Chemical Kinetics

Introduction :

In the thermodynamics, we have studied whether a reaction will take place or not and if it does then upto what extent (chemical equilibrium), In this chapter we will study about how fast a chemical reaction takes place and what are the different factors affecting this rate of chemical reaction. How to optimise the conditions as to maximse the output in optimum time. The last part of chapter will be dealing with the mechanism of a chemical reaction and catalysis.

Rate/Velocity of chemical reaction :

The rate of change of concentration with time of different chemical species taking part in a chemical reaction is known as **rate of reaction of that species**.

Rate =
$$\frac{\Delta c}{\Delta t} = \frac{\text{mol/lit.}}{\text{sec}}$$
 = mol lit⁻¹ time⁻¹ = mol dm⁻³ time⁻¹

Rate is always defined in such a manner so that it is always a positive quantity.

Types of Rates of chemical reaction :

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For a reaction R \longrightarrow P

Average rate = Total change in concentration

$$\frac{\Delta c}{\Delta t} = -\frac{\Delta [R]}{\Delta t} = \frac{\Delta [P]}{\Delta t}$$

Instantaneous rate : rate of reaction at a particular instant.

$$\mathsf{R}_{\mathsf{instantaneous}} = \lim_{t \to 0} \left[\frac{\Delta c}{\Delta t} \right] = \frac{\mathsf{d}c}{\mathsf{d}t} = -\frac{\mathsf{d}[\mathsf{R}]}{\mathsf{d}t} = \frac{\mathsf{d}[\mathsf{P}]}{\mathsf{d}t}$$

Instantaneous rate can be determined by drawing a tangent at time t on curve drawn for concentration versus time.

Initial Rate : Instantaneous rate at 't = 0' is called initial rate [slope of tangent at t = 0].



Relation between reaction rates of different species involved in a reaction :

For the reaction : $N_2 + 3H_2 \longrightarrow 2NH_3$ Rate of reaction of $N_2 = -\frac{d [N_2]}{dt}$ Rate of reaction of $H_2 = -\frac{d [H_2]}{dt}$ Rate of reaction of $NH_3 = \frac{d [NH_3]}{dt}$

These rates are not all equal. Therefore by convention the rate of a reaction is defined as

Rate of reaction $=-\frac{d [N_2]}{dt} = -\frac{1 d [H_2]}{3 dt} =$ $\overline{2}$ dt

Note : Rate of reaction value is dependent on the stoichiometric coefficients used in the reaction while rate of any species will be fixed value under given conditions.

Solved Examples

From the concentrations of R at different times given below, cauclate the average rate of the reaction: Ex.1 $R \rightarrow P$ during different intervals of time.

t/s	0	5	10	20	30
10 ³ × [R]/mol L ⁻¹	160	80	40	10	2.5

Sol. We can determine the difference in concentration over different intervals of time and thus determine the rate by dividing Δ [R] by Δ t

[R] ₁ ×10 ³	$[R]_2 \times 10^3$	<u>t</u> 2	<u>t</u> 1	$r_{av} \times 10^3$	$-[R_2 - R_1] \times 10^3$
mol L ⁻¹	mol L ⁻¹	S	S	mol L ⁻¹ s ⁻¹	$[t_2 - t_1]$
160	80	5	0	16	
80	40	10	5	8	
40	10	20	10	3	
10	2.5	30	20	0.75	

Factors affecting rate of chemical reaction :

- 1. Concentration
- 4. Catalyst 5. pH of the solution
- 2. Temperature
- 3. Nature of reactants & products
- 6. Dielectric constant of the medium.
- 8. Pressure 7. Radiations/light
- 9. Electrical & Magnetic field.

The first four factors generally affect rate of almost all reactions while other factors are specific to some reactions only. The common examples of these reactions are :

Concentration : We known from law of mass action that Rate is proportional to concentration of reactants. " So, generally rate of reaction decreases with passage of time, since concentration of reactants decreases.



Temperature :

Nature of reactants & Products : (a) Physical state of reactants :

Gaseous state > Liquid state > Solid state Decreasing order of rate of reaction.

(b) Physical size of reactants : As we decreases the particle size rate of reaction increases since surface area increases.

(c) Chemical nature of reactants :

- Ο If more bonds are to be broken, the rate of reaction will be slow.
- Ο Similarly bond strength is more, rate of reaction will be slow.

Catalyst :

- Presence of positive catalyst lower down the activation energy hence increases the rate of O reaction.
- Ο presence of negative catalyst increases activation energy hence decreases the rate of reaction.
- Radiations/light : Radiation are useful for photochemical reaction.
- Pressure : Pressure is important factor for gaseous reaction.

Rate Law (Dependence of rate on concentration of reactants) :

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law.

It can only be established by experiments.

Generally rate law expressions are not simple and these may differ for the same reaction on conditions under which the reaction is being carried out.

But for large number of reactions starting with pure reactants we can obtain simple rate laws. For these reactions : Rate \propto (conc.)^{order}

Rate = K (conc.)^{order} – differential rate equation or rate expression

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity unit of K = $(conc)^{1-order}$ time⁻¹

Note : Value of K is a constant for a given reaction, depends only on temperature

Order of reaction :

Let there be a reaction $m_1A + m_2B \longrightarrow products$.

Now, if on the basis of experiment, we find that

 $R \propto [A]^p [B]^q$ Where p may or may not be equal to m₁ & similarly q may or may not be equal to m₂. p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p + q) is **overall order of the reaction.**

Note : Order of a reaction can be 'zero' or any whole number, can be a fractional number and it can even be negative with respect to a particular reactant. But oveall order is not found to be negative for any reaction till observed.

Examples showing different values of order of reactions :

Reaction	Rate law	Order
$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$	$R = K [N_2O_5]^1$	1
$5Br^{-}(aq) + BrO_{3^{-}}(aq) + 6H^{+}(aq) \longrightarrow 3Br_{2}(\ell) + 3H_{2}O(\ell)$	R= K [Br [_]] [BrO ₃ [_]] [H ⁺] ²	1 + 1 + 2 = 4
H_2 (Para) $\longrightarrow H_2$ (ortho)	R = K [H _{2 (Para)}] ^{3/2}	3/2
$NO_{2}(g) + CO(g) \longrightarrow NO(g) + CO_{2}(g)$	R = K [NO ₂] ² [CO] ⁰	2 + 0 = 2
$2O_3(g) \longrightarrow 3O_2(g)$	$R = K [O_3]^2 [O_2]^{-1}$	2 – 1 = 1
$H_2 + CI_2$ 2 HCI	$R = K [H_2]^0 [CI_2]^0$	0 + 0 = 0

The reaction (2) does not take place in one single step. It is almost impossible for all the 12 molecules of the reactants to be in a state of encounter simultaneously. Such a reaction is called **complex reaction** and takes places in a sequence of a number of **elementary reactions**. For an elementary reaction the sum of stoichiometric coefficients = order of the reactions. But for complex reactions order is to be experimentally calculated.

Solved Examples.

Ex.2 The reaction $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$ is second order in NO and first order in Cl_2 . In a volume of 2 dm³, 5 mole of nitric oxide and 2 mol of Cl_2 were brought together, and the initial rate was 2.4×10^{-3} mole

dm⁻³ s⁻¹. What will be the rate when half of the chlorine has reacted ? 4.32×10^{-4} M sec⁻¹

Ans. Sol.

$$\begin{aligned} & \text{PI.} \quad 2\text{NO} + \text{CI}_2 \longrightarrow 2\text{NaCl} \\ & 5 & 2 \\ & 5 - 2 & 1 & 2 \\ & \text{R} = \text{k}\left(\frac{5}{2}\right)^2 \\ & 2.4 \times 10^{-3} = \text{k}\left(\frac{15}{4}\right) \\ & \text{R} = \frac{4 \times 2.4 \times 10^{-3}}{25} = \frac{4 \times 2.4 \times 10^{-3}}{25} \left[\frac{3}{2}\right]^2 \left[\frac{1}{2}\right] \\ & \text{R} = \frac{4 \times 2.4 \times 10^{-3}}{25} \times \frac{9 \times 1}{8} = 4.32 \times 10^{-4} \text{ M sec}^{-1} \end{aligned}$$



: Half life period for a 1st order reaction is a constant quantity.

Graphical Representation :

$$t = -\frac{2.303}{k} \log C_t + \frac{2.303}{R} \log C_0$$



First order growth reaction :

For bacteria multiplication or virus growth use following concept Consider a growth reaction Population (or colony) Time

0 a
dt
$$(a + x)$$

 $\frac{dx}{dt} = k (a + x) \text{ or } \frac{dx}{(a + x)} = kdt$

on integration

 $\log_a (a + x) = kt + C$

at
$$t = 0$$
; $x = 0 \Rightarrow C = \log_e a$

 $kt = -\log_e \frac{a}{(a+x)}$

or

or
$$k = \frac{2.303}{t} \log_{10} \left(\frac{a+x}{a} \right)$$

$$k = -\frac{2.303}{t} \log_{10}\left(\frac{a}{(a+x)}\right)$$

t = generation time, x = a 0.693

$$\therefore$$
 $t = \frac{0.69}{K}$

Examples of 1st order reactions :

$$1. \qquad H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

- 2. $NH_4 NO_2 \longrightarrow 2H_2O + N_2$
- 3. Radiactive decay
- All radioactive decays are always first order kinetics. •

$$\begin{array}{c} 226 \\ Ra \\ 88 \end{array} \xrightarrow{} \begin{array}{c} 222 \\ Rn + _2H^4 \\ 86 \end{array}$$

 $\label{eq:calculate} Calculate \; \frac{t_{0.75}}{t_{0.50}} \; \text{for a 1}^{\text{st}} \; \text{order reaction}$ Ex.3

Sol.
$$k = \frac{2.303}{t_{1/4}} \log \frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}} \log \frac{C_0}{\frac{C_0}{2}} \implies \frac{t_{1/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{2 \log 2}{\log 2} = 2$$

Ex.4 At least how many half-lives should elapse for a 1st order reaction A products so that the reaction is at least 95% completed ? $(\log 2 = 0.3)$ (2) 6 (1) 7 $(1) \Lambda$ () E

Sol. (1) 4 (2) 5 (3) 6 (4) 7

$$Sol. (2) \frac{100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5 \xrightarrow{t_{1/2}} 6.25 \xrightarrow{t$$

(c) Second order reaction :

2 nd order Reactions	
Two types	
$A + A \longrightarrow \text{products}$	A + B \longrightarrow products.
a a	a b O
(a – x) (a –x)	a-x b-x
$\therefore \frac{\mathrm{d}x}{\mathrm{d}t} = k \ (\mathrm{a} - \mathrm{x})^2$	Rate law
$\Rightarrow \int_{0}^{x} \frac{dx}{(a-x)^{2}} = \int k dt$	$\frac{dx}{dt} = k (a - x) (b - x)$
$\Rightarrow \left(\frac{-1}{(a-x)}\right)_{0}^{1} = kt$	$\int_{0}^{x} \frac{dx}{(a-x)(b-x)} = \int_{0}^{t} kdt$
$\Rightarrow \frac{1}{(a-x)} - \frac{1}{a} = kt$	$k = \frac{2.303}{t (a - b)} \log \frac{b (a - x)}{a (b - x)}$

(d) Psuedo first order reaction :

A second order (or of higher order) reactions can be converted into a first order reaction if the other reactant is taken in large excess. Such first order reactions are known as psuedo first order reactions.

 $\therefore \text{ For } A + B \longrightarrow \text{Products} \qquad [\text{Rate} = K [A]^1 [B]^1]$

$$k = \frac{2.303}{t (a-b)} \log \frac{b(a-x)}{a (b-x)}$$

Now if 'B' is taken in large excess b > > a.

$$\therefore \quad k = \frac{2.303}{-bt} \log \frac{a}{a-x} \qquad \Rightarrow \qquad k = \frac{2.303}{t} \log \frac{a}{a-x}$$

 \because 'b' is very large can be taken as constant

$$\Rightarrow$$
 kb = log \Rightarrow k' = log

- k' is psuedo first order rate constant
- K' will have units of first order.
- K will have units of second order.
- Examples of Pseudo 1st order reactions :
- (a) Hydrolysis of canesugar

$$\begin{array}{rcl} C_{12}H_{12}O_{11} & + & H_2O & \longrightarrow & C_6H_{12}O_6 + C_6H_{12}O_6 \\ \text{sucrose} & & \text{excess} \end{array}$$

(b) Hydrolysis of esters

$$\begin{array}{rcl} CH_{3}COOCH_{3} & + & H_{2}O & \xrightarrow{H^{+}} & CH_{3}COOH + CH_{3}OH \\ & & (excess) \end{array}$$

Table : Characterstics of First-and Second-Order Reactions of the Type A Products

	Zero Order	First-Order	Second-Order	n th order
Differential Rate law	$\frac{-\Delta A}{\Delta t} = k[A]^{\circ}$	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$	$-\frac{\Delta A}{\Delta t} = k [A]^n$
(Integrated Rate law)	$\left[A\right]_{t} = \left[A\right]_{0} - kt$	$\ln \left[A\right]_{t} = -kt + \ln \left[A\right]_{0}$	$\frac{1}{\left[A\right]_{t}} = kt + \frac{1}{\left[A\right]_{0}}$	$\frac{1}{(A_t)^{n-1}} - \frac{1}{(A_0)^{n-1}} = (n-1) \text{ kt}$
Linear graph	[A] _t versus t	In [A] versus t	$\frac{1}{[A]}$ versus t	$\frac{1}{\left(A_{t}\right)^{n-1}} \ \text{ v/s } t$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{_{1/2}} = \frac{1}{k[A]_0}$	$t_{1/2} \propto \frac{1}{(A_0)^{n-1}}$
	(depends on $[A]_0$)	(independent of $[A]_0$)	(depends on $[A]_0$)	
	[A]₀ ↑ [A] Time →	[A] ₀ (A) (A) (A) (A) (A) (A) (A) (A)		
	Graphical com	parison of differe	nt orders	
	Zero order	$ \begin{array}{c} \uparrow \\ \downarrow \\ \downarrow \\ \hline \\ \downarrow \\ \hline \\ \downarrow \\ \downarrow$	$\frac{1}{[A]} \begin{array}{ c c } 2 \text{ nd order} \\ \hline t \rightarrow \end{array}$	
	Zero order terestication of the second sec	↑ erection of the second seco	$ \begin{array}{c c} 2 & nd & order \\ & &$	-
	t Zero order t Conc. →	↑ 1 st order ↓ Conc. →	↑ 2 nd order ↑ 1/conc. →	_



Ex.5 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below :

t/s	0	100	200	300
p/Pa	4.00 × 10 ³	3.50 × 10 ³	3.00 × 10 ³	2.5 × 10 ³

Determine the order of reaction, its rate constant and half-life period.

100

Sol. It Can be seen that rate of reaction between different time intervals is :

0-100 s, rate =
$$\frac{[3.50 - 4.00] \times 10^3 \text{ Pa}}{100}$$
 = 5 Pa/s
100-200s, rate = $-\frac{[3.00 - 3.50] \times 10^3 \text{ Pa}}{100\text{ s}}$ = 5 Pa/s
200-300s, rate = $-\frac{[2.50 - 3.00] \times 10^3 \text{ Pa}}{100}$ = 5 Pa/s

We notice that the rate remains constant and therefore, reaction is of zero order. Alternatively, if we plot a p against t, it is a straight line agaion indicating it is a zero order reaction.

k = rate = 5 Pa/s

+ _	initial	concentration	or	pressure	_ 4.00	×10 ³	Pa	- 400s
1 /2 –		2k			2×5	Ра	s ⁻¹	- 4003

(A) integrated rate law method :

• It is method of hit and trial. By checking where the kinetic data (experimetal data) best fits into which integrated rate law, we determine the order. It can also be done graphically.

Ex.6 The rate of decomposition of N_2O_5 in CCl₄ solution has been studied at 318 K and the following results have been obtained :

t/min	0	135	342	683	1693
c/M	2.08	1.91	1.67	1.35	0.57

Find the order of the reaction and calculate its rate constant. What is the half-life period?

Sol. It can be shown that the rate of the reaction. We now try integrated first order equation i.e., $k = \frac{\ln (c_0/c)}{t}$

t/min	c/M	$k = \frac{\ln (c_0/c)}{t} \min^{-1}$
0	2.08	6.32 × 10 ⁻⁴
135	1.91	6.30 × 10 ⁻⁴
339	1.68	6.32 × 10 ⁻⁴
683	1.35	6.32 × 10 ^{-₄}
1680	0.72	6.31 × 10 ⁻⁴

It can be seen that the value of k is almost constant for all the experimetal results and hence it is first order reaction with $k = 6.31 \times 10^{-4} \text{ min}^{-1}$.

$$t_{_{1/2}} = \frac{0.69}{6.31 \times 10^{-4} \text{ min}^{-1}} = 1.094 \times 10^3 \text{ min}^{-1}$$

Graphical method : Alternatively, if we draw a graph between l n c against t, we obtain a straight line with slope = -k.

(B) Method of half lives :

• The half lives of each order is unique so by comparing half lives we can determine order

 $\label{eq:transformation} \mbox{for n^{th} order reaction} \qquad t_{_{1/2}} \ \propto \ \frac{1}{IR_{_{n}}I^{n-1}}$

$$\frac{t_{1/2}}{t_{1/2}} = \frac{(\dot{R_0})^{n-1}}{(R_0)^{n-1}}$$

Ex.7 In the reduction of nitric gas with hydrogen, the reaction was found to be 50% complete in 210 seconds when the initial pressure of the mixture was 200 mm. In a second experiment the time of half reaction was 140 seconds when the initial pressure was 300 mm. Calculate the total order of the reaction.

Sol. For a nth order reaction
$$(n \neq 1)$$
, $t_{1/2} \propto \frac{1}{c_0^{n-1}}$

$$\frac{210}{140} = \left(\frac{300}{200}\right)^{n-1} n = 2$$

(C) Ostwald's isolation method :

• This method is useful for reaction which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess exception that of one, so if

rate = k [A]^a [B]^b [C]^c =
$$k_0$$
 [A]^a

Then value of 'a' can be calculated by previous methods and similarly 'b' and 'c' can also be calculated.

Methods to monitor the progress of the reaction :

(A) Pressure measurement :

Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature.

This method can applied for those reaction also in which a gas is produced because of decomposition of a solid or liquid. We can get an idea about the concentration of reacting species at a particular time by measuring pressure.

- The pressure data can be given in terms of
 - (i) Partial pressure of the reactant
 - (ii) Total pressure of the reaction system
 - (iii) Pressure at only some points of time

- **Ex.8** Find the expression for K in terms of P_0 , P_t and n
- Sol. Let there is a 1^{st} order reaction, A(g) nB(g) Let initial pressure at time t 0 P₀ t = 0 $\mathbf{P}_{A} = (\mathbf{P}_{0} - \mathbf{x})$ nx t = t nP $t = \infty$ \therefore P_t (Total pressure at time 't') = P₀ - x + nx = P₀ + (n - 1) x $\therefore x = \frac{P_t - P_0}{n - 1}$ $\therefore P_{A} = P_{0} - \frac{P_{t} - P_{0}}{n-1} = \frac{P_{0}n - P_{t}}{n-1}$ $\therefore a \propto p_0$ & $a - x \propto P_A = \frac{nP_0 - P_t}{n-1}$

 $\therefore \ \mathbf{k} = \frac{2.303}{t} \ \log \ \frac{P_0(n-1)}{nP_0 - P_t} \qquad \text{or} \qquad K = \frac{2.303}{t} \ \log \frac{P_\infty - P_0}{P_\infty - P_t}$

Final total pressure after infinite time = $P_t = nP_0$

- Formula is not applicable when n = 1, the value of n can be fractional also.
- Do not remember the formula but derive it for each question.
- Ex.9 For the decomposition of azoisopropane at 270°C it was found that at t = 0, the total pressure was 33.15 mm of Hg and after 3 minutes the total pressure was found to be 46.3 mm of Hg. Calculate the value of 'k' for this reaction.

 $k = \frac{2.303}{3} \log \frac{33.15 (2-1)}{2 \times 33.15 - 46.3} = 0.1684 \text{ min}^{-1}$ Sol.

(B) Volume measurement :

(i) By measuring the volume of product formed we can monitor the progress of reactions.

Ex.10 Study of a reaction whose progress is monitored by measuring the volume of a escaping gas.

 NH_4NO_2 (s) $\xrightarrow{\Delta}$ $2H_2O(\ell) + N_2(g)$

Let, V, be the volume of N₂ collected at time 't' Sol.

 V_{∞} = be the volume of N₂, collected at the end of the reaction.

$$a \propto V_{\infty}$$

$$(a - x) \propto V_{\infty} - V_{t}$$

$$\therefore \qquad k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_{t}}$$

(C) **Optical rotation measurment :**

It is used for optically active sample. It is applicable if there is atleast one optically active species involved in chemical reaction.

The optically active species may be present in reactant or product.

It is found that $\frac{(r_{\infty}-r_{0}) \propto a}{(r_{\infty}-r_{t}) \propto (a-x)}$

(a = concentration, x = amount consumed)

where are r_0 , r_t , r_{∞} are angle of optical rotation at time t = 0, t = t and $t = \infty$

Ex.11 Study of hydrolysis of sucrose : Progress of this reaction is monitored with the help of polarimeter because a solution of sucrose is dextrorotatory and on hydrolysis, the mixture of glucose as fructose obtained becomes leavorotary. That's why this reaction is also known as inversion of cane sugar.

$$\begin{array}{ccc} C_{12}H_{22}O_{11}+H_2O & \xrightarrow{H^+} & C_6H_{12}O_6+C_6H_{12}O_6 \\ excess & glucose & fructose \end{array}$$

+52.7° -92.4°

+66.5° Let the readings in the polarimeters are

Sp. rotation

t = 0, θ_0 ; t = t, θ_1 and $at t = \infty$, θ_{∞} Then calculate rate constant 'k' in terms of these readings.

Sol. The principle of the experiment is that change in the rotation is directly proportional to the amount of sugar hydrolysed.

$$\therefore \mathbf{a} \propto \theta_1 - \theta_{\infty} \quad ; \qquad \mathbf{a} - \mathbf{x} \propto \theta_t - \theta_{\infty} \quad ; \qquad \mathbf{k} = \frac{2.303}{t} \log \left(\frac{\theta_0 - \theta_{\infty}}{\theta_t - \theta_{\infty}} \right)$$

Effect of temperature on rate of reaction :

In early days the effect of temperature on reaction rate was expressed in terms of **temperature coefficient** which was defined as the ratio of rate of reaction at two different temperature differing by 10° C(usually these temperatures were taken as 25° C and 35° C)

T.C. = $\frac{K_t + 10}{K_t} \approx 2$ to 3 (for most of the reactions)

For some reactions temperature coefficient is also found to be less than unity. for example

 $2NO + O_2 \rightarrow 2NO_2$ rate of reaction decreases on increasing temperature.

Ex.12 For a reaction T.C. = 2, Calculate $\frac{k_{40^{\circ}C}}{k_{25^{\circ}C}}$ for this reaction.

 $\frac{k_2}{k_1} = (T.C.)^{\frac{\Delta t}{10}} = (2)^{\frac{15}{10}} = (2)^{\frac{3}{2}} = \sqrt{8}$

• But the method of temperature coefficient was not exact and to explain the effect of temperature on reaction rate new theory was evolved

Arrhenius theory of reaction rate :

It was developed by max Trautz and William lewis.

It gives insight in to the energetics and mechanistic aspects of reactions.

It is based upon kinetic theory of gases.

Arrhenius proposed a theory of reaction rate which states as follows :

O A chemical reaction takes palce due to the collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).

O Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be effective the following two barriers are to be cleared.

• Energy barrier :

The minimum amount of energy which the colliding molecules must posses as to make the chemical reaction to occur is known as threshold energy.

"The minimum amount of extra energy required by reactant molecules to pariticipate in a reaction is called activation energy (E_a) "

Orientation barrier :

Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make collision effective. Following diagrams can explain importance of suitable direction for collision.





- Collision to be effective the colliding molecules must posses some certain minimum energy called threshold energy of the reaction.
- Reactant molecules having energy equal or greater than the threshold are called active molecules and those having energy less than the threshold are called passive molecules.
- **O** Concept of energy of activation (E_a)
- The extra amount of energy which the reactant molecules (having energy less than the threshold) must acquire so that their mutual collision may lead to the breaking of bond(s) and hence the energy is known as energy of activation of the reaction. It is denoted by the symbol E_a. Thus,

E_a = Threshold energy – Actual average energy,

E_a is expressed in kcals mole⁻¹ or kJ mole⁻¹.

• The essence of Arrhenius Theory of reaction rate is that there exists an energy barrier in the reaction path between reactant(s) and product(s) and for reaction to occur the reactant molecules must climb over the top of the barrier which they do by collision. The existence of energy barrier and concept of E_a can be understood from the following diagram.



or

Collision frequency is the number of collisions per unit volume per unit time. It is denoted by the symbol Z. Z is directly proportional to \sqrt{T} . By 10°C rise in temperature, so it is the fraction of the total number of effective collision that increases markedly resulting into marked increase in the reaction rate.

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$$\frac{dIIIK}{dT} = \frac{E_a}{RT^2}$$

Integrating equation 4 assuming E_a to be constant we get,

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

Fraction of molecules capable of bringing effective collisions T_1 $T_2 > T_1$ Energy $T_2 > T_1$ $T_2 > T_1$

This is integrated form of Arrhenius equation.

Where, Constant A = pre-exponential factor it is a constant for a given reaction.

From this equation it is evident that as $T \to \infty$, $k \to A$. Thus, the constant A is the rate constant of reaction at infinity temperature. The rate constant goes on increasing with temperature. So, when T approaches inifinity, k will be maximum. That is to say, A is the maximum rate constant of a

so, when I approaches inifinity, k will be maximum. That is to say, A is the maximum rate constant of a reaction.

The expontential term i.e. e^{-Ea/RT} measures the fraction of total number of molecules in the activated state or fraction of the total number of effective collisions.

$$\frac{n_{E_a}}{n} = e^{-E_a/RT}$$
 Where $n_{E_a} = no.$ of molecules of reactant in the activated state $n = total no.$ of molecules of the reactant in the reaction

• From Arrhenius Equation we have, log k =

$$g k = \left(-\frac{Ea}{2.303 R}\right)\frac{1}{T} + \log A$$

So from this it is evident that a plot of log k versus $\frac{1}{T}$ will be a straight line of the slope equal

to $-\frac{E_a}{2.303 \text{ R}}$ and intercept equal to log A as shown below :



Thus, from this plot E_a and A both can be determined accurately.

If k_1 and k_2 be the rate constant of a reaction at two different temperature T_1 and T_2 respectively, then we have

$$\log k_{1} = -\frac{E_{a}}{2.303 \text{ R}} \cdot \frac{1}{T_{1}} + \log A \text{ and } \log k_{2} = -\frac{E_{a}}{2.303 \text{ R}} \cdot \frac{1}{T_{1}} + \log A$$

Subtracting we get
$$\log \frac{k_{2}}{k_{1}} = \frac{E_{a}}{2.303 \text{ R}} \cdot \left(\frac{1}{T_{1}} - \frac{1}{T_{2}}\right)$$

General characteristics of catalyst :

- A catalyst does not initiate the reaction. It simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.
- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence ΔG° . It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst also the reaction will go to 75% of completion before the attainment of equilibrium but the time needed for this will be less than 20 minutes.
- A catalyst drives the reaction through a low energy path and hence E_a is less. That is, the function of the catalyst is to lower down the activation energy.

 E_a = Energy of activation in absence of catalyst.

 E'_{a} = Energy of activation in presence of catalyst.

 $E_a - E'_a$ = lowering of activation energy by catalyst.



Comparision of rates of reaction in presence and absence of catalyst :

If k and k_{cat} be the rate constant of a reaction at a given temperature T, and E_a and E'_a are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{cat}}{k} = \frac{Ae^{-E'a/RT}}{Ae^{-Ea/RT}} = Ae^{(E_a - E'_a)/RT}$$

Ex.13 The pyrolysis of an organic ester follows a first order process and its rate can be expressed as

$$\ln k = 78.09 - \frac{42075}{\tau}$$

where k is given in the min⁻¹. Calculate the time required for 25 percent reaction to complete at 227°C.

Sol.
$$\ln k = 78.09 - \frac{42075}{500} = -6.06$$

 $\log k = -\frac{6.06}{2.303} = -2.63$; $k = 2.344 \times 10-3 \text{ min}^{-1}$
when $x = 0.25$; $k = \frac{2.303}{t_{1/4}} \log \frac{a}{0.75 \text{ a}}$
 $t_{1/4} = \frac{2.303}{2.344 \times 10^{-3}} \log 1.333 = 122.6 \text{ min}$

Ex.14 The slope of the plot of log k vs $\frac{1}{T}$ for a certain reactionwas found to be -5.4×10^3 . Calculate the energy of activation of the reaction. If the rate constant of the reaction is 1.155×10^{-2} sec⁻¹ at 373 K, what is its frequency factor ?

Sol. (a) Slope =
$$\frac{-E}{2.303 \text{ R}} = -5.4 \times 10^3$$

 $E = 5.4 \times 10^3 \times 2.303 \times 1.987 = 24.624 \text{ cal mol}^{-1}$
(b) $E = Ae^{-E/RT}$; log 1.155 × 10⁻² = log A - $\frac{24.624}{2.303 \times 1.987 \times 373}$
or A = 3.08 × 10¹² sec⁻¹

Derivation of a suitable rate law with the help of a suitable mechanism :

Molecularity and Order :

The number of molecules that react in an elementary step is the molecularity of the elementary reaction. Molecularity is defined only for the elementary reactions and not for complex reactions. No elementary reactions involving more than three molecules are known, because of very low probability of near-simultaneous collision of more than three molecules.

The rate law for the elementary reaction

 $aA + bB \longrightarrow products$

```
rate = k[A]^{a}[B]^{b}, where a + b = 1, 2 or 3.
```

For an elementary reaction, the orders in the rate law equal the coefficients of the reactants.

While, the order is defined for complex as well as elementary reactions and is always experimentally calculated by the mechanism of the reaction, usually by the slowest step of the mechanism known as **rate determining step of the reaction.**

Comparison B/W Molecularity and order of reaction				
Molecularity of Reaction	Order of Reaction			
1. It is defined as the no. of molecules of reactant taking part in a chemical reaction eq $NH_4NO_2 \rightarrow N_2 + 2 H_2O$ m = 1	1. It is defined as the sum of the power of concentration terms that appear in rate law. NH ₄ NO ₂ \rightarrow N ₂ + 2 H ₂ O. Rate = K [NH ₄ NO ₂]			
 It is always a whole number It can neither be zero nor fractional. 	2. It may be zero , fractional or integer.			
3. It is derived from RDS in the mechanism of reaction.	3. It is derived from rate expression.			
4. It is theoretical value.	4. It is experimental value.			
5. Reactions with molecularity \geq 4 are rare.	5. Reactions with $O.R \ge 4$ are also rare.			
6. Molecularity is in independent of Pressure and temperature.	6.OR. depends upon pressure and temperature.			

Mechanism of a reaction :

Reactions can be divided into

- Elementary / simple / single step
- Complex / multi-step
- **ELEMENTARY REACTION:**
- 0 These reaction take place in single step without formation of any intermediate



- Ο For elementary reaction we can define molecularity of the reaction which is equal to no of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy
- Ο molecularity will always be a natural no
 - 1 = unimolecular one molecule gets excited (like radioectivity)
 - 2.= bimolecular
 - 3 = trimolecular
- Ο Molecularly \leq 3 because the probability of simultaneous collision between 4 or more molecules in proper orientation is very low
- Ο For elementary reaction there is only single step and hence it is going to be rate determining step so order of an elementary reaction is its molecularity

Order of elementary reaction w.r.t. reactant = stoichiometric co-efficient of the reactant H₂ +

$$I_2 \rightleftharpoons 2HI \rightarrow Simple reaction$$
 rate = k [H₂] [I₂]

$$2H_2 + 2I_2 \rightleftharpoons 4HI$$
 (not elementary)

reaction obtained by multiplying an elementary reaction with some no will not be of elementary nature $H_2 + CI_2 \implies 2HCI$ order = 0

COMPLEX REACTION:

• Reaction which proceed in more than two steps. or having some mechanism. (sequence of elementary reaction in which any complex reaction proceeds)



- For complex reaction each step of mechanism will be having its own molecularity but molecularity of net complex reaction will not be defined.
- O Order of complex reaction can be zero fractions whole no, even negative w.r.t. some species.
- Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction generally using Rate determine step (R.D.S) if given.
- O Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of interimediates.

The mechanism of any complex recation is always written in terms of elementary steps, so molecularity of each of these steps will be defined but net molecularity of complex reaction has no meaning.

The mechanism of most of the reaction will be calculated or predicted by using mainly the following approximations.

Solved Examples —

Ex.15 The thermal decomposition of N_2O_5 occurs in the following steps.

Step - I $N_2O_5 \xrightarrow{slow} NO_2 + NO_3$ Step - II $N_2O_5 + NO_3 \xrightarrow{fast} 3NO_2 + O_2$

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

suggest the rate expression.

Ans. $k [N_2O_5]$

Sol.

$$\begin{split} & \mathsf{N}_2\mathsf{O}_5 & \longrightarrow \mathsf{NO}_2 + \mathsf{NO}_3 & (\mathsf{Slow}) \\ & \mathsf{N}_2\mathsf{O}_5 + \mathsf{NO}_3 & \longrightarrow \mathsf{2NO}_2 + \mathsf{O}_2 & (\mathsf{Fast}) \\ & \mathsf{2N}_2\mathsf{O}_5 & \longrightarrow \mathsf{4NO}_2 + \mathsf{O}_2 & \mathsf{rate} = \mathsf{k} \left[\mathsf{N}_2\mathsf{O}_5\right] \end{split}$$

COMPLICATIONS IN 1ST ORDER REACTION

PARALLEL 1st ORDER REACTION

Frequently a species can react in different ways to give a variety of products. For example, toluene can be nitrated at the ortho, meta, or para positions, We shall consider the simplest case, that of two competing irreversible first-order reactions :

$$A \xrightarrow{k_1} B and A \xrightarrow{k_2} C$$

where the stoichiometric coefficients are taken as unity for simplicity. The rate law is

$$\frac{d [B]}{dt} = K_1 [A] \frac{d [C]}{dt} = K_2 [A]$$

$$\frac{-d[A]}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt}$$

$$\frac{-d[A]}{dt} = (K_1 + K_2) [A] = K_{eff} [A]$$

$$K_{eff} = K_1 + K_2$$

$$\frac{ln2}{T_{eff}} = \frac{ln2}{T_1} + \frac{ln2}{T_2} \text{ (where T represent half life)}$$

$$\frac{1}{T_{eff}} = \frac{1}{T_1} + \frac{1}{T_2} \text{ (remember)}$$

Now, $[A]_{t} = a e^{-K_{eff}t} = a e^{-(K_{1} + K_{2})t}$ $\frac{d [B]}{dt} = K_{1}[A]$ $\frac{d [B]}{dt} = K_{1}a e^{-(K_{1} + K_{2})t}$ $[B] = \left(\frac{k_{1}a}{k_{1} + k_{2}}\right) (1 - e^{-(K_{1} + K_{2})t})$ similarly, $[C] = \frac{K_{2}}{K_{1} + K_{2}} (1 - e^{-(K_{1} + K_{2})t})$ $\frac{[B]}{[C]} = \frac{K_{1}}{K_{2}}$ (remember) $K_{eff} = k_{1} + k_{2}$

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

1. For each reaction below, express the rates of change of [product] and [reactant] in the correct relationship to each other.

(a)
$$2O_3(g) \rightarrow 3O_2(g)$$

(b) $2HOF(g) \rightarrow 2HF(g) + O_2(g)$
(c) $\frac{-d[O_3]}{2dt} = +\frac{1}{3} \frac{d[O_2]}{dt}$
(c) $\frac{-d[O_3]}{dt} = \frac{2}{3} \frac{d}{dt} [O_2]$
(c) $\frac{-d[O_3]}{dt} = \frac{2}{3} \frac{d}{dt} [O_2]$
(c) $\frac{-d[HOF]}{dt} = +\frac{d[HF]}{dt} = +\frac{2d[O_2]}{dt}$

2. In a catalytic experiment involving the Haber's process, $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction was measured as rate = = 2 x 10⁻⁴ M.s⁻¹. If there were no side reactions, express the rate of reaction in terms of (a) N_2 (b) H_2 ?

Sol. Rate of Reaction $= -\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = +\frac{1}{2} \frac{d[NH_3]}{dt}$ (a) $2 \times 10^{-4} = -\frac{d[N_2]}{dt}$ (b) $2 \times 10^{-4} \times 3 = -\frac{d[H_2]}{dt} = 6 \times 10^{-4} \text{ MS}^{-1}$.

- **3.** Write the units of the rate constants for a (i) zeroth order, (ii) half order, (iii) first order, (iv) 3/2 order, (v) second order, (vi) 5/2 order, (vii) third order reactions.
- **Sol.** Unit of Rate Constant = $(Mole)^{1-n}$ (Litre)ⁿ⁻¹ Sec⁻¹ Where n is the order of Reaction (i) For Zeroth order = $Mole^{(1-0)}$ (Litre)⁽⁰⁻¹⁾ Sec⁻¹ Unit of K n = 0 Mole Litre⁽⁻¹⁾ Sec⁻¹ Similarly For others
- 4. The reaction $CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$ is second order in NO_2 and zero order in CO at temperatures less than 500K.
 - (a) Write the rate expression for the reaction.
 - (b) How will the reaction rate change if the NO₂ concentration is halved?
- Sol. (a) $\frac{-d}{dt} [CO] = \frac{-d}{dt} (NO_2) = K [NO_2]^2$ Order is zero w.r.t. CO but Conc will Still change (b) Rate of Rxn = K[NO_2]^2 of Conc of NO_2 Half The Rate Becomes One fourth 5. For a reaction A + 3B \rightarrow Product, Rate = {- d[A] / dt} = k [A]^2 [B], the expression for the rate of reaction in terms of change in the concentration of B; {- d[B]/dt} will be : (1) k[A]^2 [B] (2) k [A]^2 [3B] (3) 3k [A^2] [B] (4) (1/3) k [A^2] [B]
- **Sol.** For the given reaction

 $\frac{-d[A]}{dt} = \frac{1}{3} \frac{-d[B]}{dt} = K[A]^2[B]$ Then $\frac{-d[B]}{dt} = 3K[A]^2[B]$ Ans. (3) Gaseous cyclobutene isomerizes to butadiene in a first order process which has $k = 3.3 \times 10^{-4} \text{ s}^{-1}$ at 6. 153°C. How many minutes would it take for the isomerization to proceed 40 % to completion at this temperature. Sol. For the First order Rxn $t = \frac{2.303}{K} \log \frac{a}{(a-x)} \qquad t = \frac{2.303}{3.3 \times 10^{-4}} \log \left(\frac{100}{60}\right)$ $t = 1.54 \times 10^{+3}$ Second. = 25.66 Minute Calculate $\frac{t_{0.5}}{t_{0.25}}$ for a 1st order reaction 7. $\frac{t_{0.5}}{t_{0.25}} = \frac{\frac{2.303}{K} \log \frac{a}{(a-\frac{a}{2})}}{\frac{2.303}{K} \log \frac{a}{(a-\frac{a}{2})}} = \frac{\log 2}{(\log \frac{4}{3})}$ Sol. 8. For the reaction $A + B \longrightarrow \text{products}$ the following date were obtained : initial rate (mole/liter.sec) 0.030 0.059 0.060 0.090 0.089 [A] (mole/liter) 0.10 0.20 0.20 0.30 0.30 [B] (mole/liter) 0.20 0.20 0.30 0.30 0.50 Write the rate equation for this reaction. Be sure to evaluate k. Rate = $K[A]^{x}[B]^{y}$ Sol. From data I. .030 = K [.10]^x [.20]^y (1).059 = K [.20]^x [.20]^y From data II. (2).060 = K [.20]^x [.30]^y (3)From III. $\frac{.030}{.059} = \frac{\text{K}[.10]^{\text{x}}[.20]^{\text{y}}}{\text{K}[.20]^{\text{y}}}$ divide 1 equation by (2) \Rightarrow x = 1 Then divide (2) eguation by (3) .059 K[.20]^x[.20]^y $\frac{.059}{.060} = \frac{K[.20] [.20]}{K[.20]^{x}[.30]^{y}}$ \Rightarrow v = 0 Put the value of x and y in (1) equation $.030 = K[.10]^{1} [.20]^{0}$

$$K = \frac{.030}{10} = .3$$
 Sec-1

9. Now, let us assume that A, B and C are optically active compounds, which rotate the plane polarized light in the clockwise or anticlockwise direction.

 $A(soln.) \longrightarrow B(soln.) + C(soln.)$

Time	0	t	∞
Total rotation in degrees	r _o	r,	r _∞

Calculate the expression of rate constant.

Sol. The principle of the experiment is that change in the rotation is directally proportional to concentration.

a α (r_o - r_∞)

Then Expression For rate constant

$$\mathsf{K} = \frac{2.303}{t} \log \frac{\mathsf{r}_{o} - \mathsf{r}_{\infty}}{\mathsf{r}_{t} - \mathsf{r}_{\infty}}$$

10. The hydrolysis of cane sugar was studied using an optical polarimeter and the following readings were taken:

time (min.): 0 84 min ∞ observed rotation: 50 20 -10 (degrees) When will the mixture optically inactive? (log 2 = 0.3, log 3 = 0.48)

Sol. From the hydrolysis

Κ

$$= \frac{2.303}{t} \log \frac{(r_{o} - r_{\infty})}{r_{t} - r_{\infty}} = \frac{2.303}{84} \log \frac{50 + 10}{20 + 10}$$

$$K = \frac{2.303}{84} \times .3010$$

The time taken when sample are optically Inactive is t

$$K = \frac{2.303 \times .3010}{84} = \frac{2.303}{t} \log \frac{50 + 10}{+10}$$

t = 217.14 minute

- **11.** Temperature coefficient of the rate of a reaction is 3. How many times the rate of reaction would increase if temperature is raised by 30 K :
 - (1) 3 (2) 9 (3) 27 (4) 81
- **Sol.** For same concentration $\frac{R_1}{R_2} = \frac{K_1}{K_2} = 3^{\frac{30}{10}} = 27$ **Ans. (3)**
- 12. For a gaseous reaction A → products, the half-life of the first order decomposition at 400 K is 150 minutes and the energy of activation is 65.0 kJ mole⁻¹. What fraction of molecules of A at 400 K have sufficient energy to give the products ?
- **Sol.** $\frac{K}{A} = e \frac{-Ea}{RT}$ = Fraction of Molecule Having Sufficient Energy $\Rightarrow \frac{K}{A} = \frac{1}{\frac{65 \times 10^2}{e_{8.3 \times 400}}} = 3.13 \times 10^{-6}$
- **13.** An exothermic reaction $A \rightarrow B$ has an activation energy of 17 KJ per mole of A. The heat of reaction is -40 KJ/mole. The activation energy for the reverse reaction $B \rightarrow A$ is : (1) 75KJ per mole (2) 67KJ per mole (3) 57 KJ per mole (4) 17 KJ per mole

Sol. $\Delta H = E_A - E_B$ -40 = 17 - E_B E_B = 57

- 14. Use the diagram below to answer the following questions.(a) Is the forward reaction exothermic or endothermic?
 - (b) What is the approximate value of $\triangle E$ for the forward reaction?

 $Ea^1 = 30 \text{ KJ/Mole}$

(c) What is activation energy in each direction?

(d) A catalyst is found that lowers the activation energy of the reaction by about 10kJ/mol. How will this catalyst affect the rate of the reverse reaction?



(c) Ea = 50 KJ/Mole

- (b) $\Delta E = (Ea Ea^1) = (50 30) = 20 \text{ KJ} / \text{Mole.}$ (d) Increses
- **15.** At some temperature, the rate constant for the decomposition of HI on a gold surface is .1M.s⁻¹





 $2\text{HI} \rightarrow \text{H}_2(g) + \text{I}_2(g)$

What is the order of the reaction? How long will it take for the concentration of HI to drop from 2M to .5M Sol. From the unit of k given, the reaction is of zero order. As this reaction is of the type $2A \rightarrow$ Products, we apply

 $k_0 = \frac{x}{nt}$ where n = 2 or $k_0 = \frac{a - (a - x)}{nt}$ or $.1 = \frac{(2 - .5)}{2t}$ or t = 7.5 sec

16. The rate of a first order reaction is 0.05 mole/L/s at 10 minutes and 0.04 mole/L/s at 30 minutes after initiation. Find the half-life of the reaction

Sol. Let the concentrations of the reactant after 10 min and 30 min be C_1 and C_2 respectively. Rate after 10 min = KC₁ = 0.05 × 60 Mmin⁻¹ and Rate after 30 min = KC₂ = 0.04 × 60 Mmin⁻¹

$$\therefore \frac{c_1}{c_2} = \frac{5}{4}$$

Supposing the reaction starting after 10 minutes

 $k = \frac{2.303}{20} \log \frac{c_1}{c_2} = \frac{2.303}{20} \log \frac{5}{4} = .011159 \qquad \therefore t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{.011159} = 62.12 \text{ min.}$

17. For a chemical reaction $A+B \rightarrow Product$, the order is 1 with respect to each of A and B Find x and y from the given data.

Rate (moles/L/s)	[A]	[B]
0.10	0.1 M	.1M
0.80	х	.1M
0.40	0.2 M	у
		-

Sol. The rate law may be written as

rate = k [A] [B] Substituting the first set of data in the rate law, we get, $0.10 = k \times .1 \times .1$

k = 10Now substituting the second and third sets of data, we get, $.8 = 10 \times x \times .1$ x = 0.80 M And, $.4 = 10 \times 0.2 \times y$ y = 0.20 M.

- **18.** Find the two third life, $t_{2/3}$, of a first order reaction in which $k = 5.4 \times 10^{-14} \text{ s}^{-1}$.
- **Sol.** The rate constant k for first order reaction is expressed by relation,

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \text{or} \qquad t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Substitute,
$$t = t_{2/3}, k = 5.4 \times 10^{-14} \, \text{s}^{-1}, x = \frac{2a}{3}$$
$$t_{2/3} = \frac{2.303}{5.4 \times 10^{-14} \, \text{s}^{-1}} \log \frac{a}{a-\frac{2}{3}\alpha} = \frac{2.303}{5.4} \times 10^{14} (\log 3) \text{s}$$

 $= 0.4265 \times 0.4771 \times 10^{14} \text{s} = 2.035 \times 10^{13} \text{ s}$ Two third life of given first order reaction is 2.035 × 10¹³ s.