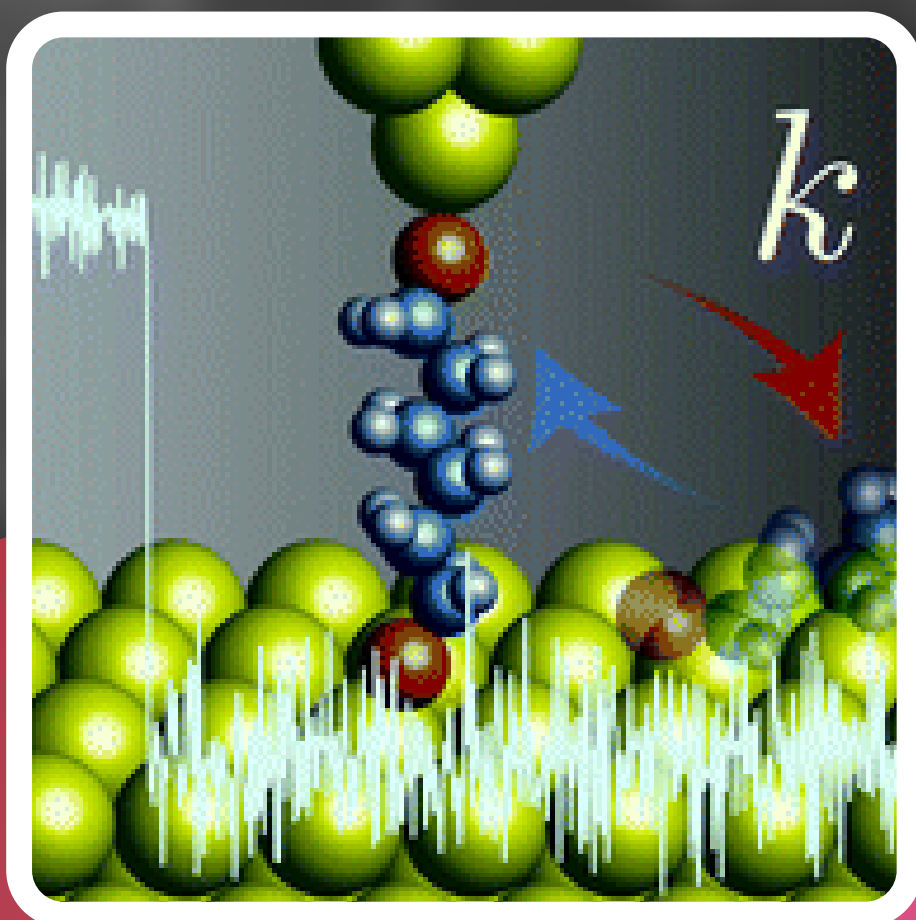


PHYSICAL CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



STUDY MATERIAL

Chemical kinetics

ENGLISH MEDIUM

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CHEMICAL KINETICS

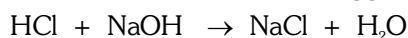
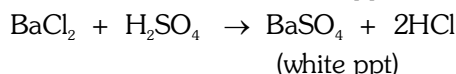
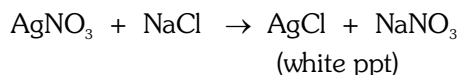
2.0 INTRODUCTION

Chemical Kinetics is the branch of physical chemistry which deals with the study of rate of reactions, the mechanism by which the reactions proceed and factors affecting rate of reaction.

On the basis of rate, chemical reaction are broadly divided into three categories :-

(a) Very fast or instantaneous reactions : Generally these reactions involve ionic species and known as ionic reactions. These reactions take about 10^{-14} or 10^{-16} seconds for completion. So, it is almost impossible to determine the rate of these reactions.

Examples :



(b) Very slow reactions : These reactions proceed very slowly, may take days or months to show any measurable change at room temperature.

Examples :

- Rusting of iron.
- Reaction between H_2 and O_2 to form H_2O at ordinary temperature in absence of catalyst.
- $\text{CO} + 2\text{H}_2 \xrightarrow{\text{at room temperature}} \text{CH}_3\text{OH}$

(c) Moderate or slow reactions : This type of reactions proceed with a measurable rates at normal temperature and we can measure the rate of these reactions easily. Mostly these reactions are molecular in nature.

Examples :

- Decomposition of H_2O_2

$$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$$
- Decomposition of N_2O_5

$$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$$
- Hydrolysis of ester

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$$
- Inversion of cane sugar in aqueous solution
- Reaction of NO with chlorine

$$\text{NO} + \text{Cl}_2 \rightarrow \text{NOCl}_2$$

2.1 RATE OF REACTION

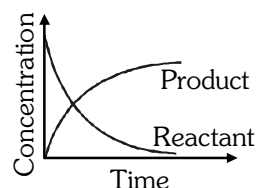
Rate of reaction is defined as the change in concentration or pressure of reactant or product per unit time. It is always a positive quantity.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactant or product}}{\text{Time taken in change}} \quad \boxed{r = \pm \frac{\Delta C}{\Delta t}}$$

Where ΔC = change in concentration in a small interval Δt
 [+] sign is used when we refer for product concentration.
 [-] sign is used when we refer for reactant concentration.

For gaseous reactions $r = \pm \frac{\Delta P}{\Delta t}$ (unit of rate = pressure time⁻¹)

$$\text{and } r = \frac{1}{RT} \times \left[\pm \frac{\Delta P}{\Delta t} \right] \quad (\text{unit of rate} = \text{M time}^{-1})$$



Types of Rate of Reactions :-
(A) Average Rate of Reaction

The rate of reaction over a certain measurable period of time during the course of reaction is called average rate of reaction. It is denoted by \bar{r} .

For a reaction $A \longrightarrow B$

$$r_{\text{average}} = \bar{r} = \left(\frac{[A]_2 - [A]_1}{t_2 - t_1} \right) = - \frac{\Delta[A]}{\Delta t}$$

Where $[A]_1$ = Concentration of reactant A at time t_1 ,

$[A]_2$ = Concentration of reactant A at time t_2 .

(B) Instantaneous Rate of Reaction

The rate of reaction at any particular instant during the course of reaction is called instantaneous rate of reaction.

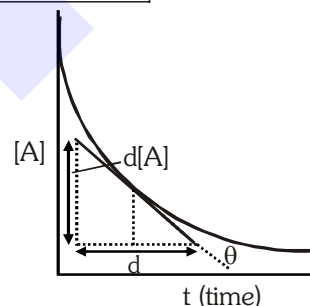
For a reaction $A \longrightarrow B$

Mathematically ; Instantaneous rate = $\lim_{\Delta t \rightarrow 0}$ (Average rate)

$$r_{\text{inst}} = \lim_{\Delta t \rightarrow 0} \left(- \frac{\Delta[A]}{\Delta t} \right) = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta[B]}{\Delta t} \right) \quad \text{or} \quad r_{\text{inst}} = (-) \frac{d[A]}{dt} = (+) \frac{d[B]}{dt}$$

Hence, Slope of the tangent at time t in plot of concentration with time gives instantaneous rate of reaction.

$$\text{Instantaneous rate of reaction} = \lim_{\Delta t \rightarrow 0} \left(\pm \frac{\Delta C}{\Delta t} \right) = \pm \frac{dC}{dt}$$


2.2 RATE OF REACTION IN THE FORM OF STOICHIOMETRY OF A CHEMICAL REACTION

Let us consider a reaction : $m_1A + m_2B \rightarrow n_1P + n_2Q$

Where, Rate of disappearance of A = $-\frac{d[A]}{dt}$

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

Rate of appearance of P = $\frac{d[P]}{dt}$

Rate of appearance of Q = $\frac{d[Q]}{dt}$

$$\text{Rate of reaction} = \frac{1}{m_1} \left(- \frac{d[A]}{dt} \right) = \frac{1}{m_2} \left(- \frac{d[B]}{dt} \right) = \frac{1}{n_1} \frac{d[P]}{dt} = \frac{1}{n_2} \frac{d[Q]}{dt}$$

- Rate of reaction is always positive; negative sign represents decrease in concentration of reactant.

Units of Rate of Reaction

Unit of rate of reaction = $\text{mol L}^{-1} \text{time}^{-1}$ i.e. ($\text{mol L}^{-1} \text{s}^{-1}$ or $\text{mol L}^{-1} \text{min}^{-1}$ or $\text{mol L}^{-1} \text{h}^{-1}$)

Illustrations

Illustration 1. For the reaction : $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. If the concentration of NO_2 increases by $1.6 \times 10^{-2} \text{ M}$ in 4 s. Calculate the following -

- (i) rate of formation of NO₂
 (ii) rate of formation of O₂
 (iii) rate of disappearance of N₂O₅
 (iv) rate of reaction

Solution. (i) Rate of formation of NO_2 : $\frac{d[\text{NO}_2]}{dt} = \frac{1.6 \times 10^{-2}}{4} = 4.0 \times 10^{-3} \text{ M/s}$

(ii) Rate of formation of O_2 : $\frac{d[O_2]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{1}{4} \times 4 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M/s}$

(iii) Rate of disappearance of N_2O_5 : $\frac{-d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \times 4 \times 10^{-3} = 2.0 \times 10^{-3} \text{ M/s}$

$$(iv) \text{ Rate of reaction} = \frac{1}{2} \left(-\frac{d[\text{N}_2\text{O}_5]}{dt} \right) = \frac{1}{2} \times 2 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M/s}$$

$$\text{or } \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{1}{4} \times 4 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M/s}$$

$$\text{or } \frac{d[\text{O}_2]}{dt} = 1.0 \times 10^{-3} \text{ M/s}$$

Illustration 2. Express the rate of reaction for the following changes :

- (a) $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
(b) $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$

Solution. (a) Rate of reaction $= \frac{1}{2} \left(-\frac{d[\text{HI}]}{dt} \right) = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt}$

(b) Rate of reaction $= \frac{1}{2} \left(-\frac{d[\text{SO}_2]}{dt} \right) = \frac{-d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$

BEGINNER'S BOX-1

1. The rate of a reaction is expressed as :

$$+\frac{1}{2}\frac{\Delta[C]}{\Delta t}=\frac{1}{3}\frac{\Delta[D]}{\Delta t}=\frac{1}{4}\left(-\frac{\Delta[A]}{\Delta t}\right)=\left(-\frac{\Delta[B]}{\Delta t}\right)$$

Then reaction is

- (1) $4A + B \rightarrow 2C + 3D$
(3) $A + B \rightarrow C + D$

- $$(2) \text{ B} + 3\text{D} \rightarrow 4\text{A} + 2\text{C}$$
- $$(4) \text{ B} + \text{D} \rightarrow \text{A} + \text{C}$$

2. In the reaction, $A + 2B \rightarrow 6C + 2D$ if $-\frac{\Delta[A]}{\Delta t}$ is $2.6 \times 10^{-2} \text{ M s}^{-1}$, what will be the value of $-\frac{\Delta[B]}{\Delta t}$?

- (1) $8.5 \times 10^{-2} \text{ M s}^{-1}$ (2) $2.6 \times 10^{-2} \text{ M s}^{-1}$ (3) $5.2 \times 10^{-2} \text{ M s}^{-1}$ (4) $7.5 \times 10^{-2} \text{ M s}^{-1}$

3. In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\ell) + 3\text{H}_2\text{O}(\text{aq})$

$$(1) \quad (-) \frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{\Delta[\text{Br}_2]}{\Delta t}$$

$$(2) \quad (-) \frac{1}{3} \frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{\Delta[\text{Br}_2]}{\Delta t}$$

$$(3) \quad (-) \frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t}$$

- (4) None of these

2.3 RATE LAW

The experimental expression of rate of reaction in terms of concentration of reactants is known as rate law. In this expression the rate of a reaction is proportional to the product of molar concentration of reactants with each term raised to the power or exponent that has to be found experimentally.

In a chemical reaction :- $aA + bB \longrightarrow \text{Product}$

The rate law is :- $\text{Rate} \propto [A]^x[B]^y$

The values of exponents x and y are found experimentally which may or may not be same as stoichiometric coefficients.

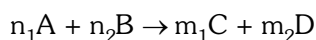
Above relationship can be written as :-

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

Where k is a proportionality constant known as rate constant.

Rate constant :

In a chemical reaction –



according to law of mass action

$$\text{Rate} = k[A]^{n_1}[B]^{n_2}$$

but according to rate law (experimental concept)

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

if $[A] = [B] = 1 \text{ mol/L}$

then, $\text{Rate} = k$

Rate of reaction at unit concentration of reactants is called as rate constant or specific reaction rate.

Rate constant does not depend on concentration of reactant but it depends on temperature and catalyst.

2.4 ORDER OF REACTION –

The sum of powers of concentration of reactants in rate law expression is known as order of reaction.

For the reaction $aA + bB \rightarrow \text{Product}$

Rate law is $\text{Rate} = k[A]^x[B]^y$

Here

x = order of reaction with respect to A

y = order of reaction with respect to B

x + y = n (overall order of reaction)

- Order of reaction may be zero, positive, negative or fractional.
- Order of reaction is an experimental quantity.

Units of rate constant :

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

$$k = \frac{r}{[A]^n} = \frac{\text{unit of rate}}{[\text{unit of concentration}]^n} = \frac{\frac{\text{mol}}{\text{L}} \times \text{time}^{-1}}{\left[\frac{\text{mol}}{\text{L}}\right]^n}$$

- Unit of $k = \left[\frac{\text{mol}}{\text{L}}\right]^{1-n} \times \text{time}^{-1}$
- For gaseous reaction unit of k may be $= (\text{atm})^{1-n} \times \text{time}^{-1}$

2.5 MECHANISM OF REACTION :**(a) Elementary reactions :**

Those reactions which completes in single step and which have exponents in rate law equal to stoichiometric coefficients of the reactants.

If $A + B \longrightarrow \text{Products}$; is an elementary reaction
then rate law will be –

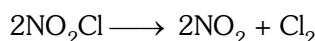
$$\text{Rate} = k[A][B]$$

- Zero order reactions can never be elementary reactions.
- For elementary reactions fractional order is not possible.

(b) Complex reactions :

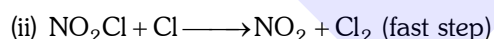
Those reactions which complete in multisteps. For these reactions a mechanism is proposed.

- For complex reactions the overall rate of reaction is controlled by the slowest step which is called as rate determining step (R.D.S.).
- In rate law expression rate of reaction depends on concentration of reactants of slowest step which must be free from intermediate.
- If R.D.S. contains intermediate, its value is solved using K_{eq} of fast step (assumed as reversible)

Example-1

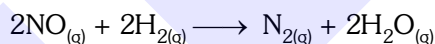
Experimentally, the rate law is $\text{Rate} = k[\text{NO}_2\text{Cl}]$

The mechanism of the reaction is given as –



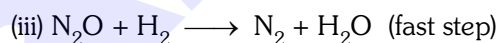
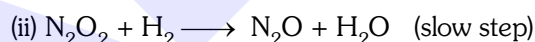
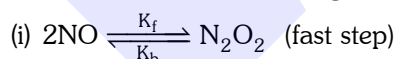
So the rate law from slowest step $\text{Rate} = k[\text{NO}_2\text{Cl}]$

In this way the predicted rate law derived from two step mechanism agrees with experimental rate law.

Example-2

experimentally the rate law is, $\text{Rate} = k[\text{NO}]^2[\text{H}_2]$

The mechanism of the reaction is given as –



The Rate law from slowest step is :

$$\text{Rate} = k[\text{N}_2\text{O}_2][\text{H}_2]$$

The rate law expression should be free from intermediate species N_2O_2 .

From fast reversible step –

$$k_f[\text{NO}]^2 = k_b[\text{N}_2\text{O}_2]$$

$$\therefore [\text{N}_2\text{O}_2] = \frac{k_f}{k_b}[\text{NO}]^2$$

and rate law becomes

$$\text{Rate} = k \left(\frac{k_f}{k_b} \right) [\text{NO}]^2 [\text{H}_2]$$

therefore, $\text{Rate} = k'[\text{NO}]^2[\text{H}_2]$

This derived rate law agrees with experimental rate law.

2.6 MOLECULARITY

Total number of molecules, atoms or ions (reacting species) participating in an elementary reaction is called as molecularity of reaction.

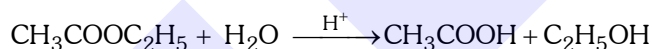
- Molecularity is a theoretical quantity.
- Molecularity can be an integer (1, 2 or 3) but it cannot be zero or negative or fractional.
- In elementary reaction molecularity is equal to its order.
- In complex reaction molecularity of each step of mechanism is defined separately.
- Total molecularity of complex reaction is meaningless.
- In complex reactions generally molecularity of slowest step is same as order of reaction which can be considered as molecularity of reaction. (Except when slowest step contain intermediate)
- Maximum value of molecularity or order is 3 because chances of effective collision of more than three molecules is very rare.

2.7 PSEUDO FIRST ORDER REACTION

A chemical reaction in which value of order of reaction is one but molecularity is more than one are known as pseudo unimolecular/pseudo first order reaction.

Example-1

Hydrolysis of ester in acidic medium.



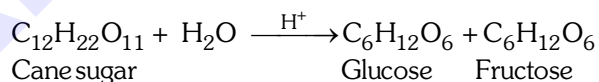
$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$$

Water is in excess then its concentration remain constant during the reaction and $[\text{H}_2\text{O}]$ is taken as constant therefore,

$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] \quad \text{where } k' = k [\text{H}_2\text{O}]$$

Example-2

Inversion of cane sugar.



$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}_2\text{O}]$$

Water is in excess then its concentration remain constant during the reaction and $[\text{H}_2\text{O}]$ is taken as constant therefore,

$$\text{Rate} = k' [\text{C}_{12}\text{H}_{22}\text{O}_{11}] \quad \text{where } k' = k [\text{H}_2\text{O}]$$

GOLDEN KEY POINTS

- Reactant taken in excess can't affect order of reaction.
- In certain complex reaction product is also considered in order calculation.
- Order of reaction is determined experimentally.

Illustrations

Illustration 3. Give the following data for the reaction : $A + B \rightarrow \text{Product}$.

Experiment No.	[A]	[B]	ROR ($\text{mol L}^{-1}\text{s}^{-1}$)
1	1	2	4
2	2	2	4
3	2	4	16

What is the rate law equation ?

Solution. We know that rate law is given by : $r = k[A]^x[B]^y$ (1)

put the values of experiment No. 1 and 2 in equation 1, we get

$$4 = k[1]^x[2]^y \quad \text{.....(2)}$$

$$\text{and } 4 = k[2]^x[2]^y \quad \text{.....(3)}$$

Now, Equation (2) is divided by (3), we get

$$1 = \left(\frac{1}{2}\right)^x \text{ i.e., } x = 0$$

Now, put the values of experiment no. 2 and 3 in equation (1), we get

$$4 = (2)^x (2)^y \quad \text{.....(4)}$$

$$16 = (2)^x (4)^y \quad \text{.....(5)}$$

Equation (4) is divided by (5), we get

$$\frac{1}{4} = \left(\frac{1}{2}\right)^y \text{ i.e., } y = 2$$

So, order of reaction with respect to 'A' is 0 and with respect to 'B' is 2 and the rate of reaction is $r = k[A]^0[B]^2 = k[B]^2$ i.e., order of reaction = 2

Illustration 4. The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and the reaction rate is given by :

$$\text{Rate} = k[\text{CH}_3\text{OCH}_3]^{3/2}$$

The rate of reaction is followed by increase in pressure in a closed vessel and the rate can also be expressed in terms of the partial pressure of dimethyl ether i.e.,

$$\text{Rate} = k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?

Solution. $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2$

$$\text{Rate} = k[\text{CH}_3\text{OCH}_3]^{3/2} = k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

Unit of rate = bar min^{-1}

$$\text{Unit of } k = \frac{\text{Rate}}{(P_{\text{CH}_3\text{OCH}_3})^{3/2}} = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2} \text{ min}^{-1}$$

Illustration 5. For a reaction ; $3A \rightarrow \text{Products}$, it is found that the rate of reaction doubles if concentration of A is increased four times, calculate order of reaction.

Solution.

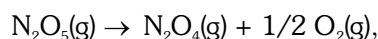
$$\text{Rate} = k[\text{Reactant}]^n \quad \text{if } [\text{Reactant}] = a ; \text{rate} = r_1$$

$$r_1 = k[a]^n \quad \text{if } [\text{Reactant}] = 4a; \text{rate} = 2r_1$$

$$2r_1 = k[4a]^n ; \frac{1}{2} = \left[\frac{1}{4}\right]^n \Rightarrow n = \frac{1}{2}$$

Illustration 6. For the decomposition, $N_2O_5(g) \rightarrow N_2O_4(g) + 1/2 O_2(g)$, the initial pressure of N_2O_5 is 114 mm and after 20 s the pressure of reaction mixture becomes 133 mm of Hg. Calculate the rate of reaction in terms of (a) change in atm s^{-1} and (b) change in molarity s^{-1} . Given that reaction is carried out at 127°C .

Solution.



$$\text{Initial pressure} \quad P \quad 0 \quad 0$$

$$\text{Pressure at } t = 20 \text{ s} \quad (P - P') \quad P' \quad P'/2$$

$$\text{Given } P = 114 \text{ mm}$$

$$\text{After 20 s, total pressure} = (P - P') + P' + (P'/2) = 133 \text{ mm}$$

$$\Rightarrow P'/2 = 19 \text{ mm} \quad P' = 38 \text{ mm}$$

$$\text{Thus rate of reaction in terms of change in pressure} = 38/20 = 1.9 \text{ mm s}^{-1}$$

$$= \frac{1.9}{760} \text{ atm s}^{-1} = 2.5 \times 10^{-3} \text{ atm s}^{-1}$$

$$\text{Also we have } PV = nRT \quad \text{or} \quad \frac{n}{V} = C = \frac{P}{RT}$$

$$\text{change in concentration in 20 second} = \Delta C = \frac{P'}{RT} \quad (\text{change in pressure})$$

$$\frac{38}{760 \times 0.0821 \times 400} = 1.52 \times 10^{-3} \text{ M}$$

$$\text{rate of reaction in terms of change in concentration} = \frac{1.52 \times 10^{-3}}{20} = 7.61 \times 10^{-5} \text{ M s}^{-1}$$

BEGINNER'S BOX-2

1. $A_2 + B_2 \rightarrow 2AB$; R.O.R. = $k[A_2]^a[B_2]^b$

$[A_2]$	$[B_2]$	Rate of reaction $[\text{Ms}^{-1}]$
0.2	0.2	0.04
0.1	0.4	0.04
0.2	0.4	0.08

order of reaction with respect to A_2 and B_2 are respectively :

(1) $a=1, b=1$ (2) $a=2, b=0$ (3) $a=2, b=1$ (4) None

2. For a reaction the initial rate is given as : $R_0 = k[A]_0^2[B]_0$ by what factor, the initial rate of reaction will increase if initial concentration of A is 1.5 times and B is tripled ?

(1) 4.5 (2) 2.25 (3) 6.75 (4) None of these

3. For $A(g) + B(g) \rightarrow C(g)$; rate = $k[A]^{1/2}[B]^2$, if initial concentration of A and B are increased by factor of 4 and 2 respectively, then the initial rate is changed by the factor :-

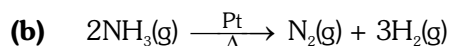
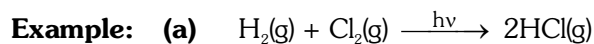
(1) 4 (2) 6 (3) 8 (4) None of these

2.8 STUDY OF DIFFERENT ORDER REACTIONS :

(A) Zero order reactions

Reactions in which rate of reaction remains independent of concentration of the reactant are said to be zero order reactions.

- Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions.

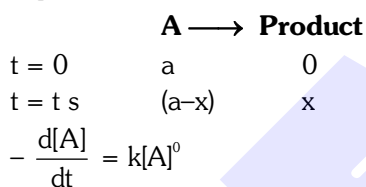


(c) Reaction between Acetone and Bromine.

(d) Dissociation of HI on gold surface.

(e) Adsorption of gases on metal surface :- At low P, rate of adsorption is proportional to surface area covered which is proportional to P or concentration of gas hence order is 1 whereas at high P, complete surface gets covered by gas & rate becomes independent of P & concentration hence order is 0.

Differential Rate Equation



$$\boxed{\frac{dx}{dt} = k[A]^0}$$

Calculation of Rate Constant

Let us take the reaction



$$-\frac{d[A]}{dt} = k[A]^0 = k$$

$$-\int d[A] = \int k dt$$

$$-[A]_t = kt + C$$

$$\text{at } t = 0 \quad [A]_t = [A]_0$$

$$-[A]_0 = k \times 0 + C$$

$$C = -[A]_0$$

On substituting the value of C

$$-[A]_t = kt - [A]_0$$

$$\boxed{[A]_t = [A]_0 - kt} \quad \text{[Integrated rate equation]}$$

$$y = c - mx$$

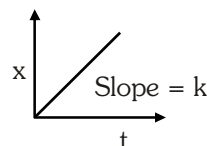
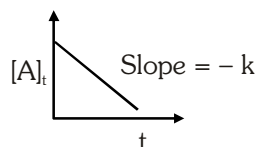
$$[A]_0 - [A]_t = kt$$

$$k = \frac{[A]_0 - [A]_t}{t} = \frac{x}{t}$$

$$\boxed{x = kt}$$

x = Amount of reactant that will change in product.

- For zero order reaction, rate of reaction is equal to rate constant



Unit of rate constant

$k = \text{mol L}^{-1} \text{s}^{-1} = \text{unit of rate of reaction.}$

Half-life period – The time in which half of the initial amount of reactant is consumed.

$$\text{At } t = t_{1/2}, [A]_t = \frac{[A]_0}{2}$$

$$\therefore k t_{1/2} = [A]_0 - \frac{[A]_0}{2} \quad \text{or} \quad t_{1/2} = \frac{[A]_0}{2k}$$

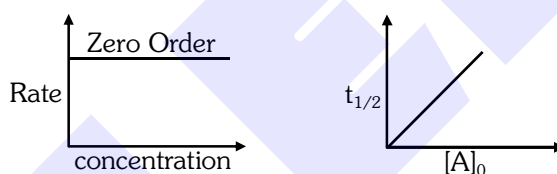
The half life period for a zero order reaction is directly proportional to the initial concentration of the reactants.

Time for completion of reaction

$$[A]_t = [A]_0 - kt$$

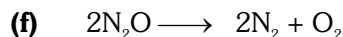
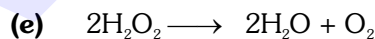
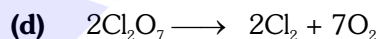
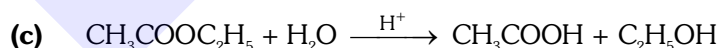
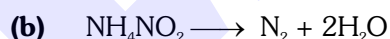
$$\text{For completion } [A]_t = 0$$

$$k = \frac{[A]_0}{t} \quad t_{100\%} = \frac{[A]_0}{k}$$

Graphical representation

(B) First order reactions

Reactions in which the rate of reaction is directly proportional to concentration of reactant.

Example :


Differential rate equation


$$t = 0 \quad a \quad 0$$

$$t = t \text{ s} \quad (a-x) \quad x$$

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

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

Calculation of rate constant

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

$$-\ln[A]_t = kt + c \quad \dots\dots\dots(i)$$

$$\text{At } t = 0; [A]_t = [A]_0 \quad \therefore C = -\ln[A]_0$$

Putting the value of C in equation (i)

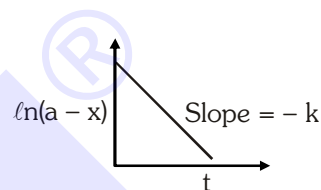
$$-\ln[A]_t = kt - \ln[A]_0$$

$$\boxed{\ln[A]_t = \ln[A]_0 - kt}$$

$$y = c - mx$$

$$\ln \frac{[A]_0}{[A]_t} = kt \quad \dots\dots\dots(ii)$$

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



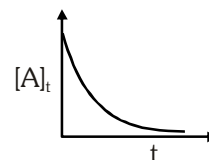
$$2.303 \log_{10} \frac{[A]_0}{[A]_t} = kt$$

$$\boxed{K = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}}$$

from equation(ii)

$$\frac{[A]_0}{[A]_t} = e^{kt}$$

$$\frac{[A]_t}{[A]_0} = e^{-kt} \Rightarrow \boxed{[A]_t = [A]_0 e^{-kt}} \quad \text{Wilhelmy equation}$$



Unit of rate constant [k = time⁻¹]

Half-life Period : The time in which half of the initial amount of reactant is consumed.

$$\text{At } t = t_{1/2} \quad ; \quad x = a/2 \quad ; \quad a-x = a/2$$

$$t_{1/2} = \frac{1}{k} \ln\left(\frac{a}{a/2}\right) \quad \text{or} \quad t_{1/2} = \frac{\ln 2}{k} = \frac{2.303}{k} (\log 2) \quad \text{or} \quad \boxed{t_{1/2} = \frac{0.693}{k}}$$

Half-life period for first order reaction is independent of the initial concentration of reactant.

Time for 3/4th of the Reaction (t_{3/4}) : The time in which 3/4th of the initial amount of reactant is consumed.

$$\text{At } t = t_{3/4} \quad ; \quad x = 3a/4 \quad ; \quad a-x = a/4$$

$$t_{3/4} = \frac{2.303}{k} (\log 4) = \frac{2.303}{k} \times 2 \log 2 = 2 \times t_{1/2}$$

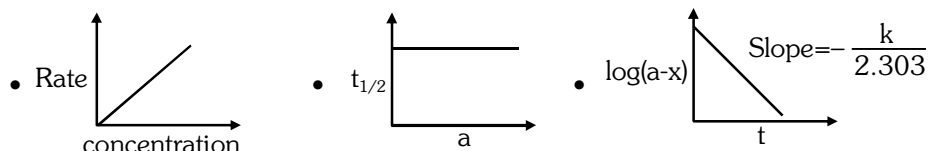
t_{3/4} for first order reaction is independent of the initial concentration of reactant.

Interval Formula

$$k = \frac{2.303}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$$

where x_1 and x_2 are the amount consumed at time t_1 and t_2 respectively.

Time required for the completion of definite fraction of the first order reaction is independent of the initial concentration of the reactant.

Graphical Representation

(C) GENERAL INTEGRATED RATE EQUATION (n^{th} order kinetics)

$$kt = \frac{1}{(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right] \quad [n \neq 1]$$

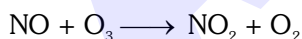
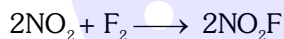
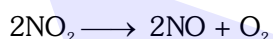
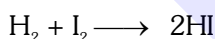
If $t = t_{1/2}$; $x = \frac{a}{2}$

Therefore $kt_{1/2} = \frac{1}{(n-1)} \left[\left(\frac{2}{a} \right)^{n-1} - \left(\frac{1}{a} \right)^{n-1} \right]$

$$kt_{1/2} = \frac{1}{(n-1)} \left[\frac{2^{n-1} - 1}{a^{n-1}} \right] \quad (n \neq 1) ; \quad t_{1/2} \propto \frac{1}{a^{n-1}}$$

(i) Second order reactions

Hydrolysis of ester by alkali (Saponification)

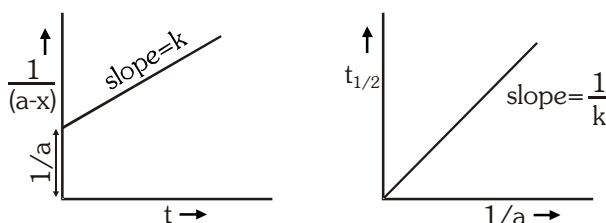


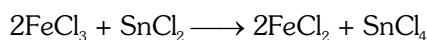
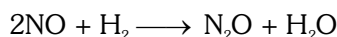
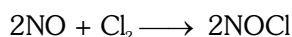
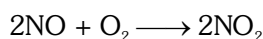
For second order : $n = 2$

$$kt = \frac{1}{(2-1)} \left[\frac{1}{(a-x)} - \frac{1}{a} \right] = \frac{1}{(a-x)} - \frac{1}{a}$$

Half life

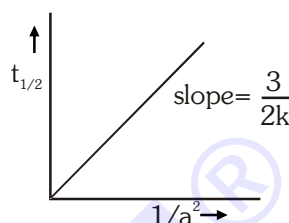
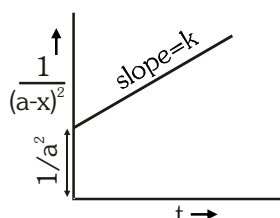
$$t_{1/2} = \frac{1}{ak}$$



(ii) Third order reactions

$$\text{for third order } n = 3 \quad kt = \frac{1}{(3-1)} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right] = \frac{1}{2} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$

$$\text{Half life } t_{1/2} = \frac{3}{2a^2k}$$

**Examples of fractional order reaction**

Reaction	Order
$\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$	1.5
$\text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2$	2.5
$\text{COCl}_2 \longrightarrow \text{CO} + \text{Cl}_2$	1.5
$\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$	1.5
$\text{CHCl}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{HCl}$	1.5

Illustrations

Illustration 7. 90% of a first order reaction was completed in 10 hours. When will 99.9% of the reaction complete ?

Solution. $k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$, $a = 100$, $x = 90$, $t = 10$

$$\text{So } k_1 = \frac{2.303}{10} \log \frac{100}{10} = 2.303 \times 10^{-1} \text{ hour}^{-1}$$

Now for 99.9% completion : $a = 100$ and $x = 99.9$

$$t = \frac{2.303}{k_1} \log \frac{100}{0.1} = \frac{2.303}{2.303 \times 10^{-1}} \times 3 = 30 \text{ hours}$$

Illustration 8. 20% of a first order reaction was completed in 5 min. When will 60% of the reaction complete?

Solution. $t = 5 \text{ min}$, $a = 100$, $x_1 = 20$

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x_1} \right) = \frac{2.303}{5} \log \frac{100}{80} = \frac{2.303}{5} \log \frac{5}{4} = \frac{2.303}{5} [\log 5 - \log 4]$$

$$k = \frac{2.303}{5} [0.6989 - 0.6020] = \frac{2.303}{5} [0.0969] = 0.0446 \text{ min}^{-1}$$

Now $x_2 = 60$

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x_2} \right)$$

$$t = \frac{2.303}{0.0446} \log \frac{100}{40} = \frac{2.303}{0.0446} [\log 5 - \log 2] = \frac{2.303}{0.0446} \times 0.3979 = 20.55 \text{ min.}$$

Illustration 9. For the first order reaction, half life is 6 min. Calculate the rate constant of the reaction ?

Solution. $t_{1/2} = \frac{0.693}{k_1} \Rightarrow k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{6} = 0.1155 \text{ min}^{-1}$

Illustration 10. A first order reaction is 90% complete in 40 min. Calculate the Half life of the reaction.

Solution. $a = 100, x = 90$
 $k_1 = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40} \log \frac{100}{10} = \frac{2.303}{40} = 5.757 \times 10^{-2} \text{ min}^{-1}$
 $t_{1/2} = \frac{0.693}{k_1} = \frac{0.693}{5.757 \times 10^{-2}} = 12.03 \text{ min.}$

Illustration 11. In a second order reaction both the reactants have equal initial concentration, the time taken for 60% completion of reaction is 3000 s. What will be the time taken for 20% of the reaction?

Solution. $k_2 = \frac{1}{t} \frac{x}{a(a-x)}, \text{ Let } a = 1,$
 $k_2 = \frac{1}{t} \frac{x}{(1-x)} = \frac{1}{3000} \left(\frac{0.6}{1-0.6} \right) = \frac{1}{3000} \times \frac{0.6}{0.4} = \frac{1}{2000}$
 So time for the 20% completion is :
 $t = \frac{1}{k_2} \frac{x}{a(a-x)} = 2000 \times \frac{0.20}{0.80} = 500 \text{ s.}$

Illustration 12. If the initial concentration of reactants are doubled then half life becomes half. Calculate order of the reaction ?

Solution. $\left(\frac{t_1}{2} \right)_1 = \left(\frac{a_2}{a_1} \right)^{n-1} \Rightarrow \left(\frac{t_1}{2} \right)_1 = \left(\frac{2a}{a} \right)^{n-1}$
 $2 = (2)^{n-1} \Rightarrow n-1 = 1 \Rightarrow n = 2$
 so, the order of the reaction will be 2.

BEGINNER'S BOX-3

- Which of the following expressions is correct for zero order and first order reactions respectively (where a is initial concentration) ?
 (1) $t_{1/2} \propto a; t_{1/2} \propto \frac{1}{a}$ (2) $t_{1/2} \propto a; t_{1/2} \propto a^0$ (3) $t_{1/2} \propto a^0; t_{1/2} \propto a$ (4) $t_{1/2} \propto a; t_{1/2} \propto \frac{1}{a^2}$
- For the zero order reaction, $A \rightarrow B + C$; initial concentration of A is 0.1 M. If $[A] = 0.08 \text{ M}$ after 10 minutes, then it's half-life and completion time are respectively :
 (1) 10 min; 20 min (2) $2 \times 10^{-3} \text{ min}; 4 \times 10^{-3} \text{ min}$
 (3) 25 min, 50 min (4) 250 min, 500 min
- For an elementary reaction, $X(g) \rightarrow Y(g) + Z(g)$ the half life period is 10 min. In what period of time the concentration of X will be reduced to 10% of original concentration?
 (1) 20 min (2) 33 min (3) 15 min (4) 25 min
- A first order reaction is 75% completed in 100 min. How long will it take for it's 87.5% completion?
 (1) 125 min (2) 150 min (3) 175 min (4) 200 min
- The rate constant for a first order reaction which has half life 480 s is :-
 (1) $1.44 \times 10^{-3} \text{ s}^{-1}$ (2) $1.44 \times \text{s}^{-1}$ (3) $0.72 \times 10^{-3} \text{ s}^{-1}$ (4) $2.88 \times 10^{-3} \text{ s}^{-1}$

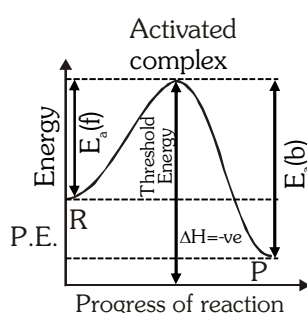
2.9 COLLISION THEORY OF CHEMICAL REACTIONS

This theory was given by Max Trautz and William Lewis. According to it, for a reaction to occur there must be collisions in between reacting molecules. Total number of collisions per second in unit volume is called collision frequency (z). Generally its value is very high for gaseous reactions (10^{25} to 10^{28} collisions/sec-cm³). But only a small fraction of these collisions are capable to convert reactant into product. These collisions are called as effective collisions.

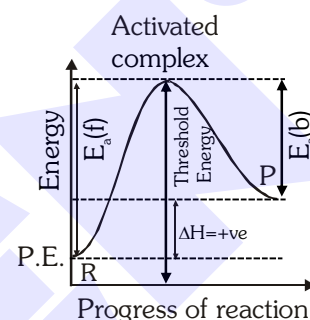
For effective collision following two conditions must be satisfied at a time :

- Reacting molecules must possess a minimum amount of energy.
- Proper orientation of collision

- Threshold energy** : The minimum energy which must be possessed by reacting molecules for a chemical reaction to occur.
- Activation energy** : The minimum extra amount of energy required by reactant molecules for converting into products.



Exothermic reaction



Endothermic reaction

- $E_a(f)$ = Activation energy for forward reaction
- $E_a(b)$ = Activation energy for backward reaction

If not specified in questions then consider E_a for forward reaction.

$$\Delta H = E_a(f) - E_a(b) \quad ; \quad \Delta H = H_p - H_R$$

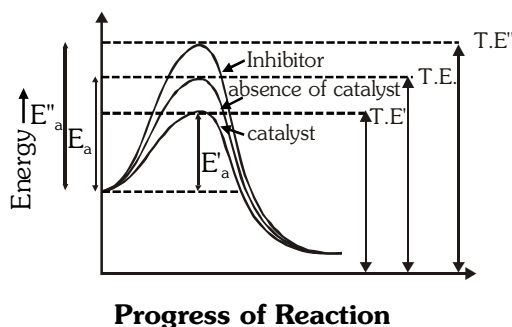
ACTIVATION ENERGY MAINLY DEPENDS UPON :

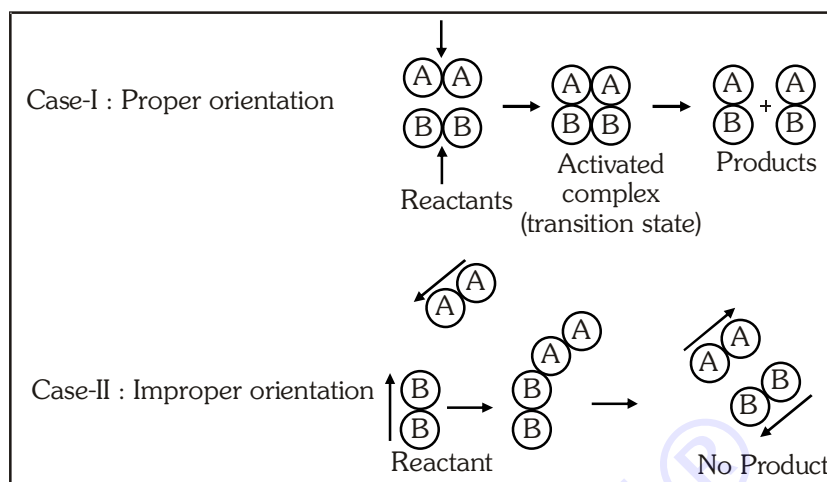
- Nature of reactant** : For different reactants, number of bonds and bond energies are different, therefore activation energy will also be different.

Reactions which have less E_a , take place at faster rate.

- Presence of catalyst** : Catalyst provide an alternative path of reaction mechanism for the reaction.

- In presence of catalyst threshold energy decreases, activation energy decreases and rate of reaction increases.
- In presence of negative catalyst (inhibitor) threshold energy increases, activation energy increases, rate of reaction decreases.



(b) Orientation :

• Limitations :

- (i) This theory is mainly applicable for gaseous reactions and also for solutions in which reacting species are molecules.
- (ii) This theory is mainly applicable for simple bimolecular reactions but fails for complex reactions.
- (iii) It considers molecules to be hard sphere and ignore structural aspect of molecules.

GOLDEN KEY POINTS

- Activated complex is most unstable complex formed in the transition state with effective collision.
- On increasing temperature E_a for reaction does not decrease but number of active molecules which are crossing the energy barrier increases therefore rate of reaction increases.
- According to Arrhenius ; rate of reaction $\propto e^{-\frac{E_a}{RT}}$ E_a = Activation energy
 R = Gas constant
 T = Temperature (in K)

Illustrations

Illustration 13 The E_a for an exothermic reaction $A \rightarrow B$ is 80 kJ mol^{-1} . Heat of reaction is 20 kJ mol^{-1} . E_a for the reaction $B \rightarrow A$ will be ?

Solution $\Delta H = E_{a(f)} - E_{a(b)} \Rightarrow -20 = 80 - E_{a(b)}$
 $E_{a(b)} = 100 \text{ kJ mol}^{-1}$

Illustration 14 For the reaction $A + B \rightleftharpoons C + D$ the activation energy is 32 kJ mol^{-1} . For the reverse reaction the E_a is 58 kJ mol^{-1} . Determine (i) Nature of reaction (ii) ΔH

Solution $\Delta H = E_{a(f)} - E_{a(b)}$
 $\Delta H = 32 - 58$
 $\Delta H = -26 \text{ kJ mol}^{-1}$ (exothermic)

Illustration 15 For an endothermic reaction

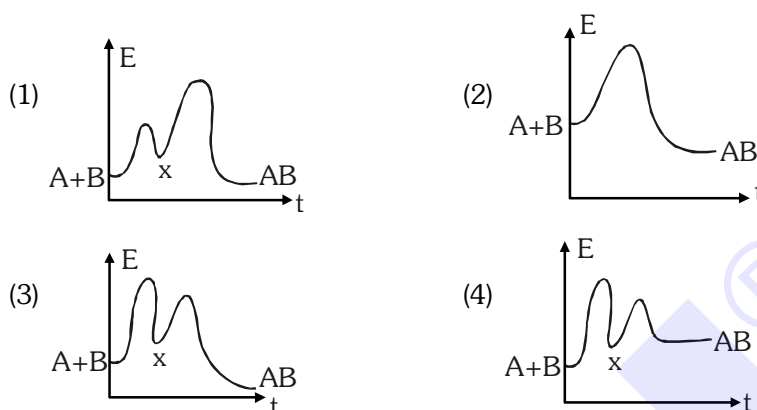
- (1) $E_a > \Delta H$
- (2) $E_a < \Delta H$
- (3) $E_a = \Delta H$
- (4) any one of the above

Solution **Ans. (1)**

Illustration 16 For an exothermic reaction
 (1) $E_a > \Delta H$ (2) $E_a < \Delta H$ (3) $E_a = \Delta H$ (4) any one of the above

Solution **Ans. (4)**

Illustration 17 An exothermic chemical reaction is occurring in two steps as follows
 (i) $A + B \rightarrow X$ (slow) (ii) $X \rightarrow AB$ (fast)
 the process of reaction can be best described by



Solution **Ans. (3)**

2.10 FACTORS AFFECTING RATE OF REACTION :

1. Nature of reactant :

(a) Physical state of reactant :

increasing order of rate of reaction – Solid < liquid < gas
 (Intermolecular attractive force decreases which provides more freedom for collisions)

(b) Physical size of particles (if reactant is solid) :

$$\text{Rate of reaction} \propto \frac{1}{\text{physical size}} \propto \text{surface area}$$

(c) **Chemical nature of reactant** : For different reacting species number of bonds broken and their bond energies are different. Therefore requirement of activation energy is also different. Now reactions having less value of activation energy will take place at faster rate.

2. Concentration of reactant : Rate of reaction \propto concentration of reactant

3. **Pressure** : Effect of pressure on Rate of reaction is negligible when reactants are solid or liquid. But if reactants are in gaseous state then rate of reaction increases on increasing pressure because number of effective collisions increases.

4. **Temperature** : On increasing temperature rate of reaction increases whether the reaction is exothermic or endothermic. When temperature increases KE of molecules increases, number of activated molecules increases thus rate of reaction increases.

Relation between rate constant and Temperature :-

(a) Generally it is found that for every 10 °C rise in temperature Rate of reaction becomes 2 to 3 times.

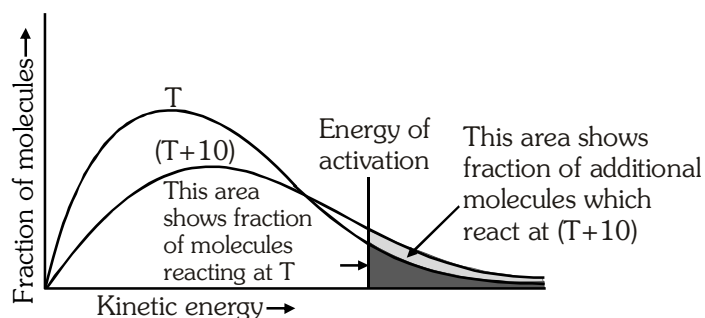
Temperature coefficient (μ) : It is defined as ratio of rate constant of a reaction at two different temperatures which will differ by 10 °C.

$$\mu = \frac{k_{T+10}}{k_T} = 2 \text{ to } 3 ; \frac{r_2}{r_1} = \frac{k_2}{k_1} = \mu^{AT/10}$$

If temperature of reaction is not specified then consider 25 °C.

(If μ is not given consider it as minimum 2)

MAXWELL AND BOLTZMANN ENERGY DISTRIBUTION CURVE



(b) Arrhenius equation

$$k = Ae^{-E_a/RT} \quad \dots(1)$$

A = Arrhenius constant / pre-exponential factor / Frequency factor

E_a = Activation energy

R = gas constant

T = Temperature (Kelvin)

- k increases with increase in temperature
If $T \rightarrow \infty$; $k = A$
- $\frac{k}{A} = e^{-E_a/RT}$ = fraction of molecules having energy $\geq E_a$
 $e^{-E_a/RT}$ = Boltzman factor

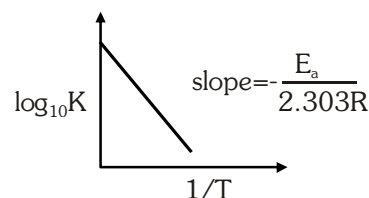
On taking logarithm for equation (1) on both sides.

$$\ln k = \ln A + \ln e^{-E_a/RT}$$

$$2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT} \quad \dots(2)$$

$y = c - mx$



- E_a of reaction can be determined by measuring rate constant at two different temperatures

At temperature T_1 :

$$\log_{10} k_1 = \log_{10} A - \frac{E_a}{2.303RT_1} \quad \dots(3)$$

At temperature T_2 :

$$\log_{10} k_2 = \log_{10} A - \frac{E_a}{2.303RT_2} \quad \dots(4)$$

Equation (4) – Equation (3) gives -

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

- From arrhenius equation - $k = Ae^{-E_a/RT}$

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

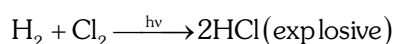
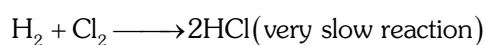
$$\frac{d}{dT}(\ln k) = \frac{d}{dT}(\ln A) + \frac{d}{dT}\left(-\frac{E_a}{RT}\right) = 0 - \frac{E_a}{R} \frac{d}{dT}(T^{-1}) = \frac{E_a}{R}(T^{-2})$$

$$\boxed{\frac{d}{dT} \ln k = \frac{E_a}{RT^2}} \quad \text{differential form of Arrhenius equation}$$

5. Presence of catalyst : In presence of catalyst E_a of reaction decreases and rate of reaction increases.

6. Exposure to radiation : Rate of some reactions also increases when reaction are carried out in the presence of radiation. (only for photochemical reaction)

e.g. formation of HCl



Illustrations

Illustration 18 A reaction whose temperature is increased from 10°C to 50°C then increase in rate of reaction will be—

Solution. We know that on increasing temperature by 10°C the rate of reaction becomes 2 to 3 times.

Note : If the value of temperature coefficient is not given then we will take 2.

$$\begin{aligned} 10^\circ\text{C} &\text{ — } 20^\circ\text{C} = 2 \text{ times} \\ 20^\circ\text{C} &\text{ — } 30^\circ\text{C} = 2^2 \text{ times} \\ 30^\circ\text{C} &\text{ — } 40^\circ\text{C} = 2^3 \text{ times} \\ 40^\circ\text{C} &\text{ — } 50^\circ\text{C} = 2^4 \text{ times} \\ &= 16 \text{ times} \end{aligned}$$

Illustration 19 For a reaction, temperature coefficient = 2, then calculate the activation energy (in kJ) of the reaction.

Solution. Let $T_1 = 25^\circ\text{C}$, $T_2 = 35^\circ\text{C}$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Given : Temperature coefficient = $\frac{k_2}{k_1} = 2$

$$T_1 = 25 + 273 = 298 \text{ K}, T_2 = 35 + 273 = 308 \text{ K}, R = 8.314$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \left(\frac{10}{298 \times 308} \right)$$

$$E_a = 52.897 \text{ kJ}$$

Illustration 20 An exothermic reaction $A \longrightarrow B$ has an activation energy of 17 kJ mol^{-1} of A. The heat of the reaction is 40 kJ . Calculate the activation energy for the reverse reaction $B \longrightarrow A$.

Solution. For the reaction $A \longrightarrow B$.

Activation energy $E_a = 17 \text{ kJ}$

$\Delta H = -40 \text{ kJ}$

$\Delta H = E_a(f) - E_a(b)$

$E_a(b) = 17 - (-40) = 57 \text{ kJ}$

Illustration 21 For first order gaseous reaction $\log k$ when plotted against $\frac{1}{T}$, gives a straight line with a slope of -8000 . Calculate the activation energy of the reaction.

Solution. Arrhenius equation $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

when curve is plotted between $\log k$ and $\frac{1}{T}$, a straight line is obtained. Slope of this line

$$= -\frac{E_a}{2.303R}$$

Then, $\frac{E_a}{2.303R} = 8000$ or $E_a = 8000 \times 2.303 \times 1.987 = 36608 \text{ Cal}$

Illustration 22 If temperature of a reaction is increased from 10°C to 100°C then how many times rate of reaction will become?

Solution 2^9 times

Illustration 23 If temperature of a reaction is increased from t_1 to t_2 then rate of reaction becomes ?

Solution $(\mu)^{t_2-t_1/10} \Rightarrow (\mu)^{\Delta T/10}$ times ; $r_{\text{new}} = r_{\text{old}} \times (\mu)^{\Delta T/10}$

Illustration 24 A reaction is carried out at 10°C . If temperature is increased by 50°C then how many times rate of reaction will become?

Solution 32 times

BEGINNER'S BOX-4

- For an endothermic reaction where ΔH represents the enthalpy of reaction in kJ mol^{-1} , the minimum value for the energy of activation will be
 (1) less than ΔH (2) more than ΔH (3) equal to ΔH (4) zero
- The activation energy of the reaction, $A + B \rightarrow C + D + 38 \text{ kcal}$ is 20 kcal , what would be the activation energy of the reaction, $C + D \rightarrow A + B$
 (1) 20 kcal (2) -20 kcal
 (3) 18 kcal (4) 58 kcal
- $\frac{k_{35^\circ}}{k_{34^\circ}} > 1$, this means that
 (1) Rate increases with the rise in temperature (2) Rate decreases with rise in temperature
 (3) rate does not change with rise in temperature (4) None of the above
- The plot of $\ln k$ versus $1/T$ is linear with slope of
 (1) $-\frac{E_a}{R}$ (2) $\frac{E_a}{R}$
 (3) $\frac{E_a}{2.303R}$ (4) $-\frac{E_a}{2.303R}$

ANSWER'S KEY

BEGINNER'S BOX-1	Que.	1	2	3		
	Ans.	1	3	3		

BEGINNER'S BOX-2	Que.	1	2	3		
	Ans.	1	3	3		

BEGINNER'S BOX-3	Que.	1	2	3	4	5		
	Ans.	2	3	2	2	1		

BEGINNER'S BOX-4	Que.	1	2	3	4		
	Ans.	2	4	1	1		