{dR}{[R]} = -k dt$$

Integrating both the sides

$$\int \frac{dR}{[R]} = -k \int dt$$

$$\Rightarrow \ln R = -kt + I \rightarrow (S)$$

at $R_0 \rightarrow$ initial conc. and $R \rightarrow$ conc. at time t

when $t = 0, R = R_0, [I = \ln R_0]$

$$\Rightarrow \ln R = -kt + \ln R_0 \rightarrow (6)$$

$$\Rightarrow \ln R - \ln R_0 = -kt$$

$$\Rightarrow \ln R_0 - \ln R = kt$$

$$\Rightarrow \frac{\ln(R_0)}{\ln(R)} = kt \rightarrow (7)$$

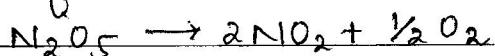
$$\Rightarrow kt = 2.303 \log \left(\frac{R_0}{R} \right)$$

$$\Rightarrow K = \frac{2.303}{t} \log \left(\frac{R_0}{R} \right) \text{ or } K = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

L (8)

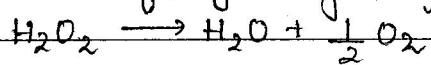
① Examples of 1st order reaction:

① decomposition of N_2O_5

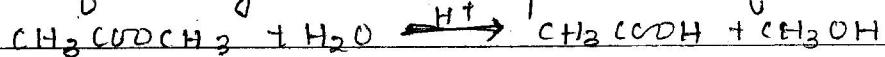


$$\text{Rate} = K [\text{N}_2\text{O}_5]^1$$

② Decomposition of hydrogen peroxide in aq sol.

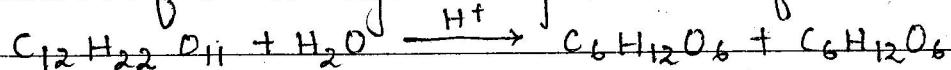


③ Hydrolysis of methyl acetate in presence of mineral acid



$$\text{Rate} = K [\text{CH}_3\text{COOCCH}_3]$$

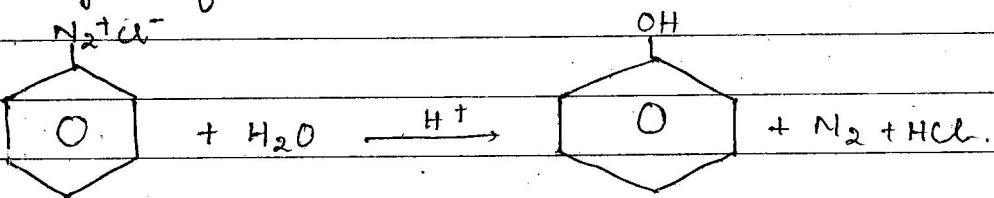
④ Inversion of cane sugar in presence of mineral acid



⑤ Decomposition of ammonium nitrite

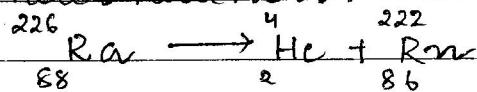


⑥ Hydrolysis of diazonium derivatives:



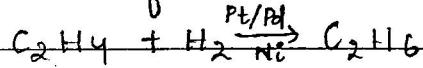
$$\text{Rate} = K [\text{C}_6\text{H}_5\text{N}_2^+ \text{Cl}^-]$$

⑦ All natural and artificial ~~radioactive~~ radioactive decay is 1st order reaction.



$$\text{Rate} = K [\text{Ra}]$$

(e) Hydrogenation of ethers:

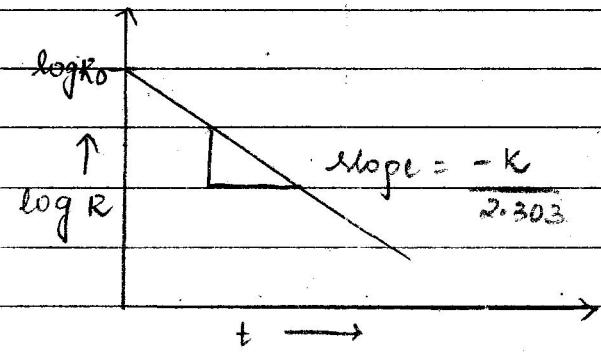
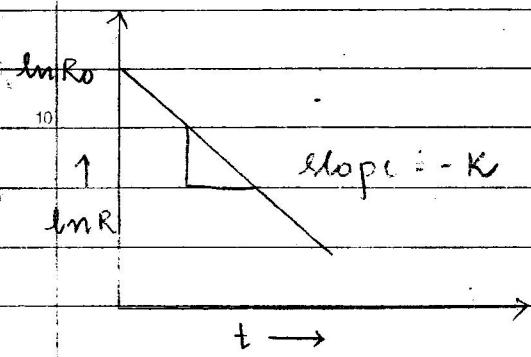


○ characteristic of 1st order reaction:

③ A change in conc. unit will not change the numerical value of K . Then

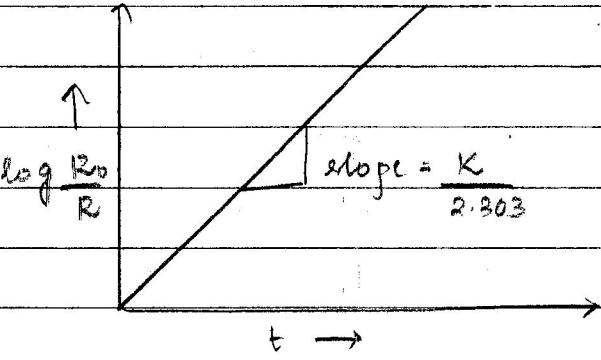
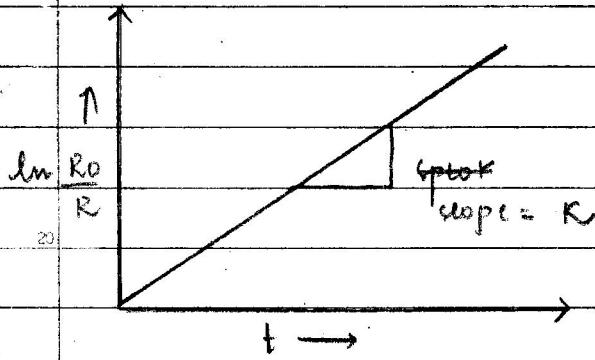
i) From eqn (6)

ii) From (6) $\log R = -\frac{Kt}{2.303} + \log R_0 \rightarrow (9)$



iii) From eqn (7)

iv) From (6) $\log \frac{R_0}{R} = \frac{Kt}{2.303} \rightarrow (10)$



v) From eqn (7) $R_0 = \frac{R}{e^{Kt}}$

vi) From eqn (10) $\log \left(\frac{R_0}{R} \right) = \frac{Kt}{2.303}$

$$\frac{R_0}{R} = \text{antilog} \left(\frac{Kt}{2.303} \right).$$

① Half life period for 1st order:

when $t = t_{1/2}$, $R = \frac{R_0}{2}$

5 $K = \frac{2.303}{t_{1/2}} \log \frac{R_0}{R_0/2}$

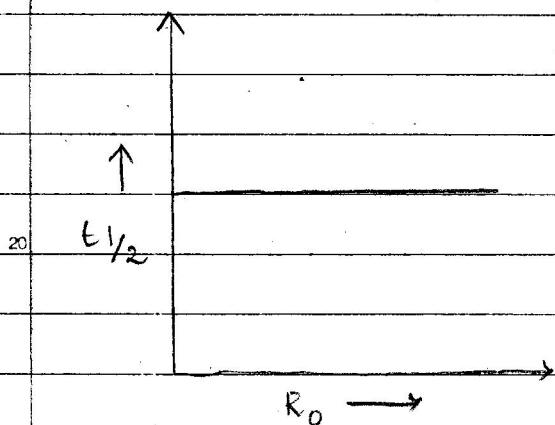
$K = \frac{2.303}{t_{1/2}} \log 2$

10 $K = \frac{2.303}{t_{1/2}} \times 0.3010$

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

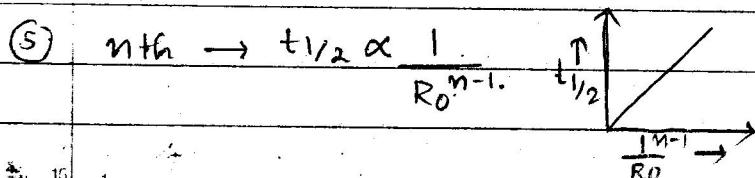
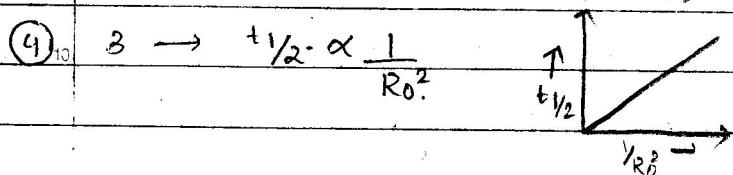
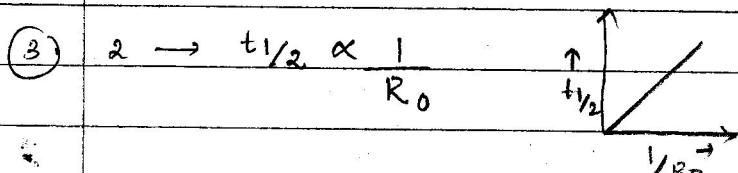
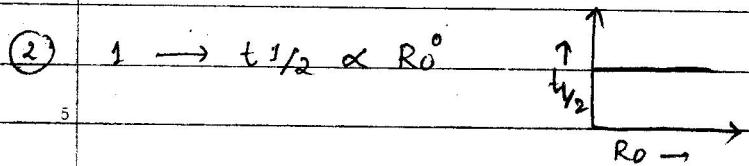
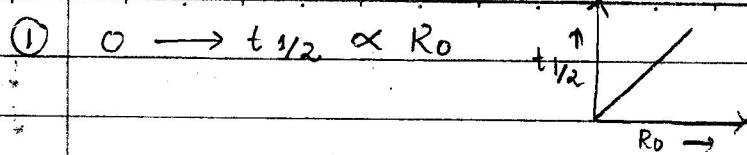
$t_{1/2} \propto R_0^0$

15 Hence half life time period is independent of initial conc.



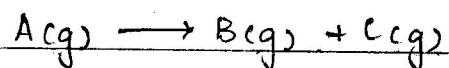
② Summary:

Order	Rate	units of K	K	$t_{1/2}$
0	$= K[R]^0$	$\text{mol l}^{-1} \text{sec}^{-1}$	$= \frac{R_0 - R}{t}$	$t_{1/2} = \frac{R_0}{2K}$
1	$= K[R]$	sec^{-1}	$= \frac{2.303}{t} \log \frac{R_0}{R}$	$= \frac{0.693}{K}$



① Kinetics of first order gas phase reaction:

when both reactant and product are in gaseous state,
in place of conc. partial pressure can be used
consider a reaction:



Initial 'P' P_i 0 0 atm

Pressure at

time t $P_i - x$ x x

According to dalton law of partial pressure.

$$P_T = P_i - x + x + x$$

$$P_T = P_i + x$$

$$x = P_T - P_i$$

$$K = \frac{2.303}{t} \log \frac{P_i^{\circ}}{P_A}$$

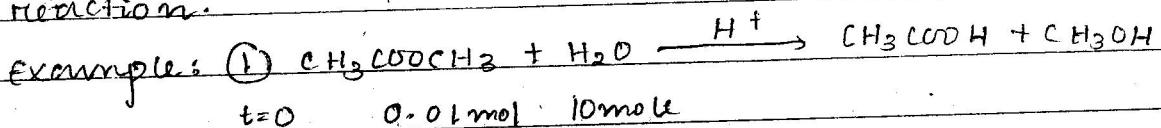
$$\Rightarrow K = \frac{2.303}{t} \log \frac{P_i^{\circ}}{P_i^{\circ} - x}$$

$$\Rightarrow K = \frac{2.303}{t} \log \frac{P_i^{\circ}}{P_i^{\circ} - P_T + P_i}$$

$$\Rightarrow K = \frac{2.303}{t} \log \left(\frac{P_i^{\circ}}{2P_i^{\circ} - P_T} \right)$$

① Pseudo first order reaction: The chemical reaction which seems to be higher order but actually a 1st order reaction is called Pseudo 1st order reaction.

OR Any chemical reaction out of two reactant, if one of the reactant conc. is excess then it is called as Pseudo 1st order reaction.



t=0 0.01 mol 10 mole

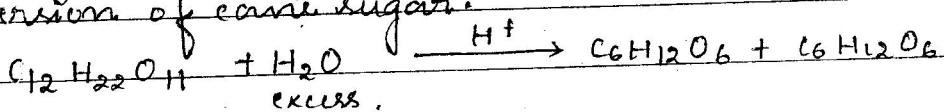
t 0 9.9 mole 0.01 mole 0.01 mole

$$\text{Rate} = k' [\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}]$$

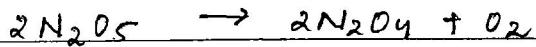
$$k' = [\text{CH}_3\text{COOCH}_3]. \quad [\because k'[\text{H}_2\text{O}] = k]$$

$$k' = \frac{k}{[\text{H}_2\text{O}]} = \frac{k}{55.55}$$

② Inversion of cane sugar.



$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$



Initial pressure 0.5 atm 0 0

$$P_T = P_i + \alpha$$

$$\Rightarrow \alpha = 0.512 - 0.5$$

$$\Rightarrow \alpha = 0.012 \text{ atm.}$$

$$K = \frac{2.303}{t} \log \frac{0.5}{0.5 - 0.012 \times 2}$$

$$K = \frac{2.303}{100} \log \frac{0.5}{0.5 - 0.012}$$

$$K = \frac{2.303}{100} \log \frac{0.500}{0.496}$$

$$K = \frac{2.303}{100} \log 1.05$$

$$K = \frac{2.303}{100} \times 0.0212$$

$$K = 4.98 \times 10^{-4} \text{ sec}^{-1}$$

Q. In a reaction between A and B, the initial rate of reaction was measured for different initial conc. of A and B as given below.

A	0.2	0.2	0.4
B	0.3	0.1	0.05
rate	6.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction w.r.t A and B?

Ans. Let Rate = $K [A]^x [B]^y$

then. $K = \frac{[0.2]^x [0.3]^y \times 1}{5.07 \times 10^{-5}} \Rightarrow 5.07 \times 10^{-5} = K [0.2]^x [0.3]^y$ → ①

then $K = \frac{5.07 \times 10^{-5}}{[0.2]^x [0.3]^y}$

$$\Rightarrow 5.07 \times 10^{-5} = K [0.2]^x [0.1]^y \rightarrow ②$$

$$\Rightarrow 1.43 \times 10^{-4} = K [0.4]^x [0.05]^y \rightarrow ③$$

Dividing eqn ② by ③ we get :

$$\Rightarrow 1 = \frac{[0.3]^y}{[0.1]^y}$$

$$\Rightarrow 1 [3]^y = 3^0$$

$$\Rightarrow y = 0.$$

Dividing eqn ② by ③ we get :

$$\Rightarrow \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{[0.4]^x}{[0.2]^x}$$

$$\Rightarrow \frac{1.43 \times 10}{5.07} = [0.2]^x$$

$$\Rightarrow \frac{14.3}{5.07} = [0.2]^x$$

$$\Rightarrow x = 1.5$$

$$\text{Rate} = K [A]^{1.5} [B]^0$$

w.r.t of A order = 1.5

w.r.t of B order = 0.

Q) Temp. dependence of the rate of a chemical reaction :

Generally increase in temp. the rate of reaction increases for the decomposition of N_2O_5 , it has been found that for a chemical reaction with rise in temp by 10°C , the rate constant nearly doubled (1.85 times)

- The temp. dependence of the rate of a chemical reaction

can be accurately explained by Arrhenius equation

- It was 1st proposed by Dutch chemist, T.H. Van't Hoff

Q. consider a reaction $A + 2B + 3C \rightarrow P$
excess

- write the rate expression?
- what is the overall order of the reaction?
- what is the unit of the rate constant?
- If conc. of A increase twice, conc. of B reduces to $\frac{1}{2}$ and conc. of C increases twice, then rate of reaction increases or decreases by how much time?

Ans. (i) Rate = $k[A][B]^2$

(ii) order = 3.

(iii) unit of rate constant = $\text{mol}^{-2}\text{L}^2\text{sec}^{-1}$

$$(iv) \text{Rate}' = [2A] \left[\frac{B}{2} \right]^2 \\ = [2A] \left[\frac{B^2}{4} \right]$$

$$= \frac{[A][B^2]}{2}$$

$$= \frac{\text{Rate}}{2}$$

decreases by $\frac{1}{2}$:

Q. For the reaction $2A + B \rightarrow A_2B$

$$\text{Rate} = k[A][B]^2$$

$$k = 2 \times 10^{-6} \text{ mol}^{-2}\text{L}^2\text{sec}^{-1}$$

(i) calculate the initial rate of reaction when $[A] = 0.1 \text{ M}$ and $[B] = 0.2$

(ii) calculate the rate of reaction when $[A]$ reduces to 0.06 M

Ans.

$$(i) \text{Rate} = 2 \times 10^{-6} \times 0.1 \times 0.04$$

$$= 8 \times 10^{-9} \text{ mol L}^{-1}\text{sec}^{-1}$$

(ii) final conc = 0.06 M

$$\text{change in conc} = 0.1 - 0.06 = 0.04 \text{ M}$$

$$\text{For 1 mole} = \frac{0.04}{2} = 0.02$$

$$\text{Final conc. of } [B] = 0.2 - 0.02 = 0.18.$$

$$\begin{aligned} \text{Rate} &= 2 \times 10^{-6} \times 0.06 \times 0.18 \times 0.18 \\ &= 0.12 \times 0.18 \times 0.18 \times 10^{-6} \\ &= 3.88 \times 10^{-9} \text{ mol l}^{-1} \text{ sec}^{-1} \end{aligned}$$

Q. Prove that time required for 99.9% is 10 times the half-life time period for a 1st order reaction.

Ans.

$$t_{99.9} = \frac{2.303}{K} \log \frac{100}{0.1} \quad t_{50} = \frac{2.303}{K} \log \frac{2}{1}$$

$$t_{99.9} = \frac{2.303}{K} \log 10^3 \quad t_{50} = \frac{0.693}{K} \rightarrow (i)$$

$$t_{99.9} = \frac{2.303}{K} \log 10$$

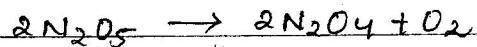
$$t_{99.9} = \frac{2.303 \times 3}{K} \rightarrow (ii)$$

dividing (i) by (ii) we get .

$$\frac{t_{99.9}}{t_{50}} = \frac{2.303 \times 3}{K} \times \frac{6K}{0.693}$$

$$t_{99.9} = 10 \times t_{50}.$$

Q. The following data were obtain during the 1st order thermal decomposition of N_2O_5 at a constant vol.



Sl. No.	time in sec.	total pressure (atm)
1	0	0.5 atm
2	100	0.512 atm

calculate the rate constant .

$$K = A e^{-E_a/RT} \rightarrow (i)$$

$K \rightarrow$ Rate constant

$A \rightarrow$ Arrhenius factor / frequency factor / preexponential factor

$E_a \rightarrow$ Activation energy

$R \rightarrow$ universal gas constant

$T \rightarrow$ Temp.

$$\frac{K}{A} = e^{-E_a/RT} \rightarrow (ii)$$

$$\ln K = \ln A - \frac{E_a}{RT} \rightarrow (iii)$$

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

$$\log K = \log A - \frac{E_a}{2.303 RT} \rightarrow (iv)$$

For two temp T_1 and T_2 , $T_2 > T_1$

For T_1 ,

$$\log K_1 = \log A - \frac{E_a}{2.303 RT_1} \rightarrow (v)$$

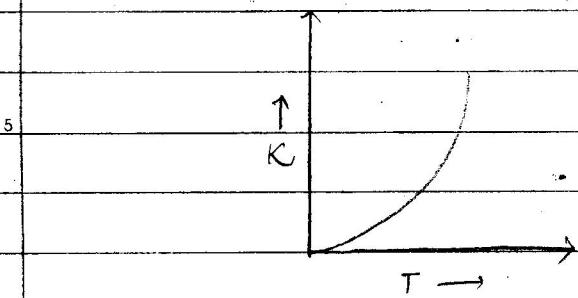
$$\text{For } T_2 \quad \log K_2 = \log A - \frac{E_a}{2.303 RT_2} \rightarrow (vi)$$

Equation (vi) - Equation (v)

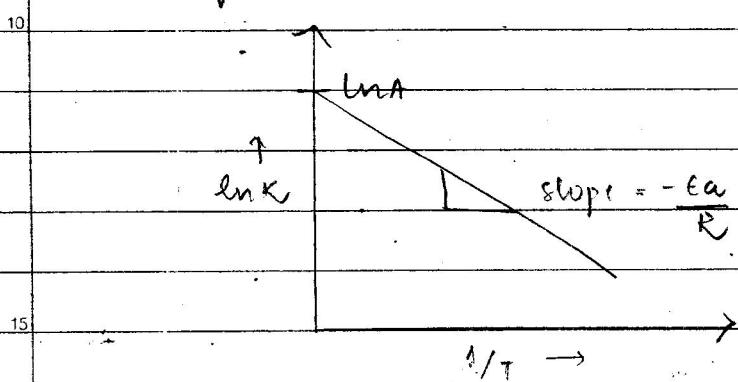
$$\log K_2 - \log K_1 = -\frac{E_a}{2.303 RT_2} + \frac{E_a}{2.303 RT_1}$$

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

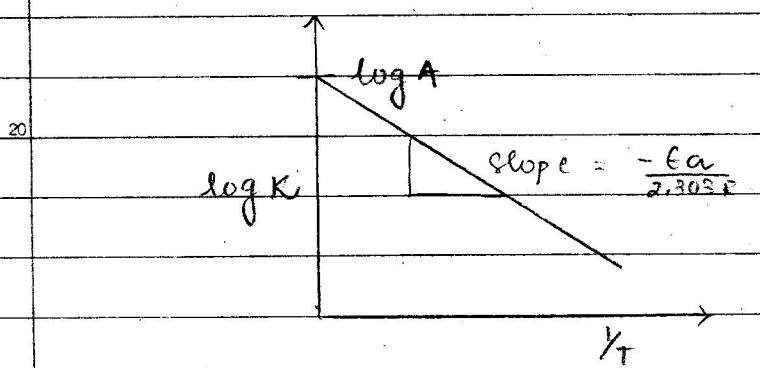
① Graphical representation:
from eqn ①



from eqn ②



From eqn ④



② Note: from eqn ②

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

fraction of molecules whose
KE equal or greater than Ea

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

$$\frac{K}{A} = \text{antilog} \left(\frac{-Ea}{2.303 RT} \right)$$

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

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

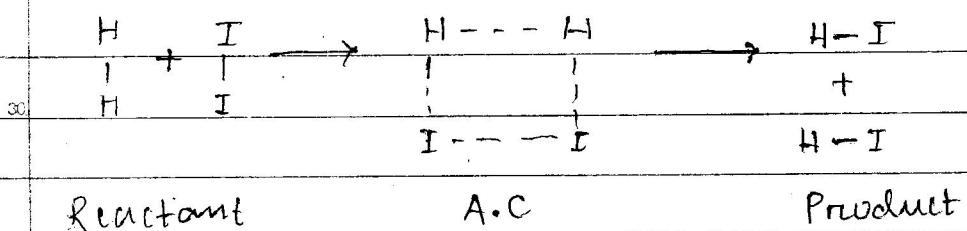
Q. The activation energy for the reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ is 209.5 kJ/mol at 581 K . calculate the fraction of molecules of reactants whose energy equal or greater than activation energy.

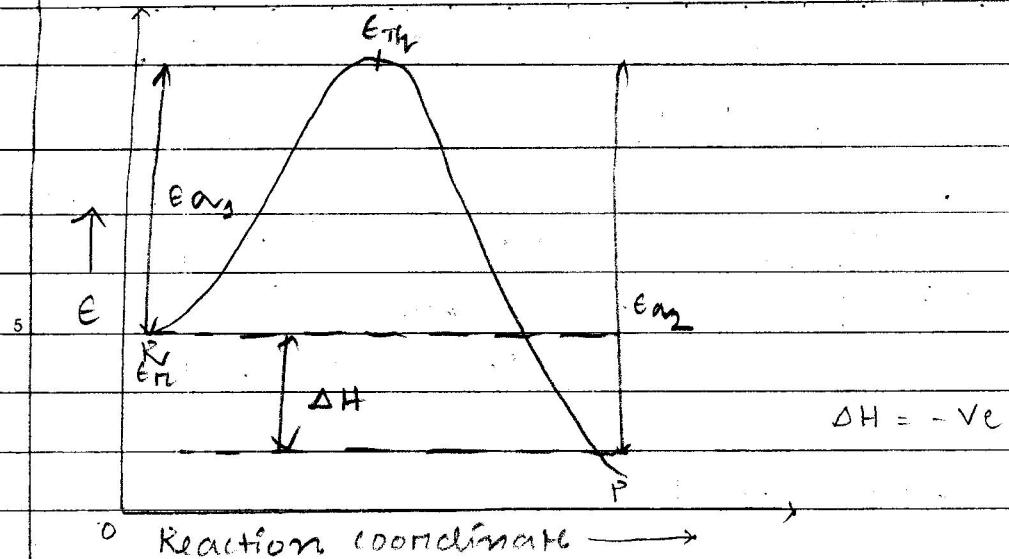
Ans. $\frac{IC}{A} = \text{antilog} \left(-\frac{209.5 \times 10^3}{2.303 \times 8.314 \times 581} \right)$.

$$= 1.462 \times 10^{-19}$$

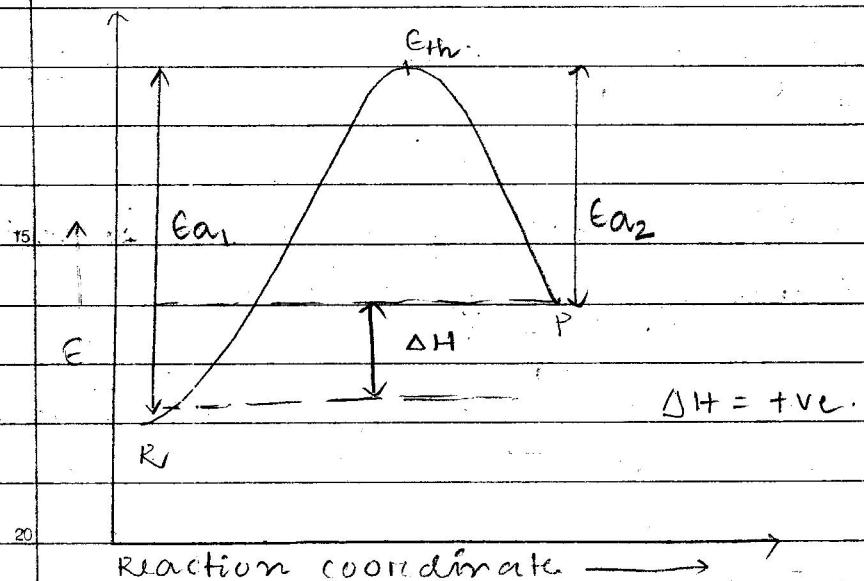
① Activation energy:

- The energy possessed by reacting molecule is called actual energy (E_{R})
- The energy at which formation of activated complex takes place is called threshold energy (E_{th})
- The extra extra amount of energy given to the reactants to get E_{th} (activated complex) is called activation energy
- Mathematically $\epsilon_a = E_{\text{th}} - E_{\text{R}}$.
- A highly reactive, short lived intermediate formed between reactant and product is called activated complex.
- example: $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$





EXOTHERMIC REACTION

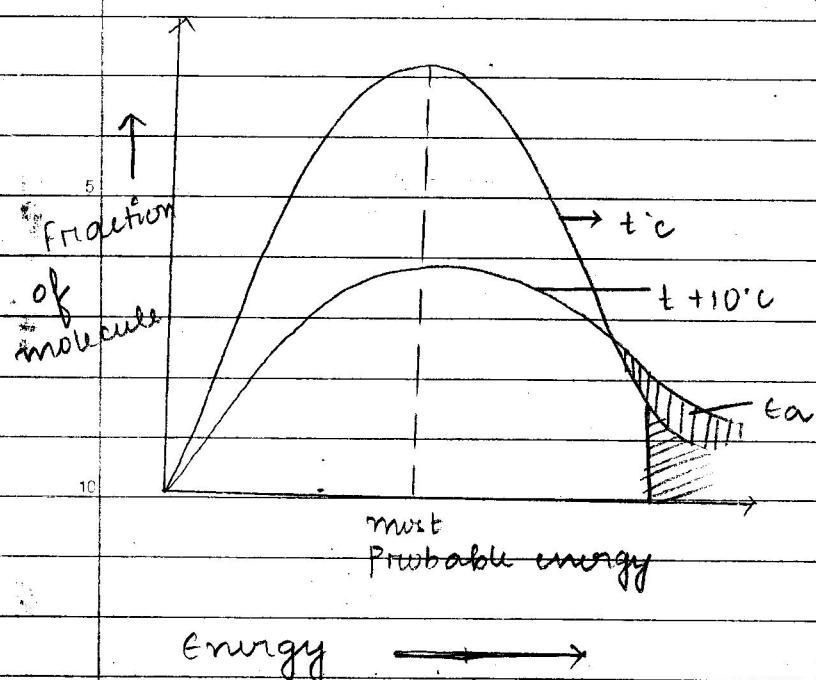


ENDOTHERMIC REACTION

Note:

- (1) ΔH value never changes for a reaction when catalyst is added. ΔH value does not change.
- (2) with increase in temp of $n \times 10^{\circ}\text{C}$, the rate of reaction increases by 2^n times.

(C) Maxwell - Boltzman Probability distribution curve:



Note: Jmp. coefficient (n) = rate constant at $t + 10^\circ\text{C}$
Rate constant at $t^\circ\text{C}$

For most of the reactions $2 < n < 3$

$$n = \frac{K(t+10^\circ\text{C})}{K(t^\circ\text{C})}$$

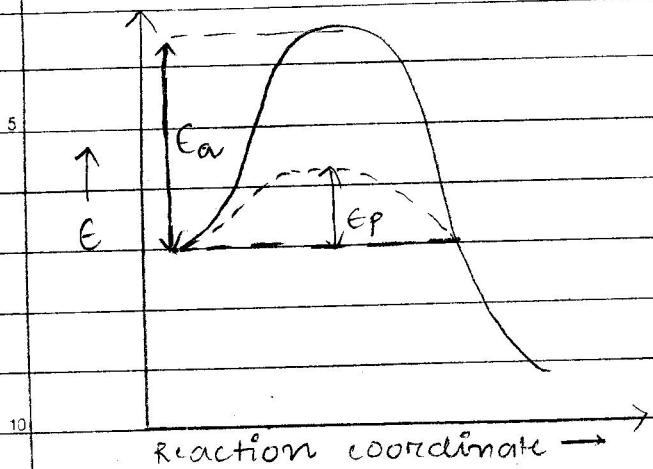
(C) Effect of catalyst on rate of a chemical reaction:

catalyst is a chemical substance which alter the rate of a chemical reaction without being consumed itself.

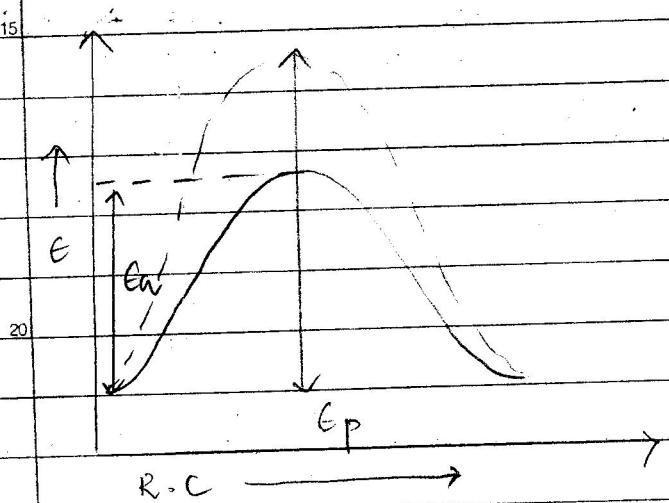
It is of two types:

- (1) +ve catalyst
- (2) -ve catalyst

① Positive catalyst: It decreases the activation energy and increases the rate of reaction



② Negative catalyst: It decreases the rate of reaction and increases the activation energy.



$$K_p = A e^{-\frac{E_p}{RT}} \rightarrow ①$$

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

$$\log \frac{K_p}{K_a} = \frac{\Delta E}{2.303RT}$$

$$\frac{K_p}{K_a} = e^{\frac{E_a}{RT} - \frac{E_p}{RT}}$$

$$\frac{K_p}{K_a} = \text{antilog} \left(\frac{\Delta E}{2.303RT} \right)$$

$$\frac{K_p}{K_a} = e^{\frac{1}{RT} (E_a - E_p)}$$

$$\ln \frac{K_p}{K_a} = \frac{1}{RT} (\Delta E)$$

- ① Note: A small amount of catalyst can catalyse a large amount of reactant.
- A catalyst does not alter Ag and ΔH value.
- A catalyst can catalyse only spontaneous reaction but does not catalyse the non-spontaneous reaction.
- A catalyst does not change the value of equilibrium constant.

② Collision theory:

The postulates of collision theory are as follows:

- (1) A chemical reaction takes place due to collision among reactant molecules.
- (2) All the collisions do not lead to the product formation when the collision is effective then only chemical reaction takes place.
- (3) Only those collision result in chemical reaction in which the colliding molecules possess a certain min. amount of energy which is called E_{th} .
- (4) Energy alone does not determine the effectiveness of the collision. When the no. of no. of effective collisions increases the rate of reaction increases.

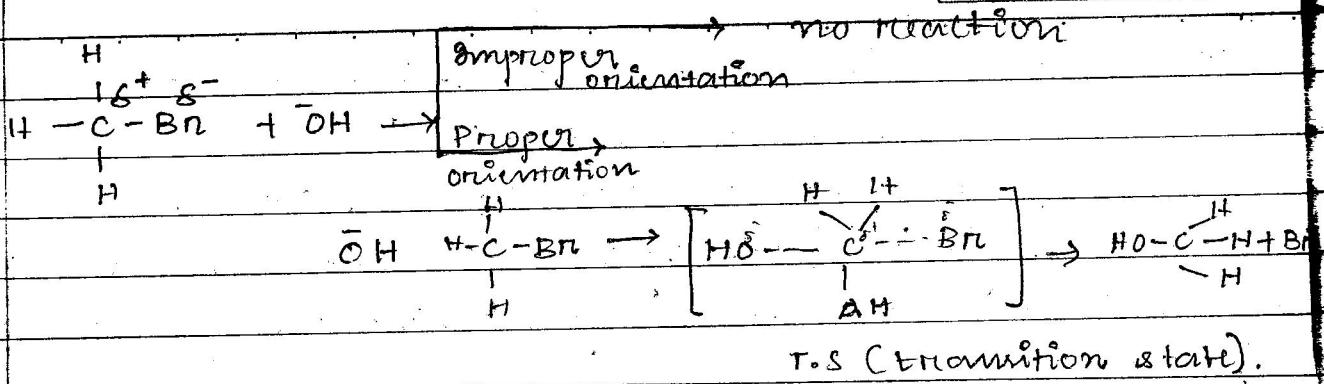
$$\text{Rate} = Z_{AB} e^{-E_a/RT}$$

where Z_{AB} = no. of effective collision.

- (5) When the reacting molecules must collide in proper orientation then the reaction takes place.

$$\text{Rate} = Z_{AB} \times P \times e^{-E_a/RT}$$

P = orientation factor



\rightarrow Effective collision: It is defined as the no. of collisions per second per unit vol. of the reaction mixture.

Q) The rate constant for the decomposition of hydrocarbon is $2.418 \times 10^{-5} \text{ sec}^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor (A)?

A_{ans.}

$$15 \quad K = 2.418 \times 10^{-5} \text{ sec}^{-1}$$

$$T = 546 \text{ K}$$

$$E_a = 179.9 \text{ kJ/mol} = 179900 \text{ J/mol}$$

$$20 \quad \log K = \log A - \frac{E_a}{2.303RT}$$

$$\log A = \log K + \frac{179900}{2.303 \times 8.314 \times 546}$$

$$25 \quad \log A = \log (2.418 \times 10^{-5}) + \frac{179900}{2.303 \times 8.314 \times 546}$$

Q. Sucrose decomposes in acidic sol. into glucose and fructose according to 1st order rate law with $t_{1/2} = 3 \text{ hr}$. What fraction of sample of sucrose remains after 8 hours.

$$t_{1/2} = 3 \text{ hr}, t = 8 \text{ hr}$$

$$t_{50\%} = \frac{2.303}{k} \log \frac{100}{50}$$

$$t = \frac{2.303}{k} \log \frac{R_0}{R}$$

$$\frac{t_{50\%}}{8} = \frac{\log 2}{\log \frac{R_0}{R}}$$

$$\frac{3}{8} = \frac{0.3}{\log \frac{R_0}{R}}$$

$$\log \frac{R_0}{R} = \frac{8}{10}$$

$$\log \frac{R_0}{R} = 0.8$$

$$\text{so, } \log \frac{R_0}{R} = 0.8$$

$$\left(\frac{R_0}{R} \right) = \text{antilog}(0.8) = 6.329$$

$$\frac{R_0}{R} = \frac{1}{6.329} = 0.158$$

Q. The decomposition of hydrocarbon follows the equation
 $k = 4.5 \times 10^{11} \text{ sec}^{-1} e^{-28000 K/T}$
 calculate Ea

$$\Rightarrow \frac{E_a}{RT} = 28000 \frac{K}{T}$$

$$\Rightarrow E_a = 28000 \text{ K} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 28000 \times 8.314 \text{ J mol}^{-1}$$

Q. The rate constant for the 1st order decomposition of H₂O₂ is log K = 14.34 - 1.25 × 10⁻⁴ K/T calculate Ea at what temp. the half-life time period becomes 256 unit

Ans

$$\frac{E_a}{2.303 RT} = 1.25 \times 10^{-4} \text{ K}$$

$$E_a = 1.25 \times 10^{-4} \times 2.303 \times 8.314 \text{ J/mol.}$$

$$= 289339.275 \text{ J/mol}$$

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

$$\log\left(\frac{0.693}{256}\right) = \log A \approx 14.34 - \frac{289339.275}{2.303 \times 8.314 \times T}$$

$$\log(0.0027) = 14.34 - \frac{289339.275}{2.303 \times 8.314 \times T}$$