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 maximise the output in optimum time. The last part of chapter will be dealing with the mechanism of a chemical reaction and catalysis.

Section (A) : Rate of reaction

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.**

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

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

Types of Rates of chemical reaction :

For a reaction $R \longrightarrow P$

Average rate = $\dfrac{\text{Total change in concentration}}{\text{Total time taken}}$

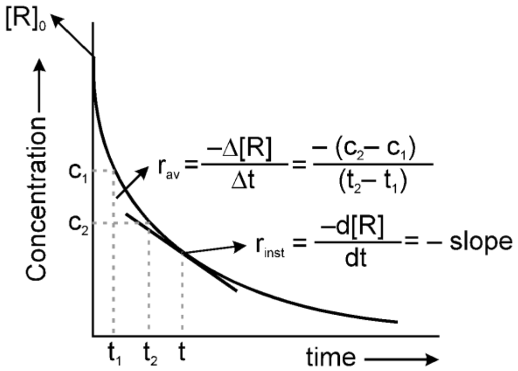
$$= \frac{\Delta c}{\Delta t} = -\frac{\Delta [R]}{\Delta t} = \frac{\Delta [P]}{\Delta t}$$

Instantaneous rate : rate of reaction at a particular instant.

$$R_{\text{instantaneous}} = \lim_{t\to 0}\left[\frac{\Delta c}{\Delta t}\right] = \frac{dc}{dt} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

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 = $-\frac{d\ [N_2]}{dt} = -\frac{1}{3}\frac{d\ [H_2]}{dt} = \frac{1}{2}\frac{d\ [NH_3]}{dt}$

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

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

t/s	0	5	10	20	30
$10^3 \times [R]/mol\ L^{-1}$	160	80	40	10	2.5

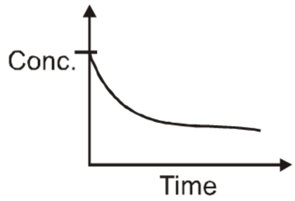
Sol. We can determine the difference in concentration over different intervals of time and thus determine the rate by dividing Δ[R] by Δt

$\frac{[R]_1 \times 10^3}{mol\ \ L^{-1}}$	$\frac{[R]_2 \times 10^3}{mol\ \ L^{-1}}$	$\frac{t_2}{s}$	$\frac{t_1}{s}$	$\frac{r_{av} \times 10^3}{mol\ \ L^{-1}\ \ s^{-1}} = \frac{-[R_2 - R_1] \times 10^3}{[t_2 - t_1]}$
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
2. Temperature
3. Nature of reactants & products
4. Catalyst
5. pH of the solution
6. Dielectric constant of the medium.
7. Radiations/light
8. Pressure
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 :

❍ If more bonds are to be broken, the rate of reaction will be slow.

❍ 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 reaction.

❍ Presence of negative catalyst increases activation energy hence decreases the rate of reaction.

- **pH of solution :**

Eg. $Fe(CN)_6^{4-} \xrightarrow{(Tl^{3+})} [Fe(CN)_6]^{3-}$

This reaction takes place with appreciable rate in acidic medium, but does not take place in basic medium.

- **Dielectric constant of the medium :** More is the dielectric constant of the medium greater will be the rate of ionic reactions.
- **Radiations/light :** Radiation are useful for photochemical reaction.
- **Pressure :** Pressure is important factor for gaseous reaction.
- **Electrical & Magnetic field :** Electric & magnetic fields are rate determining factors if a reaction involves polar species.

Section (B) : Rate law

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 ∝ (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)$^{1-\text{order}}$ 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 m_1 & similarly q may or may not be equal to m_2.

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
$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(\ell) + 3H_2O(\ell)$	$R = K\,[Br^-]\,[BrO_3^-]\,[H^+]^2$	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
$H_2 + Cl_2 \xrightarrow{h\nu} 2\,HCl$	$R = K\,[H_2]^0[Cl_2]^0$	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 dm^3, 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 ?

Ans. 4.32×10^{-4} M sec^{-1}

Sol. $2NO + Cl_2 \longrightarrow 2NOCl$

5 2

5-2 1 2

$$R = k\left(\frac{5}{2}\right)^2 \times \left(\frac{2}{2}\right)^1$$

$$2.4 \times 10^{-3} = k\left(\frac{25}{4}\right)$$

$$K = \frac{4 \times 2.4 \times 10^{-3}}{25} \qquad R, = \frac{4 \times 2.4 \times 10^{-3}}{25}\left[\frac{3}{2}\right]^2 \left[\frac{1}{2}\right]$$

$$R = \frac{4 \times 2.4 \times 10^{-3}}{25} \times \frac{9 \times 1}{8} = 4.32 \times 10^{-4} \text{ M sec}^{-1}$$

Section (C) : The integrated rate laws

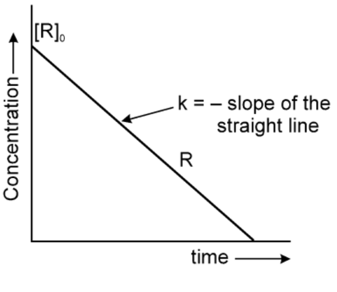
Integrated rate laws :

(a) Zero Order Reactions :

For a zero order reaction

General rate law is, Rate = k [conc.]º = constant

If C_0 is the initial concentration of a reactant and C_t is the concentration at time 't' then



$$\text{Rate} = k = \frac{C_0 - C_t}{'t'} \quad \text{or} \quad kt = C_0 - C_t \quad \text{or} \quad C_t = C_0 - kt$$

Unit of K = same as that of Rate = mol lit^{-1} sec^{-1}.

$$\text{Time for completion} = \frac{C_0}{k}$$

$t_{1/2}$ (half life period) at $t_{1/2}$, $C_t = \frac{C_0}{2}$, so $kt_{1/2} = \frac{C_0}{2}$ $\Rightarrow$ $\mathbf{t_{1/2} =} \frac{C_0}{2k}$ $\therefore t_{1/2} \propto C_0$

Examples of zero order reactions :

Generally decomposition of gases on metal surfaces at high concentrations follow zero order kinetics.

$2PH_3(g) \xrightarrow{Ni} 2P + 3H_2$ Rate = K $[PH_3]^o$

$2HI(g) \xrightarrow{Au} H_2 + I_2$

$2NH_3(g) \xrightarrow{N} N_2 + 3H_2$

$H_2 + Cl_2 \xrightarrow{hv} 2HCl$ Rate = K $[H_2]^o [Cl_2]^o$

(b) First Order Reactions :

(i) Let a 1st order reaction is

	A	$\longrightarrow$ Products	
conc.	'a'	0	t = 0
	'a–x'	.... t = 't'	

Let $\frac{dx}{dt}$ be the rate of reaction at time 't'

$\therefore \frac{dx}{dt} = k(a-x)^1$ or $\frac{dx}{a-x} = kdt.$

On solving $t = \frac{2.303}{k} \log \frac{a}{a-x}$ $k = \frac{2.303}{t} \log \frac{C_0}{C_t}$

$$\boxed{k = \frac{2.303}{t} \log \frac{C_0}{C_t}}$$

$$\boxed{\text{Wilhemy formula : } C_t = C_0 e^{-kt}}$$

$$\boxed{\text{Interval formula : } k = \frac{2.303}{(t_2 - t_1)} \log \frac{C_1}{C_2}}$$

If any substance is growing/increasing following first order kinetics then :

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

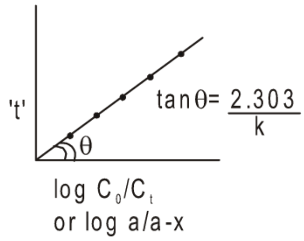
where a is initial concentration of the substance and x is the increment in its concentration after time t.

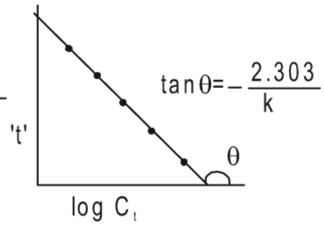
Half life time ($t_{1/2}$) $k = \frac{2.303}{t_{1/2}} \log \frac{2C_0}{C_0}$ $\Rightarrow$ $t_{1/2} = \frac{2.303 \log 2}{k} = \frac{\ell n\ 2}{k} = \frac{0.693}{k}$

$\therefore$ 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

Time	Population (or colony)
0	a
dt	(a + x)

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

on integration

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

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

$$kt = -\log_e \frac{a}{(a+x)} \qquad \text{or} \qquad k = -\frac{2.303}{t}\log_{10}\left(\frac{a}{(a+x)}\right)$$

or

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

Generation time :

At t = generation time , x = a

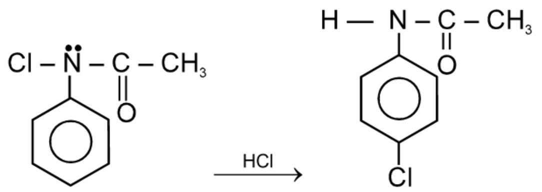
$$\therefore \quad t = \frac{0.693}{K}$$

Examples of 1st order reactions :

1. Decomposition of azoisopropane

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH-N=N-CH\!\!<\!\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}\,(g) \xrightarrow{\Delta} N_2(g) + C_6H_{14}(g)$$

2. Conversion of N–chloro acetanilide into p–chloroacetanilide



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

4. $NH_4NO_2 \longrightarrow 2H_2O + N_2$

5. Radiactive decay

- All radioactive decays are always first order kinetics.

$${}^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}_2H^4$$

Solved Examples

Ex.3 Calculate $\frac{t_{0.75}}{t_{0.50}}$ for a 1st order reaction

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

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

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

Sol. (2)
$$\underset{0\%}{100} \xrightarrow{t_{1/2}} \underset{50\%}{50} \xrightarrow{t_{1/2}} \underset{75\%}{25} \xrightarrow{t_{1/2}} \underset{87.5\%}{12.5} \xrightarrow{t_{1/2}} \underset{93.75\%}{6.25} \xrightarrow{t_{1/2}} \underset{96.875\%}{3.125}$$

(c) Second order reaction :

2nd order Reactions

Two types

$A + A \longrightarrow$ products

a a

(a – x) (a –x)

$\therefore \frac{dx}{dt} = k(a-x)^2$

$\Rightarrow \int_0^x \frac{dx}{(a-x)^2} = \int kdt$

$\Rightarrow \left(\frac{-1}{(a-x)}\right)_0^1 = kt$

$\Rightarrow \frac{1}{(a-x)} - \frac{1}{a} = kt$

$A + B \longrightarrow$ products.

a b 0

a – x b – x

Rate law

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

$\int_0^x \frac{dx}{(a-x)(b-x)} = \int_0^t kdt$

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

(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.

$\therefore$ For A + B $\longrightarrow$ Products [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.

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

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

$$\Rightarrow kb = \frac{2.303}{t} \log \frac{a}{a-x} \Rightarrow \quad k_b' = \frac{2.303}{t} \log \frac{a}{a-x}$$

- 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

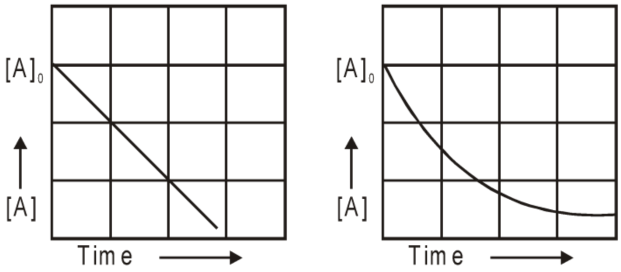
$$\underset{\text{sucrose}}{C_{12}H_{12}O_{11}} + \underset{\text{excess}}{H_2O} \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

(b) Hydrolysis of esters

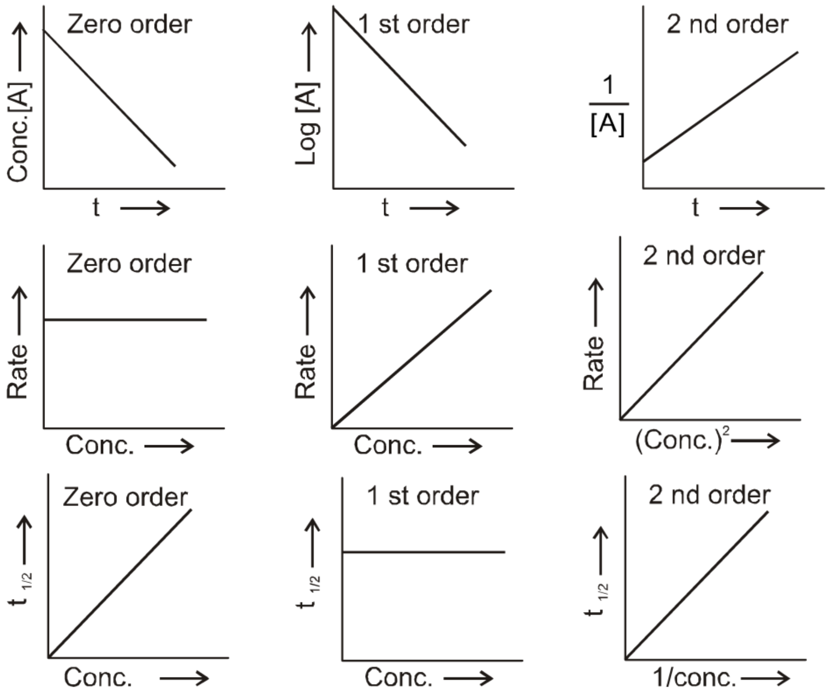
$$CH_3COOCH_3 + \underset{\text{(excess)}}{H_2O} \xrightarrow{H^+} CH_3COOH + CH_3OH$$

Table : Characterstics of First-and Second-Order Reactions of the Type A $\longrightarrow$ 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)	$[A]_t = [A]_0 - kt$	$\ln [A]_t = -kt + \ln [A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{(A_t)^{n-1}} - \frac{1}{(A_0)^{n-1}} = (n-1)\ kt$
Linear graph	$[A]_t$ versus t	$\ln [A]$ versus t	$\frac{1}{[A]}$ versus t	$\frac{1}{(A_t)^{n-1}}$ v/s t
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ (depends on $[A]_0$)	$t_{1/2} = \frac{0.693}{k}$ (independent of $[A]_0$)	$t_{1/2} = \frac{1}{k[A]_0}$ (depends on $[A]_0$)	$t_{1/2} \propto \frac{1}{(A_0)^{n-1}}$



Graphical comparison of different orders



Section (D) : Methods to determine the rate law

Methods to determine order of a reaction :

(A) Initial rate method :

- By comparision of different initial rates of a reaction by varying the concentration of one of the reactants while others are kept constant

$r = k\,[A]^a\,[B]^b\,[C]^c$ if $[B]$ = constant

$[C]$ = constant

then for two different initial concentrations of A we have

$r_{0_1} = k\,[A_0]_1{}^a$ $r_{0_2} = k\,[A_0]_2{}^a$

$$\Rightarrow \quad \frac{r_{0_1}}{r_{0_2}} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^x$$

or in log form we have $a = \dfrac{\log\ (r_{0_1}/r_{0_2})}{\log\ ([A_0]_1/[A_0]_2)}$

Solved Examples

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.

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

0–100 s, rate = $\dfrac{[3.50 - 4.00] \times 10^3\ \ \text{Pa}}{100}$ = 5 Pa/s

100–200s, rate = – $\dfrac{[3.00 - 3.50] \times 10^3\ \ \text{Pa}}{100\text{s}}$ = 5 Pa/s

200–300s, rate = – $\dfrac{[2.50 - 3.00] \times 10^3\ \ \text{Pa}}{100}$ = 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 again indicating it is a zero order reaction.

k = rate = 5 Pa/s

$t_{1/2} = \dfrac{\text{initial concentration or pressure}}{2k} = \dfrac{4.00 \times 10^3 \text{Pa}}{2 \times 5\ \ \text{Pa}\ \ s^{-1}}$ = 400s

(B) 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.

Solved Examples

Ex.6 The rate of decomposition of N_2O_5 in CCl_4 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., $k = \dfrac{\ln\ (c_0/c)}{t}$

t/min c/M $k = \dfrac{\ln\ (c_0/c)}{t}$ 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 $k = 6.31 \times 10^{-4}$ 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 ℓn c against t, we obtain a straight line with slope = – k.

(C) Method of half lives :

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

for n^{th} order reaction $t_{1/2} \propto \dfrac{1}{[R_0]^{n-1}}$

$$\frac{t_{1/2}}{t'_{1/2}} = \frac{(R'_0)^{n-1}}{(R_0)^{n-1}}$$

Solved Examples

Ex.7 In the reduction of nitric oxide 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 n^{th} order reaction ($n \neq 1$), $t_{1/2} \propto \dfrac{1}{c_0^{n-1}}$

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

(D) 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

$$\text{rate} = k\,[A]^a\,[B]^b\,[C]^c = k_0\,[A]^a$$

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

Section (E) : Methods to monitor the progress of the reaction

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

Solved Examples

Ex.8 Find the expression for K in terms of P_0 , P_t and n

Sol. Let there is a 1st order reaction, $A(g) \longrightarrow nB(g)$

Let initial pressure at time t	P_0	0	t = 0
	$P_A = (P_0 - x)$	nx	t = t
	–	nP_0	t = ∞

$\therefore P_t$ (Total pressure at time 't') $= P_0 - x + nx = P_0 + (n - 1)x$

$\therefore x = \dfrac{P_t - P_0}{n-1}$

$\therefore P_A = P_0 - \dfrac{P_t - P_0}{n-1} = \dfrac{P_0 n - P_t}{n-1}$

$\therefore a \propto p_0$ & $a - x \propto P_A = \dfrac{nP_0 - P_t}{n-1}$

$\therefore$ **k =** $\dfrac{2.303}{t}$ **log** $\dfrac{P_0(n-1)}{nP_0 - P_t}$ or $K = \dfrac{2.303}{t}$ **log** $\dfrac{P_\infty - P_0}{P_\infty - P_t}$

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

- 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.

Solved Examples

Ex.9 For the decomposition of azoisopropane at 270ºC 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.

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

(B) Volume measurement :

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

Solved Examples

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

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

Sol. Let, V_t be the volume of N_2 collected at time 't'

V_∞ = be the volume of N_2, collected at the end of the reaction.

$$a \propto V_\infty$$

$$(a - x) \propto V_\infty - V_t$$

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

(ii) By titration method : By measuring the volume of titrating agent we can monitor amount of reactant remaining or amount of product formed at any time. It is the titre value . Here the milliequilivents or millimoles are calculated using valence factors.

Solved Examples

Ex.11 Study of acid hydrolysis of an ester.

$$CH_3COOCH_3 + \underset{(excess)}{H_2O} \xrightarrow[(HCl)]{H^+} CH_3COOH + CH_3OH$$

The progress of this reaction is monitered or dertermined by titrating the reaction mixture at different time intervals against a standard solution of NaOH using phenolphthalein as indicator. Findout rate constant of the reaction in terms of volume of NaOH consumed at t = 0, V_0 , at t = ∞, V_∞ & at time t, V_t .

Sol. Let, V_0 = vol. of NaOH used at t = 0 [this is exciusively for HCl.]

V_t = vol. of NaOH used at 't'

V_∞ = vol. of NaOH used at t = ∞

$a \propto V_\infty - V_0$

$a - x \propto V_\infty - V_t$; $x \propto V_t - V_0$

$a \propto V_\infty - V_0$; $k = \dfrac{2.303}{t} \log \dfrac{V_\infty - V_0}{V_\infty - V_t}$

Section (F) : Effect of Temperature

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 10^0C(usually these temperatures were taken as 25^0C and 35^0 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.

Solved Examples

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

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

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

Arrhenius theroy 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 :

❍ A chemical reaction takes place 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).

❍ 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.

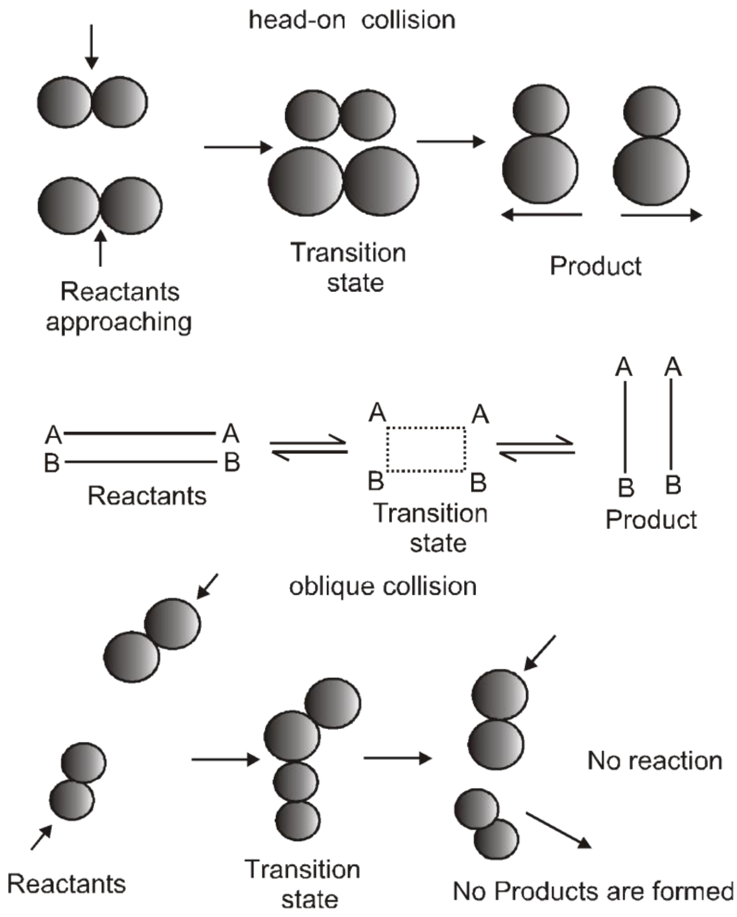
- **Energy barrier :**

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 activaiton 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.

❍ At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the reaction.

Passive molecules $\rightleftharpoons$ Active molecules, $\Delta H = +ve$

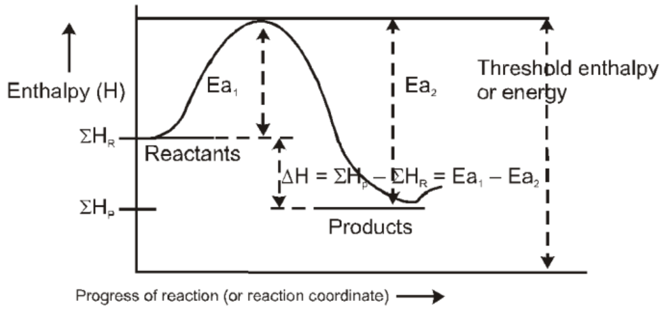
❍ Concept of energy of activation (E_a)

● 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,

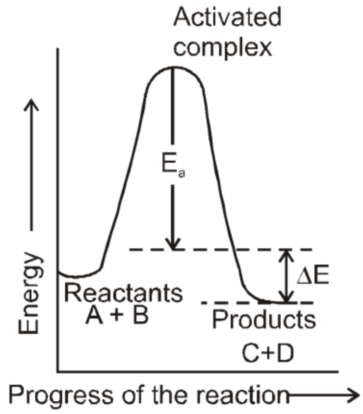
E_a is expressed in kcals mole^{-1} or kJ mole^{-1}.

- 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.

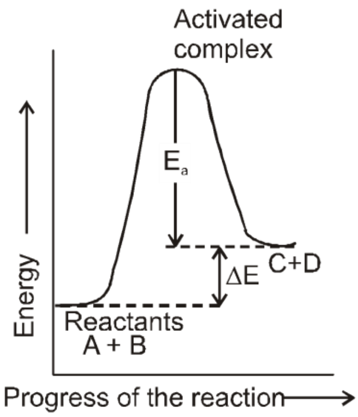


ΣH_R = Summation of enthalpies of reactants
ΣH_P = Summation of enthalpies of reactants
ΔH = Enthalpy change during the reaction
Ea_1 = Energy of activation of the forward reaction
Ea_2 = Energy of activation of the backward reaction

From the figure above it can be concluded that the minimum activation energy of any exothermic reaction will be zero while minimum activation energy for any endothermic reaction will be equal to ΔH.
Greater the height of energy barrier, greater will be the energy of activation and more slower will be the reaction at a given temperature.



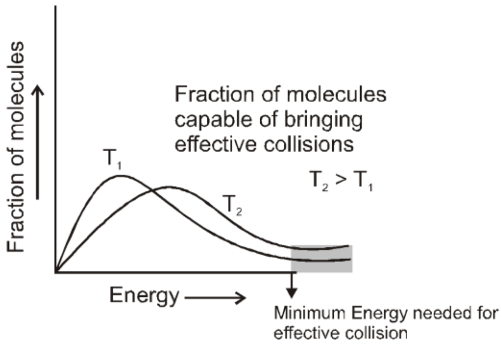
(Exothermic)



(Endothermic)

Rate of any chemical reaction = Collision frequency × fraction of the total number of effective collision
= Collision frequency × fraction of the total number of collision in which K.E. of the colliding molecules equals to E_a or exceeds over it.

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 10ºC 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.



Arrhenius equation $\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$

Integrating equation 4 assuming E_a to be constant we get,

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

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 inifinty, k will be maximum. That is to say, A is the maximum rate constant of a reaction.

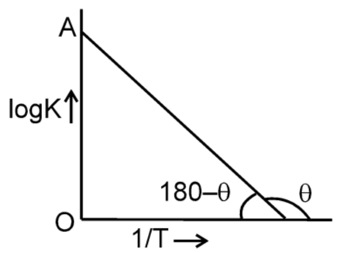
- The expontential term i.e. $e^{-Ea/RT}$ measures the fraction of total number of molecules in the activated state or fraction of the total number of effective collisions.

$\frac{n_{E_a}}{n} = e^{-E_a/RT}$ Where n_{Ea} = 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, $\log k = \left(-\frac{Ea}{2.303\ R}\right)\frac{1}{T} + \log A$

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



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

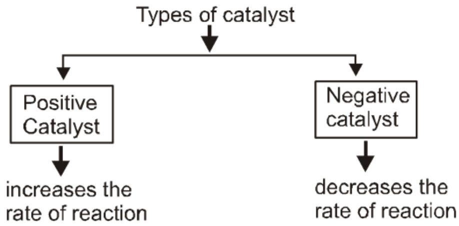
If k_1 and k_2 be the rate constant of a reaction at two different temperature T_1 and T_2 respectively, then we have log $k_1 = -\dfrac{E_a}{2.303\ R}.\dfrac{1}{T_1} + \log A$ and log $k_2 = -\dfrac{E_a}{2.303\ R}.\dfrac{1}{T_1} + \log A$

Subtracting we get

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

Catalyst and catalysis :

A **catalyst** is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called **catalysis**.



Catalyst are generally foreign substances but sometimes one of the product may act as a catalyst and such catalyst is called **"auto catalyst"** and the phenomena is called **auto catalysis**.

Examples of catalysis

(a) Thermal decomposition of $KClO_3$ is found to be accelerated by the presence of MnO_2. Here MnO_2 (foregin substance) acts as a catalyst.

$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 \uparrow + [MnO_2]$$

● MnO_2 can be received in the same composition and mass at the end of the reaction.

(b) In the permanganate titration of oxalic acid intially there is slow discharge of the colour of permanganate solution but afterwards the discharge of the colour become faster. This is due to the formation of $MnSO_4$ during the reaction which acts as a catalyst for the same reaction. Thus, $MnSO_4$ is an **"auto catalyst"** for this reaction. This is an example of auto catalyst.

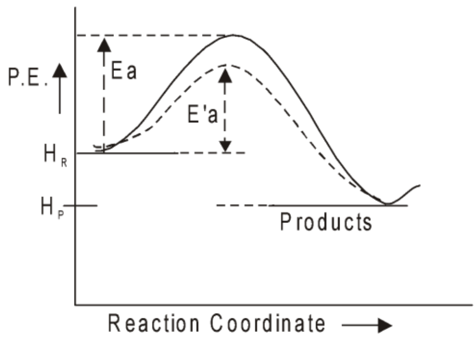
$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_2 \longrightarrow K_2SO_4 + 8H_2O + 10CO_2$$

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^o.

  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.

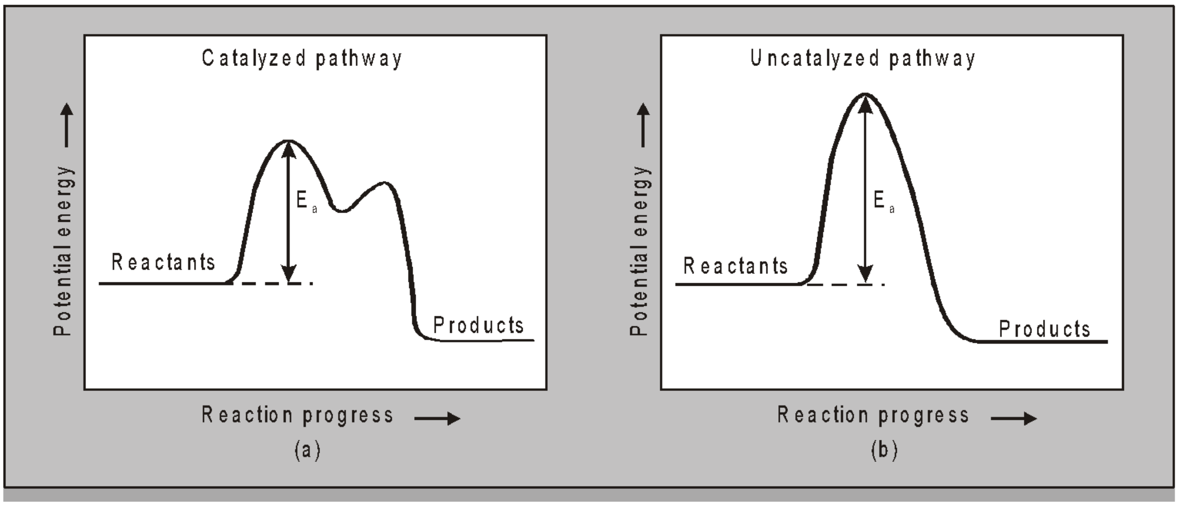
Comparision of rates of reaction in presence and absence of catalyst :

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

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

Since $E_a - E'_a$ is positive so $k_{cat} > k$. the ratio $\frac{k_{cat}}{k}$ gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature.

The rate of recation in the presence of catalyst at any temperature T_1 may be made equal to the rate of reaction in absence of catalyst but for this sake we will have to raise the temperature. Let this temperature be T_2 this $e^{-E'_a/RT_1} = e^{-E_a/RT_2}$ or $\frac{E'_a}{T_1} = \frac{E_a}{T_2}$



Solved Examples

Ex.13 For the reaction $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$ under the same concentration conditions of the reactants, the rate of the reaction at 250°C is 1500 times as fast as the same reaction at 150°C. Calculate the activation energy of the reaction. If the frequency factor is 2.0×10^{10} M^{-1} sec^{-1}, calulate the rate constant of the reaction at 150°C.

Sol. $\log \frac{K_2}{K_1} = \frac{E}{2.303\ R}\left[\frac{T_2 - T_1}{T_1\ T_2}\right]$

$\log 1500 = \frac{E}{2.303 \times 2} \times \frac{100}{523 \times 423}$

$E = \frac{3.1761 \times 2.303 \times 2 \times 523 \times 423}{100} = 32.36\ \text{kcal mol}^{-1}$

$\log K = \log A - \frac{E}{2.303\ RT} = \log(2.0 \times 10^{10}) - \frac{32360}{2.303 \times 2 \times 423} = 10.301 - 16.609 = -6.308$

$K = 4.92 \times 10^{-7}$ litres mol^{-1} sec^{-1}

Ex.14 The pyrolysis of an organic ester follows a first order process and its rate can be expressed as

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

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

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

$\log k = -\frac{6.06}{2.303} = -2.63$; $k = 2.344 \times 10–3\ min^{-1}$

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

Ex.15 The slope of the plot of log k vs $\frac{1}{T}$ for a certain reaction was 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 $= \frac{-E}{2.303\ R} = -5.4 \times 10^3$

$E = 5.4 \times 10^3 \times 2.303 \times 1.987 = 24.624$ cal mol^{-1}

(b) $E = Ae^{-E/RT}$; $\log 1.155 \times 10^{-2} = \log A - \frac{24.624}{2.303 \times 1.987 \times 373}$

or $A = 3.08 \times 10^{12}$ 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

$$aA + bB \longrightarrow \text{products} \qquad \text{rate} = k[A]^a[B]^b, \text{ where } a + b = 1, 2 \text{ or } 3.$$

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 reactart taking part in a chemical reaction eq $NH_4NO_2 \rightarrow N_2 + 2H_2O$ m = 1	It is defined as the sum of the power of concnentraction terms that appear in rate law. $NH_4NO_2 \rightarrow N_2 + 2H_2O$. Rate = $k[NH_4NO_2]$
2	It is always a whole number. It can neither be zero nor fractional.	It may be zero, fractional or integer.
3	It is derived from RDS in the mechanism of reaction.	It is derived from rate expression.
4	It is theoretical value.	It is experimental value.
5	Reactions with molecularity > 4 are rare.	Reactions with order of reaction > 4 are also rare.
6	Molecularity is in independent of Pressure and temperature.	Order of reaction depends upon pressure and temperature.

Section (G) : Mechanism of reactions

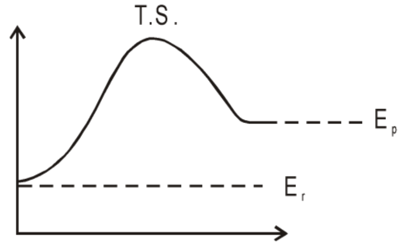
Mechanism of a reaction :

Reactions can be divided into

- Elementary / simple / single step
- Complex / multi-step

- **ELEMENTARY REACTION :**

❍ These reaction take place in single step without formation of any intermediate



- 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
- molecularity will always be a natural no

  1 = unimolecular one molecule gets excited (like radioactivity)

  2 = bimolecular

  3 = trimolecular
- Molecularly $\leq$ 3 because the probabilty of simaltaneous collision between 4 or more molecules in proper orientation is very low
- 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

  $H_2 + I_2 \rightleftharpoons 2HI \rightarrow$ Simple reaction rate = k $[H_2]$ $[I_2]$

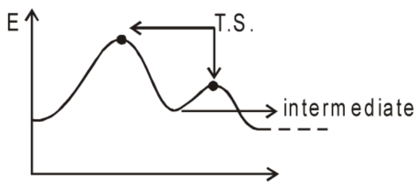
  $2H_2 + 2I_2 \rightleftharpoons 4HI$ (not elementary)

  reaction obtained by multiplying an elementary reaction with some no will not be of elementary nature

  $H_2 + Cl_2 \rightleftharpoons 2HCl$ 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 procceds)



- For complex reaction each step of mechanism will be having its own molecularity but molecularity of net complex reaction will not be defined.
- 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.
- 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.16 The thermal decomposition of N_2O_5 occurs in the following steps.

Step - I $N_2O_5 \xrightarrow{\text{slow}} NO_2 + NO_3$

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

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

suggest the rate expression.

Ans. k $[N_2O_5]$

Sol. $N_2O_5 \longrightarrow NO_2 + NO_3$ (Slow)

$N_2O_5 + NO_3 \longrightarrow 2NO_2 + O_2$ (Fast)

$2N_2O_5 \longrightarrow 4NO_2 + O_2$ rate = k $[N_2O_5]$

Radioactivity

* All radioactive disintegration follow Ist order kinetics.

$A \longrightarrow B + C$

Int. nuclie N_0

At time t. N

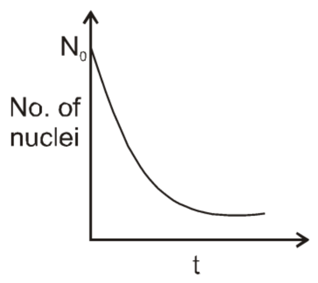
decay constant

$$\boxed{\frac{-dN}{dt} = \lambda N}$$ No. of nuclei of A at time t

rate decay(A)

* λ = Not dependent on temperature.

$\frac{-dN}{dt} = \lambda N$; $\int \frac{-dN}{N} = \int \lambda \ dt$



$$\boxed{N = N_0 e^{-\lambda t}}$$

$$\boxed{\lambda = \frac{1}{t} \ln\left(\frac{N_0}{N}\right)} \quad ; \quad \boxed{\frac{A_0}{A} = \frac{N_0}{N} = \frac{n_0}{n} = \frac{w_0}{w}}$$

n_0 = initial moles ; w_0 = initial weight

$\lambda = \frac{1}{t} \ln\left(\frac{w_0}{w}\right)$ (w = weight of A remaining after time t)

$$\boxed{\lambda = \frac{1}{t} \ln\left(\frac{w_0}{w_0 - x}\right)}$$

Half life :

$t = t_{1/2}$; $N = \frac{N_0}{2}$

$\lambda = \frac{1}{t_{1/2}} \ln \left(\frac{N_0}{N_0/2}\right)$

$\lambda = \frac{\ln 2}{t_{1/2}}$

$$\boxed{t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}}$$

Average life :

$$\boxed{T_{avg.} = \frac{1}{\lambda} = 1.44 \quad t_{1/2}}$$

$T_{avg.} = \frac{\int_0^\infty dN \,.\, t}{N_0} = \frac{1}{\lambda}$ $\left(\because \frac{-dN}{dt} = \lambda N \text{ and } N = N_0e^{-\lambda t}, \therefore dN = -\lambda N_0e^{-\lambda t}\, dt\right)$

Unit of activity :

* Curie (C_i) = 3.7×10^{10} dps

  Millicurie (mC_i) = 3.7×10^{7} dps

  Microcurie (μC_i) = 3.7×10^{4} dps

* Rutherford (1 Rd) = 1×10^{6}dps

Application of radioactivity :

1. Carbon dating : (used for wooden object)

In living matter existing in nature : ${}_6C^{14}$ (radio active) : ${}_6C^{12}$ (stable) = 1 : 10^{12}

In upper atmosphere :

$${}_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1p^1$$

Ratio of radioactive carbon in dead animals / trees decreases with respect to time.

$t = \frac{1}{\lambda} \ln \left(\frac{A_0}{A}\right)$

Half life of ${}_6C^{14}$ = 5770 yrs.

A = activity of old wood piece. ; A_0 = activity of fresh wood piece.

2. Age of rocks or minerals

${}_{92}U^{238}$ (radioactive) $\longrightarrow$ ${}_{82}Pb^{206}$ (stable)

Reaction :

$$_{92}U^{238} \longrightarrow {}_{82}Pb^{206} + x\,{}_2He^4 + y\,{}_{-1}e^0$$

$$_zX^A \longrightarrow {}_{z-2}X'^{A-4} + {}_2He^4$$

$$_zY^A \longrightarrow {}_{z+1}Y'^A + {}_{-1}e^0$$

Number of α-particles = $\dfrac{\text{difference of mass no.}}{4} = \dfrac{238-206}{4} = 8$

$238 = 206 + 4x + 0$ .....(1)

$92 = 82 + 2x - y$ .....(2)

On solving (1) and (2),

$x = 8$; $y = 6$

$$_{92}U^{238} \longrightarrow {}_{82}Pb^{206} + 8({}_2He^4) + 6({}_{-1}e^0)$$

At time t w g y g

$t = \dfrac{1}{\lambda}\ln\left(\dfrac{w_0}{w}\right)$

$t = \dfrac{1}{\lambda}\ln\left(\dfrac{w_0}{w_0 - x}\right)$

$w = w_0 - x$

∴ $w_0 = w + x$

1 mole or 238 g U provide 206 g of Pb

∴ $\dfrac{238}{206}$ g U provide 1 g Pb

∴ $\dfrac{238}{206} \times y$ g U provide y g Pb

$x = \dfrac{238}{206} \times y$; $w_0 = w + \dfrac{238}{206} \times y$

$$_{92}U^{238} \longrightarrow {}_{82}Pb^{206} + 8\,{}_2He^4 + 6\,{}_{-1}e^-$$

V(in mL) collected

$n_{He} = \dfrac{PV}{RT}$ .... (1)

$t = \dfrac{1}{\lambda}\ln\left(\dfrac{n_0}{n}\right)$

$n = \dfrac{w}{238}$ .... (2)

$n_0 = n + \dfrac{n_{He}}{8}$

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) $2HOF(g) \rightarrow 2HF(g) + O_2(g)$

Sol. (a) $\frac{-d[O_3]}{2dt} = +\frac{1}{3}\frac{d[O_2]}{dt}$ (b) $-\frac{1}{2}\frac{d[HOF]}{dt} = +\frac{d[HF]}{2dt} = +\frac{d[O_2]}{dt}$

$\frac{-d[O_3]}{dt} = \frac{2}{3}\frac{d}{dt}[O_2]$ $\frac{-d[HOF]}{dt} = +\frac{d[HF]}{dt} = +\frac{2d[O_2]}{dt}$

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 = 2×10^{-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) $2 \times 10^{-4} \times 3 = -\frac{d[H_2]}{dt} = 6 \times 10^{-4}$ 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 NO_2 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 → 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)**

6. Gaseous cyclobutene isomerizes to butadiene in a first order process which has k = 3.3 x 10^{-4} s^{-1} at 153ºC. How many minutes would it take for the isomerization to proceed 40 % to completion at this temperature .

Sol. For the First order Rxn

$$t = \frac{2.303}{k}\log\frac{a}{(a-x)} \qquad t = \frac{2.303}{3.3\times10^{-4}}\log\left(\frac{100}{60}\right)$$

$t = 1.54 \times 10^{+3}$ Second. = 25.66 Minute

7. Calculate $\frac{t_{0.5}}{t_{0.25}}$ for a 1^{st} order reaction

Sol. $$\frac{t_{0.5}}{t_{0.25}} = \frac{\frac{2.303}{K}\log\frac{a}{(a-\frac{a}{2})}}{\frac{2.303}{K}\log\frac{a}{(a-\frac{a}{4})}} = \frac{\log 2}{(\log\frac{4}{3})}$$

8. For the reaction A + B –→ 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.

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

From data I. $.030 = K [.10]^x [.20]^y$ (1)

From data II. $.059 = K [.20]^x [.20]^y$ (2)

From III. $.060 = K [.20]^x [.30]^y$ (3)

divide 1 equation by (2)

$$\frac{.030}{.059} = \frac{k[.10]^x[.20]^y}{k[.20]^x[.20]^y} \quad \Rightarrow x = 1$$

Then divide (2) equation by (3)

$$\frac{.059}{.060} = \frac{k[.20]^x[.20]^y}{k[.20]^x[.30]^y} \quad \Rightarrow y = 0$$

Put the value of x and y in (1) eguation

$.030 = K[.10]^1 [.20]^0$

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

9. Decomposition of H_2O_2.

$$H_2O_2 \longrightarrow H_2O(\ell) + \frac{1}{2}O_2(g)$$

The progress of this reaction is measured by titrating the reaction mixture with $KMnO_4$ at different time intervals. Calculate rate constant of the reaction in terms of volume of $KMnO_4$ consumed at time t = 0, V_0 and at time t, V_t.

Sol. Assume the decomposetion of H_2O_2 is a first order reaction

$H_2O_2 \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$

$KMnO_4$ React Only with the H_2O_2 them

For Ist order reaction $K = \frac{2.303}{t}\log\frac{a}{(a-x)}$

Then $a \alpha Vo$

and $(a - x) \alpha Vt$

Then $K = \frac{2.303}{t}\log\left(\frac{Vo}{Vt}\right)$

10. 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)**

11. The reaction

$A + B \longrightarrow$ products

is first order with respect to both A and B has a rate constant of 6.0 mol^{-1} sec^{-1}. at 27°C. Calculate the initial rate of the reaction at 47°C when equal volumes of A and B of concentration 0.02 moles litre^{-1} in each are mixed. The activation energy of the energy of the reaction is 42 kJ mol^{-1} .

Sol. Reaction $A + B \longrightarrow$ Product

We know $\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta E}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta E}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$\log\left(\frac{K_2}{6}\right) = \frac{42 \times 10^3[320 - 300]}{2.303 \times 8.3 \times 300 \times 320} = \frac{840}{1835.03}$

$\log \frac{K_2}{6} = .4577$

$\frac{K_2}{6} = \text{anti log}\ (.4577)$

$K_2 = 2.863 \times 6 = 17.178$

Rate at 47°C will be

The $Rate_2 = 17.178 \times [.01] \times [.01]$

$Rate_2 = 17.178 \times 10^{-4} = 1.7178 \times 10^{-3}$

12. For a gaseous reaction $A \longrightarrow$ 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 $\Rightarrow \frac{K}{A} = \frac{1}{e^{\frac{65 \times 10^2}{8.3 \times 400}}} = 3.13 \times 10^{-6}$

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 :

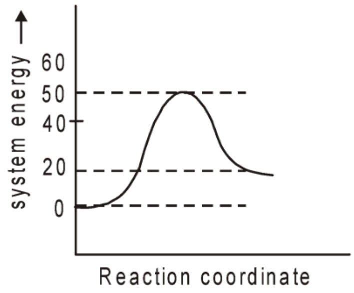
(1) 75KJ per mole (2) 67KJ per mole (3) 57 KJ per mole (4) 17 KJ per mole

Sol. $\Delta H = E_A - E_B$

$-40 = 17 - E_B$

$E_B = 57$

14. Use the diagram below to answer the following questions.

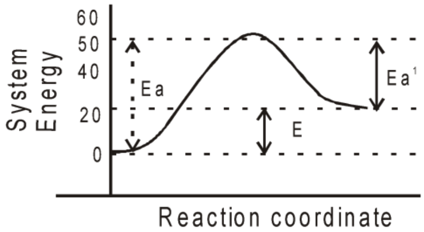


(a) Is the forward reaction exothermic or endothermic?

(b) What is the approximate value of Δ *E* for the forward reaction?

(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?



Sol.

(a) Forward Rxn are endothermic

(b) $\Delta E = (Ea - Ea^1) = (50 - 30) = 20$ KJ / Mole.

(c) Ea = 50 KJ/Mole Ea^1 = 30 KJ/Mole

(d) Increses

15. At some temperature, the rate constant for the decomposition of HI on a gold surface is .1M.s^{-1}

$$2HI \rightarrow H_2(g) + I_2(g)$$

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 → 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 = 7.5sec

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 = $KC_1 = 0.05 \times 60$ Mmin^{-1} and Rate after 30 min = $KC_2 = 0.04 \times 60$ Mmin^{-1}

$$\therefore \frac{C_1}{C_2} = \frac{5}{4}.$$

Supposing the reaction starting after 10 minutes

$$k = \frac{2.303}{20}\log\frac{C_1}{C_2} = \frac{2.303}{20}\log\frac{5}{4} = .011159 \quad \therefore t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{.011159} = 62.12 \text{ min.}$$

17. For a chemical reaction A+B → 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	x	.1M
0.40	0.2 M	y

Sol. The rate law may be written as

rate = k [A] [B]

Substituting the first set of data in the rate law, we get,

$0.10 = k \times .1 \times .1$

$k = 10$

Now 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. In the decomposition of H_2O_2 at 300 K, the energy of activation was found to be 16 kcal/ mole, while it decreased to 10 kcal/ mole when the decomposition was carried out in the presence of a catalyst at 300 K, How many times is the catalysed reaction faster than the uncatalysed one?

Sol. Suppose E_1 and E_2 are the energies of activation when the reaction is carried out in the absence and presence of a catalyst respectively.

Thus, $k_1 = Ae^{-E_1/RT}$; $k_2 = Ae^{-E_2/RT}$

Taking log, $\ln k_1 = \ln A - \frac{E_1}{RT}$

$\ln k_2 = \ln A - \frac{E_2}{RT}$

$\therefore$ $\ln k_2 - \ln k_1 = -\frac{E_2}{RT} + \frac{E_1}{RT}$ or $\ln \frac{k_2}{k_1} = \frac{1}{0.002 \times 300}(16 - 10) = \frac{6}{0.002 \times 300}$

$2.303 \log \frac{k_2}{k_1} = 10$

$\log \frac{k_2}{k_1} = \frac{10}{2.303} = 4.342$ Taking antilog $\frac{k_2}{k_1} = 2.190 \times 10^4$

19. In Arrhenius's equation for a certain Reaction, the value of A and E (activation energy) are $6 \times 10^{13}\ s^{-1}$ and 98.6kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be 20 minutes?

Sol. $k = Ae^{-E/RT}$

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

$2.303 \log k = 2.303 \log A - \frac{E}{RT}$ or $\log k = \log A - \frac{E}{2.303RT}$ .....(1)

Given that $A = 6 \times 10^{13}\ s^{-1}$, $E = 98.6$ kJ mol^{-1}

$t_{1/2} = 20 \times 60$ s.

For first-order reaction $k = \frac{0.6932}{t_{1/2}} = \frac{0.6932}{1200}\ s^{-1}$

Thus (1) becomes,

$$\log \frac{0.6932}{1200} = \log (6 \times 10^{13}) - \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T}$$

[$R = 8.314 \times 10^{-3}$ kJ/K/mol]

T = 302.26 K.

20. The decomposition of N_2O_5 according to the equation

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

is a first-order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.

Sol. $2N_2O_5 \rightarrow 4NO_2 + O_2$

at t = 0 a

After 30 min: $a - x$ $2x$ $x/2$

$\therefore$ $(a - x) + 2x + \frac{x}{2} = 284.5$ or $a + \frac{3x}{2} = 284.5$ ....(1)

After complete decompositon of N_2O_5.

$2N_2O_5 \rightarrow 4NO_2 + O_2$

0 2a a/2

$\therefore$ $2a + \frac{a}{2} = 584.5$ or $\frac{5a}{2} = 584.5$ ....(2)

From (1) and (2), we get,

$a = 233.5$, $x = 34$

Thus, for a first-order reaction of the type $2A \rightarrow$ products

$$k = \frac{1}{2t} \log \frac{a}{a - x}$$

$$k = \frac{2.303}{2 \times 30} \log \frac{233.5}{233.5 - 34} = 2.625 \times 10^{-3}\ min^{-1}$$

21. Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide :

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

The rate law for this reaction is

rate = $k\,[NO]^2[O_2]$

Propose a mechanism for the above reaction.

Sol. The rate law indicate that order of reaction is 2 w.r.t. NO and 1 w.r.t. O_2. The possible mechanism for given reaction may be

$$NO + O_2 \underset{}{\overset{K_1}{\rightleftharpoons}} NO_3 \quad \text{... (fast step)}$$

$$NO_3 + NO \xrightarrow{K_2} NO_2 + NO_2 \quad \text{... (slow step)}$$

Overall reaction, (by addition of two steps)

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

As slowest step of mechanism of reaction determine the rate of reaction,

∴ rate = k_2 $[NO_3][NO]$

But $[NO_3] = k_1 [NO][O_2]$ (∴ NO_3 is an intermediate species, and its formation is in equilibrium state)

∴ rate = $k_1k_2 [NO][O_2][NO] = k[NO]^2[O_2]$

(where k is rate constant and $k = k_1k_2$) The above expression of rate law derived from proposed mechanism is same as in given data.

22. The decomposition of a compound is found to follow a first order rate law. If it takes 15 minutes for 20 percent of original material to react, calculate (i) the specific rate constant, (ii) the time at which 10 percent of the original material remains unreacted, (iii) the time it takes for the next 20 percent of the reactant left to react first 15 minutes.

Sol. (i) Specific rate constant, k for first order reaction is given by,

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{15} \log \frac{100}{100-20} = \frac{2.303}{15} \times 0.0969 \text{ min}^{-1}$$

$$= 0.0148 \text{ min}^{-1} = 1.48 \times 10^{-2} \text{ min}^{-1}$$

(ii) When 10% of original reactant remains unreacted, 90% of reaction is complete. We are required to calculate $t_{90\%}$ of reaction.

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{100-90} = \frac{2.303}{0.0148} \times \log 10$$

$$= 155.6 \text{ minutes}$$

(iii) After first 15 minutes. 80% of reactant is left unreacted.

∴ a = 80 a – x = 80 – 20% of 80

$$= 80 - \frac{20}{100} \times 80 = 80 - 16$$

Time for next 20% of reactant left to react is given by

$$t = \frac{2.303}{k} \log \frac{80}{80-16}$$

$$= \frac{2.303}{0.0148} \times \log \frac{80}{64} = \frac{2.303}{0.0148} \times 0.0969 = 15 \text{ minutes}$$

23. Find the two third life, $t_{2/3}$, of a first order reaction in which $k = 5.4 \times 10^{-14}\ s^{-1}$.

Sol. The rate constant k for first order reaction is expressed by relation,

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

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

$$t_{2/3} = \frac{2.303}{5.4\times10^{-14}s^{-1}}\log\frac{a}{a-\frac{2}{3}a} = \frac{2.303}{5.4} \times 10^{14}(\log 3)s$$

$$= 0.4265 \times 0.4771 \times 10^{14}s = 2.035 \times 10^{13}\ s$$

Two third life of given first order reaction is 2.035×10^{13} s.

24. First order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete ?

Sol. Use the following relation to calc00ulate k, rate constant of first order reaction.

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

Here, t = 20 minutes, a = 100 x = 15 (for completion of 15% of reaction)

$$20 = \frac{2.303}{k}\log\frac{100}{100-15}$$

$\therefore$ Rate constant, $k = \frac{2.303}{k}\log\frac{100}{85} = \frac{2.303}{20} \times \frac{0.0706}{1} = 0.00813\ min^{-1}$

Again use the relation for completion of 60% of reaction :

$$t_{60\%} = \frac{2.303}{k}\log\frac{a}{a-x}$$

Now, a = 100, a – x = 100 – 60

$$= \frac{2.303}{0.00813}\log\frac{100}{100-60} = \frac{2.303}{0.00813}\log\frac{100}{40} = \frac{2.303}{0.00813} \times \frac{(0.3979)}{1} = 112.7 \text{ minutes}$$

The 60% completion of reaction will take 112.7 minutes.

25. A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction.

Sol. Let initial conc. of reactant be a, then conc. after 10 minutes will be, a– x = a– 20% of a= 80% of

$$a = \frac{80}{100} \times a = \frac{4a}{5} = 0.8a$$

For the first order recation, rate constant k can be expressed as,

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{10}\log\frac{a}{0.8a} = \frac{2.303}{10}\log\frac{5}{4} = \frac{2.303}{10}(\log 5 - \log 4)$$

$$\frac{2.303}{10}(0.6990 - 0.6021) = 0.02232\ min^{-1}$$

Knowing the rate constant, k we can find time for 75% completion of reaction again by using the relation.

$k = \frac{2.303}{t} \log \frac{a}{a-x}$;

$a - x = a - 75\%$ of $a = \frac{a}{4}$, $t = t_{75\%}$

$t_{75\%} = \frac{2.303}{0.2232} \times \log \frac{a}{a/4} = \frac{2.303}{0.2232} \times \log 4 = \frac{2.303}{0.2232} \times \frac{0.6021}{1} = 62.125$ min

26. For a first order reaction, show that time required for completion of 99.9% of reaction is 3 times the time required for completion of 90% of the reaction.

or

Show that, $t_{99.9\%} = 3t_{90\%}$ for a first order reaction.

Sol. For a first order reaction, we know that

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

$\therefore \quad t_{99.9\%} = \frac{2.303}{k} \log \frac{a}{a-.999a} = \frac{2.303}{k} \log 10^3 = \frac{3 \times 2.303}{k}$ ... (i)

and $\quad t_{90\%} = \frac{3 \times 2.303}{k} \log \frac{a}{a-0.90a} = \frac{2.303}{k} \log 10 = \frac{2.303}{k}$ ... (ii)

Now divide (i) by (ii)

$$\frac{t_{99.9\%}}{t_{90\%}} = \frac{3 \times 2.303}{k} \times \frac{k}{2.303} = \frac{3}{1}$$

$t_{99.9\%} = 3t_{90\%}$