Chemical Kinetics & Radioactivity

Introduction :

In the thermodynamics, we have studied whether a reaction will take place or not and if it does then upto what extent. In this chapter (chemical kinetics) 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 chemical reaction and Dependence of Rate : Basic

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.**

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

For gaseous reactions, when concentration of gases is expressed in terms of their partial pressure, then units of rate equation will be atms^{-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 $R \longrightarrow P$

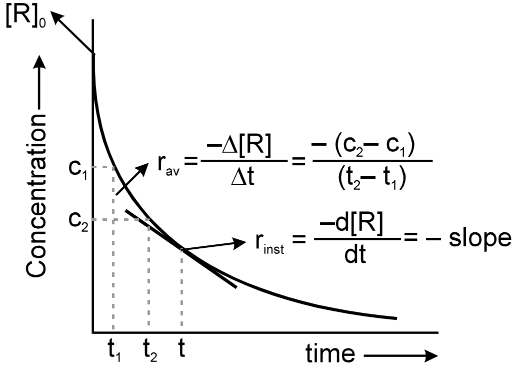
Average rate $= \dfrac{\text{Total change in concentration}}{\text{Total time taken}} = \dfrac{\Delta c}{\Delta t} = -\dfrac{\Delta[R]}{\Delta t} = \dfrac{\Delta[P]}{\Delta t}$

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 $N_2 = -\dfrac{d[N_2]}{dt}$;   Rate of reaction of $H_2 = -\dfrac{d[H_2]}{dt}$

Rate of reaction of $NH_3 = \dfrac{d[NH_3]}{dt}$

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

Rate of reaction $= -\dfrac{d[N_2]}{dt} = -\dfrac{1}{3}\dfrac{d[H_2]}{dt} = \dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

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, calculate the average rate of the reaction: $R \rightarrow P$ during different intervals of time.

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

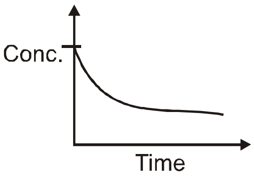
Sol. We can determine the difference in concentration over different intervals of time and thus determine the rate by dividing $\Delta[R]$ by Δt.

$\dfrac{[R]_1 \times 10^3}{\text{mol L}^{-1}}$	$\dfrac{[R]_2 \times 10^3}{\text{mol L}^{-1}}$	$\dfrac{t_2}{s}$	$\dfrac{t_1}{s}$	$\dfrac{r_{av} \times 10^3}{\text{mol L}^{-1}\ s^{-1}} = \dfrac{-[R_2 - R_1] \times 10^3}{[t_2 - t_1]}$
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 and products
4. Catalyst	5. pH of the solution	6. Dielectric constant of the medium.
7. Radiations/light	8. Pressure	9. Electrical and magnetic field.

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



1. **Effect of concentration :** We known from law of mass action that Rate is proportional to concentration of reactants. “So rate of reaction decreases with passage of time, since concentration of reactants decreases.

2. **Effect of temperature :** Most of the chemical reactions are accelerated by increases in T. This will be discussed in detail further.

3. **Effect of nature of reactants and Products :**

(a) Physical state of reactants :

Gaseous state > Liquid state > Solid state

Decreasing order of rate of reaction.

Because collisions in homogeneous system are more effective than heterogenous system.

(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.

4. **Effect of 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.

5. **Effect of pH of solution :** Few reactions take place only in a particular medium.

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

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

6. **Effect of dielectric constant of the medium :** More is the dielectric constant of the medium greater will be the rate of ionic reactions.

7. **Effect of radiations/light :** Radiation are useful for photochemical reaction.

8. **Effect of pressure :** Pressure is important factor for gaseous reaction.

9. **Effect of electrical & Magnetic field :** Electric and magnetic fields are rate determining factors if a reaction involves polar species.

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.)$^{\text{order}}$

Rate = K (conc.)$^{\text{order}}$ ***This is the differential rate equation or rate expression/Rate law.***

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity

unit of K = $(\text{conc})^{1-\text{order}}\ \text{time}^{-1}$

K depend on temperature only and not on concentration.

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 and 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, it can be a fractional number and it can even be negative with respect to a particular reactant. But overall order is not found to be negative for any reaction till observed.

Examples showing different values of order of reactions :

	Reaction	Rate law	Order
(i)	$2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$	$R = K[N_2O_5]^1$	1
(ii)	$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(\ell) + 3H_2O(\ell)$	$R= K[Br^-]\,[BrO_3^-]\,[H^+]^2$	1 + 1 + 2 = 4
(iii)	H_2 (Para) $\longrightarrow H_2$ (ortho)	$R = K[H_{2(Para)}]^{3/2}$	3/2
(iv)	$NO_2\,(g) + CO(g) \longrightarrow NO\,(g) + CO_2\,(g)$	$R = K[NO_2]^2[CO]^0$	2 + 0 = 2
(v)	$2O_3(g) \longrightarrow 3O_2\,(g)$	$R = K[O_3]^2\,[O_2]^{-1}$	2 – 1 = 1
(vi)	$H_2 + Cl_2 \xrightarrow{h\nu} 2\,HCl$	$R = K[H_2]^0[Cl_2]^0$	0 + 0 = 0

The reaction (ii) 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 rate of a certain reaction depends on concentration according to the equation : $\dfrac{-dC}{dt} = \dfrac{K_1C}{1+K_2C}$

What will be the order of reaction, when concentration (C) is : (a) very-very high, (b) very-very low.

Sol. (a) $\dfrac{-dC}{dt} = \dfrac{K_1C}{1+K_2C} = \dfrac{K_1}{\dfrac{1}{C}+K_2}$

if C is very-very high then $\dfrac{1}{C}$ being small may be neglected.

$\therefore\quad \dfrac{-dC}{dt} = \dfrac{K_1}{K_2}$ = constant, i.e., zero order reaction.

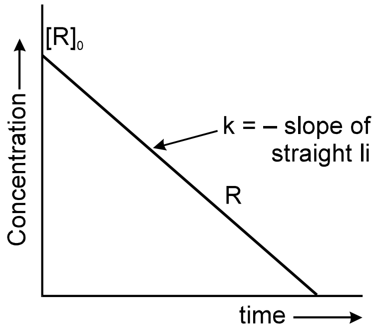
(b) If C is very-very low $1 + K_2C \approx K'$

$\therefore\quad \dfrac{-dC}{dt} = \dfrac{K_1C}{K'} = \left(\dfrac{K_1}{K'}\right) \times$ concentration i.e., I order reaction.

Section (B) : Integrated rate law : Zero and First Order Reaction

(a) Zero order reactions :

For a zero order reaction



General rate law is, Rate = k $[\text{conc.}]^0$ = constant

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

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

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

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

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

$\therefore t_{1/2} \propto C_0$

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 $[PH_3]^o$

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

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

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

(b) First Order Reactions :

(i) Let a 1st order reaction is

A	⟶	Products	
'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 $t = \frac{2.303}{k}\log\frac{a}{a-x}$ or $k = \frac{2.303}{t}\log\frac{C_0}{C_t}$

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

$$\boxed{\begin{array}{c}\text{Wilhemy formula :}\\ C_t = C_0\,e^{-kt}\end{array}}$$

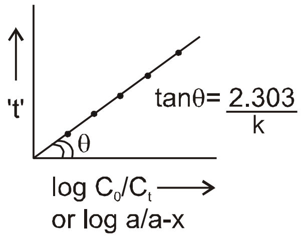
$$\boxed{\begin{array}{c}\text{Interval formula :}\\ k = \dfrac{2.303}{(t_2 - t_1)}\log\dfrac{C_1}{C_2}\end{array}}$$

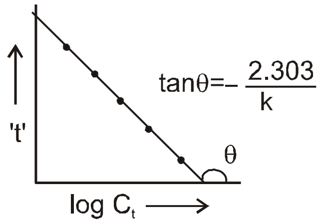
Half life time ($t_{1/2}$) $k = \frac{2.303}{t_{1/2}}\log\frac{2C_0}{C_0}$ $\Rightarrow$ $t_{1/2} = \frac{2.303\log 2}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$

$\therefore$ Half life period for a 1st order reaction is a constant quantity.

Graphical representation :

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





First order growth reaction :

For bacteria multiplication or virus growth use following concept

Consider a growth reaction

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

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

on integration

$\log_e(a+x) = kt + C$ at $t = 0 \,;\, x = 0 \Rightarrow C = \log_e a$

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

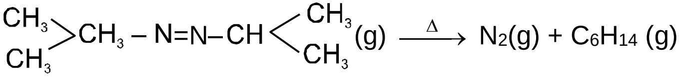
$$\boxed{k = \frac{2.303}{t}\log_{10}\left(\frac{a+x}{a}\right)}$$

Generation time :

At t = generation time, x = a $\therefore$ $t = \frac{0.693}{K}$

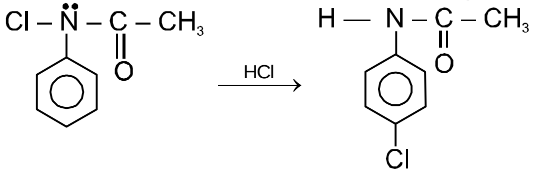
Examples of 1st order reactions :

1. Decomposition of azoisopropane



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

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



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

4. $NH_4NO_2 \longrightarrow 2H_2O + N_2(g)$

5. Radioactive decay

All radioactive decays are always first order kinetics.

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

Solved Examples

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

Sol. $k = \frac{2.303}{t_{3/4}}\log\frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}}\log\frac{C_0}{\frac{C_0}{2}}$ $\Rightarrow$ $\frac{t_{3/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{2\log 2}{\log 2} = 2$

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)

(A) 4 (B) 5 (C) 6 (D) 7

Sol. **(B)** $100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5 \xrightarrow{t_{1/2}} 6.25 \xrightarrow{t_{1/2}} 3.125$

0% 50% 75% 87.5% 93.75% 96.875%

Section (C) : Integrated Rate law : Second Order & Pseudo first order reaction

(a) Second Order reaction :

2^{nd} order Reactions
Two types

$A + A \longrightarrow$ products

a a

(a – x) (a –x)

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

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

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

$\Rightarrow \dfrac{1}{(a-x)} - \dfrac{1}{a} = kt$ or $\dfrac{1}{C_t} - \dfrac{1}{C_0} = kt$

$A + B \longrightarrow$ products.

a b 0

a – x b – x

Rate law

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

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

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

(b) Pseudo 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 pseudo 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.

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

□ 'b' is very large can be taken as constant $\Rightarrow$ $kb = \dfrac{2.303}{t} \log \dfrac{a}{a-x} \quad \Rightarrow \quad k' = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$

- k′ is pseudo first order rate constant
- K' will have units of first order
- K will have units of second order.

- **Examples of Pseudo 1^{st} order reactions :**

(a) Hydrolysis of canesugar :

$C_{12}H_{12}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

sucrose excess glucose fractose

(b) Hydrolysis of esters :

$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$

excess

Solved Examples

Ex-5. Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below :

t/min	0	30	60	90
c/M	0.8500	0.8004	0.7538	0.7096.

Show that it follows a pseudo first order reaction as the concentration of H_2O remains nearly constant (51.2 M) during the course of the reaction. What is the value of k in the equation?

rate = k $[CH_3COOCH_3]\,[H_2O]$

Sol. For pseudo first order reaction, the reaction should be first order with respect to the ester when $[H_2O]$ = constant. From the above data we note

t	c	$k\{H_2O\}$ = min^{-1}
0	0.8500	–
30	0.8004	2.004×10^{-3}
60	0.7538	2.002×10^{-3}

90	0.7096	2.005×10^{-3}

It can be seen that k $[H_2O]$ is constant and equal to 2.004×10^{-3} min^{-1} and hence it is pseudo first order reaction. We can now determine k from

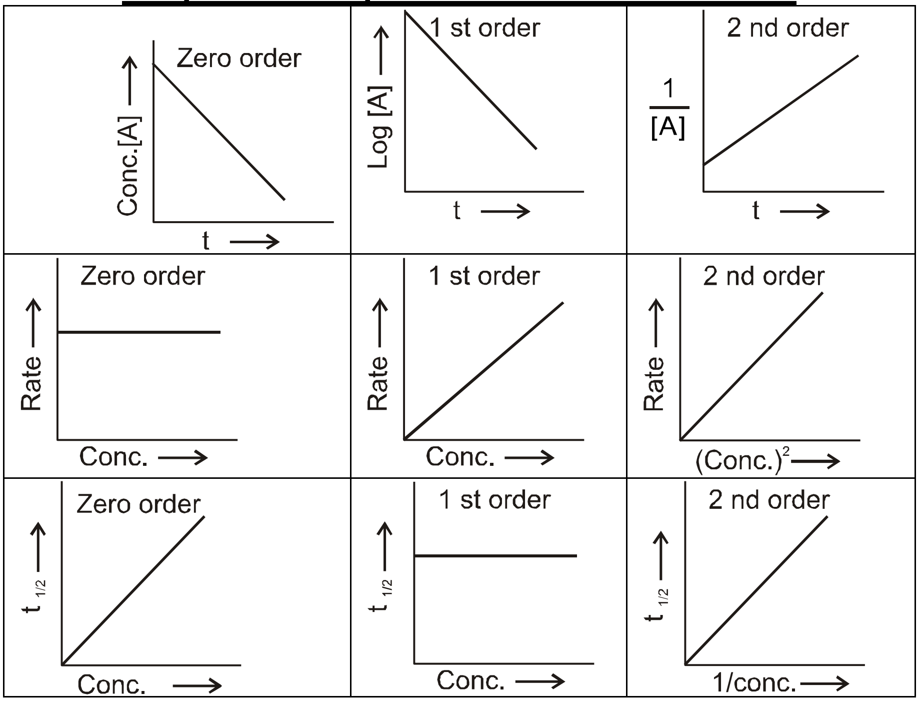
$$k\,[H_2O] = 2.004 \times 10^{-3}\ min^{-1}$$
$$k\,[51.2\ M] = 2.004 \times 10^{-3}\ min^{-1}$$
$$k = 3.914 \times 10^{-5}\ M^{-1}\ min^{-1}$$

It has the units of a second order reaction.

Table : Characteristics of Zero, First, Second and nth Order Reactions of the Type A $\longrightarrow$ Products

	Zero Order	**First-Order**	**Second-Order**	**nth order**
Differential Rate law	$\frac{-d[A]}{dt} = k[A]^0$	$\frac{-d[A]}{dt} = k[A]$	$\frac{-d[A]}{dt} = k[A]^2$	$\frac{-d[A]}{dt} = k[A]^n$
(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	$[A]_t$ v/s t	$\ln [A]$ v/s t	$\frac{1}{[A]}$ v/s 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 $[A]_0$)	$\mathbf{t_{1/2}} \propto \frac{1}{(A_0)^{n-1}}$
Unit	mol L^{-1} s^{-1}	s^{-1}	mol^{-1} Ls^{-1}	$\frac{(conc.)^{1-n}}{t}$

Graphical comparison of different orders



Section (D) : Experimental method to calculate order and rate law of reaction and methods to monitor the progress of reaction

Methods to determine order of a reaction :

(A) Initial rate method :

- By comparison 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

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

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

Or in log form we have $$\boxed{a = \frac{\log\left(r_{0_1}/r_{0_2}\right)}{\log\left([A_0]_1/[A_0]_2\right)}}$$

(B) integrated rate law method :

- It is method of hit and trial. By checking where the kinetic data (experimental 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 these data will not satisfy the integrated rate law of zero order. 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}
342	1.67	6.32×10^{-4}
683	1.35	6.32×10^{-4}
1693	0.57	6.31×10^{-4}

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

$$t_{1/2} = \frac{0.693}{6.31 \times 10^{-4}\ \text{min}^{-1}} = 1.094 \times 10^3\ \text{min}^{-1}$$

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 nth order reaction $t_{1/2} \propto \frac{1}{[C_0]^{n-1}}$ $\Rightarrow$ $\frac{t_{1/2}}{t'_{1/2}} = \frac{(C'_0)^{n-1}}{(C_0)^{n-1}}$

Solved Examples

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 ≠ 1), $t_{1/2} \propto \frac{1}{c_0^{n-1}}$

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

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

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

$$\begin{array}{llll} & A(g) & \longrightarrow & nB(g) & \\ \text{Let initial pressure at time t} & P_0 & & 0 & t = 0 \\ & P_A = (P_0 - x) & & nx & \end{array}$$

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

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

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

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

$\therefore \quad \mathbf{k = \dfrac{2.303}{t} \log \dfrac{P_0(n-1)}{nP_0 - P_t}}$

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.

(B) Volume measurement :

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

Solved Examples

Ex-9. Study of a reaction whose progress is monitored by measuring the volume of a escaping gas.

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

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.

$a \propto V_\infty$ and $x \propto V_t$

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

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

Section (E) : Method to monitor the progress of Reactions (Titration Method and Optical Activity Method)

(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 milliequivalent or millimoles are calculated using valence factors.

Solved Examples

Ex-10. From the following data show that the decomposition of hydrogen peroxide in aqueous solution is a first-order reaction. What is the value of the rate constant?

Time in minutes	0	10	20	30	40
Volume V in ml	25.0	20.0	15.7	12.5	9.6

where V is the number of ml of potassium permagnate required to react with a definite volume of hydrogen peroxide solution.

Sol. The equation for a first order reaction is $2H_2O_2 \xrightarrow{\Delta} 2H_2O\ (□) + O_2\ (g)$

the volume of $KMnO_4$ used, evidently corresponds to the undecomposed hydrogen peroxide.

Hence the volume of $KMnO_4$ used, at zero time corresponds to the initial concentration a and the volume used after time t, corresponds to (a – x) at that time. Inserting these values in the above equation, we get

When $t = 10$ min. $k_1 = \frac{2.303}{10} \log \frac{25}{20.0} = 0.022318\ \text{min}^{-1} = 0.000372\ \text{s}^{-1}$

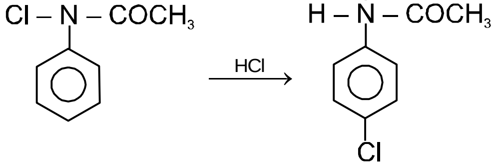
when $t = 20$ min. $k_1 = \frac{2.303}{20} \log \frac{25}{15.7} = 0.023265\ \text{min}^{-1} = 0.000387\ \text{s}^{-1}$

when $t = 30$ min. $k_1 = \frac{2.303}{30} \log \frac{25}{12.5} = 0.02311\ \text{min}^{-1} = 0.000385\ \text{s}^{-1}$

when $t = 40$ min. $k_1 = \frac{2.303}{40} \log \frac{25}{9.6} = 0.023932\ \text{min}^{-1} = 0.0003983\ \text{s}^{-1}$

The constancy of k, shows that the decomposition of H_2O_2 in aqueous solution is a **first order** reaction. The average value of the rate constant is $0.0003879\ \text{s}^{-1}$.

Ex-11. Conversion of N-chloro acetanilide into p-chloroacetanilide



The above reaction is first order reaction and its progress is monitored by iodometric titration in which liberated iodine is titrated against a standard solution of Hypo using starch as indicator. Given that in this reaction KI does not react with the product (p–chloro acetanilide). Calculate the rate constant of the reaction. Given that volume of hypo consumed at t = 0 is V_0 and at time 't', V_t

Sol. Let, V_0 = volume of hypo consumed at t = 0

Similarly V_t = volume of hypo consumed at t = 't'

$\therefore\ a \propto V_0$ {□ KI reacts with the reactant only}

$a - x \propto V_t$

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

Ex-12. Study of acid hydrolysis of an ester.

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

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

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

V_t = vol. of NaOH used at 't'

V_∞ = vol. of NaOH used at $t = \infty$

$a \propto V_\infty - V_0$

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

$x \propto V_t - V_0$

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

(C) Optical rotation measurement :

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

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

It is found that $(r_\infty - r_0) \propto a$ (a = initial concentration, x = amount consumed)

$(r_\infty - r_t) \propto (a - x)$

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

Solved Examples

Ex-13. 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 laevorotatory. That's why this reaction is also known as inversion of cane sugar.

$$\underset{}{C_{12}H_{22}O_{11}} + \underset{\text{excess}}{H_2O} \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Sp. rotation $+66.5^o$ $+52.7^o$ -92.4^o

Let the readings in the polarimeter are

$t = 0,\ \theta_0$; $t = $ 't', θ_t and at $t = \infty$, θ_∞

Then calculate rate constant 'k' in terms of these readings.

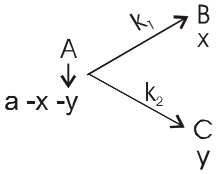
Sol. The principle of the experiment is that change in the rotation is directly proportional to the amount of sugar hydrolysed.

$\therefore \quad a \propto \theta_0 - \theta_\infty \quad ; \quad a - x \propto \theta_t - \theta_\infty$

$$k = \frac{2.303}{t}\log\left(\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}\right)$$

Section (F) : Complication in 1st Order Reaction

PARALLEL 1st ORDER REACTION OR COMPETING FIRST-ORDER REACTIONS



At $t = 0$ $[A] = a$ $[B] = [C] = 0$

Calculate effective $t_{1/2}$ for [A], [B], [C] & [B] / [C]

$$\frac{d[B]}{dt} = k_1[A] \quad ; \quad \frac{d[C]}{dt} = k_2[A]$$

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

$$\frac{-d[A]}{dt} = (k_1 + k_2)[A] = k_{eff}[A]$$

$k_{eff} = k_1 + k_2$

$$\frac{\ell n2}{T_{eff}} = \frac{\ell n2}{T_1} + \frac{\ell n2}{T_2} \quad \text{(where T represent half life)}$$

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

Now, $[A]_t = ae^{-k_{eff}t} = ae^{-(k_1+k_2)t}$

$$\frac{d[B]}{dt} = k_1[A]$$

$$\frac{d[B]}{dt} = k_1 ae^{-(k_1+k_2)t}$$

$$[B] = \left(\frac{k_1 a}{k_1+k_2}\right)(1 - e^{-(k_1+k_2)t})$$

similarly $[C] = \dfrac{k_2 a}{k_1+k_2}(1 - e^{-(k_1+k_2)t})$

$$\boxed{\frac{[B]}{[C]} = \frac{k_1}{k_2}} \quad \text{(remember)}$$

$k_{eff} = k_1 + k_2$

$A_{eff} .e^{-Ea/RT} = A_1\, e^{-Ea1/RT} + A_2 e^{-Ea2/RT}$

on differentiating

$$-\frac{E_a}{R}\left(\frac{-1}{T^2}\right) A_{eff}.e^{-Ea/RT} = -\frac{E_{a_1}}{R}\left(\frac{-1}{T^2}\right) A_1\, e^{-Ea1/RT} - \frac{E_{a_2}}{R}\left(\frac{-1}{T^2}\right) A_2 e^{-Ea2/RT}$$

$$\frac{Ea}{RT^2} \times \frac{Ea_1}{RT^2} k_{eff} = k_1 + \frac{Ea_2}{RT^2} k_2$$

$$E_a \times k_{eff} = E_{a1} k_1 + E_{a2} k_2$$

$$\boxed{E_a = \frac{E_{a_1}k_1 + E_{a_2}k_2}{k_1 + k_2}}$$

Section (G) : Temperature dependence of rate

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 10ºC (usually these temperatures were taken as 25ºC and 35ºC)

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

Solved Examples

Ex-14. For a reaction T.C. = 2, Calculate $\frac{k_{40^\circ C}}{k_{25^\circ C}}$ for this reaction.

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

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

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Arrhenius theory of reaction rate :

It was developed by Max Trautz and William lewis.

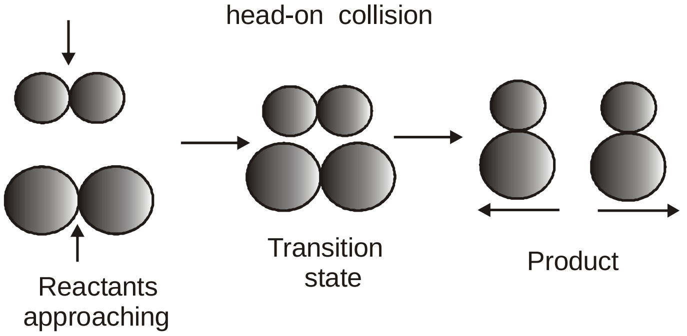
It gives insight in to the energetics and mechanistic aspects of reactions.

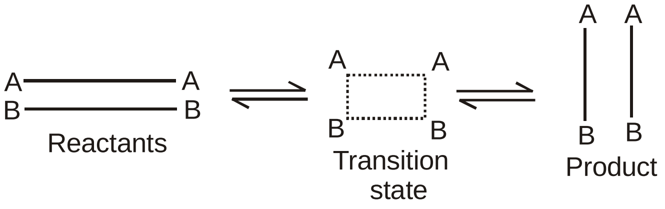
It is based upon kinetic theory of gases.

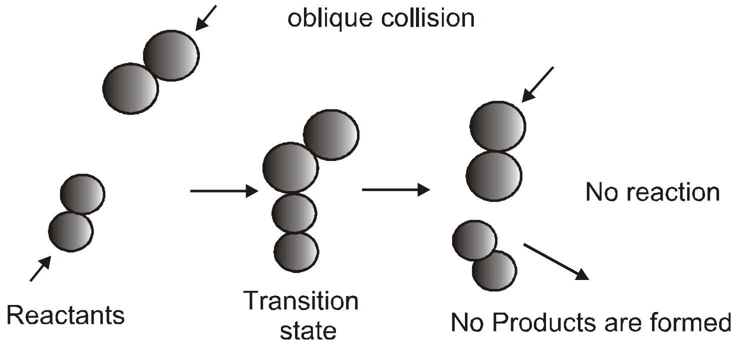
Arrhenius proposed a theory of reaction rate which states as follows :

- 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 cleared.

- **Energy barrier :** The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur is known as threshold energy.
  "The minimum amount of energy required by reactant molecules to participate 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.







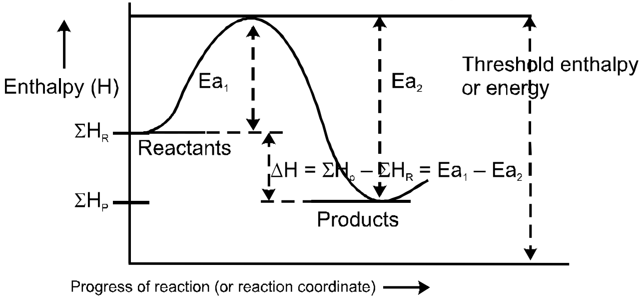
- Collision to be effective the colliding molecules must possess some certain minimum energy called threshold energy of the reaction.
- Reactant molecules having energy equal or greater than the threshold are called active molecules and those having energy less than the threshold are called passive molecules.
- 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,

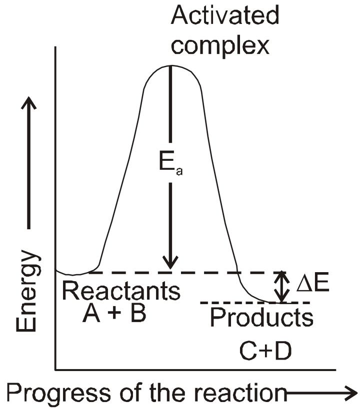
  E_a = Threshold energy – Actual average energy

  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.

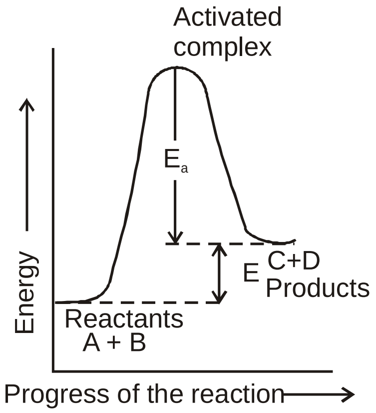


ΣH_R = Summation of enthalpies of reactants
ΣH_P = Summation of enthalpies of products
ΔH = Enthalpy change during the reaction
Ea_1 = Energy of activation of the forward reaction
Ea_2 = Energy of activation of the backward reaction

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.



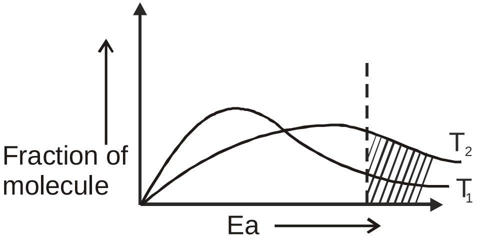
(Exothermic)



(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.
From maxwellian distribution it is found that fraction of molecules having excess energy greater than threshold energy lead to the formation of product.



$T_2 > T_1$

$e^{-E_a/RT}$ → represents fraction of molecules having energy greater E_a

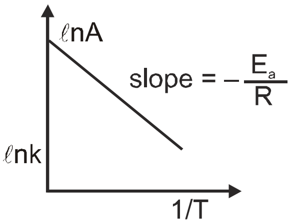
rate $\propto e^{-E_a/RT}$

dependence of rate on temperature is due to dependence of k on temperature.

$k \propto e^{-E_a/RT}$
$k = Ae^{-E_a/RT}$ **[Arrhenius equation]**

A is pre exponential factor / frequency factor representing collisions taking place with proper orientation.
A and E_a are independent of temperature generally.
E_a = min K. E. that colliding molecules must have to reach transition state.

$\ell n k = \ell n A - \frac{E_a}{RT}$



$E_a \geq 0$

❖ As T → ∞, K → A

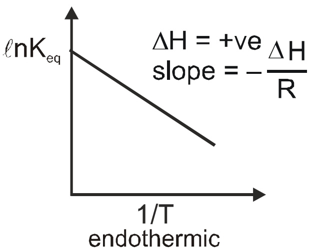
REVERSIBLE REACTIONS

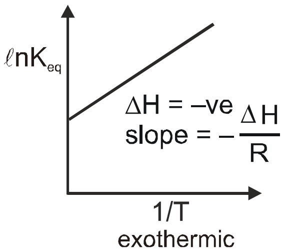
$k_f = A_f e^{-E_{af}/RT}$

$k_b = A_b e^{-E_{ab}/RT}$

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f e^{-E_{af}/RT}}{A_b e^{-E_{ab}/RT}} = \left(\frac{A_f}{A_b}\right) e^{-(E_{af}-E_{ab})/RT}$$

$$\ell n\, K_{eq} = -\frac{\Delta H}{RT} + \ell n\left(\frac{A_f}{A_b}\right)$$





At temperature T_1, rate constant = k_1
At temperature T_2, rate constant = k_2

$$\ell n k_1 = \ell n A - \frac{E_a}{RT_1} \Rightarrow \ell n k_2 = \ell n A - \frac{E_a}{RT_2} \Rightarrow \ell n \frac{k_2}{k_1} = \frac{E_a}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\} \text{ (remember)}$$

Solved Examples

Ex-15. Two Ist order reactions are initially having equal rate at a particular temprature. Temprature of both the reaction is increased by same amount. Calculate rate of which reaction will increase by greater amount (reaction with low E_a or high E_a)

Sol.
$$\ell n\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\} \qquad .....(i)$$

$$\ell n\left(\frac{k_2'}{k_1}\right) = \frac{E_a'}{R}\left[\frac{1}{T_1} - \frac{1}{T_2'}\right] \qquad .....(ii)$$

Equation (i) – (ii).

$$\ell n\left(\frac{k_2}{k_2'}\right) = \frac{\Delta T}{R}(E_a - E_a,) \qquad \text{if } E_a > E_a, \qquad k_2 > k_2'$$

or $\quad k = A e^{-E_a/RT} \quad$ or $\quad \frac{dk}{dT} = \frac{-Ea}{R}\left(\frac{-1}{T^2}\right) A e^{-E_a/RT}$

temprature coeff. of rate constant $\frac{1}{K}\frac{dk}{dT} = \frac{E_a}{RT^2}$ or $\frac{\Delta k}{k.\Delta T}$ = fractional change / unit temp. rise

Ex-16. Explain on the basis of temprature coeff. of rate const. that equilibrium of endothermic reaction shifts in forward direction on increasing temprature while equilibriums of exothermic shift back.

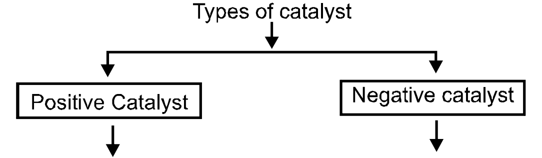
$$\ell n\left(\frac{K_{eq_1}}{K_{eq_2}}\right) = \frac{\Delta H}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}$$

Sol. $\Delta H = E_{af} - E_{ab} > 0$ (for endothermic)
$E_{af} > E_{ab}$
on increasing temp. $k_f\uparrow$ more than k_b
equilibrium will shift in forward direction.

Section (H) : Catalyst dependence of rate and type of Reaction and Determination of rate law and order with the help of given mechanism

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 acts as a catalysts.

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

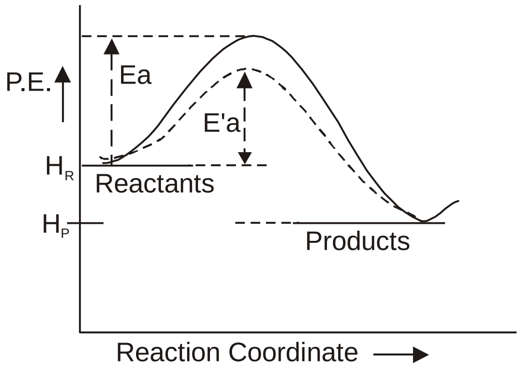
- MnO_2 can be received in the same composition and mass at the end of the reaction.

(b) In the permanganate titration of oxalic acid initially 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.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 8H_2O + 10CO_2 + 2MnSO_4$$

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 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.

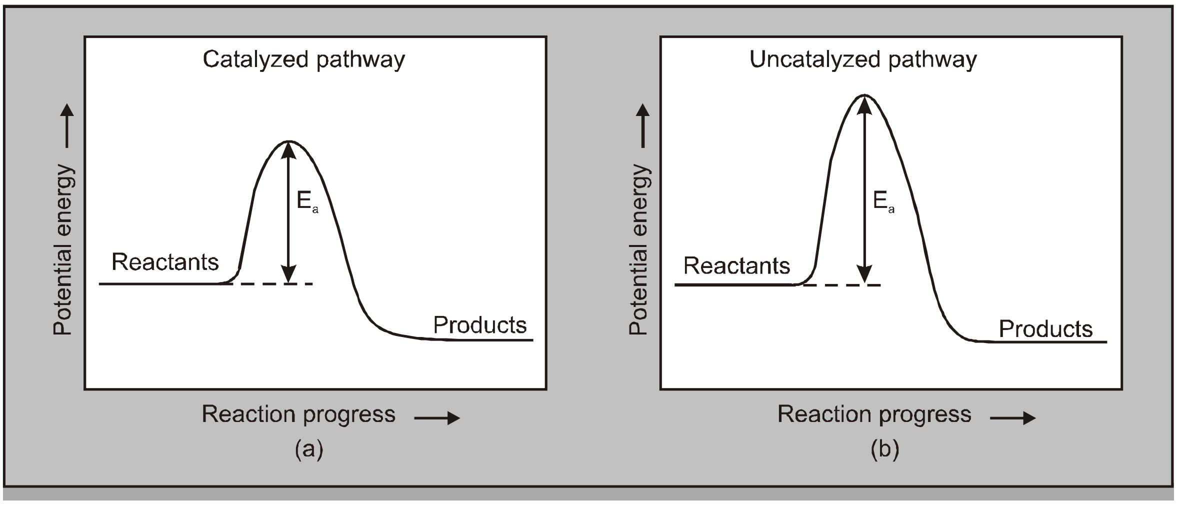
Comparison of rates of reaction in presence and absence of catalyst :

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

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

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 reaction 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, $e^{-E'_a/RT_1} = e^{-E_a/RT_2}$ or $\frac{E'_a}{T_1} = \frac{E_a}{T_2}$



(a) (b)

Solved Examples

Ex-17. 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}, calculate the rate constant of the reaction at 150°C.

Sol. $\log\frac{k_2}{k_1} = \frac{E}{2.303R}\left[\frac{T_2 - T_1}{T_1\ T_2}\right]$

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

$E = \frac{3.1761 \times 2.303 \times 2 \times 523 \times 423}{100} = 32.36$ 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-18. The pyrolysis of an organic ester follows a first order process and its rate constant 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 ; $k = \frac{2.303}{t_{1/4}} \log\frac{a}{0.75a}$

$t_{1/4} = \frac{2.303}{2.344 \times 10^{-3}} \log 1.333 = 123.06$ min

Ex-19. 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 = $\frac{-E}{2.303R} = -5.4 \times 10^3$

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

(b) $K = Ae^{-E/RT}$; $\log 1.155 \times 10^{-2} = \log A - \frac{24.624}{2.303 \times 1.987 \times 373}$ or $A = 1.764 \times 10^3$ sec^{-1}

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 (RDS) 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.

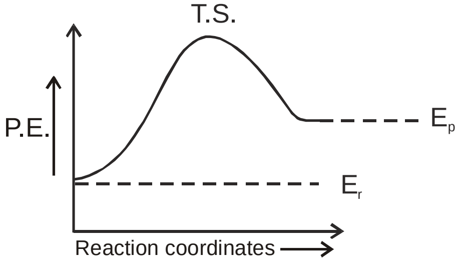
4	It is theoretical value.	It is experimental value.
5	Reactions with molecularity > 4 are rare.	Reactions with order of reaction > 4 are also rare.
6	Molecularity is in independent of Pressure and temperature.	Order of reaction depends upon pressure and temperature.

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 number.
    1 = unimolecular one molecule gets excited (like radioactivity)
    2 = bimolecular
    3 = trimolecular
  - Molecularly ≤ 3 because the probability of simultaneous 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

$H_2 + I_2 \rightleftharpoons 2HI$ (Simple reaction)

rate = k $[H_2]$ $[I_2]$

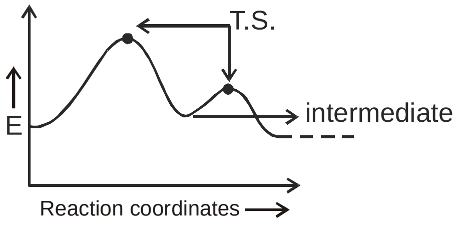
$2H_2 + 2I_2 \rightleftharpoons 4HI$ (not elementary)

reaction obtained by multiplying an elementary reaction with some number 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 intermediates.

The mechanism of any complex reaction 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.

CALCULATION OF RATE LAW/ ORDER

(A) MECHANISM IN WHICH R.D.S. GIVEN

(i) If R.D.S. involves only reactant, product or catalyst on reactant side
rate law of R.D.S. = rate law of reaction

Solved Examples

Ex-20. Calculate order and rate law of reaction

$2NO_2 + F_2 \longrightarrow 2NO_2F$ with help of mechanism

I	$NO_2 + F_2 \xrightarrow{K_1} NO_2F + F$	(slow)	molecularity = 2 for both
II	$NO_2 + F \xrightarrow{K_2} NO_2F$	(fast)	

According to RDS

Rate = $k_1\,[NO_2]\,[F_2]$

Ex-21. Calculate rate law

$3ClO^- \longrightarrow ClO_3^- + 2Cl^-$

$2ClO^- \xrightarrow{K_1} ClO_2^- + Cl^-$ (slow)

$ClO_2^- + ClO^- \xrightarrow{K_2} ClO_3^- + Cl^-$ (fast)

Rate = $k_1[ClO^-]^2$

(ii) RDS is having intermediate on reactant side

To calculate order, we have to specify [intermediate] in expression of rate law in terms of conc. of [R], [P] or catalyst with the help of some equilibrium step given in mechanism.

Solved Examples

Ex-22. $2O_3 \longrightarrow 3O_2$

$O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ (fast eq. step)

(intermediate)

$O + O_3 \xrightarrow{k_3} 2O_2$ (slow)

From R.D.S., rate = $k_3\,[O_3]\,[O]$

According to equilibrium step.

$$K_{eq.} = \frac{k_1}{k_2} = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \left[\frac{k_1[O_3]}{k_2[O_2]}\right]$$

$$\text{Rate} = k_3[O_3]\,[O] = k_3[O_3]\left[\frac{k_1[O_3]}{k_2[O_2]}\right].$$

$$\text{Rate} = \frac{k_1k_3}{k_2}\,\frac{[O_3]^2}{[O_2]}$$

Ex-23 $H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br^-} C_6H_5N_2^+ + 2H_2O$

intermediate

$H^+ + HNO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2NO_2^+$ (fast) equilibrium step

intermediate

$H_2NO_2^+ + Br^- \xrightarrow{k_3} NOBr + H_2O$ (slow)

$NOBr + C_6H_5NH_2 \xrightarrow{k_4} C_6H_5N_2^+ + Br^- + H_2O$ (fast)

Sol. $r = k_3[Br^-]\,[H_2NO_2^+]$

$$K_{eq} = \frac{k_1}{k_2} = \frac{[H_2NO_2^+]}{[H^+][HNO_2]}$$

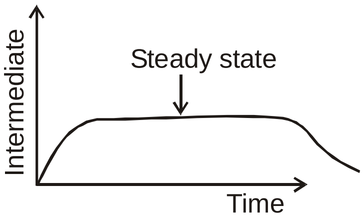
$$[H_2NO_2^+] = \left[\frac{k_1}{k_2}\right][H^+]\,[HNO_2]$$

$$r = \frac{k_1k_3}{k_2}\,[H^+]\,[HNO_2]\,[Br^-].$$

(B) **MECHANISMS IN WHICH RDS NOT SPECIFIED**

STEADY STATE APPROXIMATION

Initially, for most of the cases only reactants are taken and hence the rate of production of intermediate is large in comparison to its rate of consumption but after some time rate of consumption of intermediate will become equal to its rate of production. This is known as steady state of reaction. Finally when reaction is going to get completed, rate of consumption will become more then rate of production. But for most of the times reaction remains at steady state. So rate law of reaction during steady state can be taken to be final or net rate law of reaction.



At steady state $\frac{d\,[\text{intermediate}]}{dt} = 0$

Solved Examples

Ex-24 $2O_3 \longrightarrow 3O_2$

$O_3 \xrightarrow{k_1} O_2 + O$

$O_2 + O \xrightarrow{k_2} O_3$

$O_3 + O \xrightarrow{k_3} 2O_2$

Sol. Rate = $\frac{-1}{2}\frac{d[O_3]}{dt} = \frac{1}{3}\frac{d[O_2]}{dt}$

$$\frac{d[O_3]}{dt} = -\,k_1\,[O_3] + k_2\,[O_2][O] - k_3\,[O_3]\,[O]$$

$$\frac{d[O_2]}{dt} = k_1\,[O_3] - k_2\,[O_2]\,[O] + k_3\,[O_3]\,[O]$$

At steady state $\frac{d[O]}{dt} = 0$

$$\frac{d[O]}{dt} = k_1\,[O_3] - k_2\,[O_2]\,[O] - k_3[O_3]\,[O] = 0$$

$$[O] = \frac{k_1[O_3]}{k_2[O_2]+k_3[O_3]}$$

$$\frac{d[O_3]}{dt} = -\,k_1\,[O_3] + \frac{\{k_2[O_2]\ \ k_1[O_3]\}}{k_2[O_2]+k_3[O_3]} - \frac{k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$$

$$= -\,k_1\,[O_3] + \frac{k_1k_2[O_2]\ \ [O_3]-k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$$

$$= \frac{-k_1k_2[O_2][O_3]-k_1k_3[O_3]^2+k_1k_2[O_2][O_3]-k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]} = \frac{-2k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$$

$$\left[\frac{-1}{2}\frac{d}{dt}[O_3]\right] = \frac{k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$$

$$\text{Rate} = -\frac{1}{2}\frac{d}{dt}[O_3]$$

So, Rate (r) = $\frac{k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$

if 3rd step is RDS then $k_1 >> k_3$

$k_2 >> k_3$

$$r = \frac{k_1 k_3 [O_3]^2}{k_2 [O_2]}$$

Ex-25 $H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br} C_6H_5N_2^+ + 2H_2O$

$H^+ + HNO_2 \xrightarrow{k_1} H_2NO_2^+$

$H_2NO_2^+ \xrightarrow{k_2} H^+ + HNO_2$

$H_2NO_2^+ + Br^- \xrightarrow{k_3} NOBr + H_2O.$

$NOBr + C_6H_5NH_2 \xrightarrow{k_4} C_6H_5N_2^+ + H_2O + Br^-$

Sol. $\frac{d[H_2NO_2^+]}{dt} = k_1 [H^+][HNO_2] - k_2 [H_2NO_2^+] - k_3 [H_2NO_2^+][Br^-] = 0$

$$[H_2NO_2^+] = k_1 \frac{[H^+][HNO_2]}{k_2 + k_3[Br^-]}$$

$$\text{rate} = \frac{d}{dt}[C_6H_5NH_2] = \frac{d}{dt}[HNO_2]$$

$$\frac{d}{dt}[C_6H_5NH_2] = k_4 [NOBr][C_6H_5NH_2]$$

$$\frac{d}{dt}[NOBr] = -k_4 [C_6H_5NH_2][NOBr] + k_3 [Br^-][H_2NO_2^+] = 0$$

$$[NOBr] = \frac{k_3[Br^-][H_2NO_2^+]}{k_4[C_6H_5NH_2]}$$

$$r = \frac{k_4 k_3 [Br^-][H_2NO_2^+]}{k_4[C_6H_5NH_2]}[C_6H_5NH_2]$$

$$r = \frac{k_1 k_3 [Br^-][H^+][HNO_2]}{k_2 + k_3[Br^-]}$$

Section (I) : Radio Activity

* All radioactive disintegration follow Ist order kinetics.

$$A \longrightarrow B + C$$

Int. nuclie N_0

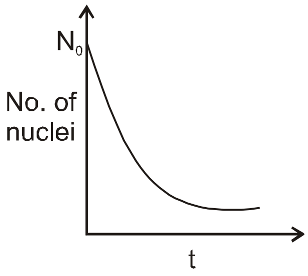
At time t. N

decay constant

$$\boxed{\frac{-dN}{dt} = \lambda N}$$

No. of nuclei of A at time t

rate decay(A)



* λ = Not dependent on temperature.

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

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

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

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 :

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

$T_{avg.} = \frac{\int_0^\infty dN.t}{N_0} = \frac{1}{\lambda}$ (□ $\frac{-dN}{dt} = \lambda N$ and $N = N_0 e^{-\lambda t}$, $\therefore$ $dN = -\lambda N_0 e^{-\lambda t}\,dt$)

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 :

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

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

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

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

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

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

On solving (1) and (2),

$x = 8$; $y = 6$

$$_{92}U^{238} \longrightarrow {}_{82}Pb^{206} + 8({}_{2}He^{4}) + 6({}_{-1}e^{0})$$

At time t w g y g

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

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

$w = w_0 - x$

$\therefore$ $w_0 = w + x$

1 mole or 238 g U provide 206 g of Pb

$\therefore$ $\frac{238}{206}$ g U provide 1 g Pb

$\therefore$ $\frac{238}{206} \times y$ g U provide y g Pb

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

$$_{92}U^{238} \longrightarrow {}_{82}Pb^{206} + 8{}_{2}He^{4} + 6{}_{-1}e^{-}$$

V(in mL) collected

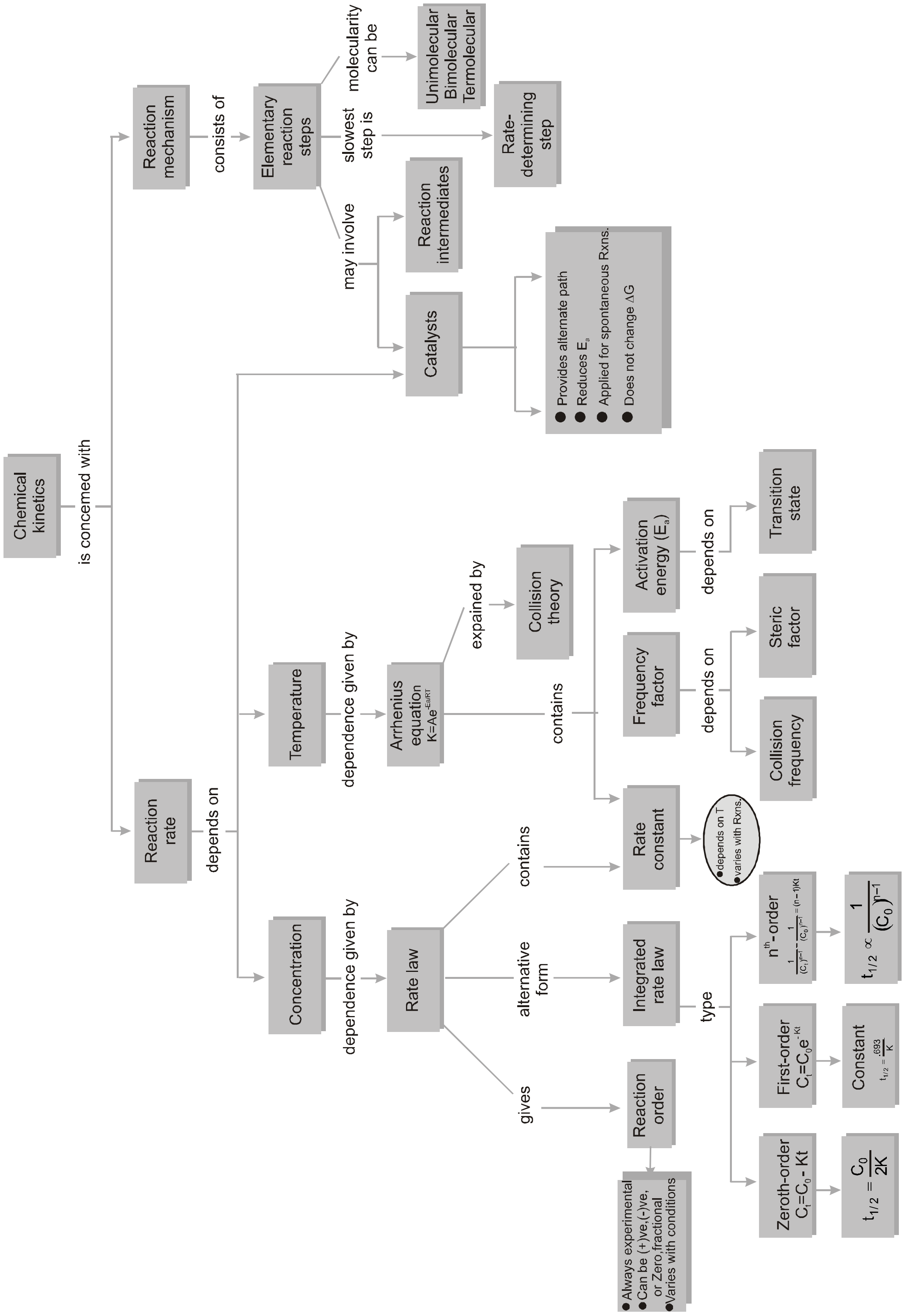
$n_{He} = \frac{PV}{RT}$ .... (1)

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

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

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

Summary



MISCELLANEOUS SOLVED PROBLEMS (MSPS)

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

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

Ex-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}.

Ex-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

Ex-4. The reaction $CO(g) + NO_2(g) \rightarrow CO_2 + NO$ 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

Ex-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 :

(A) $k[A]^2[B]$ (B) $k[A]^2[3B]$ (C) $3k[A^2][B]$ (D) $(1/3)k[A^2][B]$

Sol. **(C)** For the given reaction

$$\frac{-d[A]}{dt} = \frac{1}{3}\frac{-d[B]}{dt} = K[A]^2[B]$$

then $\frac{-d[B]}{dt} = 3K[A]^2[B]$

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

Sol. For the First order Rxn

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

$t = 1.54 \times 10^{+3}$ Second. $= 25.80$ Minute

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

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

Ex-8. For the reaction A + B $\longrightarrow$ 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. $0.030 = K\,[0.10]^x\,[0.20]^y$ (1)

From data II. $0.059 = K\,[0.20]^x\,[0.20]^y$ (2)

From III. $0.060 = K\,[0.20]^x\,[0.30]^y$ (3)

divide 1 equation by (2)

$$\frac{0.030}{0.059} = \frac{K[0.10]^x[0.20]^y}{K[0.20]^x[0.20]^y} \quad \Rightarrow \quad x = 1$$

Then divide (2) equation by (3)

$$\frac{0.059}{0.060} = \frac{K[0.20]^x[0.20]^y}{K[0.20]^x[0.30]^y} \quad \Rightarrow \quad y = 0$$

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

$0.030 = K[0.10]^1\,[0.20]^0$

$$K = \frac{0.030}{0.10} = 0.3\ \text{sec}^{-1}$$

Ex-9. The following data is for the decomposition of ammonium nitrite in aqueous solution.

Volume of N_2 in cc.	Time (minutes)
6.25	10
9.00	15
11.40	20
13.65	25
35.05	infinity

The order of the reaction is

Sol. $NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(l)$

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

$a \alpha V_\infty$

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

Then from the given data we assume the Rxn is first order Then

$$K = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

From Ist data $K = \frac{2.303}{10}\log\frac{35.05}{(35.05-6.25)} = 1.96 \times 10^{-2}\ \text{sec}^{-1}$

IInd data $K = \frac{2.303}{15}\log\frac{35.05}{(35.05-9)} = 1.96 \times 10^{-2}\ \text{sec}^{-1}$

IIIrd data $K = \frac{2.303}{20}\log\frac{35.05}{(35.05-11.40)} = 1.96 \times 10^{-2}\ \text{sec}^{-1}$

From these relation the value of K are same the reaction will be First order

Ex-10. 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 decomposition 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 $a \alpha\ V_o$ and $(a - x) \alpha\ V_t$

Then $K = \frac{2.303}{t} \log \left(\frac{V_0}{V_t}\right)$

Ex-11. $A \xrightarrow{D} B + C$

Time	0	t	∞
Volume of reagent	V_1	V_2	V_3

The reagent reacts with only B, C and D. Find k.

Sol.

	$A \xrightarrow{\quad D \quad}$	B	+ C
at t = 0	a	0	0
t = t	(a – x)	x	x
t = ∞	o	a	a

at t = 0 only D. React

after t = 0 reagent react with B.C.D.

$2a\ \alpha\ (V_3 - V_1)$

$A\ \alpha\ \frac{(V_3 - V_1)}{2}$

$2x\ \alpha\ (V_2 - V_1)$

$2(a - x)\ \alpha\ (V_3 - V_1 - V_2 + V_1)$

$(a - x)\ \alpha\ \frac{(V_3 - V_2)}{2}$

Then, $K = \frac{1}{t} \ln \frac{(V_3 - V_1)}{(V_3 - V_2)}$

Ex-12. $A \rightarrow B + C$

Time	0	t
Volume of reagent	V_1	V_2

The reagent reacts with A, B and C. Find k.

Sol.

	A →	B +	C
t = 0	a	0	0
t = t	(a – x)	x	x

$a \alpha\ V_1$

$(a - x) + x + x\ \alpha\ V_2$

$(a + x)\ \alpha\ V_2$

$(a - x)\ \alpha\ (2V_1 - V_2)$; $K = \frac{1}{t} \ln \frac{[A]_o}{[A]_t} = \frac{1}{t} \ln \frac{V_1}{(2V_1 - V_2)}$

Ex-13. $A \rightarrow B + C$

Time	T	∞
Volume of reagent	V_2	V_3

Reagent reacts with all A, B and C and have 'n' factors in the ratio of 1 : 2 : 3 with the reagent. Find k.

Sol.

	A →	B + C	
t = 0	a	0	0
t = t	(a– x)	x	x

$t = \infty$ 0 a a

Reagent React with all A, B, C. and have ‘n’ factor in the Ratio 1 **:** 2 **:** 3

$$(2a + 3a)\ \alpha\ V_3$$

$$a\ \alpha\ \frac{V_3}{5}$$

$$(a - x) \times 1 + 2x + 3x\ \alpha\ V_2$$

$$(a + 4x)\ \alpha\ V_2$$

$$\frac{V_3}{5} + 4x\ \alpha\ V_2$$

$$x\ \alpha\ \frac{1}{4}\left(V_2 - \frac{V_3}{5}\right) \quad \Rightarrow \quad (a - x)\ \alpha\ \frac{V_3}{5} - \frac{1}{4}\left(V_2 - \frac{V_3}{5}\right)$$

$$(a\text{-}x)\ \alpha\ \frac{5(v_3 - v_2)}{20} \quad \Rightarrow \quad K = \frac{1}{t}\ \ln \frac{4V_3}{5(v_3 - v_2)}$$

Ex-14. 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.

$$A(\text{soln.}) \longrightarrow B(\text{soln.}) + C(\text{soln.})$$

Time	0	t	∞
Total rotation in degrees	R_0	r_t	r_∞

Calculate the expression of rate constant.

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

$$a\ \alpha\ (r_0 - r_\infty)$$

$$(a - x)\ \alpha\ (r_t - r_\infty)$$

Then Expression For rate constant

$$K = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

Ex-15. The hydrolysis of cane sugar was studied using an optical polarimeter and the following readings were taken.

time (min.) :	0	84 min	∞
observed rotation (degrees) :	50	20	–10

When will the mixture optically inactive? (log 2 = 0.3, log 3 = 0.48)

Sol. From the hydrolysis

$$K = \frac{2.303}{t} \log \frac{(r_0 - r_\infty)}{r_t - r_\infty} = \frac{2.303}{84} \log \frac{50 + 10}{20 + 10}$$

$$K = \frac{2.303}{84} \times 0.3010 = 8.252 \times 10^{-3}$$

The time taken when sample are optically Inactive is t

$$K = \frac{2.303 \times 0.3010}{84} = \frac{2.303}{t} \log \frac{50 + 10}{+10}$$

$$t = 217.14 \text{ minute}$$

Ex-16. The optical rotation of sucrose in 0.5 M HCl at 35^{0}C at various time intervals are given below. Show that the reaction is first order.

Time (minutes)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	–11.1

Sol. If reaction first order the value of K same in First-Order Expression

$$K = \frac{2.303}{t} \log \frac{(r_0 - r_\infty)}{r_t - r_\infty}$$

$$K = \frac{2.303}{10} \log \frac{32.4 + 11.1}{28.8 + 11.1} = \frac{0.03751 \times 2.303}{10} = 8.63 \times 10^{-3}$$

$$K = \frac{2.303}{20} \log \frac{32.4 + 11.1}{25.5 + 11.1} = 8.63 \times 10^{-3}$$

$$K = \frac{2.303}{30} \log \frac{32.4 + 11.1}{22.4 + 11.1} = 8.63 \times 10^{-3}$$

$$K = \frac{2.303}{40} \log \frac{32.4 + 11.1}{19.6 + 11.1} = 8.63 \times 10^{-3}$$

The reaction show 1st order kinetics

Ex-17. 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 :
(A) 3 (B) 9 (C) 27 (D) 81

Sol. **(C)** For same concentration $\frac{R_2}{R_1} = \frac{K_2}{K_1} = 3^{\frac{30}{10}} = 27.$

Ex-18. The reaction A + B ⟶ products is first order with respect to both A and B has a rate constant of 6.0 L 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 0.01 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 ⟶ Product

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

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

$$\log\left(\frac{K_2}{6}\right) = \frac{42\times10^3[320-300]}{2.303\times8.3\times300\times320} = \frac{840}{1835.03}$$

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

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

$K_2 = 2.863 \times 6 = 17.178$

Rate at 47°C will be

The $Rate_2 = 17.178 \times [0.01] \times [0.01]$

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

Ex-19. An exothermic reaction A → 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 → A is :
(A) 75 KJ per mole (B) 67 KJ per mole (C) 57 KJ per mole (D) 17 KJ per mole

Sol. **(C)** $\Delta H = E_A - E_B$

$-40 = 17 - E_B$

$E_B = 57$

Ex-20. The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in sec^{-1}) K_1 and K_2 respectively. The energy of activations for the two reactions are 152.30 kJ mol^{-1} and 157.7 kJ mol^{-1} as well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions.

Sol. Rate constant will be same.

$K_1 = K_2$

$$A_1 e^{\frac{-Ea_1}{RT}} = A_2 e^{\frac{-Ea_2}{RT}}$$

$$T = \frac{Ea_2 - Ea_1}{2.303\log\left(\frac{A_2}{A_1}\right)\times R} \Rightarrow T = \frac{157.7 - 152.3}{2.303\times8\times\log\left(\frac{10^4}{10^3}\right)} \Rightarrow T = 282K$$

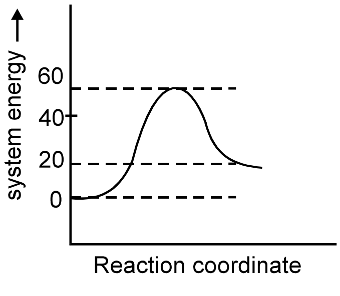
Ex-21. Use the diagram below to answer the following questions.

(a) Is the reaction exothermic or endothermic?

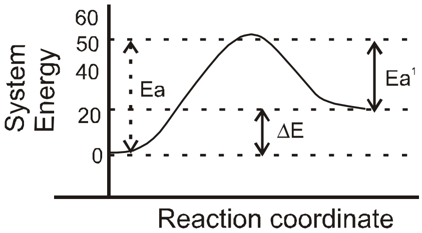
(b) What is the approximate value of Δ *E* for the forward reaction?

(c) What is activation energy in each direction?

(d) A catalyst is found that lowers the activation energy of the reaction by about 10 kJ/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) $Ea_f = 50$ KJ/Mole, $Ea_b = 30$ KJ/Mole (d) Increases

Ex-22. 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 = $KC_1 = 0.05 \times 60$ and Rate after 30 min = $KC_2 = 0.04 \times 60$

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

Supposing the reaction starting after 10 minutes

$$k = \frac{2.303}{20}\log\frac{c_1}{c_2} = \frac{2.303}{20}\log\frac{5}{4} = 0.011159$$

$$\therefore \quad t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{0.011159} = 62.12 \text{ min.}$$

Ex-23. 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	0.1M
0.80	x M	0.1M
0.40	0.2 M	y M

Sol. The rate law may be written as

rate = k [A] [B]

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

$0.10 = k \times 0.1 \times 0.1 \quad \Rightarrow \quad k = 10$

Now substituting the second and third sets of data, we get,

$0.8 = 10 \times x \times 0.1 \quad \Rightarrow \quad x = 0.80$ M

and, $0.4 = 10 \times 0.2 \times y \quad \Rightarrow \quad y = 0.20$ M.

Ex-24. 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, $\ln k_1 = \ln A - \frac{E_1}{RT}$

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

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

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

$$\log\frac{k_2}{k_1} = \frac{10}{2.303} = 4.342$$

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

Ex-25. In Arrhenius`s equation for a certain Reaction, the value of A and E (activation energy) are 6×10^{13} s^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be 20 minutes ?

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

$\text{In } k = \text{In } A - \frac{E}{RT}$

$2.303 \log k = 2.303 \log A - \frac{E}{RT}$ 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.

Ex-26. 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 decomposition 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 → products

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

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

Ex-27. The complexation of Fe^{2+} with the chelating agent dipyridyl has been studied kinetically in both forward and reverse directions.

$Fe^{2+} + 3\ \text{dipy} \rightarrow Fe(\text{dipy})_3^{2+}$

Rate (forward) = $(1.80 \times 10^{13})\ [Fe^{2+}]\ [\text{dipy}]^3$

and rate (reverse) = $(1.20 \times 10^{-4})\ [Fe\,(\text{dipy})_3^{2+}]$

Find the stability constant for the complex.

Sol. At dynamic equilibrium,

rate of formation of complex = rate of its decomposition

$(1.8 \times 10^{13})\ [Fe^{2+}]\ [\text{dipy}]^3 = (1.20 \times 10^{-4})\ [Fe(\text{dipy})_3^{2+}]$

$K_s = \frac{[Fe(\text{dipy})_3{}^{2+}]}{[Fe^{2+}][\text{dipy}]^3} = \frac{1.8 \times 10^{13}}{12 \times 10^{-4}} = 1.5 \times 10^{17}$

Ex-28. The approach to the following equilibrium was observed kinetically from both directions.

$PtCl_4^{2-} + H_2O \rightleftharpoons Pt(H_2O)Cl^{-}_3 + Cl^{-}$ at 25°C It was found that

$-\frac{d[PtCl]^{2-}}{dt} = (4.8 \times 10^{-5})\ [PtCl_4]^{2-} - (2.4 \times 10^{-3})\ [Pt(H_2O)Cl^{-}_3]\ [Cl^{-}]$

Calculate the equilibrium constant for the complexation of Cl^{-} with Pt(II).

Sol. At equilibrium, $\frac{d[PtCl_4]^{2-}}{dt} = 0$

Hence, $4.8 \times 10^{-5}\ [PtCl^{2-}_4] = 2.4 \times 10^{-3}\ [Pt(H_2O)Cl^{-}_3]\ [Cl^{-}]$

or $$K = \frac{[PtCl_4]^{2-}}{[Pt(H_2O)Cl_3^-][Cl^-]} = \frac{2.4\times10^{-3}}{4.8\times10^{-5}} = 50.$$

Ex-29. Some $PH_3(g)$ is introduced into a flask at 600°C containing an inert gas PH_3 proceeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. The total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant for the reaction:

Time (s)	0	60	120	∞
p mm (Hg)	262.40	272.90	275.51	276.40

$$4PH_3 \rightarrow P_4 + 6H_2$$

Sol. Let the initial Partial pressures of PH_3 and the inert gas be p and p' mm respectively and p' mm of PH_3 decomposes at different time intervals.

Initial partial pressure (P)

$$4PH_3 \rightarrow P_4 + 6H_2$$

Partial pressure at different times: $p - p'$ $\quad p'/4 \quad$ $6p'/4$

As given, at t = 0 seconds.

$$p + p' = 262.40 \qquad ...(1)$$

and, t = 60 second $$p - p' + \frac{p'}{4} + \frac{6p'}{4} + p' = 272.90 \qquad ...(2)$$

At t = ∞: $$\frac{p}{4} + \frac{6p}{4} + p' = 276.40. \qquad ...(3)$$

Solving, equations (1), (2) and (3), we get,

$$p = 18.67 \text{ and } p' = 14.$$

Similarly, at t = 120 seconds

$$p - p' + \frac{p'}{4} + \frac{6p'}{4} + p' = 275.51. \qquad ...(4)$$

Solving, equations (1), (4) and (3), we get

$$p = 18.67 \text{ and } p' = 17.48.$$

As the given reaction is of the type nA → products, where n = 4, we have the following equation for first-order kinetics

$$k_1 = \frac{2.303}{4t}\log\frac{a}{a-x} = \frac{2.303}{4t}\log\frac{p}{p-p'}.$$

Thus, at t = 60s; $$k_1 = \frac{2.303}{4\times60}\log\frac{18.67}{18.67-14} = 5.8\times10^{-3}\ s^{-1}$$

t = 120s; $$k_1 = \frac{2.303}{4\times120}\log\frac{18.67}{18.67-17.48} = 5.8\times10^{-3}\ s^{-1.}$$

As the values of k_1 are constant, the given reaction following the first order kinetics.