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:

$AgNO_3 + NaCl \longrightarrow \underset{\text{(white ppt)}}{AgCl} + NaNO_3$

$BaCl_2 + H_2SO_4 \longrightarrow \underset{\text{(white ppt)}}{BaSO_4} + 2HCl$

$HCl + NaOH \longrightarrow NaCl + HO$

(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.
- $CO + 2H_2 \xrightarrow{\text{at room temperature}} CH_3OH$

(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.

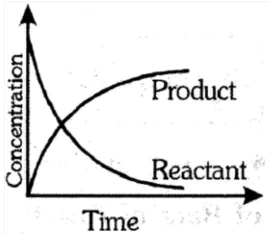
Examples:

- Decomposition of H_2O_2
  $2H_2O_2 \longrightarrow 2H_2O + O_2$
- Decomposition of N_2O_5
  $2N_2O_5 \longrightarrow 4NO_2 + O_2$
- Hydrolysis of ester
  $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$
- Inversion of cane sugar in aqueous solution
- Reaction of NO with chlorine
  $NO + Cl_2 \longrightarrow NOCl_2$

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.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactant or product}}{\text{Time taken in change}}$$



$$r = \pm\frac{\Delta C}{\Delta t}$$

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})

and $r = \frac{1}{RT} \times \left[\pm \frac{\Delta P}{\Delta t}\right]$ (unit of rate = 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 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

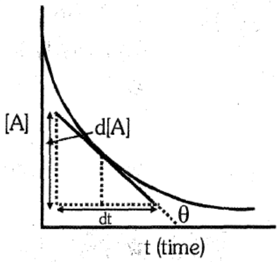
(B) Instantaneous Rate of Reaction

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 = $\lim\limits_{\Delta t \to 0}(\text{Average rate})$

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



Instantaneous rate of reaction = $\lim\limits_{\Delta t \to 0}\left(\pm \frac{\Delta C}{\Delta t}\right) = \pm \frac{dC}{dt}$

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

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

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 or Q = $\frac{d[Q]}{dt}$

Rate or 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 = mol L^{-1} time^{-1} i.e. (mol L^{-1} s^{-1} or mol L^{-1} min^{-1} or mol L^{-1} h^{-1})

Illustrations

Illustrations 1. For the reaction: $2N_2O_5 \longrightarrow 4NO_2 + O_2$. If the concentration of NO_2 increases by 1.6×10^{-2} M in 4 s. Calculate the following -

(i) rate of formation of NO_2 (ii) rate of formation of O_2

(iii) rate of disappearance of N_2O_5 (iv) rate of reaction

Solution.(i) Rate of formation of NO_2 : $\frac{d[NO_2]}{dt} = \frac{1.6\times10^{-2}}{4} = 4.0\times10^{-3}$ M/s

(ii) Rate of formation of O_2 : $\frac{d[O_2]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{4}\times4\times10^{-3} = 1.0\times10^{-3}$ M/s

(iii) Rate of disappearance of N_2O_5 : $\frac{-d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\times4\times10^{-3} = 2.0\times10^{-3}$ M/s

(iv) Rate of reaction = $\frac{1}{2}\left(-\frac{d[N_2O_5]}{dt}\right) = \frac{1}{2}\times2\times10^{-3} = 1.0\times10^{-3}$ M/s

or $\frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{4}\times4\times10^{-3} = 1.0\times10^{-3}$ M/s

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

(a) $2HI \longrightarrow H_2 + I_2$

(b) $2SO_2 + O_2 \longrightarrow 2SO_3$

Solution. (a) Rate of reaction = $\frac{1}{2}\left(-\frac{d[HI]}{dt}\right) = \frac{d[H_2]}{dt} = \frac{d[I_2]}{dt}$

(b) Rate of reaction = $\frac{1}{2}\left(-\frac{d[SO_2]}{dt}\right) = \frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[SO_3]}{dt}$

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

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

2. In the reaction, $A + 2B \rightarrow 6C + 2D$ if the initial rate $(-)\frac{\Delta[A]}{\Delta t}$ at t = 0 is 2.6×10^{-2} M s^{-1}, what will be the value of $(-)\frac{\Delta[B]}{\Delta t}$ at t = 0 ?

(1) 8.5×10^{-2} M s^{-1}

(2) 2.6×10^{-2} M s^{-1}

(3) 5.2×10^{-2} M s^{-1}

(4) 7.5×10^{-2} 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

$\underline{BrO_3^-}\,(aq) + 5Br^{-1}\,(aq) + 6H^+\,(aq) \rightarrow \underline{Br_2}\,(\lambda) + 3H_2O(aq)$

(1) $(-)\dfrac{\Delta[BrO_3^-]}{\Delta t} = \dfrac{\Delta[Br_2]}{\Delta t}$

(2) $(-)\dfrac{1}{3}\dfrac{\Delta[BrO_3^-]}{\Delta t} = \dfrac{\Delta[Br_2]}{\Delta t}$

(3) $(-)\dfrac{\Delta[BrO_3^-]}{\Delta t} = \dfrac{1}{3}\dfrac{\Delta[Br_2]}{\Delta t}$

(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 :- $aA + bB \longrightarrow$ Product

The rate law is :- 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 -

$$n_1A + n_2B \rightarrow m_1C + m_2D$$

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 mol/L

then, 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	$aA + bB \rightarrow$ Product
Rate law is	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 :

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 → Products ; is an elementary reaction

then rate law will be -

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 Keq of fast step (assumed as reversible)

Exarnple-1

$$2NO_2Cl \longrightarrow 2NO_2 + Cl_2$$

Experimentally, the rate law is Rate= $k[NO_2Cl]$

The mechanism of the reaction is given as-

(i) $NPO_2Cl \longrightarrow NO_2 + Cl$ (slow step)

(ii) $NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$ (fast step)

So the rate law from slowest step Rate = $k[NO_2Cl]$

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

Example-2

$$2NO_{(g)} + 2H_{2(g)} \longrightarrow N_{2(g)} + 2H_2O_{(g)}$$

experimentally the rate. law is, Rate = $k\,[NO]^2[H_2]$

The mechanism of the reaction is given as -

(i) $2NO \underset{k_b}{\overset{K_f}{\rightleftharpoons}} N_2O_2$ (fast step)

(ii) $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow step)

(iii) $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast step)

The rate law from slowest step is:

Rate = $k[N_2O_2][H_2]$

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

From fast reversible step -

$$k_f[NO]^2 = k_b[N_2O_2]$$

$$[N_2O_2] = \frac{k_f}{k_b}[NO]^2$$

and rate law becomes

$$\text{Rate} = k\left(\frac{k_f}{k_b}\right)[NO]^2[H_2]$$

therefore, Rate = $[NO]^2[H_2]$

This derived rate law agree 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 ARST 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.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k\,[CH_3COOC_2H_5][H_2O]$$

Water is in excess then its concentration remain constant during the reaction and $[H_2O]$ is taken as constant therefore,

Rate = $k'\,[CH_3COOC_2H_5]$ Where $k' = k\,[H_2O]$

Example-2

Inversion of cane sugar.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = k[C_{12}H_{22}O_{11}][H_2O]$$

Water is in excess then its concentration remain constant during the reaction and $[H_2O]$ is taken as constant

therefore,

Rate = k' $[C_{12}H_{22}O_{11}]$ where k' = k$[H_2O]$

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 $\rightarrow$ Product

Experiment No.	[A]	[B]	rate
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

$4 \quad k[1]^x[2]^y$ ……..(2)

and $4 \quad k[2]^x[2]^y$ ……..(3)

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

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

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

$4 = (2)^x\,(2)^y$ ……..(4)

$16 = (2)^x\,(4)^y$ ……..(5)

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

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

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 :

$$\text{Rate} = k[CH_3OCH_3]^{3/2}$$

The rate of reaction is followed by increase in pressure in a c1osed vessel and the rate can also be expressed in terms of the partial pressure of dimethyl ether i.e.,

$$\text{Rate} = k\left(P_{CH_3OCH_3}\right)^{3/2}$$

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

Solution. $CH_3OCH_3 \longrightarrow CH_4 + CO + H_2$

$$\text{Rate} = k[CH_3OCH_3]^{3/2} = k\left(P_{CH_3OCH_3}\right)^{3/2}$$

Unit of rate = bar min^{-1}

$$\text{Unit of k} = \frac{\text{Rate}}{k\left(P_{CH_3OCH_3}\right)^{3/2}} = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2}\ \text{min}^{-1}$$

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

Solution. Rate= k[Reactant]^n if (Reactant] = a ; rate= r_1

$r_1 = k[a]^n$ if [Reactant]= 4a; 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, $N_2O_{5(g)} \rightarrow N_2O_{4(g)} + 1/2O_{2(g)}$, 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.

	$N_2O_{5(g)} \rightarrow$	$N_2O_{4(g)}$ +	$1/2O_2(g)$
Initial pressure	P	0	0
Pressure at t = 20 s	(P - P')	P'	P'/2

Given P = 114 mm

After 20 s, total pressure = (P–P') + P' + (P'/2) = 133 mm

$\Rightarrow$ P'/2 = 19 mm P' = 38 mm

Thus rate of reaction in terms of change in pressure = 38/20 = 1. 9 mm s^{-1}

$$= \frac{1.9}{760}\ \text{atm s}^{-1} = 2.5\times10^{-3}\ \text{atm s}^{-1}$$

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

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

$$= \frac{38}{760\times0.0821\times400} = 1.52\times10^{-3}\ \text{M}$$

$\therefore$ rate of reaction in terms o change in concentration = $\frac{1.52\times10^{-3}}{20} = 7.61\times10^{-5}\ \text{Ms}^{-1}$

BEGINNER'S BOX-2

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

Initial $[A_2]$	**Initial $[B_2]$**	**Rate of reaction $[Ms^{-1}]$**
0.2	0.2	0.4
0.1	0.4	0.4
0.2	0.4	0.8

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.

Example: **(a)** $H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl(g)$

(b) $2NH_3(g) \xrightarrow[\Delta]{Pt} N_2(g) + 3H_2(g)$

(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

	A ⟶	**Product**
t = 0	a	0
t = t s	(a-x)	x

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

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

Calculation of Rate Constant

Let us take the reaction

$A \longrightarrow \text{Product}$

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

$$-\int d[A] = \int kdt$$

$-[A]_t = kt + C$

at t = 0 $[A]_t = [A]_0$

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

$C = -[A]_0$

On substituting the value of C

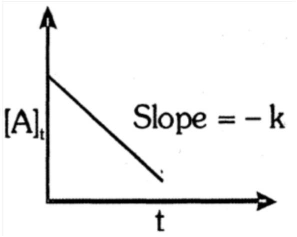
$-[A]_t = kt - [A]_0$

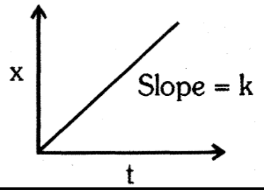
$[A]_t = [A]_0 - kt$ [Integrated rate equation]

$y = c - mx$

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

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





$x = kt$

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

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

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

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

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

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

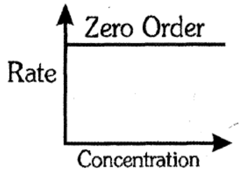
Time for completion of reaction

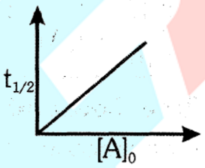
$$[A]_t = [A]_0 - kt$$

For completetion $[A]_t = 0$

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

Graphical representation





(B) First order reactions

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

Example: (a) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

(b) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(c) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

(d) $2Cl_2O_7 \longrightarrow 2Cl_2 + 7O_2$

(e) $2H_2O_2 \longrightarrow 2H_2O + O_2$

(f) $2N_2O \longrightarrow 2N_2 + O_2$

(g) All radioactive decay

Differential rate equation

$$A \longrightarrow \text{Product}$$

$t = 0$	a	0
$t = t$ s	$(a-x)$	x

$$-\frac{d[A]}{dt} = k[A] \qquad \frac{dx}{dt} = k(a-x)$$

Calculation of rate constant

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

$-\ln[A] = kt + c$ .... (i)

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

Putting the value of C in equation (i)

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

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

$y = c - mx$

$\ln\frac{[A]_0}{[A]_t} = kt$ ....(ii) $kt = \ln\left(\frac{a}{a-x}\right)$

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

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

From equation (ii)

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

$\frac{[A]_0}{[A]_t} = e^{-kt}$ $\Rightarrow [A]_t = [A]_0 e^{-kt}$ while my equation

Unit of rate constant [k = time^{-1}]

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

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

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

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.

At $t = t_{3/4}$; $x = 3_{a/4}$; $a-x = a/4$

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

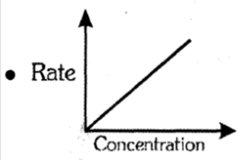
$t_{3/4}$ for first order reaction is independent of the initial concentration of reactant.

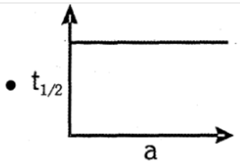
Interval Formula $k = \frac{2.303}{t_2 - t_1}\log\frac{a-x_1}{a-x_2}$

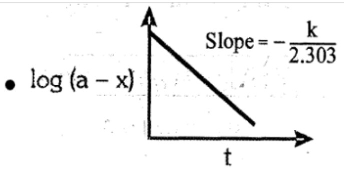
where x_1 and x_2 are the amount consumed at time t1 and t2 respectively.

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)

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

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

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

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

(i) Second order reactions

Hydrolysis of ester by alkali (Saponification)

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

$H_2 + I_2 \longrightarrow 2HI$

$2HI \longrightarrow H_2 + I_2$

$2NO_2 \longrightarrow 2NO + O_2$

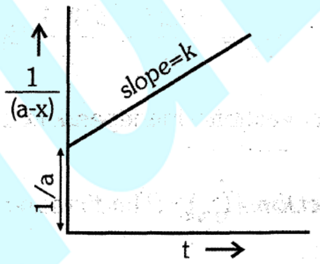
$2NO_2 + F_2 \longrightarrow 2NO_2F$

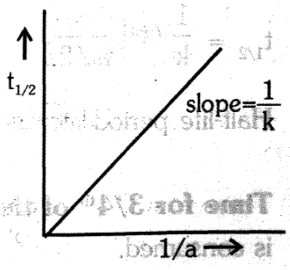
$NO + O_3 \longrightarrow NO_2 + O_2$

$2Cl_2O \longrightarrow 2Cl_2 + O_2$

For second order : n =2 $\quad kt = \frac{1}{(2-1)}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] = \frac{1}{(a-x)} - \frac{1}{a}$

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





(ii) Third order reactions

$2NO + O_2 \longrightarrow 2NO_2$

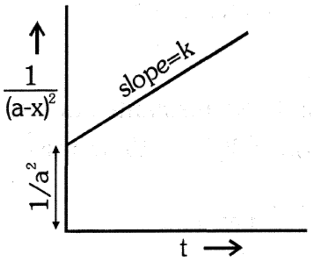
$2NO + Cl_2 \longrightarrow 2NOCl$

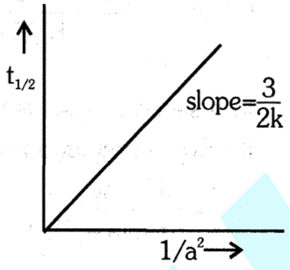
$2NO + H_2 \longrightarrow N_2O + H_2O$

$2FeCl_3 + SnCl_2 \longrightarrow 2FeC1_2 + SnCl_4$

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

Half life $t_{1/2} = \dfrac{2}{2a^2k}$





Examples of fractional order reaction

Reaction	Order
$H_2 + Br_2 \longrightarrow 2HBr$	1.5
$CO + Cl_2 \longrightarrow COCl_2$	2.5
$COCl_2 \longrightarrow CO + Cl_2$	1.5
$CH_3CHO \longrightarrow CH_4 + CO$	1.5
$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$	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. $k_1 = \dfrac{2.303}{t}\log\dfrac{a}{a-x}$, a = 100, x = 90, t = 10

So $$k_1 = \frac{2.303}{10}\log\frac{100}{10} = 2.303\times10^{-1}\ \text{hour}^{-1}$$

Now for 99.9% completion : a = 100 and x = 99. 9

$$T = \frac{2.303}{k_1}\log\frac{100}{0.1} = \frac{2.303}{2.303\times10^{-1}}\times3 = 30 \text{ hours}$$

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

Solution. t = 5 min , a = 100, $x_1 = 20$

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x_1}\right) = \frac{2.303}{5}\log\frac{100}{80} = \frac{2.303}{5}\log\frac{5}{4} = \frac{2.303}{5}[\log5-\log4]$$

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

Now $x_2 = 60$

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

$$t = \frac{2.303}{0.0446}\log\frac{100}{40} = \frac{2.303}{0.0446}[\log5-\log2] = \frac{2.303}{0.0446}\times0.3979 = 20.55 \text{ Min.}$$

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

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

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

Solution. a = 100, x = 90

$$k_1 = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{40}\log\frac{100}{10}\ \frac{2.303}{40} = 5.757\times10^{-2}\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k_1} = \frac{0.693}{5.757\times10^{-2}} = 12.03\ \text{min.}$$

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 200 % of the reaction?

Solution. $k_2 = \dfrac{1}{t}\dfrac{x}{a(a-x)}$, 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. $\dfrac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\dfrac{a_2}{a_1}\right)^{n-1} \Rightarrow \dfrac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\dfrac{2a}{a}\right)^{n-1}$

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

So, the order of the reaction will be 2.

BEGINNER'S BOX-3

1. Which of the following expressions is correct for zero order and first order reactions respectively (where a is initial concentration) ?

(1) $t_{1/2} \propto a;\ t_{1/2} \propto \dfrac{1}{a}$

(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) $t_{1/2} \propto a;\ t_{1/2} \propto \dfrac{1}{a^2}$

2. For the zero order reaction, $A \rightarrow B + C$; initial concentration of A is 0.1 M. If [A] = 0. 08 M after 10 minutes, then it's half-life and completion time are respectively :

(1) 10 min; 20 min

(2) 2×10^{-3} min; 4×10^{-3} min

(3) 25 min, 50 min

(4) 250 min, 500 min

3. For an elementary reaction, $X(g) \rightarrow Y(g) + Z(g)$ the half life period is 10 min. Jn 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

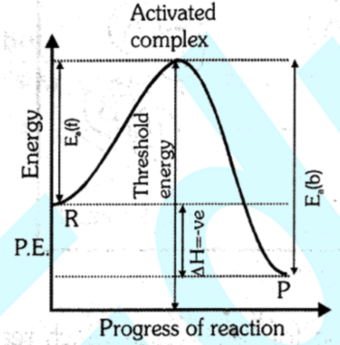
4. A first order reaction is 75% completed in 100 min. How long will it take for it's 87.5% completion?
(1) 125 min (2) 150 min (3) 175 min (4) 200 min

5. The rate constant for a first order reaction which has half life 480 s is :-
(1) $1.44\times10^{-3}\ s^{-1}$ (2) $1.44\ \times s^{-1}$ (3) $0.72\times10^{-3}\ s^{-1}$ (4) $2.88\times10^{-3}\ s^{-1}$

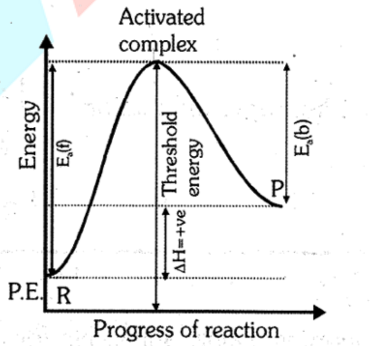
2.9 COLLISION THEORY OF CHEMICAL REACTIONS

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-cm^3). 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 :
(a) Reacting molecules must post a minimum amount of energy.
(b) Proper orientation of collision

- **Threshold energy :** The minimum energy which must be possesed 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

1. E_a (f) = Activation energy for forward reaction
2. E_a (b) = Activation energy for backward reaction

If no specified in questions then consider E_a for forward reaction.

$$\Delta H = E_{a(f)} - E_{a(b)} \quad ; \quad \Delta H = H_P - H_R$$

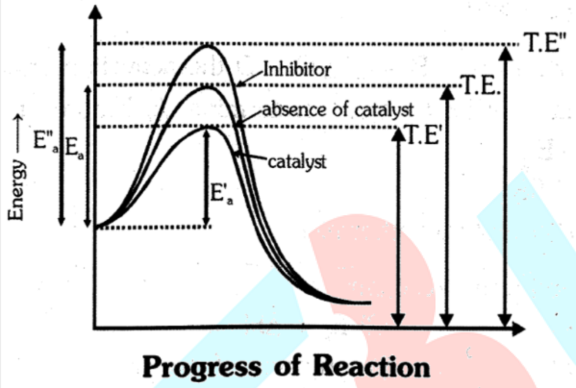
ACTIVATION ENERGY MAINLY DEPENDS UPON :\

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

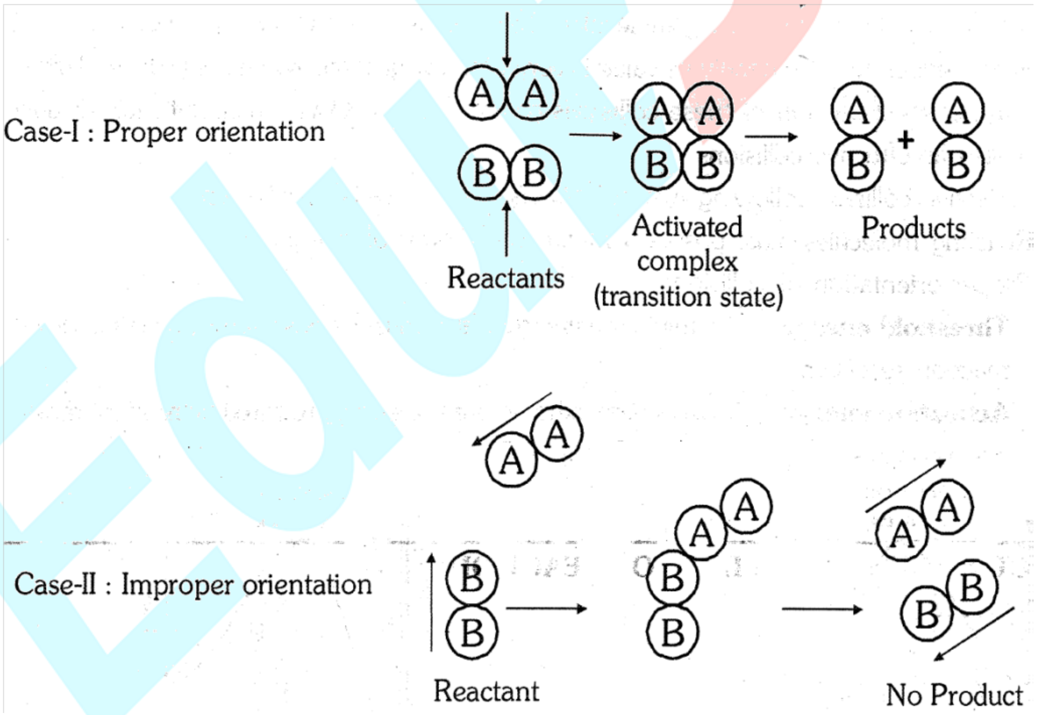
Reactions which have less Ea, take place at faster rate.

(ii) **Presence of catalyst :** Catalyst provide an alternative path of reaction mechanism for the reaction.

- In presence of catalyst thresheld 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 Ea 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 $e^{\frac{E_a}{RT}}$ E_a = Activation energy
  R = Gas constant
  T = Temperature (in K)

Illustrations

Illustration 13. The E_a for an exothermic reaction A→B is 80 kJ/mol. Heat of reaction is 20 kJ/mol. E_a for the reaction B→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 ‡ˆ† C + D the activation energy is 32 kJ mol^{-1}. For 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

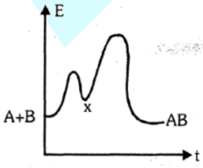
(1) $E_a > \Delta H$
(2) $E_a < \Delta H$
(3) $E_a = \Delta H$
(4) any one of the above

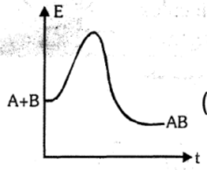
Solution **Ans. (4)**

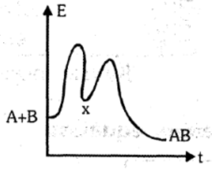
Illustration 17. An exothermic chemical reaction is occuring in two steps as follows

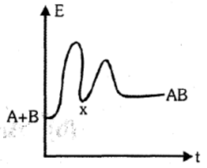
(i) $A + B \rightarrow X$ (slow)
(ii) $X \rightarrow AB$ (fast)

the process of reaction can be best described by

(1)


(2)


(3)


(4)


Solution **Ans. (4)**

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 $\propto$ concentratiol1 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 endothertnic. 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.

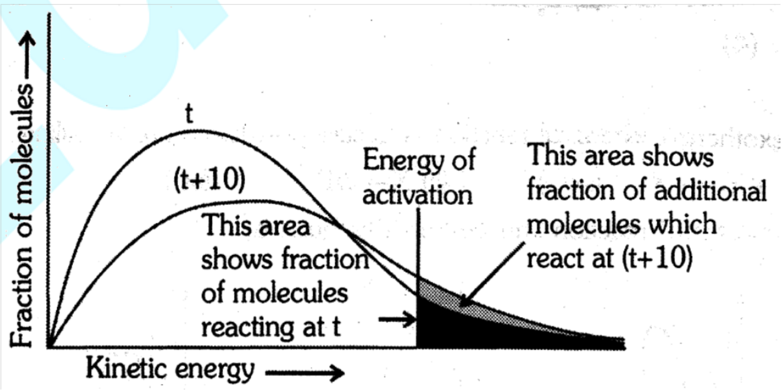
Temperature coefficient (μ): It is defined as ratio of rate constant of a reaction at two different temperatures which will be differ by 10°C.

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

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**

$k = Ae^{-E_a/RT}$ …….(1)

A = Arrhenius constant / pre-exponential factor / Frequency factor
E_a = Activation energy
R = gas constant
T = Temperature (Kelvin)

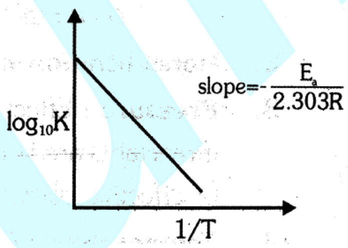
- k increases with increase in temperature

If T→ ∞ ; k = A

- $\frac{k}{A} = e^{-E_a/RT}$ = fraction of molecules having energy ≥ E_a

$e^{-E_a/RT}$ = Boltzman factor

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



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

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

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

$$y = c - mx$$

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

At temperature T_1 :

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

At temperature T_2 :

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

Equation (4) – Equation (3) gives –

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

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

- From Arrhenius equation – $k = A\,e^{-E_a/RT}$

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

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

$\frac{d}{dt}\ln k = \frac{E_a}{RT^2}$ 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
   $H_2 + Cl_2 \longrightarrow 2HCl$ (very slow reaction)
   $H_z + Cl_2 \xrightarrow{hv} 2HCl$(explosive)

GOLDEN KEY POINTS

- **PHOTO CHEMICAL REACTION**
  Reactions which occur in presence of light are photochemical reaction i.e., reaction which do not occur in dark.
  Example : (i) $H_2 + Cl_2 \xrightarrow{hv} 2HCl$ (ii) Photo synthesis (iii) Vision

- In photochemical reaction, each molecule of the reacting substance absorbs one quantum (single photon) of radiation and is activated to form the product.
- For every reaction, a certain amount of energy is required .
- Higher the intensity of light greater will be the rate of reaction .
- For these reactions, the value of ΔG may be positive or negative .
- Temperature have no significant effect.
  Mechanism : $Cl_2 + hv \longrightarrow Cl_2^*$ (activated molecule)
  Primary step of reaction : $Cl_2^* \longrightarrow Cl + Cl$
  Secondary step of reaction : $H_2 + Cl \longrightarrow HCl + H$
  $Cl_2 + H \longrightarrow HCl + Cl$
  Final step of reaction : $Cl + Cl \longrightarrow Cl_2$

- **Quantum yield (or quantum efficiency):**
  The quantum efficiency yield (ϕ) of a photochemical reaction may be expressed as

$$\phi = \frac{\text{Number of molecules reacted or product formed}}{\text{Number of photons absorbed}}$$

- Application of Photochemical Reaction
  (i) In photography (ii) In photo printing (iii) In photosynthesis
  (iv) In vision (v) In electronic industries (vi) In many polymerization reactions

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 1 0°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.

10°C - 20°C = 2 times
20°C – 30°C = 2^2 times
30°C – 40°C = 2^3 times
40°C – 50°C = 2^4 times = 16 times

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

Solution. Let $T_1 = 25°C$, $T_2 = 35°$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

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

$T_1 = 25 + 273 = 298$ k, $T_2 = 35 + 273 = 308$ k, R = 8.314

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

$E_a = 52.897$ kJ

Illustration 20 An exothermic reaction $A \longrightarrow B$ has an activation energy of 7 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 $E_a = 17$ kJ

$\Delta H = -40$ kJ

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

$E_a(b) = 17 - (-40) = 57$ 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 $k = Ae^{-Ea/RT}$

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

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 $E_a = 8000 \times 2.303 \times 1.987 = 36608$ Cal

Illustration 22 If temperature of a reaction is increased from 10°C to 10°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 ; $r_{new} = r_{old} \times (\mu)^{\Delta T/10}$

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

1. 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

2. The activation energy of the reaction, $A + B \rightarrow C + D + 38$ 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

3. $\frac{k_{35^\circ}}{k_{34^\circ}} > 1$, 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

4. The plot of *l*n 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 KEY

BEGINNER'S BOX-1

1.	(1)	**2.**	(3)	**3.**	(3)

BEGINNER'S BOX-2

1.	(1)	**2.**	(3)	**3.**	(3)

BEGINNER'S BOX-3

1.	(2)	**2.**	(3)	**3.**	(2)	**4.**	(2)	**5.**	(1)

BEGINNER'S BOX-4

1.	(2)	**2.**	(4)	**3.**	(1)	**4.**	(1)