CHAPTER 6

CHEMICAL KINETICS

The branch of physical chemistry which deals with the study of the rate or speed or velocity of the chemical reactions proceeding under given conditions of the temperature, pressure and concentration is called as Chemical kinetics.

The different chemical reactions take different time to complete, out of them some reactions are very fast and some are slow. For example the reaction between $AgNO_3$ & NaCl in aqueous solution is fast, reaction between Na metal & water is vigorous, most of the organic reactions are slow & take measurable time to complete. While reaction between H_2 & O_2 to form water in absence of a catalyst or an electric discharge is so slow that it takes years together to complete. Wenzel C. F. was the first person to introduce the word chemical velocity or velocity of reaction & is defined as "The ratio of amount of the substance expressed in gram molecules, transformed in the process to the time within which it is transformed." Or "it is the rate of change of concentration of the reactant". Study of rate of chemical reaction gives us the knowledge of the behavior of different matters. We are able to control the reactions by knowing the influence of different factors on the rate of reactions. Thus chemical kinetics is explained in terms of following aspects.

i) Rate of reactions & Rate law
ii) Mechanism of the reaction.
iii) Effect of concentration, temperature, pressure & Catalyst on the rate of reaction

The knowledge of reaction kinetics is of great importance & utility in selecting optimum conditions for all industrial processes.

Rate or Velocity or Speed of Chemical Reaction

Let us consider a simple reaction of the type

$$\underset{\textbf{reactant}}{A} \rightarrow \underset{\textbf{product}}{B}$$

Here reactant 'A' is consumed and product 'B' is formed. As the reaction proceed concentration of reactants decreases while the concentration of product increases.

The rate or speed or velocity of a chemical reaction is defined as-

'The change in concentration of any one of the reactant or product per unit time' is called as rate of reaction.

OR

'The rate of change of concentration of either reactant or product per unit time' is called as rate of reaction.

Example: Consider dissociation of H_2O_2 to give H_2O & O_2

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Thus rate of reaction = $\frac{\text{Decrease in concentration of } H_2O_2}{\text{Time taken}}$

= $\frac{\text{Increase in conc. of } H_2O \text{ \& } O_2}{\text{Time taken}}$

Since, the concentration is usually expressed in mole /lit & the time taken in sec or min., then the unit of rate of reaction is therefore **mole /lit/sec.** Thus rate of reaction does not remain constant throughout the reaction hence we can consider rate of a reaction at a particular instant which is defined as follows " the rate of a reaction at any time is defined as the change in the concentration of any one of the reactant or product per unit time at that particular instant of time."

It is denoted as

Thus, Rate = $r = \frac{dx}{dt} = -\frac{dC_A}{dt} = +\frac{dC_B}{dt}$ ………....(l)

Where, dx is the change in concentration of either reactant or product, dt is the time interval.

According to law of mass action rate of any chemical reaction directly varies with the active mass of the reactants i.e. C_A or [A]

$\therefore r = \frac{dx}{dt} = -\frac{dC_A}{dt} = +\frac{dC_B}{dt} \alpha C_A$

OR

$r = -\frac{dC_A}{dt} = kC_A$

OR

$r = -\frac{d[A]}{dt} = k[A]$ …………..(2)

Where,

- dC_A or d[A] is infinitesimally decrease in the concentration of 'A' in an infinitesimal interval of time'dt'. Negative sign indicates decrease in concentration of 'A'.
- dC_B or d[B] is infinitesimally increase in the concentration of 'B' in an infinitesimal interval of time'dt'. Positive sign in equation indicates the concentration of product is increasing, with time.
- k is known as the rate constant of a reaction.

Velocity Constant or Rate Constant

Consider a simple reaction of the type

$$\underset{\text{Reactant}}{A} \rightarrow \underset{\text{product}}{P}$$

Rate of this reaction is given by

Rate α [A]

= k [A]

Or for a reaction

$A + B \longrightarrow P$ or $A + A \longrightarrow P$

Rate α [A] [B] or Rate = k [A] [B]

Rate α [A] [A] or Rate = k $[A]^2$

Here, k is called as velocity constant or specific reaction rate. If concentration of each reactant is unity, then rate of reaction = k, thus at fixed temperature, specific reaction rate or velocity constant is equal to the rate of the reaction when concentration of each reactant is unity.

Factors Influencing the Rate of Reaction

The following factors influence (affect) the rate of chemical reactions.

1) Concentration of reactants : As a reaction proceeds the reactants are consumed, therefore the concentration of the reactant decreases with the passage of time. It is observed experimentally that the rate of reaction also decreases as the time passes. This clearly indicates that the rate of reaction is directly proportional to the concentration of the reactants.

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

The rate of above reaction get doubled, when the concentration of the reactant A is doubled.

Similarly, $A + B \longrightarrow \text{Product}$

The rate of this reaction becomes four times the initial rate if concentration of A & B is doubled. Thus the increase in concentration of the reactants increases the effective collision rate of the molecules.

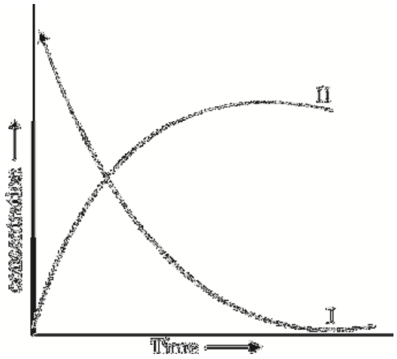

Fig.6.1 Concentration versus time plot

ii) Effect of temperature : The increase in temperature leads to increase in the rate of the reaction. It is observed that for all those reactions which are exothermic (heat evolving) rate decreases, while rate of endothermic reactions increase with increase in temperature.

iii) Solvent : Solvent also plays the important role in determining rate of reactions. Rate of reaction increases or decreases with change of solvent, which depends upon the nature of the reaction.

iv) Catalyst : The rate of certain reactions increase due to presence of certain substances in the reacting system, known as catalyst. So, catalyst increases the rate of reaction.
e.g. MnO_2 speeds up decomposition of potassium chlorate.

v) Pressure: Rate of the gas phase reactions are also affected by pressure. Higher the pressure more is the rate of reaction. Thus concentration and pressure affect the rate of reaction in the same manner.

Order of Reaction

Determination of rate of reaction reveals that all the molecules of the reactants represented by the chemical equations do not determine the rate of reaction but only those molecules whose concentration changes measurably during the reaction determine the rate of reaction. Hence "The number of reacting molecules whose concentration changes appreciably as a result of chemical reaction is known as order of the reaction." Or the order of reaction is also defined as "The power to which the concentration of the reactant is to be raised to get the rate of reaction"

Thus

Rate α $[\text{Reactant}]^n$

Where, n is the number of moles of reactant, then 'n' becomes order of reaction.

For a reaction,

$$mA + nB \longrightarrow \text{Products}$$

Rate = $k\,[A]^m[B]^n$

Hence the order of reaction = (m+n)

So the order of reaction may also be defined as, *"The sum of the powers of the concentration terms of the rate determining equations".*

Molecularity of a Reaction : Definition-"*The number of reacting species (atoms, molecules or ions) taking part in a chemical reaction is known as molecularity of a reaction."*

- Molecularity of a reaction is always a whole number.
- When the reaction involved single species atom, molecule or ion to carry out a chemical reaction then such reaction is called as unimolecular reaction.

In general it is represented as

$$A \longrightarrow \text{product}$$

For example

i) $Br_2 \longrightarrow 2Br$

ii) $H_2O_{2\,(l)} \longrightarrow H_2O_{(l)} + \frac{1}{2}O_2$

- The reaction in which two molecules are involved in a chemical reaction is said to be bimolecular reaction.

In general it is represented as

$A + A \longrightarrow \text{product}$

OR $A + B \longrightarrow \text{product}$

For example

i) $2HI \longrightarrow H_2 + I_2$

ii) Hydrolysis of methyl acetate in presence of mineral acid

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

- A reaction in which three molecules of reactants are involved to form the product is known as trimolecular reaction.

In general it is represented as

$3A \longrightarrow$ product

OR $2A + B \longrightarrow$ product

OR $A + B + C \longrightarrow$ product

For example

i) $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$

ii) $2NO_{(g)} + Cl_{2(g)} \longrightarrow 2\,NOCl_{(g)}$

Difference between Order and Molecularity

Molecularity	**Order of reaction**
1.It is a total number of molecules taking part in chemical reactions	1. It is the sum of powers of concentration terms in rate equation
2.It is theoretical concept	2. It can be determined experimentally.
3. It is always a whole number	3. It can be whole number as well as fraction.
4. It can never be zero.	4. It can be zero.
5. It has no significance for a complex reaction & can be expressed for each elementary step in case of a complex reaction.	5. It is always the same for over all reaction whether the reaction is complex or simple.
Ex.- $(CH_3)_3C\text{-}Br + KOH \longrightarrow (CH_3)_3C\text{-}OH$ Molecularity =2	$(CH_3)_3C\text{-}Br + KOH \quad (CH_3)_3C\text{-}OH$ Order of Reaction =1

Zero Order Reactions :

The reactions of first, second & third order depends upon the concentration terms of the reactants but there are certain reactions whose velocity or rate do not depend on the concentration of any one of the reactant. The velocity or rate is constant throughout the reaction; such reactions are called as zero order reactions.

"A reaction is said to be zero order when its rate is independent of the initial concentration of all the reactants."

Consider-

	A	→ Product
At time, t = 0	a	0
t = t,	(a-x)	x

Suppose 'a' mol dm^{-3} is initial concentration and (a - x) mol dm^{-3} be the concentration of reactant after time 't'. The rate of above reaction is given as -

$$\text{Rate} = r = \frac{dx}{dt} = k_0\,(a - x)^0 \qquad \text{………..(3)}$$

Where, 'k_0' is a rate constant or velocity constant

$$\therefore \frac{dx}{dt} = k_0 \qquad [\because (a - x)^0 = 1]$$

$$\text{i.e. } dx = k_0\,dt \qquad \text{………..(4)}$$

Integrating equation (4) within the limits,

$$\int_{x=o}^{x=x} dx = \int_{t=o}^{t=t} k_0 \ dt$$

$x = k_0t$ ………....(5)

This is zero order rate law equation.

Characteristics of Zero Order Reaction

1) Unit of k_0

We know that for zero order reaction, the rate law equation is

$x = k_0t$

$k_0 = \frac{x}{t} = \frac{moldm^{-3}}{sec} = \text{mol dm}^{-3}\ \text{sec}^{-1}$

2) Half life : Half life of reaction is the time required to complete half of the reaction. It is represented by $t_{1/2}$.

The zero order rate law equation is

$x = k_0t$

Thus, when $t = t_{1/2}$, $x = \frac{a}{2}$

Substitute these values in above equation

We get, $\frac{a}{2} = k_0t_{1/2}$

$\because t_{1/2} \ \alpha \ a$

Hence half life of zero order reaction is directly proportional to initial concentration of reactant.

3) The graphical representation

The zero order rate law equation is $x = k_0t$

This is in the form of $y = m x$

i.e. when the graph is plotted between 'x' values on Y-axis and 't' values on X-axis. Straight line is obtained with slope k_0 as shown in Figure 2.

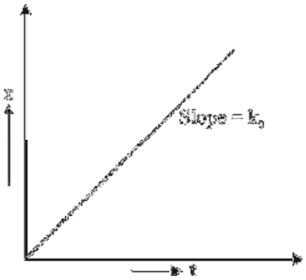

Fig.6.2 plot of 'x' versus 't'

Examples of Zero Order Reaction

i) Reaction between acetone and Bromine

$CH_3COCH_3 + Br_2 \rightarrow CH_3COCH_2Br + HBr$

This reaction proceeds with the same rate irrespective of concentration of Br_2 and so reaction is said to be zero order with respect to Br_2.

ii) Reaction of acetone and iodine

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

The reaction is zero order with respect to iodine concentration since reaction rate is independent of concentration of iodine.

iii) Decomposition of HI at the surface of gold

$$2HI \xrightarrow{\text{gold surface}} H_2 + I_2$$

Gold metal acts as a catalyst. At sufficiently high pressure catalyst surface is completely covered by HI molecule.

Even though pressure is increased or the concentration is increased, then there is no change in the rate of reaction & thus it is zero order reaction.

iv) Photochemical combination of H_2 & Cl_2 to form HCl

$$H_2 + Cl_2 \xrightarrow[\text{U.V. light}]{\text{Sunlight}} 2HCl$$

Reaction can be studied by taking H_2 & Cl_2 over water in a glass tube & then mixture is exposed to sunlight or U.V. light. The water rises at the same rate as the rate of disappearance of H_2 & Cl_2. The concentrations of gases in the gaseous phase do not change with time & hence it is zero order reaction.

First Order Reaction :

When only one molecule is taking part in the reaction & whose concentration changes appreciably as a result of chemical reaction to form a product is known as first order reaction. It can be represented as,

	A →	Product
At time, t = 0	a	0
t = t,	(a-x)	x

Suppose 'a' mole dm^{-3} be the initial concentration of reactant 'A' and 'x' mol dm^{-3} be the concentration of product after time 't'. The rate of the reaction is given as-

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

$$\text{i-e. } \frac{dx}{dt} = k_1 (a - x) \qquad \ldots\ldots\ldots(6)$$

Where, k_1 is first order rate constant (or velocity constant). Equation (6) can be written as-

$$\frac{dx}{(a-x)} = k_1\, dt \qquad \ldots\ldots\ldots..(7)$$

Integrating the equation (7), we get

$$\int \frac{dx}{(a-x)} = \int k_1\, dt$$

$$-In\,(a\text{-}x) = k_1 t + C \qquad \ldots\ldots\ldots\ldots(8)$$

Where 'C' is integration constant which can be evaluated from initial condition of reaction as at t = 0, x = 0, putting in (8) we get,

$\therefore -\text{In}\ a = C$ ………(9)

Putting the value of C in eq. (9) we get,

$-\text{In}\ (a - x) = k_1\ t - \text{In}\ a$

$\text{In}\ a - \text{In}\ (a - x) = k_1\ t$

$k_1 = \frac{1}{t}\ \text{In}\left(\frac{a}{a-x}\right)$ (since, $\log_e x = 2.303 \log_{10} x$)

$k_1 = \frac{2.303}{t} \log_{10}\left(\frac{a}{a-x}\right)$ …….(10)

This equation is known as the integrated rate law for first order reaction.

Characteristics of First Order reaction:

1) Unit of k_1

We know that the first order reaction

$A \longrightarrow \text{Product}$

Rate α [A]

Rate = k_1 [A]

K_1 = Rate / [A]

But rate is expressed in number of moles/lit/sec. or number of moles/dm^3/sec.

And concentration of reactant is expressed in mole /lit. or mole/dm^3.

$$K_1 = \frac{\text{moles/lit/sec}}{\text{Moles/lit}} \quad \text{or} \quad \frac{\text{moles/dm}^3\text{/sec}}{\text{moles/dm}^3}$$

$= 1/\text{sec} \qquad K_1 = \text{sec}^{-1}$

Thus the unit of rate constant of first order reaction is 's^{-1}'

2) Graphical representation

We know that,

$k_1 = \frac{2.303}{t} \log_{10}\left(\frac{a}{a-x}\right)$

$k_1 t = 2.303 \log_{10}\left(\frac{a}{a-x}\right)$

$\log_{10}\left(\frac{a}{a-x}\right) = \left(\frac{k_1}{2.303}\right) \times t$

This is in the form of $y = m\ x$

Hence, when a graph is plotted between $\log_{10}\left(\frac{a}{a-x}\right)$ and 't' we get a straight line passing through origin and having slope $\frac{k_1}{2.303}$ shown in figure 6.3.

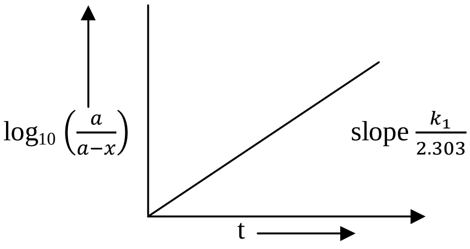

Fig. 6.3 The plot of log a/ (a-x) versus time (t)

Now, $k_1t = 2.303 \log_{10}\left(\frac{a}{a-x}\right)$

OR $k_1t = 2.303 \log_{10} a - 2.303 \log_{10} (a - x)$

OR $2.303 \log_{10}(a - x) = -k_1t + 2.303 \log_{10} a$

OR $\log_{10} (a - x) = -\left(\frac{k_1}{2.303}\right)t + \log_{10} a$ ……...(11)

This is in the form of $y = m x + C$

Thus, when a graph is plotted between $\log_{10}(a - x)$ and 't' we get a straight line with slope $-\left(\frac{k_1}{2.303}\right)$ and intercept $\log_{10} a$ as shown in figure 6.4

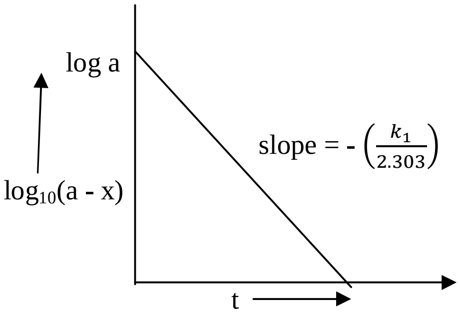

Fig.6.4. The plot of $\log_{10}$ (a-x) versus time

3) Half life

It is the time required to complete the half of reaction. It is represented by $t_{1/2}$. The first order rate law equation is

$$k_1 = \frac{2.303}{t} \log_{10}\left(\frac{a}{a-x}\right)$$

Thus, when = $t_{1/2}$, $x = \frac{a}{2}$

Substitute these values in above equation, we get

$$k_1 = \frac{2.303}{t_{1/2}} \log_{10}\left(\frac{a}{a-\frac{a}{2}}\right)$$

$$k_1 = \frac{2.303}{t_{1/2}} \log_{10}\left(\frac{a}{2a-a/2}\right)$$

$$k_1 = \frac{2.303}{t_{1/2}} \log_{10}\left(\frac{a}{a/2}\right)$$

$$k_1 = \frac{2.303}{t_{1/2}} \log_{10}\left(\frac{2a}{a}\right)$$

$$k_1 = \frac{2.303}{t_{1/2}} \log_{10} 2 \qquad \text{Since } \log_{10} 2 = 0.3010$$

$$t_{1/2} = \frac{2.303}{k_1} \times 0.3010 = \frac{0.693}{k_1} = \text{Constant}$$

Thus, the time taken for completion of half of the first order reaction is independent of the initial concentration of the reactant.

Examples of First Order Reactions:

Example 1 Conversion of Ethene to Ethane

$C_2H_4 + H_2 \rightarrow C_2H_6$

Example 2 Decomposition of H_2O_2

In presence of finely divided Pt, H_2O_2 in solution decomposes as:

This reaction is supposed to take place in two steps as-

i) $H_2O_2 \rightarrow H_2O + O$ (slow)
ii) $O + O \rightarrow O_2$ (fast)

In this first step is slow step & is called rate determining step & thus rate depends upon the concentration of **H_2O_2 & hence it is first order reaction**. The progress of the reaction can be followed by two ways-

a) By collecting O2 gas evolved
b) By titrating remaining H_2O_2 against standard KMnO4 solution using acid

In the first method volume of oxygen collected (Vt) at any time will be proportional to H_2O_2 decomposed (x) while the final volume at time 't' (Vt) will be proportional to concentration of H_2O_2 present at that time.

Therefore, $V_o \ \alpha \ a \quad \& \quad Vt \ \alpha \ (a-x)$

$V_o = k\,a \quad \& \quad Vt = k(a-x)$

Putting these values in first order rate equation

$$k_1 = \frac{2.303}{t} \log_{10}\left(\frac{a}{a-x}\right) \qquad \text{……..(12)}$$

$$k_1 = \frac{2.303}{t} \log_{10}\left(\frac{Vo}{Vt}\right) \qquad \text{……..(13)}$$

Eqn 13) is a first order equation from which k_1 can be calculated.

Pseudo-Order Reactions :

When one of the reactants of the bimolecular reaction is taken in large excess, then the reaction confirms to a unimolecular reaction. Such bimolecular reactions are called as pseudo-unimolecular reaction or pseudo-order reactions.

The reaction which appears to be bimolecular but in fact it is first order is called pseudo unimolecular reaction.

OR

'A reaction in which one of the reactants if present in a large excess shows a different order is known as Pseudo-order reaction'.

The reaction is in fact bimolecular but behaves as a first order reaction is known as Pseudo first order reaction. Pseudo-first order reaction may also be called Pseudo unimolecular reaction.

For example

i) Hydrolysis of methyl acetate in presence of mineral acid.

$$CH_3COOCH_3 + H_2O_{\text{(Excess)}} \xrightarrow{H^+} CH_3COOH + CH_3OH$$

In above reaction water is taken in a large excess so that its concentration does not change appreciably during the reaction and rate of reaction depends only on the concentration of methyl acetate so that it is Pseudo-unimolecular reaction.

ii) Inversion of cane sugar in the presence of mineral acid.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O_{(Excess)} \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Actually above reaction is bimolecular as it involves two molecules of reactants but follows first order rate equation as water is present in large excess. Hence this is an example of Pseudo-unimolecular reaction.

Problem (1) The decomposition of H_2O_2 was studied by titrating it at different intervals of time with potassium permanganate ($KMnO_4$). Calculate the velocity constant from the following data, if the reaction is of the first order.

t (min)	0	10	22	40
Vol. of $KMnO_4$ (dm^3)	25.0	20.0	15.5	9.6

Solution : Given that

Vo = a = 25

We know that for decomposition of H_2O_2 by titrating with potassium permanganate ($KMnO_4$), rate law equation is-

$$k_1 = \frac{2.303}{t} \log_{10}\left(\frac{V_O}{V_t}\right)$$

i) When, t = 10 min, V_t = 20.0 ml

$$\therefore K_{11}' = \frac{2.303}{10} \log_{10}\left(\frac{25}{20}\right)$$

$= 0.0223 \text{ min}^{-1}$

ii) When, t = 22 min, V_t = 15.5 ml

$$\therefore K_2'' = \frac{2.303}{22} \log_{10}\left(\frac{25}{15.5}\right)$$

$= 0.0217 \text{ min}^{-1}$

iii) When, t = 40 min, V_t = 9.6 ml

$$\therefore K_3''' = \frac{2.303}{40} \log_{10}\left(\frac{25}{9.6}\right)$$

$= 0.0239 \text{ min}^{-1}$

$$\therefore K_1 = \frac{K_1' + K_2'' + K_3'''}{3} = \frac{0.0223+0.0217+0.0239}{3}$$

$= 0.0226 \text{ min}^{-1}$

The K_1 values are found to be nearly same by using first order equation & hence it is first order reaction.

Problem (2) The decomposition of H_2O_2 reaction was determined by titrating equal volumes of the decomposing mixture against standard $KMnO_4$ solution at regular intervals, the following data were obtained.

t (min)	0	10	20	30
Vol. of $KMnO_4$ (cc)	25.0	16.1.	10.4	7.1

Show that the reaction is first order reaction.

Solution : For decomposition of H_2O_2 reaction following first order equation is used

$$k_1 = \frac{2.303}{t} \log_{10}\left(\frac{V_O}{V_t}\right) \qquad \text{......(1)}$$

i) When t=10 , Vt= V_{10} = 16.1 & Vo = 25

$$k = \frac{2.303}{10} \log_{10}\left(\frac{25}{16.1}\right)$$

$$k_1 = 0.2303 \log_{10} (1.55)$$

k1 =0.2303 x 0.190

k1 = 0.0438 min^{-1}

ii) When t=20 , Vt= V_{20} = 10.4& Vo = 25

$$k = \frac{2.303}{20} \log_{10}\left(\frac{25}{10.4}\right)$$

$$k_1 = 0.1151 \log_{10} (2.40)$$

k1 =0.1151 x 0.3802

k1 = 0.0437 min^{-1}

iii) When t=30 , Vt= V_{30} = 7.1 & Vo = 25

$$k = \frac{2.303}{30} \log_{10}\left(\frac{25}{7.1}\right)$$

$$K_1 = 0.07676 \log_{10}(3.521)$$

K_1 =0.07676 x 0.5466

K_1 = 0.0419 min^{-1}

The K_1 values are found to be nearly same by using first order equation & hence it is first order reaction.

Example : Hydrolysis of Methyl Acetate :

The reaction is catalyzed by mineral acid as;

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

This reaction involves two molecules, but the concentration of H_2O does not change appreciably. Hence the reaction is Pseudo unimolecular reaction or Pseudo first order reaction. Acetic acid produced during the reaction is titrated with standard alkali solution. The mineral acid is used as catalyst also reacts with the alkali solution. Equals volumes of reaction mixture are withdrawn at different time intervals & titrated with standard solution of NaOH. If V_o is the volume of alkali required at time, t = 0, it will correspond to the concentration of mineral acid & V_t volume correspond to the acetic acid formed & mineral acid. Hence,

$x = (V_t - V_0) = (T_t - T_o)$ ml & $a \equiv (V_\infty - V_0) = (T_\infty - T_o)$ ml

$(a-x) \equiv (V_\infty - V_0) - (V_t - V_0) \equiv (V_\infty - V_t)$ ml

Or $(a-x) = ((T_\infty - T_o) - (T_t - T_o)$

Thus, the equation (13) becomes :

$$\therefore k_1 = \frac{2.303}{t}\log_{10}\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right) = \frac{2.303}{t}\log_{10}\left(\frac{T_\infty - T_0}{T_\infty - T_t}\right)$$

Where To, Tt & T∞ be the titre value at time zero & at time ‘t’ & at infinite time respectively.

Problem (3) Following data was obtained in the hydrolysis of ethyl acetate at 25°C in presence of 0.35 N hydrochloric acid which was used as a catalyst.

Time (seconds)→	0	1200	4500	7140	∞
ml. of alkali used→	24.36	25.85	29.32	31.42	47.15

From this data, show that hydrolysis of methyl acetate is a first order reaction.

Solution : Given that

V_0 = a =24.36 and V_∞=47.15

We know that for acid hydrolysis of methyl acetate rate law equation is-

$$k_1 = \frac{2.303}{t}\log_{10}\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

i) At, t = 1200 s, $k_1 = \frac{2.303}{1200}\log_{10}\left(\frac{47.15-24.36}{47.15-25.85}\right)$

$= 5.64 \times 10^{-5}\ s^{-1}$

ii) At, t = 4500 s, $k_1 = \frac{2.303}{4500}\log_{10}\left(\frac{47.15-24.36}{47.15-29.32}\right)$

$= 5.46 \times 10^{-5}\ s^{-1}$

iii) At, t = 7140 s, $k_1 = \frac{2.303}{7140}\log_{10}\left(\frac{47.15-24.36}{47.15-31.42}\right)$

$= 4.46 \times 10^{-5}\ s^{-1}$

Since, k_1 is nearly constant, this reaction follows first order kinetics.

Example 3 : Inversion of Cane - Sugar The inversion or hydrolysis of cane sugar takes place in presence of mineral acid as follows

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Cane sugar	glucose	fructose
(dextro-ratatory)	(dextro-ratatoiy)	(laevo-ratatory)

The given reaction is bimolecular as it involves two molecules of reactants but follows first order rate equation as water is present in large excess. Hence this is an example of Pseudo-unimolecular reaction.

The initial solution of sucrose is dextro-ratatory but on hydrolysis in presence of hydrochloric acid, it gives glucose (dextro-ratatory) and fructose (laevo- ratatory) in equal amounts the laevo-rotation of fructose is -92° while dxtro-rotation of glucose is +52.5°. The mixture, therefore on whole, is laevo-ratatory. For this reason the reaction is known as inversion of cane sugar. The progress of the reaction can be followed by measuring the change in angle of rotation by means of polarimeter. Change in angle of rotation is directly proportional to the change of concentration of sugar (x) to glucose and fructose. The angle of rotation of plane polarized light decreases with time. The total change in angle of rotation produced at the end of reaction gives the initial concentration 'a'

Let r_0 be the initial rotation

r_∞ be the final rotation

rt be the rotation at time t

Then,

a α $(r_0 - r_\infty) \rightarrow$ Initial concentration of cane sugar

x α $(r_0 - r_t) \rightarrow$ The concentration of sugar at time t

$\therefore$ (a - x) α $(r_0 - r_\infty) - (r_0 - r_t)$

OR (a-x) α $(r_t - r_\infty)$

Substituting these values in equation,

$$k_1 = \frac{2.303}{t} \log_{10}\left(\frac{a}{a-x}\right)$$

we get, $k_1 = \frac{2.303}{t} \log_{10}\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right)$

Problem (4) A 20% solution of cane sugar is inverted by 0.5 N HC1 at 25°C. The angle of rotation of cane sugar at various time intervals are given below

Time (second)→	0	72	368	460	680	∞
Rotation (degrees)→	+24.1	+21.4	+12.4	+10	+5.5	-10.7

From this data, show that inversion of cane sugar is a first order reaction.

Solution : Given that

$r_0 = 24.1$ and $r_\infty = -10.7$

We know that for inversion of cane sugar rate law equation is-

$$k_1 = \frac{2.303}{t} \log_{10}\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right)$$

Also, $r_0 - r_\infty = 24.1 - (-10.7) = 24.1 + 10.7 = 34.8$

i) At, t = 72s, $k_1 = \frac{2.303}{72} \log_{10}\left(\frac{34.8}{21.4-(-10.7)}\right)$

$= 1.12 \times 10^{-3}\ s^{-1}$

ii) At, t = 368s, $k_1 = \frac{2.303}{368} \log_{10}\left(\frac{34.8}{12.4-(-10.7)}\right)$

$= 1.11 \times 10^{-3}\ s^{-1}$

iii) At, t = 460s, $k_1 = \frac{2.303}{460} \log_{10}\left(\frac{34.8}{10-(-10.7)}\right)$

$= 1.13 \times 10^{-3}\ s^{-1}$

iv) At, t = 680s, $k_1 = \frac{2.303}{680} \log_{10}\left(\frac{34.8}{5.5-(-10.7)}\right)$

$= 1.12 \times 10^{-3}\ s^{-1}$

Since, k_1 is nearly constant, this reaction follows first order kinetics.

Problem (5) : Optical rotation of sucrose in 0.9N HCl at various time as given in the following table:

Time (min.)→	0	10	20	30	40	∞
Rotation (degrees)→	+32.4	+28.8	+25.5	+22.4	+19.6	-14.1

Show that hydrolysis of cane sugar is first order reaction .

Solution: If the reaction is to be of first order the k1 values can be calculated by using equation

$$k_1 = \frac{2.303}{t} \log_{10} \left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right)$$

Also, $r_0 - r_\infty = 32.4 - (-14.1) = 46.5$

i) At, t = 10min, $k_1 = \frac{2.303}{10} \log_{10} \left(\frac{46.5}{28.8-(-14.1)}\right)$

$$k_1 = \frac{2.303}{10} \log_{10} \left(\frac{46.5}{42.9)}\right)$$

$$k_1 = \frac{2.303}{10} \log_{10} (1.083)$$

$$k_1 = \frac{2.303}{10} \text{ x o.o349}$$

$= 0.00805$ min-1

ii) At, t = 20min, $k_1 = \frac{2.303}{20} \log_{10} \left(\frac{46.5}{39.6)}\right)$

=.0.00802 min-1

iii) At, t = 30, $k_1 = \frac{2.303}{30} \log_{10} \left(\frac{46.5}{36.5}\right)$

= 0.00807 min-1

iv) At, t = 40min, $k_1 = \frac{2.303}{40} \log_{10} \left(\frac{46.5}{33.7)}\right)$

= 0.00805 min-1

The k_1 values are found to be nearly same by using modified first order equation & hence it is first order reaction.

Second Order Reactions :

When two molecules react together and whose concentration change appreciably as a result of chemical reaction to give product are called as second order reactions.

or

The reaction whose rate depends upon the concentration of two reactants is called as second order reaction.

In general, second order reactions are represented as follows

$$2A \rightarrow \text{Product}$$

OR $$A + B \rightarrow \text{Product}$$

Case I : Two reactants with equal initial concentration. Consider any one of above reaction

$$2A \rightarrow \text{Product}$$

At time, t = 0 a 0

t = t, (a - x) x

Suppose ‘a’ mole dm^{-3} be the initial concentration of reactant A and ‘x’ mol dm^{-3} be the concentration of product after time ‘t’. The rate of the reaction is given as-

$$r = \frac{dx}{dt} \ \alpha \ (a\text{-}x)^2$$

i.e. $$\frac{dx}{dt} = k_2\,(a - x)^2 \qquad \ldots\ldots\ldots\ldots\ldots (14)$$

Where, k_2 is second order rate constant (or velocity constant) of second order reaction.

Equation (14) can be written as-

$$\frac{dx}{(a-x)^2} = k_2\,dt$$

Integrating above equation, we get

$$\int \frac{dx}{(a-x)^2} = \int k_2\,dt$$

$$1/(a\text{-}x) = k_2t + c\ , \qquad \ldots\ldots\ldots\ldots\ldots (15)$$

Where, c= integration constant

When x= 0, t = 0

Putting in equation (15) we get,

$$\frac{1}{a} = C \qquad \ldots\ldots\ldots\ldots\ldots(16)$$

From equations (15) and (16) we get,

$$\frac{1}{(a-x)} = k_2t + \frac{1}{a}$$

$$k_2t = \frac{1}{(a-x)} - \frac{1}{a}$$

$$k_2t = \frac{x}{a(a-x)}$$

$$k_2 = \frac{1}{t}\,\frac{x}{a(a-x)} \qquad \ldots\ldots\ldots\ldots\ldots(17)$$

This equation (17) is known as second order kinetic equation or integrated rate law of second order reaction.

Case II Two reactants with different initial concentration,

i.e. A + B → Product

At time, t = 0 a b 0

t = t, (a-x) (b-x) x

Suppose ‘a’ & ‘b’ are the initial concentrations in mol/dm^3 of A & B respectively. Let x mol/dm^3 of A & B have reacted in time t. Then concentration of A & B after time t will be (a-x) & (b-x) mol/dm^3 respectively. The rate law equation is

$$r = \frac{dx}{dt} \ \alpha \ (a\text{-}x)\,(b\text{-}x)$$

i.e. $$\frac{dx}{dt} = k_2\,(a\text{-}x)\,(b\text{-}x) \qquad \ldots\ldots\ldots\ldots(18)$$

Where, k_2 is second order rate constant (or velocity constant) of second order reaction.

Equation (18) can be written as-

$\frac{dx}{(a-x)\,(b-x)} = k_2dt$ ………..... (19)

L.H.S of eq (19) resolving into partial fraction as

$\frac{dx}{(a-x)\,(b-x)} = \left(\frac{C}{(a-x)} + \frac{D}{(b-x)}\right)$ ……….. (20)

Where C & D are constants,

Taking L.C.M. of R.H.S. of eq(20) we get,

$\frac{dx}{(a-x)\,(b-x)} = \left(\frac{C(b-x)+}{(a-x)}\frac{D(a-x)}{(b-x)}\right)$

dx = C(b-x) + D (a-x) ………..(21)

when x = b putting in R.H.S. of eq(22),

dx = D(a-b), hence D = dx/ (a-b) …..(23)

when x= a , we get

dx = C(b-a) = -C (a-b)……. (24)

putting (22) & (23) in eq (24)

we get,

$\frac{dx}{(a-x)\,(b-x)} = 1/(a-b)\left(\frac{dx}{(b-x)} - \frac{dx}{(a-x)}\right)$ ………..... (25)

From eq (20) & (25), we get

$1/(a-b)\left(\frac{dx}{(b-x)} - \frac{dx}{(a-x)}\right) = k_2dt$ …..(26)

Integrate equation (26), we get

$\frac{1}{(a-b)}\left[\int \frac{dx}{b-x} - \int \frac{dx}{a-x}\right] = \int k_2dt$

$\frac{1}{(a-b)}$ [- In(b -x)- (-In (a - x)] = k_2t +C

$\frac{1}{(a-b)}$ [In (a - x)- In(b - x)] = k_2t +C

$\frac{1}{(a-b)}\left[\ln\frac{(a-x)}{(b-x)}\right] = k_2t + c$ …………… (27)

Where, C is integration constant & evaluated as-

At, t = 0, x = 0

$\frac{1}{(a-b)}$ [- In b - (-In (a)] = C

OR $\frac{1}{(a-b)}$ [In a - lnb] = C

OR $\frac{1}{(a-b)} \ln\frac{a}{b} = C$ …………….(28)

Hence equation (20) becomes-

$\frac{1}{(a-b)} \ln\frac{(a-x)}{(b-x)} = k_2t + \frac{1}{(a-b)} \ln\frac{a}{b}$

$\frac{1}{(a-b)} \ln\frac{(a-x)}{(b-x)} - \frac{1}{(a-b)} \ln\frac{a}{b} = k_2t$

$$\frac{1}{(a-b)}\left[\ln\frac{(a-x)}{(b-x)}-\ln\frac{a}{b}\right]=k_2\,t$$

$$\frac{1}{(a-b)}\ln\left(\frac{b(a-x)}{a(b-x)}\right)=k_2t$$

$$\therefore k_2=\frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)}$$

$$k_2=\frac{2.303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)} \qquad \text{…………….(29)}$$

Equation (29) is second order kinetic equation or integrated rate law for second order reaction with different initial concentration.

Characteristics of second order reaction:

i) Unit of second order reaction:

We know that rate law for the second order reaction is

$$k_2=\frac{1}{t}\frac{x}{a(a-x)}$$

$$k_2=\frac{1}{sec}\frac{moldm^{-3}}{moldm^{-3}.moldm^{-3}}$$

$$k_2=\frac{1}{sec}\frac{1}{moldm^{-3}}$$

$$k_2 = dm^3mol^{-1}\,sec^{-1}$$

ii) Half life Half life of reaction is the time required to complete half of the reaction. It is represented by $t_{1/2}$.

The second order rate law equation

$$k_2=\frac{1}{t}\frac{x}{a(a-x)}$$

Thus, when = $t_{1/2}$, x = $\frac{a}{2}$

Substitute these values in above equation, we get

$$k_2=\frac{1}{t_{1/2}}\frac{\frac{a}{2}}{a\left(a-\frac{a}{2}\right)}$$

OR $k_2=\frac{1}{t_{1/2}}\frac{\frac{a}{2}}{a\times\frac{a}{2}}$

OR $k_2=\frac{1}{t_{1/2}}\frac{1}{a}$

OR $\frac{1}{t_{1/2}}=\frac{1}{k_2}\frac{1}{a}$

OR $t_{1/2}\ \alpha\ \frac{1}{a}$

Thus the time required for completion of definite fraction of the second order reaction is inversely proportional to initial concentration of reactant.

iii) Graphical representation:

We have, $k_2 = \frac{1}{t}\frac{x}{a(a-x)}$

OR $k_2t = \frac{1}{(a-x)} - \frac{1}{t}$

OR $\frac{1}{(a-x)} = k_2t + \frac{1}{t}$

This is in the form of $y = m\,x + C$

Thus when the graph is plotted between, $\frac{1}{(a-x)}$ and time't' we get a straight line, not passing through origin slope, k_2 and intercept $\frac{1}{t}$ as shown in Figure 5.

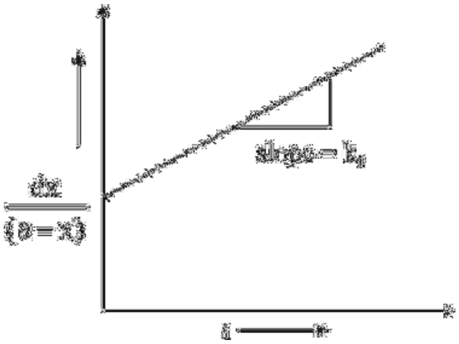

Fig. 6.5. Plot of 1/a-x versus time 't'

iv) The second order rate constant (k_2) depends on initial concentration of the reactants

Let the reaction is started with new initial concentration m times the original concentration. Then initial concentration will be ma, the concentration after time t will be 'm (a-x)' & that of the product will be mx.

We have, $k_2 = \frac{1}{t}\frac{a}{a(a-x)}$

The new equation with new concentration will be,

$$k_2' = \frac{1}{t}\frac{mx}{ma.m(a-x)}$$

$$= \frac{1}{m}\left(\frac{1}{t}\frac{a}{a(a-x)}\right)$$

$$\therefore k_2' = \frac{1}{m}k_2$$

Hence the new value of velocity constant is $\frac{1}{m}$ times the original value.

v) When one of the reactants is present in large excess, a second order reaction behaves as first order.

For the reaction of type, $A + B \rightarrow P$, we have the rate equation as-

$$k_2 = \frac{2.303}{(a-b)t}\log_{10}\frac{b(a-x)}{z(b-x)}$$

Let ‘A’ is in the large excess compared to B. Then, a » b. So that a - x ≈ a and a - b ≈ a

$$\therefore k_2 = \frac{2.303}{ta} \log_{10} \frac{b.a}{a(b-x)}$$

$$k_2' = k_2 a = \frac{2.303}{t} \log_{10} \frac{b}{(b-x)}$$

$$\therefore k_2' = k_1$$

$$\left\{Since, k_1 = \frac{2.303}{t} log_{10} \left(\frac{b}{(b-x)}\right)\right\}$$

Examples of Second Order Reaction :

Example 1 Saponification of ethyl acetate (hydrolysis of ethyl acetate by an alkali) with equal initial concentration of ester and alkali. The reaction can be written as-

$CH_3COOC_2H_5 + NaOH \rightarrow$	CH_3COONa +	C_2H_5OH
Ethyl Acetate	Sodium Acetate	Ethyl Alcohol

As the rate of reaction depends on concentration of both the reactants, the reaction is of second order. The progress of reaction is studied by titrating same volume of the reaction mixture against standard acid solution at regular time intervals. The volume of acid required for titration corresponds to un-reacted alkali or ester (a - x) and volume required initially will give initial concentration of reactant as 'a'. Thus,

$$a \equiv V_0$$

$$a - x \equiv V_t$$

OR $$a-(a-x) \equiv V_0-V_t$$

OR $$x \equiv V_0 - V_t$$

Hence the rate equation second order reaction,

$$k_2 = \frac{1}{t} \frac{a}{a(a-x)} \text{ becomes}$$

$$k_2 = \frac{1}{t} \frac{V_0 - V_t}{V_t[V_0-(V_0-V_t)]}$$

OR $$k_2 = \frac{1}{t} \frac{V_0 - V_t}{V_0 \times V_t}$$

Problem (6) In the hydrolysis of ethyl acetate using equal concentration of ester and NaOH, the following results were obtained.

Show that the reaction follows second order kinetics.

Time (min)	0	5	15	25
Vol. of HC1 (ml)	16.0	10.24	6.13	4.32

Show that the reaction follows second order kinetics.

Solution : Given that

$$V_0 = 16 \text{ ml}$$

We know that for basic hydrolysis of ethyl acetate, rate law equation is-

$$k_2 = \frac{1}{t} \frac{V_0 - V_t}{V_0 \times V_t}$$

$$\therefore \text{At, } t = 5 \text{ min, } k_2 = \frac{1}{5} \times \frac{(16-10.24)}{16 \times 10.24} = 0.0070 \text{ ml}^{-1} \text{ min}^{-1}$$

At, t = 15 min, $k_2 = \frac{1}{15} \times \frac{(16-6.13)}{16\times6.13} = 0.0067\ ml^{-1}\ min^{-1}$

At, t = 25 min, $k_2 = \frac{1}{25} \times \frac{(16-4.32)}{16\times4.32} = 0.0067\ ml^{-1}\ min^{-1}$

Since values of k_2 are nearly the same, the reaction follows second order, kinetics.

Example 2 : Thermal decomposition of acetaldehyde

The reaction is represented as-

$CH_3CHO_{(g)} \rightarrow CH_{4(g)} + CO_{(g)}$

Thus the kinetics of the reaction can be studied by the increase in pressure of the gaseous reaction mixture. Let initial pressure of acetaldehyde is P_i & suppose after time 't' its pressure decreases by 'x', which gives CH_4 & CO. Thus at time 't', pressure of CH_4 & CO will be 'x'. Thus total pressure P of reaction mixture will be-

$P = (P_i - x) + x + x$

OR $P = P_i + x$

OR $x = P - Pi$

Now, $a = P_i$ and $a - x = P_i - x$

Hence, the rate equation of second order reaction,

$k_2 = \frac{1}{t}\frac{x}{a(a-x)}$ becomes

$$k_2 = \frac{1}{t}\frac{x}{Pi(Pi-x)}$$

Problem (7) The thermal decomposition of acetaldehyde was studied at 518°C with following result.

Time (sec)	42	73	105	170
$x=(P-P_i)$ mm	34	54	74	114

If initial pressure is 363 mm, show that the reaction follows second order kinetics.

Solution :

Given that, $P_i = 363$ mm

We know that for thermal decomposition of acetaldehyde

$$k_2 = \frac{1}{t}\frac{x}{Pi(Pi-x)}$$

Thus, at t = 42 sec., $k_2 = \frac{1}{42}\frac{34}{363(363-34)} = 6.80 \times 10^{-6}$ mm of $Hg^{-1}s^{-1}$

at t = 73 sec., $k_2 = \frac{1}{73}\frac{54}{363(363-54)} = 6.6 \times 10^{-6}$ mm of $Hg^{-1}s^{-1}$

at t= 105 sec., $k_2 = \frac{1}{105}\frac{74}{363(363-74)} = 6.70 \times 10^{-6}$ mm of $Hg^{-1}s^{-1}$

at t= 170 sec., $k_2 = \frac{1}{170}\frac{34}{363(363-114)} = 7.40 \times 10^{-6}$ mm of $Hg^{-1}s^{-1}$

As the values of are nearly same, the reaction follows second order kinetics.

Example 3 : Reaction between $K_2S_2O_8$ and KI having equal initial concentration.

The reaction is represented as -

$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$

This is an example of second order reaction as the rate of this reaction is depend on the concentration of potassium per sulphate and potassium iodide. The rate of this reaction can be studied by measuring the rate of liberation of iodine by titrating it against the standard hypo solution at different interval of time. The titer values 'V_t' are proportional to the amount of iodine formed and hence the gives the amount of reactant per sulphate consumed (x) at different time intervals of time i.e. $x = V_t$.

The initial concentration 'a' of per sulphate corresponds to titer value at infinite time i.e. $a = V_\infty$.

Hence, the rate equation of second order reaction,

$k_2 = \frac{1}{t}\frac{x}{a(a-x)}$ becomes

$k_2 = \frac{1}{t}\frac{V_t}{V_\infty(V_\infty - V_t)}$

Problem (8) The reaction between $K_2S_2O_8$ & KI was studied at 25^0C with following result. Show that the reaction follows second order kinetics.

Time (min)	10	20	30	∞
Vol. of hypo (ml)	2.3	3.7	4.7	10

Solution

Given that, $V_\infty = 10$ ml

We know $k_2 = \frac{1}{t}\frac{V_t}{V_\infty(V_\infty - V_t)}$

Thus, at t = 10 min., $k_2 = \frac{1}{10}\frac{2.3}{10(10-2.3)} = 2.98 \times 10^{-3}\ ml^{-1}\ min^{-1}$

at t = 20 miu., $k_2 = \frac{1}{20}\frac{3.7}{10(10-3.7)} = 2.94 \times 10^{-3}\ ml^{-1}\ min^{-1}$

at t = 30 min, $k_2 = \frac{1}{30}\frac{4.7}{10(10-4.7)} = 2.96 \times 10^{-3}\ ml^{-1}\ min^{-1}$

As the values of k_2 are nearly same, the reaction follows second order kinetics.

Methods for Determination of Order of Reaction:

The order of reaction cannot calculate from chemical equation. The mechanism of the reaction can only be determined after determining the order of reaction. Therefore to determine the order of reaction, following methods are conveniently used.

1. Integration Method
2. Van't Hoffs Differential Method
3. Equifractional Change Method or Half Life Method
4. Graphical Method
5. Ostwald's Isolation Method

1. Integration Method :

In this method the reaction is carried out actually with known initial concentration 'a' of the reactants. The amount of reactants consumed 'x' after different time intervals't' are determined. Then these values of a, x and t are substituted in first, second & third order rate equations. The equation which gives the satisfactory constant values of velocity constant or rate constant (k) gives the order of the reaction. This method is referred as trial & error method and used for the simple reactions.

2.Van't Hoffs Differential Method:

Vant Hoff in 1884 suggested that the rate of the equation of n^th^ order is proportional to the n^th^ power of concentration.

$$\therefore -\frac{dc}{dt} \alpha C^n$$

$$\text{OR } -\frac{dc}{dt} = k\,C^n \qquad \text{……………..(30)}$$

Where 'C' is the concentration of reacting substance

Taking $\log_{10}$ to both side of equation (30) and simplifying we get,

$$\text{Log}_{10}\left(-\frac{dc}{dt}\right) = \log_{10}k + n\log_{10}C \qquad \text{……………..(31)}$$

Suppose, we start with two experiments having initial concentration C_1 & C_2. Then

$$\log_{10}\left(-\frac{dc_1}{dt}\right) = \log_{10}k + n\log_{10}C_1 \qquad \text{…………….(32)}$$

$$\log_{10}\left(-\frac{dc_2}{dt}\right) = \log_{10}k + n\log_{10}C_2 \qquad \text{…………….(33)}$$

Taking equation (32) - (33), we get

$$\log_{10}\left(-\frac{dc_1}{dt}\right) - \log_{10}\left(-\frac{dc_2}{dt}\right) = n\,(\log_{10}C_1 - \log_{10}C_2)$$

$$\therefore n = \frac{\log 10\left(-\frac{dc_1}{dt}\right) - \log 10\left(-\frac{dc_2}{dt}\right)}{(\log 10C1 - \log 10C2)} \qquad \text{…………….(34)}$$

Using equation (34), the order i.e. value of 'n' can be known from $(\frac{dc_1}{dt})$ & $(\frac{dc_2}{dt})$ values. These values can be measured by plotting 'C' against 't' The slope of the curve gives the value of $\frac{dc}{dt}$.

3. Equifractional Change Method or Half Life Method :

It has been proved that half life of zero order reaction is proportional to initial concentration of reactant. Half life of first order reaction is independent of initial concentration of the reactant & inversely proportional to initial concentration for second order & so on. If 't' is the time required for completion of half of the reaction i.e. half life of n* order reaction, then in general we can write,

$$t \propto \frac{1}{a^{n-1}} \qquad \text{……………..(35)}$$

Let, t_1 & t_2 are the times of half life or equifractional change when initial concentrations are a_1 & a_2 respectively. Then equation (35) becomes,

$$t_1 \propto \frac{1}{{a_1}^{n-1}} \qquad \text{……………..(36)}$$

$$\& \qquad t_2 \propto \frac{1}{{a_2}^{n-1}} \qquad \text{……………..(37)}$$

From equation (36) &(37) we get,

$$\frac{t_2}{t_1} = \frac{a_1^{(n-1)}}{a_2^{(n-1)}} \qquad \text{………………..(38)}$$

$$\left(\frac{a_1}{a_2}\right)^{(n-1)}$$

Taking logarithum to both sides of equation (38) and simplifying, we get,

$$\log_{10}\left(\frac{t_2}{t_1}\right) = (n-1)\log_{10}\left(\frac{a_1}{a_2}\right)$$

OR $$(n-1) = \frac{\log_{10}\left(\frac{t_2}{t_1}\right)}{\log_{10}\left(\frac{a_1}{a_2}\right)}$$

OR $$(n-1) = \frac{\log_{10}t_2 - \log_{10}t_1}{\log_{10}a_1 - \log_{10}a_2}$$

OR $$n = 1 + \frac{\log_{10}t_2 - \log_{10}t_1}{\log_{10}a_1 - \log_{10}a_2} \qquad \text{……………..(39)}$$

From this equation (39) we can determine the order of reaction 'n' by knowing the a_1, a_2, t_1 and t_2.

4. Graphical Method :

If amount of reactant decomposed (x) is plotted against time 't' then slope of the graph gives value of $\frac{dx}{dt}$. We can easily determine $\frac{dx}{dt}$ at any time from the graph shown in figure 6.6(A) by drawing tangent at the point i.e.

$$\tan\theta = \frac{dx}{dt} = \frac{AB}{BC}$$

Number of such $\frac{dx}{dt}$ values are determined at different points.

We know, if 'a' is the initial concentration & 'x' is the amount of reactant decomposed in time 't' then,

$\frac{dx}{dt} = k\,(a-x)$ for first order reaction

$\frac{dx}{dt} = k\,(a-x)^2$ for second order reaction

$\frac{dx}{dt} = k\,(a-x)^3$ for third order reaction

Thus, if the plot of $\frac{dx}{dt}$ against (a-x) is straight line, then the reaction is first order. If the plot of $\frac{dx}{dt}$ against $(a-x)^2$ is a straight line then the reaction is of second order. If the plot $\frac{dx}{dt}$ against $(a-x)^3$ is a straight line, then the reaction if of third order reaction as shown in figure 6.6(B).

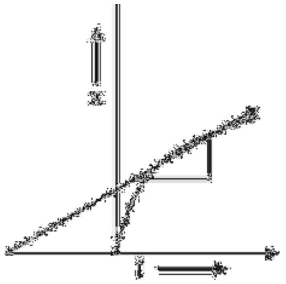

Fig. 6.6(A)

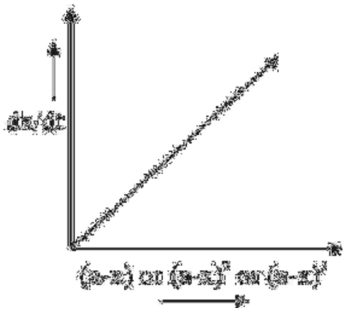

Fig. 6.6(B)

5. Ostwald's Isolation Method :

In this method all the reactants except one are taken in large excess, so that their concentration remains constant throughout this change. Thus the order of the reaction is determined with respect to that isolated reactant which is not taken in large excess. The experiment is repeated by isolating each reactant in turn. The total order of the reaction will be given by the sum of the order of reaction w.r.t. different reactants.

Let the reaction as- n_1 A + n_2 B + n_3 C → product

rate = $\frac{dx}{dt} = k\, C_A^{n_1}.\, C_B^{n_2}.\, C_C^{n_3}$

In the first experiment, the reactants B and C are taken in large excess and the order of reaction is determined w.r.t. A, which gives order = n_1. Then, take A and C in large excess and the order of reaction is determined w.r.t. B, which gives order = n_2. Now, take A and B in large excess and the order of reaction is determined w.r.t. C, which gives order = n_3.

Total order of reaction (n)= $n_1 + n_2 + n_3$.

Problems (7) In Hambly's experiment following results were obtained.

Time (sec)	0	72	157	312
(a-x) mol/dm^3	0.0916	0.0656	0.0512	0.0348

Find the order of reaction

Solution : Given that at t = 0, (a - x) ≡ a = 0.0916, As the concentration at various time intervals (a - x) are given we use integration method,

Thus, for first order reaction, the values of rate constant k_1 are given by using equation

$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$

At, t = 72 min, $k_1 = \frac{2.303}{72} \log_{10} \frac{0.0916}{0.0656} = 0.00462\ \text{min}^{-1}$

At, t = 157 min, $k_1 = \frac{2.303}{157} \log_{10} \frac{0.0916}{0.0512} = 0.00370\ \text{min}^{-1}$

At, t = 312 min, $k_1 = \frac{2.303}{312} \log_{10} \frac{0.0916}{0.0348} = 0.00308\ \text{min}^{-1}$

As k_1 values are not constant the reaction is not first order.

Now, for second order reaction, the values of rate constant k_2 hi are given by using equation,

$k_2 = \frac{1}{t}\frac{x}{a\times(a-x)}$ $dm^3\ mol^{-1}$

At, t = 72 min, $k_2 = \frac{1}{72}\times\frac{0.026}{0.0916\times0.0656} = 0.0601 dm^3 mol^{-1}\ min^{-1}$

At, t = 157 min, $k_2 = \frac{1}{157}\times\frac{0.0568}{0.0916\times0.0512} = 0.0548 dm^3 mol^{-1}\ min^{-1}$

At, t = 312 min, $k_2 = \frac{1}{312}\times\frac{0.0568}{0.0916\times0.0348} = 0.0571 dm^3 mol^{-1}\ min^{-1}$

As k_2 values are nearly constant, the reaction is of second order.

Problem (8) The study of decomposition of phosphine gave the following data-

Pressure (mm)	707	79	37.5
Half life period (sec)	84	84	84

What is the order of reaction?

Solution : We know that for first order reaction the half life time is independent of initial concentration (pressure). $t_{1/2} = \frac{2.303}{k_1}$ x 0.3010 $= \frac{0.693}{k_1}$ = Constant

Hence, this reaction is first order.

Problem (9) As a certain temperature, the half life periods for the catalytic decomposition of ammonia were found to be -

Pressure (mm)	50	100	200
Half life period (sec)	3.52	1.82	1.00

Find out the order of reaction?

Solution : We know that using half life die order of reaction can be determine by equation

$n = 1 + \frac{\log_{10}t_2 - \log_{10}t_1}{\log_{10}a_1 - \log_{10}a_2}$

Thus, i) For, $a_1 = 50$, $t_1 = 3.52$ and $a_2 = 100$, $t_2 = 1.82$

$\therefore n = 1 + \frac{\log_{10}1.82 - \log_{10}3.52}{\log_{10}50 - \log_{10}100}$

$= 1.88 \approx 2$

ii) For, $a_1 = 100$, $t_1 = 1.82$ and $a_2 = 200$, $t_2 = 1.00$

$\therefore n = 1 + \frac{\log_{10}1.00 - \log_{10}1.82}{\log_{10}100 - \log_{10}200}$

$= 1.95 \approx 2$

Thus the order is two

Problem (10) From the work of L.T. Reicher on action of bromine on fumaric acid, the following data was obtained.

Ist Expt.	IInd Expt.

t (min)	Concentration	t (min)	concentration
0	8.87	0	3.81
95	7.87	132	3.51

Find out the order.

Solution : For Ist Experiment

Let, mean concentration is $C_2 = \frac{8.87+7.87}{2} = 8.37$

$$\& \ \frac{-dc_1}{dt} = -\left(\frac{7.87-8.87}{95-0}\right) = 0.0106$$

For IInd Experiment

Let, mean concentration is $C_2 = \frac{3.81+3.51}{2} = 3.66$

$$\& \ \frac{-dc_2}{dt} = -\left(\frac{3.51-3.81}{132-0}\right) = 0.00227$$

We know, $n = \frac{log_{10}\frac{-dc_1}{dt} - log_{10}\frac{-dc_2}{dt}}{log_{10}C_1 - log_{10}C_2}$

$$= \frac{log_{10}0.0106 - log_{10}0.00227}{log_{10}8.37 - log_{10}3.66} = 1.62 \approx 2$$

Hence the reaction is second order.

Effect of Temperature on Reaction Rates

It is observed that as the temperature of chemical reaction increases, the rate or velocity of chemical reaction increases. Reactions which are very slow at ordinary temperature become fast or even explosive at higher temperature with increase in temperature, the rates of all reaction do not increase to same extent. In homogeneous reactions, rate is doubled or tripled for each 10°C rise of temperature.

This increase in the reaction rate with temperature is expressed in the form of temperature co-efficient. Definition-*'The ratio of rate constants of a reaction at two different temperatures separated by 10°C' is called as temperature co-efficient.*

Generally the two temperatures are taken as 25°C and 35°C.

$\therefore$ Temperature Co-efficient $= \frac{k_{35^0C}}{k_{25^0C}} = 2$ to 3

OR Temperature Co-efficient $= \frac{k_{(t+10)^0C}}{k_{t^0C}}$

Where, k_t → Rate constant at t° C

$k_{(t+10)}$ → Rate constant at (t + 10)°C

The Increase in rate of reaction with temperature means that the reaction has a positive temperature coefficient. For homogeneous gaseous reaction, the value of temperature co-efficient is 2 to 3. Thus with 10°C rise of temperature, specific reaction rate becomes double or triple.

Example :

i) The temperature coefficient for the dissociation of HI is 1.8

$2HI \rightleftharpoons H_2 + I_2$

ii) The temperature coefficient for the reaction of methyl iodide with sodium ethaoxide is 2.9.

$CH_3I + C_2H_5ONa \longrightarrow CH_3O\ C_2H_5 + NaI$

Arrhenius Equation:

To explain the increase in the rate of reaction with increase in temperature, Arrhenius (Nobel prize 1903) has put forward the following empirical equation.

$$k = A\, e^{-\frac{Ea}{RT}} \qquad \text{…………(40)}$$

Where, A = Arrhenius constant (Frequency factor or pre-exponential factor)

R = Gas constant 8.314 J $K^{-1}mol^{-1}$

T = Temperature (K).

E_a= Energy of activation.

Taking logarithm on both sides of equation (40) we get,

$$\log_e k = \log_e\left(A\, e^{-\frac{Ea}{RT}}\right)$$

OR $\log_e k = \log_e A + \log_e e^{-\frac{Ea}{RT}}$

$\log_e k = \log_e A - Ea/RT$ ($\log_e e=1$)

$2.303\log_{10} k = 2.303\log_{10} A - Ea/RT$ ($\log_e x=2.303\log_e x$)

Divide 2.303 on both side, we get

OR $$\log_{10} k = \log_{10} A - \frac{Ea}{2.303RT} \qquad \text{……………(41)}$$

OR $$\log_{10} k = \left(-\frac{Ea}{2.303R}\right)\frac{1}{T} + \log_{10} A$$

This in the form of y = m x + C

Thus plot of $\log_{10}k$ versus $\frac{1}{T}$ gives a straight line with slope $\frac{Ea}{2.303R}$ and intercept $\log_{10} A$ Thus we determined the energy of activation of a reaction, from the slope of the line shown in figure 6.7.

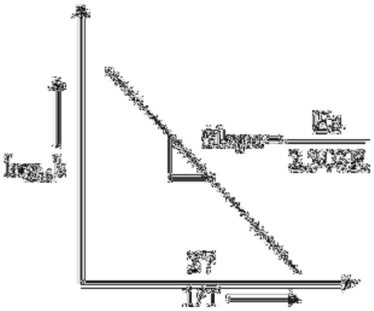

Fig.6.7 Plot of $\log_{10}k$ versus 1/T

Concept of Activation Energy :

According to collision theory, the rate of a reaction is proportional to the total number of collisions taking place between the reactant molecules. However, it is observed that all collisions are not effective. The collision between only those molecules is effective or fruitful which possess certain minimum amount of energy known as *threshold energy* which is equal to or greater than the activation energy. Thus, before the reaction occurs, molecules must be activated i.e. they possess threshold energy.

'The activation energy is the minimum energy which the molecules must absorb to go into activated state, before the reaction can take place.'

Activated state and activation energy is shown in the energy profile diagram in figure 6.8.

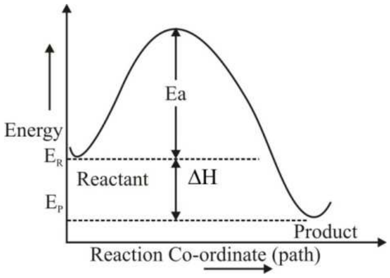

Fig.6.8 Plot of reaction rate versus energy

Thus activation energy exists an energy barrier between reactants and products. If the reactant molecules can cross this energy barrier, they will convert into products. The reactant molecules can cross the energy barrier only when they possess the minimum energy which is equals to or greater than activation energy E_a.

Therefore, the activation energy can be defined as 'It is the minimum energy possess by reactant molecules which is equals to or greater than activation energy E_a required to cross the energy barrier and convert into products'.

Determination of energy of activation by using Arrhenius equation at two different temperatures:

We have logarithmic form of Arrhenius equation as-

$$\log_{10} k = \log_{10} A - \frac{Ea}{2.303RT} \qquad \text{from equation (1)}$$

Consider T_1 and T_2 are two temperatures at which constants are k_1 and k_2 then

$$\log_{10} k_1 = \log_{10} A - \frac{Ea}{2.303RT} \qquad \text{................(42)}$$

$$\log_{10} k_2 = \log_{10} A - \frac{Ea}{2.303RT_2} \qquad \text{................(43)}$$

Subtracting equation (42) from (43), we have

$$\log_{10} k_2 - \log_{10} k_1 = \left(\log_{10} A - \frac{Ea}{2.303RT_2}\right) - \left(\log_{10} A - \frac{Ea}{2.303RT}\right)$$

OR $$\log_{10} k_2 - \log_{10} k_1 = \left(\frac{Ea}{2.303RT_1} - \frac{Ea}{2.303RT_2}\right)$$

OR $$\log_{10} \frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

OR $$\log_{10} \frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad \text{...............(44)}$$

Thus by knowing the values of T_1, T_2, $k_1$and k_2 the activation energy calculated.

Problem (11) Trichloroacetic acid in aniline solvent decomposes to give chloroform & carbon dioxide. The rate constant for this first order reaction is 4.0 x 10^{-5} min^{-1} & at 25°C & 8.0 x 10^{-4} min^{-1} at 45°C. Calculate the energy of activation for this reaction. (R= 8.314 J K$_{-}$ $_{1}$mol^{-1})

Solution Given that

$k_1 = 4.0 \times 10^{-5}$, $k_2 = 8.0 \times 10^{-4}$
T_1= 25 +273 , T_1 = 45 + 273
= 298 K =318 K
R = 8.314Jk^{-1}mor^{-1} E_a = ?

We know that from equ (3 8)

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

$$\log\frac{8.0\times10^{-4}}{4.0\times10^{-5}} = \frac{Ea}{2.303\times8.314}\left(\frac{318-298}{318\times298}\right)$$

∴ E_a = 118.03 k j mol^{-1}

Problem (12) The value of rate constant for the decomposition of nitrogen peroxide is 3.46 x 10^{-5} min^{-1} & at 25°C & 4.87 x 10^{-3} mm^{-1} at 65°C. Calculate the energy of activation for this reaction. (R= 8.314 J K^{-1}mol^{-1})

Solution : Given that

$k_1 = 3.46 \times 10^{-5}$, k_2 = 4.87 X 10^{-3}
T_1= 25 +273, T_2 = 65 + 273
= 298 K =338 K
R= 8.314 Jk^{-1}mol^{-1} E_a =?

We know that from equation (38)

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

$$\log\frac{4.87\times10^{-3}}{3.46\times10^{-5}} = \frac{Ea}{2.303\times8.314}\left(\frac{338-298}{338\times298}\right)$$

∴ E_a = 103.584 k J mol^{-1}

Problem (13) Benzene diazomium chloride decomposes in presence of water according to first order Kinetics. If the velocity constant at 25°C is 2.8 x 10^{-3} min^{-1} & the activation energy is 49.74 k J mol^{-1}, find the velocity constant at 35°C. (R= 8.314 J K^{-1}mol^{-1})

Solution :

Given that
$k_1 = 2.8 \times 10^{-3}$, k_2 = ?
T_1 = 25 + 273, T_2 = 35 + 273
= 298 K = 308 K
R= 8.314J K^{-1}mol^{-1} E_a = 49.74 k J mol^{-1}

We know that from equ (38)

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

$$\therefore \log\frac{K_2}{2.8\times10^{-3}}=\frac{49.74\times10^3}{2.303\times8.314}\left(\frac{308-298}{308\times298}\right)$$

$$\therefore K_2 = 5.37 \text{ x } 10^{-3} \text{ min}^{-1}$$

Problem (14) For a given reaction at 25°C, rate constant doubles when temperature is increased by 10°C. Calculate the energy of activation for this reaction.
(R= 8.314 J $K^{-1}mol^{-1}$)

Solution :
Given that

When, $T_1 = 25 + 273 = 298K$, $k_1 = k$
$T_2 = 35 + 273 = 308K$, $k_2 = 2k$
$R = 8.314J\ K^{-1}mol^{-1}$ $E_a = ?$

We know that from equ (38)

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

$$\therefore \log\frac{2k}{k}=\frac{Ea}{2.303\times8.314}\left(\frac{308-298}{308\times298}\right)$$

$$\therefore Ea = 53.2414 \text{ k J mol}^{-1}$$

Problem (15) : The activation energy of the change

$$NH_4CNO \xrightarrow{27\ ^{O}C} NH_2CONH_2$$

Ammonium cyanate urea is 23.2 Kcal. The value of A is 4.27 x 10 ^{12}lit/mol/sec. Calculate rate constant k of the reaction.

Solution : According to Arrhenius equation,

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

Given: A =4.27 x 10 ^{12}lit/mol/sec,
R = ideal gas constant = 1.987 Cal
& Ea = 23.2 Kcal = 23200 Cal.
& T = 273+27 = 300 K

Putting these values in the above equation,
We get,

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

$$\log_{10}k = \log_{10} (4.27\text{x}10^{12}) - \frac{23200}{2.303\ X\ 1.987\ X\ 300}$$

$$= \log(4.27) + 12 \ - \ (23200\ /1372.81)$$

$$= 0.6304 + 12 \ - \ (16.89)$$

$$= 12.6304 - 16.89$$

$$\log_{10}k = -5.7404$$

Taking antilog,

k = Anti.(-5.7404)

= 5.500×10^{-5}

EXERCISE

FILL IN THE BLANKS

1. The rate of reaction _________ on increase the concentration of reactants.
2. The hydrolysis of methyl acetate catalyzed by base is _________ order kinetics
3. The total number of molecules taking part in the reaction is called as _________
4. The ratio of rate constant of a reaction at two different temperature separated by 10° is called as_________
5. The minimum energy possesses by reactant molecules required to cross the energy barrier and convert into products is called as_________

CHOOSE THE CORRECT ALTERNATIVES

1. The rate of reaction $\frac{dx}{dt}$= k $[A]^a[B]^a$ for which the order of reaction is

   a) a+b b) a-b c)a d) b
2. Decomposition of H_2O_2 is a reaction of

   a) First order b) Second order c) Third order d) Zero order
3. The acid catalyzed hydrolysis of methyl acetate is

   a) First order reaction b) Second order reaction

   c) Third order reaction d) Zero order reaction
4. The unit of rate constant for a second order reaction is

   a) mol $dm^{-3}s^{-1}$ b) dm_{-3} mol^{-1} s^{-1}

   c) dm^3 $mol^{-1}s^{-1}$ d) s^{-1}.
5. The reaction A+B → Product in which when concentration of A is doubled, the rate is doubled, when concentration of B is doubled the rate of the reaction is unchanged. The order of reaction is

   a) Second order b) Third order

   c) Zero order d) First order
6. If 'a' is the initial concentration of reactant, then time required for completion of definite fraction ($t_{1/2}$) of the second order reaction is proportional to

   a) $\frac{1}{a}$ b) a c) Constant d) $\frac{1}{a^2}$
7. The minimum energy possess by reactant molecules required to cross the energy barrier and convert into products is called as

   a) zero point energy b) threshold energy

   c) activation energy d) both b or c

ANSWER THE FOLLOWING QUESTIONS IN ONE SENTENCE

1. What is the unit of rate constant for a first order reaction? (Ans. = s^{-1})
2. What is the unit of rate constant for a zero order reaction? (Ans. = mol $dm^{-3}s^{-1}$)
3. Define velocity or speed of reaction?
4. What is meant half life of reaction?
5. Define molecularity of reaction?

ANSWER THE FOLLOWING QUESTIONS IN DETAIL.

1. Define
   i) Pseudo-unimolecular reaction
   ii) Order of reaction.
   iii) Energy of activation
   iv) Half life of reaction
   v) Rate of reaction.
   vi) Zero order Reaction
   vii) Temperature coefficient
   viii) Molecularity of reaction
2. Discuses the effect of temperature on the rate of reaction.
3. Explain zero order Reaction with suitable example.
4. How order of reaction is determine by Ostwald's isolation method?
5. Show that the time for half change of first order reaction is constant.
6. Derive the rate of reaction for first order reaction.
7. Show that the second order reaction half life period its initially proportional to initial concatenation of reactant.
8. Describe graphical method for the determination of order of the reaction.
9. Explain van't Hoff differential method for the determination of order of reaction.
10. Describe half change or equifractional change method for the determination of order of reaction.
11. What is zero order reaction? Derive the equation of rate constant of zero order reaction.
12. Describe the effect of temperature on the rate of reaction

Problems :

13. In the study of kinetics of saponification of ethyl acetate using equal concentrations of ester and alkali, following data was obtained. Show that this reaction follows second order kinetics.

Time (min)	0	4.9	10.0	23.7
Vol. of std acid (ml.)	47.6	38.9	32.6	22.8

14. From following data show that the decomposition of H_2O_2 is first order reaction.

Time (sec)	0	100	200
Vol. of $KMnO_4$ (dm^3)xl0^5	22.8	13.38	8.28

15. Methyl acetate was subjected to hydrolysis in 0.1 N HC1 at 30°C. 2 ml of the reaction mixture was withdrawn and titrated against the standard NaOH at definite time intervals. The following data was obtained. Show that this reaction follows first order kinetics.

Time (min)	0	75	119	183	∞
Vol. of std alkali (ml.)	19.24	24.20	26.60	29.32	42.03

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