CHEMICAL KINETICS

Chemical kinetics is the branch of physical chemistry that deals with the study of rate of reactions and the factors governing rate of reaction.

Important applications of kinetic studies are given below :
1. In determination of rates of reactions and factors governing rates.
2. In predicting the conditions for maintaining the reaction rate
3. In determination of yield of reaction in certain time period.
4. In calculating the time required for completion of a reaction.
5. In deciding the mechanism of a reaction.

1. TYPES OF REACTIONS

On the basis of reaction rates, the chemical reactions have been classified into the following three groups:-

(i) Very fast or instantaneous reactions : These reactions occur at a very fast rate. Generally these reactions involve ionic species and known as ionic reactions.
These reactions take about 10^{-14} seconds for completion.

Examples : (i) $AgNO_3 + NaCl \rightarrow \underset{(PPt.)}{AgCl} + NaNO_3$ (Precipitation reaction)

(ii) $\underset{(acid)}{HCl} + \underset{(base)}{NaOH} \rightarrow \underset{(salt)}{NaCl} + H_2O$ (Neutralization reaction)

(ii) Moderate reaction : These type of reactions proceed with a measurable rates at normal temperature. In this a large number of bonds have to be broken in reactants molecules and a large number of new bonds have to be formed in product molecules. Mostly these reactions are molecular in nature.
Examples :
(i) Decomposition of H_2O_2 : $2H_2O_2 \rightarrow 2H_2O + O_2$
(ii) Decomposition of N_2O_5 : $2N_2O_5 \rightarrow 2N_2O_4 + O_2$
(iii) Hydrolysis of ester : $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$
(iv) Reaction of NO with chlorine : $NO + Cl_2 \rightarrow NOCl_2$
(v) Inversion of cane sugar in aqueous solution : $C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6+H_{12}O_6}$

(vi) $2FeCl_3(aq.) + SnCl_2 \rightarrow 2FeCl_2(aq.) + SnCl_4(aq.)$
(vii) $NO_2 + CO \rightarrow NO + CO_2$
(viii) Decolourisation of acidified potassium permanganate with sodium oxalate.

(iii) Very slow reactions : These reactions are extremely slow and take months together to show any measurable change. The rate of such type of reactions are very slow. So, it is also very difficult to determine the rate of these reactions.
Examples :
(i) Rusting of iron : $Fe_2O_3 + xH_2O \rightarrow \underset{\text{Hydrated ferric oxide (Rust)}}{Fe_2O_3.xH_2O}$

(ii) Reaction between H_2 and O_2 to form H_2O at ordinary temperature in absence of catalyst.
(iii) Reaction of atmospheric H_2S on basic lead acetate paint.

White basic lead acetate paint $\xrightarrow[H_2S]{\text{atmospheric}}$ Blackening of paint very slowly

(due to formation of Pbs)

Note : The chemical reactions can be slowed down or speed up by changing conditions under which they occur. e.g. $CO + 2H_2 \xrightarrow[\text{temp.}]{\text{At room}} CH_3OH$ (very slow reaction)
The reaction can be speeded up by maintaining temperature around 400°C, pressure about 300 atm and using a catalyst containing ZnO and Cr_2O_3.

2. RATE OF REACTION

The change in concentration of either reactant or product per unit time.

Formula : $r = \frac{dc}{dt}$

dc is change in concentration of reactant or product in a small time interval dt.

Example : $N_2 + 3H_2 \rightarrow 2NH_3$

(i) Rate of formation of ammonia $= + \frac{d[NH_3]}{dt}$

(ii) Rate of disappearance of nitrogen $= -\frac{d[N_2]}{dt}$

(iii) Rate of disappearance of hydrogen $= -\frac{d[H_2]}{dt}$

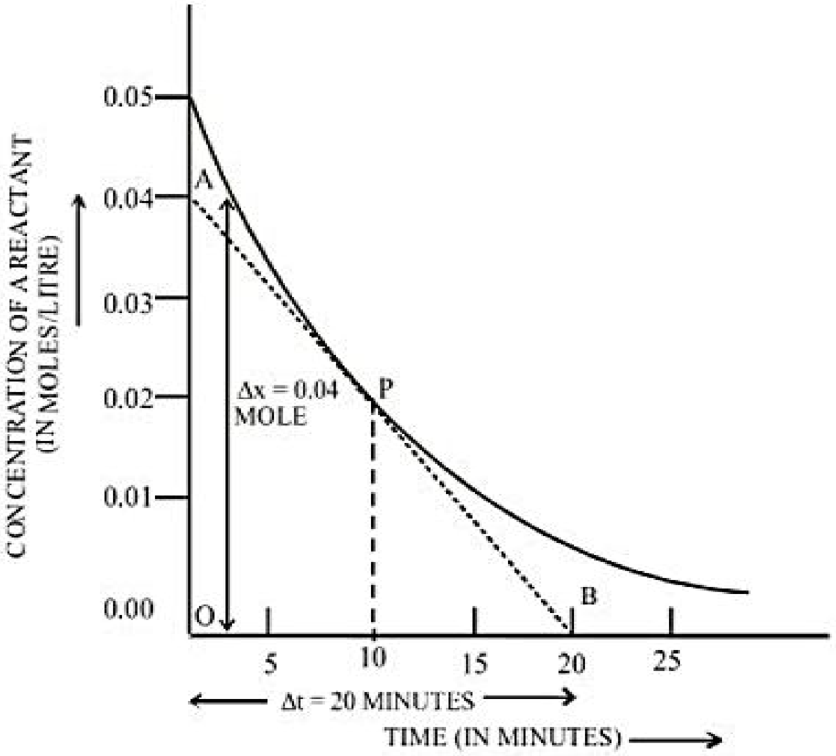
$$\text{Rate of reaction} = +\frac{1}{2}\frac{d[NH_3]}{dt} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$$

2.1 AVERAGE RATE AND INSTANTANEOUS RATE OF REACTION

A difficulty arises in stating the rate of reaction as above. This is because according to the Law of Mass Action, the rate of reaction depends upon the molar concentrations of reactants which keep on decreasing with the time (while those of the products keep on increasing). Therefore, the rate of reaction does not remain constant throughout.
Thus the rate of reaction as defined above is the 'average rate of reaction' during the time interval chosen.
To know the rate of reaction at any instant of time during the course of a reaction, we introduce the term 'instantaneous rate of reaction' which may be defined as follows :
The rate of reaction at any instant of time is the rate of change of concentration (i.e. change of concentration per unit time) of any one of the reactants or products at that particular instant of time.
To express the instantaneous rate of reaction, as small interval of time (dt) is chosen at that particular instant of time during which the rate of reaction is supposed to be almost constant. Suppose the small change in concentration is dx in the small interval of time dt. Then the rate of reaction at that instant is given by $\frac{dx}{dt}$.

2.2 Measurement of the Rate of Reaction

In order to measure the rate of a reaction, the progress of the reaction is followed by studying the concentration of one of the reactants or products at different intervals of time. The most common practice to do so is to withdraw small amount of the reaction mixture (2 cm^3 or 5 cm^3) at different intervals of time, cool it down immediately to nearly 0° C to arrest the reaction (called freezing the reaction) and then find out the concentration of the reactant or the product by suitable method usually by titration against a suitable reagent. However, this method is not preferred when some observable property like volume, pressure, optical rotation etc. changes with time and can be observed directly at different intervals of time without stopping the reaction. It is important to mention that except concentration, all other factors (like temperature etc.) which affect the rate of the reaction are kept constant during the kinetic study of the reaction.



If concentration of one of the reactants is studied at different intervals of time and these values are plotted against the corresponding times, a graph of the type shown in figure may be obtained.

2.3 Calculation of instantaneous rate of reaction

To know the rate of the reaction at any time t, a tangent is drawn to the curve at the point corresponding to that time figure and it is extended on either side so as to cut the axes, say at the points A and B. Then

$$\text{Rate of reaction} = \frac{\text{Change in the concentration}}{\text{Time}}$$

$$= \frac{\Delta x}{\Delta t} = \frac{OA}{OB} \text{ Slope of the tangent}$$

Thus the slope of the tangent gives the rate of reaction.

For example, from the (figure) in the present case, at time t = 10 minutes, $\Delta x = 0.04$ mole and $\Delta t = 20$ minutes $= 20 \times 60 = 1200$ seconds, therefore, rate of reaction at the end of 10 minutes will be $0.04/1200 = 3.33 \times 10^{-5}$ mol L^{-1} s^{-1}.

2.4 Calculation of the average rate of reaction :

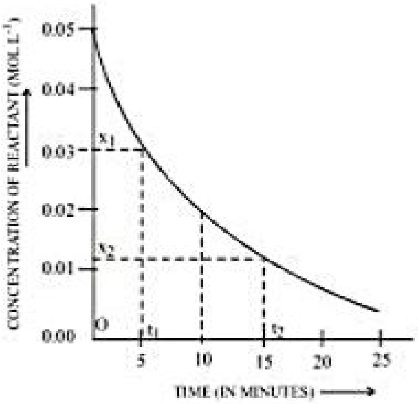
To calculate the average rate of reaction between any two instants of time say t_1 and t_2, the corresponding concentrations x_1 and x_2 are noted from the graph. Then

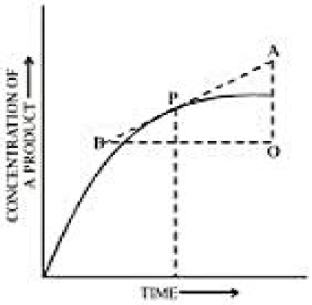
$$\text{Average rate of reaction} = \frac{x_2 - x_1}{t_2 - t_1}$$

For example, from the (figure) between the time interval 5 to 15 minutes,

$$\text{Average rate } = \frac{0.03 - 0.012}{15 - 5} = \frac{0.018}{10} = 0.0018 \text{ and mol L}^{-1}\text{ min}^{-1}$$

If concentration of one of the products is plotted against time, the type of curve obtained and the rate of reaction at any instant of time are calculated as shown in the figure.





Illustration

1. Decomposition of N_2O_5 is expressed by the equation,

$$N_2O_5 \longrightarrow 2NO_2 + ½O_2$$

If in a certain time interval, rate of decomposition of N_2O_5 is 1.8×10^{-3} mol litre^{-1} min^{-1}, what will be the rates of formation of NO_2 and O_2 during the same interval ?

Sol. The rate expression for the decomposition of N_2O_5 is

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = 2 \times \frac{\Delta[O_2]}{\Delta t}$$

So $$\frac{\Delta[NO_2]}{\Delta t} = 2\frac{\Delta[N_2O_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3}$$
$$= 3.6 \times 10^{-3} \text{ mol litre}^{-1}\text{ min}^{-1}$$

and $$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3}$$
$$= 0.9 \times 10^{-3} \text{ mol litre}^{-1}\text{ min}^{-1}$$

[Magnitude of rate is always positive and hence = $\frac{\Delta[N_2O_5]}{\Delta t}$ is taken positive.

2. A gaseous reaction : $2A(g) + B(g) \rightarrow 2C(g)$,

Show a decrease in pressure from 120 mm to 100 mm in 10 minutes. The rate of appearance of C is

(A) 2 mm/min (B) 4 mm/min (C) 10 mm/min (D) 12 mm/min.

Ans. (B)

Sol. Suppose 2p is the pressure of C after 10 min.

Fall in pressure of A = 2p ; Fall in pressure of B = p

Total fall in pressure = (2p + p) – 2p = p = 20 mm

Pressure of C = 2p = 40 mm

Rate of appearance of C = 40/10 = 4 mm/min

3. For the reaction : $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Given : $\frac{d[NO]}{dt} = 3.6 \times 10^{-3}\ \text{mol}\ l^{-1}\ s^{-1}$

Calculate : (i) rate of disappearance of ammonia (ii) rate of formation of water

Sol. From the eqn. it is clear that

Rate $= -\frac{1}{4}\frac{d[NH_3]}{dt} = \frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$ Thus : $-\frac{1}{4}\frac{d[NH_3]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$

or $-\frac{d[NH_3]}{dt} = \frac{d[NO_2]}{dt} = 3.6 \times 10^{-3}\ \text{mol}\ l^{-1}\ s^{-1}$ Also $\frac{1}{4}.\frac{d[NO]}{dt} = \frac{1}{6}.\frac{d[H_2O]}{dt}$

$$\frac{3}{2}.\frac{d[NO]}{dt} = \frac{d[H_2O]}{dt}$$

$$\frac{3}{2} \times 3.6 \times 10^{-3} = \frac{d[H_2O]}{dt}$$

$$5.4 \times 10^{-3} = \frac{d[H_2O]}{dt}$$

Exercise

In a reaction the concentration of a reactant (A) changes from 0.200 mol litre^{-1} to 0.150 mol litre^{-1} in 10 minutes. What is the average rate of reaction during this interval?

Ans. 0.005 mol litre^{-1} min^{-1}

2.5 Factors Affecting the Rate of Reaction

(i) **Concentration :** According to law of mass action greater is the conc. of the reactants, the more rapidly the reaction proceeds.

(ii) **Pressure (Gaseous reaction) :** On increasing the pressure, volume decreases and conc. increases and hence the rate increases.

(iii) **Temperature :** It is generally observed that rise in temperature increases the reaction rate. It has been found that rate is either doubled or tripled for every 10°C rise in temperature.

(iv) **Nature of the reactants :** The rate depends upon specific bonds involved and hence on the nature of reactants.

(v) **Surface area of the reactants :** In heterogeneous reactions, more powered is the form of reactants, more is the rate. [as more active centres are provided]

(vi) **Catalyst :** Affects the rate immensely.

3. LAW OF MASS ACTION, RATE LAW AND RATE CONSTANT

3.1 Law of mass action :

(Guldberg and Wage 1864) This law relates rate of reaction with active mass or molar concentration of reactants. According to this law, "At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reactions."

Active mass = Molar concentration of the substance

$$= \frac{\text{Number of gram mole of the substance}}{\text{Volume in litres}} = \frac{W/M}{V} = \frac{n}{V}$$

Where W = mass of the substance, M is the molecular mass in grams, 'n' is the number of g moles and V is volume in litre.

Consider the following general reaction, $m_1A_1 + m_2A_2 + m_3A_3 \rightarrow \text{Products}$

$$\text{Rate of reaction} \propto [A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}$$

3.2 Rate law :

The actual relationship between the concentration of reacting species and the reaction rate is determined experimentally and is given by the expression called rate law.

For any hypothetical reaction, $aA + bB \rightarrow cC + dD$

Rate law expression may be, $\text{rate} = k[A]^m[B]^n$

Where m and n are constant numbers or the powers of the concentrations of the reactants A and B respectively on which the rate of reaction depends.

(i) Rate of chemical reaction is directly proportional to the concentration of the reactants.

(ii) The rate law represents the experimentally observed rate of reaction, which depends upon the slowest step of the reaction.

(iii) Rate law cannot be deduced from the relationship for a given equation. It can be found by experiment only.

3.3 Rate constant :

Consider a simple reaction, $A \rightarrow B$. If C_A is the molar concentration or active mass of A at a particular instant, then, $\frac{dx}{dt} \propto C_A$ or $\frac{dx}{dt} = kC_A$; Where k is a **proportionality constant,** called **velocity constant** or **rate constant** or **specific rate of a reaction.**

At a fixed temperature, if $C_A = 1$, then $\text{Rate} = \frac{dx}{dt} = k$

"Rate of a reaction at unit concentration of reactants is called rate constant."

(i) The value of rate constant depends on, Nature of reactant, Temperature and Catalyst

(It is independent on concentration of the reactants)

(ii) Unit of rate constant : $\left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \sec^{-1}$ or $= \left[\frac{\text{mol}}{\text{litre}}\right]^{1-n} \times \sec^{-1}$

Where n = order of reaction

3.4 Difference between Rate law and Law of mass action

Rate law	*Law of mass action*
It is an experimentally observed law.	It is a theoretical law.
It depends on the concentration terms on which the rate of reaction actually depends	It is based upon the stoichiometry of the equation
Example for the reaction, $aA + bB \rightarrow$ Product Rate $= k\,[A]^m\,[B]^n$	Example for the reaction, $aA + bB \rightarrow$ Products Rate $= k\,[A]^a\,[B]^b$

3.5 Difference between Rate of reaction and Rate constant

Rate of reaction	*Rate constant*
It is the speed with which reactants are converted into products.	It is proportionality constant.
It is measured as the rate of decrease of the concentration of reactants or the rate of increase of concentration of products with time.	It is equal to rate of reaction when the concentration of each of the reactants is unity.
It depends upon the initial concentration of the reactants.	It is independent of the initial concentration of the reactants. It has a constant value at fixed temperature.

4. ORDER OF REACTION

The order of a reaction may be defined as the sum of the powers to which conc. terms must be raised in an experimentally determined rate equation :

For the reaction : $aA + bB \rightarrow$ product

Experimental rate equation : $r = k\,[A]^m\,[B]^n$

order with respect to A = m

order with respect to B = n

Total order = m + n

m and n may or may not be equal to a and b.

Note : Order may be zero, fractional, integer or negative.

Example :

Reaction	**Experimental rate equation**	**order**
$H_2 + Cl_2 \rightarrow 2HCl$	$r = k$	zero
$H_2 + Br_2 \rightarrow 2HBr$	$r = k\,[H_2]\,[Br_2]^{1/2}$	one and half
$H_2 + I_2 \rightarrow 2HI$	$r = k\,[H_2]\,[I_2]$	two

Examples of fractional order reaction

Reaction : $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$
$v = k\,[CO]^2\,[Cl_2]^{1/2}$, order = 2.5

Reaction : $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$
$v = k\,[COCl_2]^{3/2}$, order = 1.5

Illustration

1. The dimensions of rate constant of a second order reaction involves :
(A) time and concentration (B) neither time nor concentration
(C) time only (D) concentration only

Ans. (A)

Sol. $$k = \frac{\text{Rate}}{[A]^2} = \frac{\text{mol}\,L^{-1}S^{-1}}{(\text{mol}\,L^{-1})^2} = \frac{s^{-1}}{\text{mol}\,L^{-1}} = (\text{mol}\;L^{-1})^{-1}\,s^{-1}$$

2. The rate constant of a reaction has same units as the rate of reaction. The reaction is of
(A) zero order (B) first order (C) second order (D) none of these

Ans. (A)

Sol. For a zero order reaction, $r = k[A]^o$. Thus the units of k are the same as that of rate of reaction.

3. On which of the following factors, the rate constant does not depend ?
(A) Temperature (B) Concentration (C) Presence of catalyst (D) Nature of reactants

Ans. (A)

Sol. Rate constant is independent of the conc. of the reactants.

Exercise

The rate constant of n^{th} order has units
(A) $\text{litre}^{1-n}\text{mol}^{1-n}\text{sec}^{-1}$ (B) $\text{mol}^{1-n}\text{litre}^{1-n}\text{sec}$ (C) $\text{mol}^{1-n^2}\ \text{litre}^{n^2}\ \text{sec}^{-1}$ (D) $\text{mol}^{1-n}\text{litre}^{n-1}\text{sec}^{-1}$

Ans. (D)

5. MOLECULARITY

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction. The reaction can be unimolecular when one reacting species is involved, for example, decomposition of ammonium nitrite.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Bimolecular reactions involve collision between two species, for example, dissociation of hydrogen iodine.

$$2HI \longrightarrow H_2 + I_2$$

Trimolecular reactions involve simultaneous collision between three reacting species, for example,

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

Molecularity of a reaction is :

(i) Always a whole number (not zero) and never a fraction.

(ii) The probability that more than three molecules can collide and react simultaneously is very small. Hence, the molecularity greater than three is not observed.

Thus, from the above discussion we can conclude the following:

(a) Order of a reaction is an experimentally determined quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

(b) Order is defined to elementary as well as complex reactions whereas molecularity is defined only for elementary reactions. For complex reaction molecularity has no meaning.

(c) For an elementary reaction order and molecularity are same.

Example

$N_2O_4 \rightarrow 2NO_2$ ...... unimolecular

$H_2 + I_2 \rightarrow 2HI$ ...... bimolecular

$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$ ...... trimolecular

Note : If the reaction takes place in two or more steps then the overall molecularity of the reaction is monitored by the slow or rate determining step.

5.1 Difference Between Molecularity and Order of Reaction

Molecularity	Order of Reaction
1. Molecularity can neither be zero nor fractional	Order of a reaction can be zero, fractional or integer
2. It is independent of pressure and temperature	It depends upon pressure and temperature
3. It is assigned for each step of mechanism separately	It is assigned for overall reaction as well as each step of reaction.
4. It is the number of molecules of reactants concentration terms taking part in elementary step of a reaction.	It is sum of power raised to the concentration of the rate expression.
5. Molecularity of reaction cannot be negative	Order of a reaction may have negative value.

6. INTEGRATED RATE LAWS FOR DIFFERENT ORDER OF REACTIONS

Differential rate law (rate = $\frac{dx}{dt}$ = K.[Conc.]^n) expressed the dependance of rate of reaction on concentration of reactants. Upon integrating the differential rate law, we get integrated rate law expression which is a concentration-time equation from which we can calculate concentration at any time (t) or the time required for an initial concentration to reach any particular value. The integrated rate law expression for different reactions have been discussed below :

6.1 Zero order reaction :

Zero order reaction : Reaction whose rate is not affected by concentration or in which the concentration of reactant do not change with time are said to be of zero order reaction.

Calculation of Rate Constant : Let us take the reaction

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

conc. at t = 0 a 0

$$\frac{dx}{dt} = k[A]^0, \quad \frac{dx}{dt} = k; \qquad dx = k\,dt$$

$$\text{or, } \int_0^x dx = \int_0^t k\,dt$$

conc. of A at, time t = 0 is $[A]_0 = a$ (say)

Integrated rate equation, $k = \frac{x}{t}$; The rate of reaction is independent of the concentration of the reacting substance.

Half life period of zero order reaction : When $t = t_{1/2}$; $x = \frac{a}{2}$; $t_{1/2} = \frac{a}{2k}$ or $t_{1/2} \propto a$; The half life period is directly proportional to the initial concentration of the reactants.

Unit of Rate constant : = $\frac{\text{mole}}{\text{lit.sec.}}$; Unit of rate of reaction = Unit of rate constant.

Characteristics of zero order reactions:

(i) Concentration of reactant decreases linearly with time.

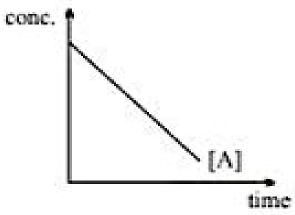
(ii) Unit of k is **mol l^{-1} time^{-1}**.

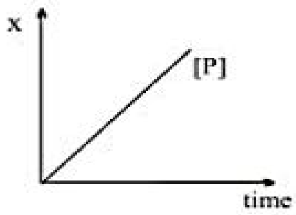
(iii) Time required for the 100% completion of reaction is $\frac{[A]_0}{k}$

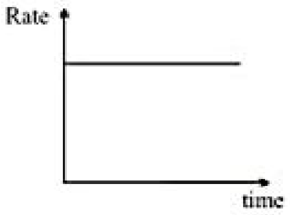
(iv) $t_{1/2} = \frac{[A]_0}{2k}$

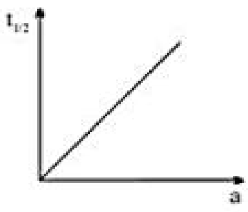
(v) Zero order reaction must be a complex reaction

(vi) Graph related with zero order reactions.









Examples :

(i) $H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$ (ii) $N_2O(g) \xrightarrow[\text{Surface}]{\text{hot Pt.}} N_2(g) + \frac{1}{2} O_2(g)$

(iii) $2NH_3(g) \xrightarrow[\text{surface}]{\text{Mo or W}} N_2 + 3H_2$ (iv) Enzyme catalysed reaction

Substrate(S) $\xrightarrow{\text{Enzyme(E)}}$ product (P).

Illustration

The rate constant for a zero order reaction is 2×10^{-2} mol $L^{-1}sec^{-1}$, if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.

Ans. 0.75 M

Sol. $2 \times 10^{-2} \times 25 = [A_0 - 0.25]$

$0.5 = A_0 - 0.25 \qquad \therefore A_0 = 0.75$

Exercise

A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

Ans. 1.2 hr

6.2 First order reactions

For the reaction : $A \longrightarrow$ Products

Rate of reaction $\propto [A]$.

For the reaction : $2A \longrightarrow$ Products

Rate of reaction $\propto [A]$ only.

For the reaction : $A + B \longrightarrow$ Products

Rate of reaction $\propto [A]$ or $[B]$ only.

Let us consider the simplest case viz.

$A \longrightarrow$ Products

Suppose we start with 'a' moles per litre of the reactant A. After time t, suppose x moles per litre of it, have decomposed. Therefore, the concentration of A after time t = (a – x) moles per litre. Then according to Law of Mass Action.

Rate of reaction $\propto (a - x)$

$$\text{i.e.,} \quad \frac{dx}{dt} \propto (a - x) \quad \text{or} \quad \frac{dx}{dt} = k(a - x) \qquad \text{.....(1)}$$

where k is called the rate constant or the specific reaction rate for the reaction of the first order. The expression for the rate constant k may be derived as follows :

Equation (1) may be rewritten in the form

$$\frac{dx}{a - x} = kdt \qquad \text{.....(2)}$$

Integrating equation (2), we get $\int \frac{dx}{a-x} = \int kdt$

or $$k = \frac{1}{t} \ln \frac{a}{a-x} \qquad .....(3)$$

or $$k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad .....(4)$$

Equation (4) is sometimes written in another form which is obtained as follows :

If the initial concentration is $[A]_0$ and the concentration after time t is [A], then putting $a = [A]_0$ and $(a - x) = [A]$ equation (iv) becomes

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \qquad ..... (5)$$

Further, putting $a = [A]_0$ and $(a - x) = [A]$ in eqn. (3), we get

$$kt = \ln \frac{[A]_0}{[A]}$$

which can be written in the exponential form as

$$\frac{[A]_0}{[A]} = e^{kt} \quad \text{or} \quad \frac{[A]}{[A]_0} = e^{-kt}$$

$$\text{or} \qquad [A] = [A]_0\, e^{-kt} \qquad ..... (6)$$

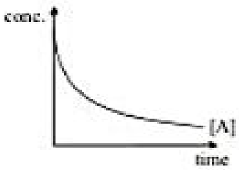
Characteristics of First Order Reaction :

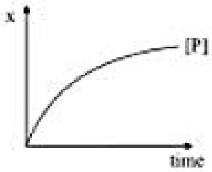
(i) Unit of rate constant is time^{-1}.

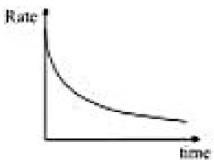
(ii) $t_{1/2} = \frac{0.693}{k}$ (Half-life)

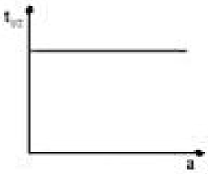
(iii) **log (a – x)** v/s **t** is a straight line with slope $-\frac{k}{2.303}$.

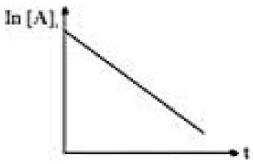
(iv) Graph related with first order reactions.











Examples:

(i) Radioactive disintegration is a first order reaction.

(ii) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Inversion}]{H^+ \text{ catalysed hydrolysis}} C_6H_{12}O_6 + C_6H_{12}O_6.$

(glucose) (fructose)

(iii) Mineral acid catalyzed hydrolysis of esters.

(iv) Decomposition of H_2O_2 in aqueous solution.

Illustration

1. A reaction which is of first order with respect to reactant '*A*' has a rate constant of 6.0 min^{-1}. If we start with $[A] = 0.5 \text{ mol L}^{-1}$, when will $[A]$ reach the value of 0.05 mol L^{-1}.

(A) 0.384 min (B) 0.15 min (C) 3 min (D) 3.84 min

Ans. (A)

Sol. $t = \dfrac{2.303}{k} \log \dfrac{a}{a-x}$

Or $t = \dfrac{2.303}{6} \log \dfrac{0.5}{0.05} = \dfrac{2.303}{6} \log 10 = \dfrac{2.303}{6} = 0.384$ min.

2. The reaction

$N_2O_5 \text{ (in } CCl_4) \rightarrow 2\,NO_2 + \frac{1}{2}\ O_2\text{ (g)}$ is first order in N_2O_5 with rate constant equal to $6.2 \times 10^{-4} \text{ s}^{-1}$.

What is the value of rate of reaction when $[N_2O_5] = 1.25 \text{ mol L}^{-1}$?

(A) $7.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (B) $6.35 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

(C) $5.15 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ (D) $3.85 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

Ans. **(A)**

Sol. Reaction rate $= k\,[N_2O_5] = 6.2 \times 10^{-4}.\ 1.25 = 7.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

3. A first order reaction is 20 % completed in 10 minutes. Calculate the time taken for the reaction to go to 80 % completion.

Sol. Applying first order equation,

$$k = \frac{2.303}{t} \log_{10} \frac{100}{(100-20)} = \frac{2.303}{10} \log_{10} \frac{100}{80} = 0.0223 \text{ min}^{-1}$$

Again applying first order equation,

$$t = \frac{2.303}{k} \log_{10} \frac{100}{(100-80)} = \frac{2.303}{0.0223} \log_{10} \frac{100}{20} = 72.18 \text{ min}$$

4. The rate of the first order reaction X → products is $7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$. What will be the value of rate constant when the concentration of X is 0.5 mol L^{-1}?

(A) $3.75 \times 10^{-4} \text{ s}^{-1}$ (B) $2.5 \times 10^{-5} \text{ s}^{-1}$ (C) $1.5 \times 10^{-3} \text{ s}^{-1}$ (D) $8.0 \times 10^{-4} \text{ s}^{-1}$

Ans. **(B)**

Sol. Rate of reaction $= 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$

$= \dfrac{7.5 \times 10^{-4}}{60} \text{ mol L}^{-1} \text{ s}^{-1} = 1.25 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$

Rate of reaction = k [concentration. of reactant X]

Or $k = \dfrac{1.25 \times 10^{-5}}{0.5} = 2.5 \times 10^{-5} s^{-1}$

Exercise

In a first order reaction, the concentration of the reactants is reduced to 25% in 1 hour. The half life period of the reaction is

(A) $2h$ (B) $4h$ (C) $\frac{1}{2}h$ (D) $\frac{1}{4}h$

Ans. (C)

6.3 Second Order Reaction :

(i) For the given reaction.

$nA \longrightarrow$ products

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

Integrated rate equation $k = \frac{1}{t}\cdot\frac{x}{a(a-x)}$ or $kt = \frac{1}{a-x} - \frac{1}{a}$.

Is the above rate constant w.r.t. reaction or disappearance.

(ii) For the given reaction.

	A +	B $\longrightarrow$ products
at time t = 0	a	b
at time t = t	a − x	b − x

differential rate equation $\frac{dx}{dt} = k\,(a-x)\,(b-x)$.

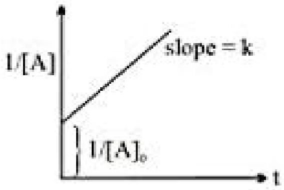
Integrated rate equation $k = \frac{2.303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}$

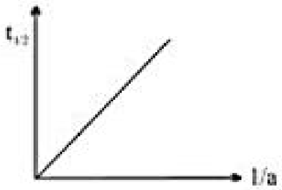
Characteristics of Second Order Reaction :

(i) Unit of rate constant L mol^{-1} $time^{-1}$.

(ii) $t_{1/2} \propto a^{-1}$ (In general $t_{1/2} \propto a^{(1-n)}$; n = order of reactions).

(iii) 2^{nd} order reaction conforms to first order when one of the reactant is in excess.





Examples:

(i) Saponification (hydrolysis of esters catalysed with alkali).

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

(ii) Hydrogenation of ethane $C_2H_4 + H_2 \xrightarrow{100°C} C_2H_6$.

(iii) $2\,O_3 \longrightarrow 3\,O_2$.

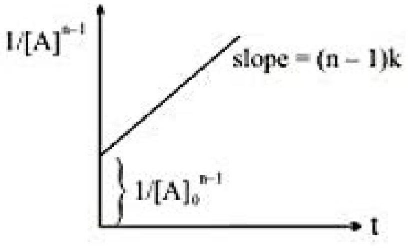
6.4 nth Order reaction

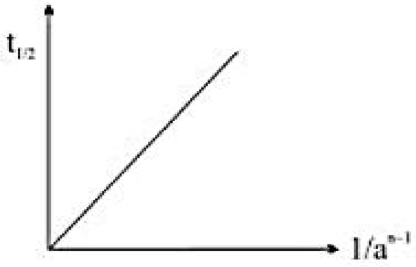
Consider the reaction

$nA \rightarrow \text{Product}$

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

$$t_{1/2} = \frac{1}{k(n-1)}\cdot\left[\frac{2^{n-1}-1}{a^{n-1}}\right]$$





What is the 'k' involved in the rate law rate constant w.r.t. reaction or w.r.t. disappearance

7. METHODS OF DETERMINATION OF ORDER OF REACTIONS

A few methods commonly used are given below :

(i) **Hit & Trial Method** : It is method of using integrated rate equations, where the experimental values of a, x & t are put into these equations. One which gives a constant value of k for different sets of a, x & t correspond to the order of the reaction.

(ii) **Graphical Method** :
(i) A plot of $\log(a-x)$ versus 't' gives a straight line for the First order reaction.
(ii) A plot of $(a-x)^{-(n-1)}$ versus 't' gives a straight line for any reaction of the order n except $n = 1$.

(iii) **Half Life Method** : The half life of nth order reaction is given by $t_{1/2} \propto 1/a^{n-1}$
By experimental observation of the dependence of half life on initial concentration we can determine n, the order of reaction. $n = 1 + \dfrac{\log(t_{1/2})_2 - \log(t_{1/2})_1}{\log(a_0)_1 - \log(a_0)_2}$.

(iv) **Initial rate method.** Initial rate method is used to determine the order or reaction in cases where more than one reactant is used. It involves the determination of the order of different reactants separately. A series of experiments are performed in which concentration of one particular reactant is varied whereas conc. of other reactants are kept constant. In each experiment the initial rate is determined from the plot of conc. vs. time, e.g., if conc. of A is doubled, and initial rate of reaction is also doubled, order of reaction w.r.t A is 1.

Illustration

1. The following result have been obtained during kinetic studies of the reaction.

$$A + B \longrightarrow C + D$$

Experiment	[A]/M	[B]/M	Initial rate of formation of $D/M\sec^{-1}$
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

(i) Determine the rate law of above reaction

(ii) Find the rate constant of above reaction in $(\text{mole/L})^{1-n}\sec^{-1}$

Sol. $r_1 =$ $6\times10^{-3} = k\,[A].\,[B]$

$6\times10^{-3} = k\,[0.1]^m\,[0.1]^n$ ....(i)

$r_2 =$ $7.2\times10^{-2} = k\,(0.3)^m\,(0.2)^n$ ....(ii)

$r_3 =$ $2.88\times10^{-1} = k\,(0.3)^m\,(0.4)^n$ ....(iii)

$r_4 =$ $2.40\times10^{-2} = k\,(0.4)^m\,(0.1)^n$ ....(iv)

eg. (iii)/(ii) $\dfrac{2.88}{0.72} = 4 = \left(\dfrac{0.4}{0.2}\right)^n = 2^n \Rightarrow n = 2$

doing (iv)/(i) $\dfrac{2.40}{0.6} = (4)^m$

$\Rightarrow m = 1$

rate law $= -\dfrac{d[A]}{dt} = \mathbf{k\,[A]^1\,[B]^2}$; $\mathbf{k = \dfrac{6\times10^{-3}}{10^{-3}} = 6\ M^{-2}\ sec^{-1}}$

2. The catalytic decomposition of N_2O by gold at 900°C and at an initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

(i) What is the order of the reaction?

(ii) Calculate the rate constant.

(iii) How much of N_2O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?

[2021013194]

Ans. (i) first order (ii) $k = 1.308\times10^{-2}\ \text{min}^{-1}$ (iii) 73%

Sol. $N_2O \longrightarrow \text{Product}$

$$K = \frac{1}{t}\ \ln\frac{A_0}{A_t}$$

$$= \frac{1}{53}\ \ln\frac{A_0}{A_{0/2}} = \frac{\ln 2}{53}$$

$$= \frac{1}{100}\ln\frac{100}{27}$$

order = 1st order

$$K = \frac{\ln 2}{53}$$

$$X\% = \frac{600 \times 73}{100} = 6 \times 73 \text{ mmHg}$$

Exercise

The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

Ans. Zero order

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8. CALCULATION OF FIRST ORDER RATE CONSTANT USING DIFFERENT PARAMETERS

(I) In terms of pressure

$A(g) \longrightarrow B(g) + C(g)$

$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_T}$$

where

P_0 = Initial partial pressure of A

P_T = Total pressure of gaseous system at time 't'

(II) Decomposition of H_2O_2 in aqueous solution (In terms of volume of reagent $KMnO_4$ required in titration against H_2O_2).

$H_2O_2 \longrightarrow H_2O + O_2$

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

where

V_0 = Volume of $KMnO_4$ required in titration of H_2O_2 sample taken initially

V_t = Volume of $KMnO_4$ required in titration of same volume of H_2O_2 sample at time 't'.

(III) Acid catalysed hydrolysis of ester(In terms of volume of reagent NaOH required in titration)

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

NaOH reacts with H^+ and CH_3COOH.

$$k = \frac{2.303}{t} \log \left(\frac{V_\infty - V_0}{V_\infty - V_t} \right)$$

where

V_0 = volume of NaOH required in titration when reacted with H^+ (at start)

V_t = volume of NaOH required in titration when reacted with H^+ and CH_3COOH at time 't'.

V_∞ = volume of NaOH required in titration when reaction is completed

(IV) Inversion of cane sugar (In terms of angle of rotation)

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Inversion}]{H^+ \text{ catalysed hydrolysis}} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}.$$

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

where

r_0 = initial angle of rotation of the sample

r_t = angle of rotation after time t

r_∞ = angle of rotation after completion of reaction

(V) Oxide layer formation:

$$k = \frac{1}{t}\ln\frac{\tau_{max}}{\tau_{max} - \tau}$$

where

τ_{max} = Thickness of oxide layer after ∞ times

τ = Thickness of oxide layer at time 't'.

(VI) Bacterial Growth:

$$k = \frac{1}{t}\ln\frac{a+x}{a}$$

Illustration

1. From the following data show that decomposition of H_2O_2 in aqueous solution is first order.

Time (in minutes)	0	10	20
Volume (in c.c. of $KMnO_4$)	22.8	13.3	8.25

Ans. First order

Sol. $$K = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

$$K_1 = \frac{2.303}{t}\log\frac{22.8}{13.3} = 0.05$$

$$K_2 = \frac{2.303}{t}\log\frac{22.8}{8.25} = 0.05$$

∴ It is first order reaction

2. The following data were obtained in experiment on inversion of cane sugar.

Time (minutes)	0	60	120	180	360	∞
Angle of rotation (degree)	+13.1	+ 11.6	+ 10.2	+9.0	+5.87	–3.8

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

Ans. 966 min

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

$K_1 = \frac{2.303}{60}\log\frac{13.1+3.8}{11.6+3.8} = 0.00155$

$K_2 = 0.001566$ $(K_1 = K_2)$

$\therefore$ It is first order reaction

$t = \frac{2.303}{0.001566}\log\frac{13.1+3.8}{0+3.8}$

$t \approx 966$ min

3. The reaction given below, rate constant for disappearance of A is $7.48 \times 10^{-3}\ \text{sec}^{-1}$. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec.

$$2A(g) \longrightarrow 4B(g) + C(g)$$

Ans. 0.180 atm, 47.69 sec

Sol. (i) $2A \rightarrow 4B + C$

$P^0 - 2x \quad\quad 4x \quad x$

$t = \frac{2.303}{7.48\times10^{-3}}\log\frac{0.1}{0.1-0.3} = 47.815$

(ii) $\frac{100\times7.48\times10^{-3}}{2.303} = \log\frac{0.1}{y}$

$y = 0.04732$

$a - 2x = 0.1 - 2x$

$x = 0.02634$

$P_t = P^0 + 3x = 0.18$ atm

4. In this case we have

$A \xrightarrow{1^{st}\ \text{order}} B + C$

Time	t	∞
Total pressure of A + B+C	P_2	P_3

Find k.

Ans. $k = \frac{1}{t} ln\frac{P_3}{2(P_3 - P_2)}$

Sol. $A \rightarrow B + C$

At infinite P_3 it means initially P of A is $P_{3/2}$ which converts into B and C $\left[\frac{P_3}{2} + \frac{P_3}{2} = P_3\right]$

$a_0 = P_{3/2}$

$A \rightarrow B + C$

$$\frac{P_3}{2}-x \quad x \quad x$$

$$\frac{P_3}{2}+x=P_2$$

$$x=P_2-\frac{P_3}{2}$$

$$k=\frac{1}{t}\ \ln\frac{P_3/2}{P_3/2-P_2+\dfrac{P_3}{2}}=\frac{1}{t}\ \ln\frac{P_3}{2(P_3-P_2)}$$

5. At 100°C the gaseous reaction $A \longrightarrow 2B + C$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction and (d) the half life period of the reaction?

Given : $ln\left(\frac{90}{47}\right)=0.65$

Ans. (a) 90 mm, (b) 47 mm, (c) 6.49×10^{-2} per minutes, (d) 10.677 min.

Sol.

	A	$\longrightarrow$ 2B	+ C	
$t = 0$	P_0			
$t = 10$	$P_0 - x$	$2x$	x	$176 = P_0 + 2x$
$t = \infty$	0	$2P_0$	P_0	$270 = 3P_0$

(a) $P_0=\frac{270}{3}=90$

$x=\frac{176-90}{2}=43$

(c) $K=\frac{1}{10\times 60}\ \ln\frac{90}{90\times 43}$

(d) $t_{1/2}=\frac{\ln 2}{K}$

Exercise

The reaction $AsH_3(g) \longrightarrow As(s)+\frac{3}{2}H_2(g)$ was followed at constant volume at 310°C by measuring the gas pressure at intervals Show from the following figures that reaction is of first order.

Time (in hrs)	0	5	7.5	10
Total pressure (in mm)	758	827	856	882

Ans. First order

9. ELEMENTARY PARALLEL PATH REACTIONS

$$\begin{tikzcd}[row sep=small] & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$

Let the initial concentration of A be$[A]_0$ and let after time t, the concentrations of A,B and C be [A],[B] and [C], respectively. It is obvious that

$$[A]_0 = [A] + [B] + [C]$$

The differential rate experisions are

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

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

The overall-rate of disappearance of A is given as

$$-\frac{d[A]}{dt} = [k_1 + k_2]\,[A]$$

$$[\,k_1 + k_2]\,t = ln\,\frac{[A]_0}{[A]_t}$$

$$\%\text{ of B in products} = \frac{k_1}{k_1 + k_2} \times 100$$

$$\%\text{ of C in products} = \frac{k_2}{k_1 + k_2} \times 100$$

Some examples of parallel reactions

(i) $$\begin{tikzcd}[row sep=small] & C_6H_6 + N_2 + HCl + CH_3CHO \\ C_6H_5N = NCl + CH_3CH_2OH \arrow[ur] \arrow[dr] & \\ & C_6H_6\ OC_2H_5 + N_2HCl \end{tikzcd}$$

(ii) $$\begin{tikzcd}[row sep=small] & CH_3CH_3OH + KBr \\ CH_3CH\ _2Br + KOH \arrow[ur] \arrow[dr] & \\ & CH_2 = CH_2\ + KBr + H_2O \end{tikzcd}$$

Illustration

1. Consider the reaction,

A, B and C all are optically active compound . If optical rotation per unit concentration of A, B and C are 60°, –72°, 42° and initial concentration of A is 2 M then select write statement (s).

(A) Solution will be optically active and dextro after very long time
(B) Solution will be optically active and levo after very long time
(C) Half life of reaction is 15 min
(D) After 75% conversion of A into B and C angle of rotation of solution will be 36°.

Ans. (A), (D)

Sol. After very long time concentration of B = $\frac{1}{3}\times 2$

After very long time concentration of C = $\frac{2}{3}\times 2 \Rightarrow \frac{4}{3}$

Angle of rotation after reaction = $\frac{2}{3}\times(-72)+\frac{4}{3}\times 42 \Rightarrow 8°$

$$(t_{1/2})_1=\frac{0.693}{6.93\times10^{-2}}=10\text{ min}$$

$$(t_{1/2})_2=\frac{0.693}{13.86\times10^{-2}}=5\text{ min}$$

$\because k_{\text{overall}}=k_1+k_2$

$$\left(\frac{1}{t_{1/2}}\right)_{\text{overall}}=\left(\frac{1}{t_{1/2}}\right)_1+\left(\frac{1}{t_{1/2}}\right)_2$$

$t_{\text{overall}}=\frac{10}{3}$ min.

After 75% conversion of A into B and C
Concentration of A = 0.5 M

Concentration of B = $\frac{1}{3}\times1.5 \Rightarrow 0.5\text{M}$

Concentration of C = $\frac{2}{3}\times1.5 \Rightarrow 1\text{M}$

$\therefore$ Angle of rotation $=0.5\times60°+42°\times1-72°\times0.5 \Rightarrow 36°$]

2. $$\begin{tikzcd}[row sep=small] & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$ $k_1 = x\ \text{hr}^{-1}; k_1 : k_2 = 1 : 10$. Calculate $\frac{[C]}{[A]}$ after one hour from the start of the reaction. Assuming only A was present in the beginning.

Ans. $\frac{[C]}{[A]} = \frac{10}{11}(e^{11x} - 1)$

Sol. $\frac{k_1}{k_2} = \frac{1}{10}$

$k_1 = x \qquad k_2 = k_1 \times 10 = x \times 10$

$k_1 + k_2 = x + 10\,x = 11\,x$

$$\frac{[B]_t}{[C]_t} = \frac{1}{10} \Rightarrow B_t = \frac{[C_t]}{10}$$

For parallel reaction

$$-\frac{d[A]}{dt} = [k_1 + k_2]\,A$$

$$\ln\frac{[A_0]}{[A_t]} = (k_1 + k_2)\,t$$

$$\ln\frac{[A_t + B_t + C_t]}{A_t} = (k_1 + k_2)\,t$$

$$\ln\frac{\left[A_t + \frac{C_t}{10} + C_t\right]}{A_t} = (k_1 + k_2)\,t \qquad \Rightarrow \qquad \ln\left[1 + \frac{11C_t}{10A_t}\right] = (x + 10x)\,t$$

$$1 + \frac{11C_t}{10A_t} = e^{11x} \qquad \because (t = 1\ \text{hr given})$$

$$\frac{[C_t]}{[A_t]} = (e^{11x} - 1)\,\frac{10}{11}$$

Exercise

For a reaction $$\begin{tikzcd}[row sep=small] & y \\ x \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & z \end{tikzcd}$$, calculate value of ratio, $\frac{[x]_t}{[y]+[z]}$ at any given instant t.

Ans. $\frac{1}{e^{(K_1+K_2)t} - 1}$

10. REVERSIBLE OR OPPOSING REACTIONS

Reversible reactions are these in which products formed converted back into reactants simultaneously.

$$\text{Reactants} \xrightleftharpoons[\text{Backward reactions}]{\text{Forward reactions}} \text{Products}$$

Kinetics of reversible reactions (First order opposed by first order) :

Consider a reversible reaction in which forward and backward reactions follow first order.

$$A \xrightleftharpoons[K_b]{K_f} B$$

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

K_f and K_b are rate constants of forward and backward reactions respectively.

$$\frac{dx}{dt} = K_f[A] - K_b[B]$$

$$\frac{dx}{dt} = K_f[[A]_0 - x] - K_b \cdot x \qquad \text{........(1)}$$

But at equilibrium $\frac{dx}{dt} = 0$; (since concentrations become constant) and x represents $x_{eq.}$ (equilibrium concentration of B).

At equilibrium rate of forward reaction is equal to rate of backward reaction.

$$K_f[[A]_0 - x_{eq.}] = K_b \cdot x_{eq.}$$

or $$x_{eq.} = \frac{K_f[A]_0}{[K_f + K_b]} \qquad \text{.........(2)}$$

Also $$K_b = \frac{K_f[[A]_0 - x_{eq.}]}{x_{eq.}} \qquad \text{.........(3)}$$

Putting values of x_{eq} and K_b in eq. (1)

$$\frac{dx}{dt} = K_f[[A]_0 - x] - \frac{K_f[[A]_0 - x_{eq.}] \cdot x}{x_{eq.}}$$

$$= K_f \cdot [A]_0 - K_f \cdot x - \frac{K_f[A]_0 \cdot x}{x_{eq.}} + K_f \cdot x$$

or, $$\frac{dx}{dt} = \frac{K_f[A]_0}{x_{eq.}}[X_{eq.} - x] \qquad \text{.........(4)}$$

On integrating the equation (4), we get

$$\text{or}\qquad -\ln[x_{eq.} - x] = K_f \frac{[A]_0}{x_{eq.}} \cdot t + C \qquad \text{.........(5)}$$

at $t = 0$, $x = 0$, and $C = -\ln x_{eq.}$

putting value of C in eq. (5)

$$\text{or}\qquad -\ln[x_{eq.} - x] + \ln x_{eq.} = K_f \frac{[A]_0}{x_{eq.}} \cdot t \qquad \text{.........(6)}$$

$$\text{or}\qquad K_f \cdot t \cdot \frac{[A]_0}{x_{eq.}} = \ln\left[\frac{x_{eq.}}{x_{eq.} - x}\right] \qquad \text{.........(7)}$$

From eqs. (2) and (7)

$$\frac{(K_f + K_b)x_{eq.}}{[A]_0} \cdot t \cdot \frac{[A_0]}{x_{eq.}} = \ln\left[\frac{x_{eq.}}{x_{eq.} - x}\right]$$

$$\text{or}\qquad (K_f + K_b) \cdot t = \ln\left[\frac{x_{eq.}}{x_{eq.} - x}\right] \qquad \text{.........(8)}$$

$$\text{or}\qquad (K_f + K_b) \cdot t = 2.303 \log\left[\frac{x_{eq.}}{x_{eq.} - x}\right] \qquad \text{.........(9)}$$

The equilibrium constant of such reversible reactions,

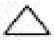
$$K_C = \frac{[B]_{eq.}}{[A]_{eq.}} = \frac{x_{eq.}}{[A_0] - x_{eq.}} = \frac{K_f}{K_b}$$

If $[B]_0$ is not equal to zero, the relation for such reversible reaction shows

$$K_f \cdot t = 2.303 \left[\frac{[B]_0 + x_{eq.}}{[A]_0 + [B]_0}\right] \log\left[\frac{x_{eq.}}{x_{eq.} - x}\right] \qquad \text{.........(10)}$$

Example of reversible reactions :

(i) $H_2 + I_2 \underset{K_b}{\overset{K_f}{\rightleftharpoons}} 2HI$

(ii)  $\underset{K_b}{\overset{K_f}{\rightleftharpoons}} CH_3CH = CH_2$

(iii) $NH_4CNO \underset{K_b}{\overset{K_f}{\rightleftharpoons}} NH_2CONH_2$

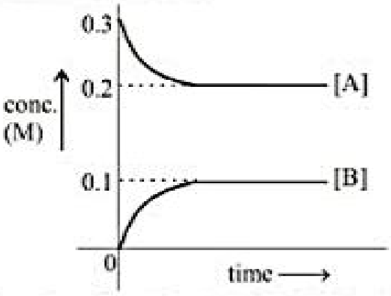
(iv) $CO + NO_2 \underset{K_b}{\overset{K_f}{\rightleftharpoons}} CO_2 + NO$

Illustration

Consider a reversible reaction :

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Which is a first order in both the directions ($k_1 = \frac{1.38}{3} \times 10^{-2}\ \text{min}^{-1}$). The variation in concentration is plotted with time as shown below.



Calculate the time (in minute) at which 25 % of A would be exhausted. [$\ell n\, 2 = 0.69$]

Sol. $k_{eq} = \frac{0.1}{0.2} = \frac{1}{2} = \frac{k_1}{k_2}$

$k_2 = \frac{2}{3} \times 1.38 \times 10^{-2}$

$\ell n \frac{0.1}{0.1 - 0.075} = (k_1 + k_2)\, t$

$2 \times 0.69 = 1.38 \times 10^{-2} \times t$

$t = 100$ min.

11. SEQUENTIAL OR CONSECUTIVE REACTIONS :

In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.

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

Let the initial concentration of A be $[A]_0$ and let after time t, the concentrations of A, B and C be [A], [B] and [C], respectively. It is obvious that

$$[A]_0 = [A] + [B] + [C] \qquad ....(1)$$

Differential Rate Law : The differential rate expressions are

$$-\frac{d[A]}{dt} = k_1[A] \qquad ....(2)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad ....(3)$$

$$\frac{d[C]}{dt} = k_2[B] \qquad ....(4)$$

On integrating equation (2), we get

$$[A] = [A]_0 e^{-k_1t} \qquad ....(5)$$

Substituting [A] from equation (5) into equation (3), we get

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1t} - k_2[B]$$

$$\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1t}$$

Integrated Rate Law : Multiplying the above expression throughout by exp (k_2t), we get

$$\frac{d[B]}{dt} + k_2[B]e^{k_2t} = k_1[A]_0 e^{-(k_1-k_2)t}$$

The left side of the above expression is equal to $d([B]e^{k_2t}) / dt$. Hence, the above expression can written as , $d\{[B]\, e^{k_2t}\} = k_1[A]_0\, e^{-(k_1-k_2)t}\, dt$

Integrating the above expression with [B] = 0 at t = 0, we get

$$[B]e^{k_2t} = k_1[A]_0\left[\frac{e^{-(k_1-k_2)t}}{-(k_1-k_2)} + \frac{1}{k_1-k_2}\right]$$

$$[B] = k_1[A]_0\left[\frac{e^{-k_1t}}{-(k_2-k_1)} + \frac{e^{-k_2t}}{k_1-k_2}\right]$$

$$[B]_t = \frac{k_1[A]_0}{(k_2-k_1)}\left[e^{-k_1t} - e^{-k_2t}\right] \qquad ....(6)$$

Substituting equations (5) and (6) in equation (1), we get

$$[A]_0 = [A]_0 e^{-k_1t} + [A]_0\left(\frac{k_1}{k_2-k_1}\right)(e^{-k_1t} - e^{-k_2t}) + [C]$$

or $$[C] = [A]_0\left[1 - \frac{1}{k_2-k_1}(k_2e^{-k_1t} - k_1e^{-k_2t}\right] \qquad ....(7)$$

Figure (1) Illustrates the general appearance of the variations of concentrations of A, B and C during the progress of the reaction.

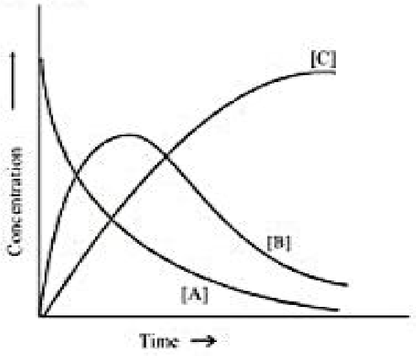


Fig. 1: Typical variations of concentration of A, B and C during the progress of the reaction $A \rightarrow B \rightarrow C$.

In general concentration of A decreases exponentially, the concentration of B initially increases upto a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value $[A]_0$, when all A has changed into C.

Maximum Concentration of B : Equation (6) is

$$[B] = [A]_0 \left(\frac{k_1}{k_2 - k_1}\right)\{e^{-k_1 t} - e^{-k_2 t}\}$$

At the maximum concentration of B, we have

$$\frac{d[B]}{dt} = 0$$

Hence, differentiating equation (6) with respect to t, we get

$$\frac{d[B]}{dt} = [A]_0 \left(\frac{k_1}{k_2 - k_1}\right)\{-k_1 e^{-k_1 t} - k_2 e^{-k_2 t}\} \qquad \text{.......(8)}$$

Equating equation (8) to zero, we get

$$-k_1 e^{-k_1 t_{max}} + k_2 e^{-k_2 t_{max}} = 0$$

or $$\frac{k_1}{k_2} = e^{(k_1 - k_2)t_{max}}$$ or $$\ln\left(\frac{k_1}{k_2}\right) = (k_1 - k_2)t_{max}$$

or $$t_{max} = \frac{1}{k_1 - k_2}\ln\left(\frac{k_1}{k_2}\right) \qquad \text{.......(9)}$$

substituting equation (9) in equation (6), we get

$$[B]_{max} = [A]_0 \left(\frac{k_2}{k_1}\right)^{k_2/(k_1 - k_2)} \qquad \text{.......(10)}$$

Examples of consecutive reactions :

(i) Several radioactive decay

$$Pb \xrightarrow{-\beta} Bi \xrightarrow{-\beta} Po$$

(ii)


$$CH_2-CH_2 \text{ (with O bridging)} \xrightarrow{K_1} (CH_3CHO) \xrightarrow{K_2} CH_4 + CO$$

Illustration

How much time would be required for the B to reach maximum concentration for the reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C. \text{ Given } k_1 = \frac{ln2}{4}, k_2 = \frac{ln2}{2}.$$

Ans. t = 4 min

Sol. $k_1 = 0.173$

$k_2 = 0.3466$

$$t_{max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} = 4 \text{ min}$$

Exercise

For the first order consecutive reactions.

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

the reaction is started with some amount of A. Match the given observation (column I) with the time (column II) related with the above reaction.

Column I **(Observation)**	**Column II** **(Time)**
(A) Rate of formation of C is maximum	(P) At time 't' = $t_{1/2}$ of A (Given $k_2 = 2k_1$)
(B) $[B]_t = [C]_t$	(Q) At time 't' = $\frac{1}{(k_2 - k_1)} ln\left(\frac{k_2}{k_1}\right)$
(C) $[A]_t = [B]_t$	(R) At time 't' when rate of formation of B is maximum
	(S) At time 't' = $\frac{ln\left(\frac{2k_1 - k_2}{k_1}\right)}{k_1 - k_2}$

Ans. (A) P, Q (B) R, P (C) S

12. RATE LAW AND MECHANISM

As already mentioned in the reaction:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

Obeys the following third order kinetics

$$\text{Rate } \alpha\ [NO]^2\ [H_2]$$

The kinetics is not in tune with chemical equation. As the law of mass action suggests each concentration term should be raised to power 2, but this is not supported by experimental facts. Under this condition we are led to believe that the reaction does not occur according to the chemical equation as written. That is the reaction is not elementary but is complicated. In order to explain the observed rate law following mechanism has been proposed.

I $NO + NO \rightleftharpoons N_2O_2$ (fast and reversible)
II $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)
III $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

The step II being the slowest i.e., the rate - determining step (R.D.S.). Note that the rate of formation of N_2 cannot be faster than the rate of formation of N_2O. So, the rate of overall reaction or rate of formation of N_2 will be equal to the rate of step II which according to law of mass action may be given as.

Rate of overall reaction = Rate of step II = $k[N_2O_2][H_2]$
Where k = rate constant of step II

The conc. of the intermediate (N_2O_2) may be evaluated by applying law of mass action upon the equilibrium existing in step I as mentioned below.

$$K_c = \frac{[N_2O_2]}{[NO]^2} \quad \text{or} \quad [N_2O_2] = K_c[NO]^2$$

Putting this in the rate expression, we get

$$\text{Rate} = k.k_c[NO]^2[H_2] = k_{obs}[NO]^2[H_2]$$

Where $k_{obs} = k.k_c$ = observed rate constant of the reaction

$$\text{Rate} \propto [NO]^2[H_2]$$

This is the same rate - law as observed experimentally.

Illustration

1. Rate law for ozone layer depletion is

$$\frac{d[O_3]}{dt} = \frac{K[O_3]^2}{[O_2]}$$

Give the probable mechanism of reaction?

Sol. $O_3 \rightleftharpoons O_2 + O$ (fast reaction)
$O_3 + O \longrightarrow 2O_2$ (slow reaction, rate constant k')
Rate = $k'[O_3][O]$ ....[1]

$$K_c = \frac{[O_2][O]}{[O_3]} \text{ or } [O] = K_c\frac{[O_3]}{[O_2]}, \quad \text{(equilibrium constant } K_c)$$

putting the value in (1)

$$\text{From (1)} \quad \text{Rate} = k'.[O_3].K_c\frac{[O_3]}{[O_2]} = k'.K_c.\frac{[O_3]^2}{[O_2]} = k.\frac{[O_3]^2}{[O_2]}$$

$k = k' \times K_c$.

2. In hypothetical reaction $A_2 + B_2 \longrightarrow 2AB$ follows the mechanism as given below:
$A_2 \rightleftharpoons A + A$ (fast reaction)
$A + B_2 \longrightarrow AB + B$ (slow reaction)
$A + B \longrightarrow AB$ (fast reaction)
Give the rate law and order of reaction.

Sol. Slowest step is rate determining.
Rate = $k[A][B_2]$ ......(1)
Here [A] should be eleminated.

$$K_c = \frac{[A][A]}{[A_2]} = \frac{[A]^2}{[A_2]}$$

$$[A] = K_c^{1/2}[A_2]^{1/2}$$

From (1). Rate $= k K_c^{1/2}[A_2]^{1/2}[B_2]$

$= K[A_2]^{1/2}[B_2]$

Order $= 1 + 1/2 = 3/2$

3. For the formation of phosgene from CO(g) and chlorine,

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$$

The experimentally determined rate equation is,

$$\frac{d[COCl_2]}{dt} = k[CO][Cl_2]^{3/2}$$

Is the following mechanism consistent with the rate equation?

(i) $Cl_2 \rightleftharpoons 2Cl$ (fast)
(ii) $Cl + CO \rightleftharpoons COCl$ (fast)
(iii) $COCl + Cl_2 \rightleftharpoons COCl_2 + Cl$ (slow)

Sol. Multiplying equation (ii) by 2 and adding (i), we get:

$$Cl_2 + 2CO \rightleftharpoons 2COCl$$

$$K = \frac{[COCl]^2}{[Cl_2][CO]^2}$$

$[COCl] = (K)^{1/2}[Cl_2]^{1/2}[CO]$ ...... (i)

Slowest step is rate determining, hence

Rate $= k[COCl][Cl_2]$ ...... (ii)

From (i) and (ii), we get

Rate $= kK^{1/2}[Cl_2]^{1/2}[Cl_2][CO]$

Rate $= k'[Cl_2]^{3/2}[CO]$ $[k' = k.k^{1/2}]$

Thus, rate law is in accordance with the mechanism.

Exercise

For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested:

$2NO \rightleftharpoons N_2O_2$ equilibrium constant K_1 (fast)

$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$ (slow)

$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$ (fast)

Establish the rate law for given reaction.

Ans. $r = K[NO]^2[H_2]$, where $K = k_2 \times K_1$

13. CATALYST

Berzelius used the term catalyst for the first time for the substances which accelerate the rate of chemical reaction. Now the term catalyst has been used for the foreign substances which influence the rate of a reaction and the phenomenon is known as catalysis. Usually two terms are used for catalysis :

Positive Catalysis : The phenomenon in which presence of catalyst accelerates the rate of reaction.

Negative catalysis : The phenomenon in which presence of catalyst retards the rate of reaction. Such substances are also known as inhibitors or negative catalyst.

13.1 Characteristics of Catalyst

(i) A catalyst remains unchanged chemically at the end of reaction, however its physical state may change. e.g. MnO_2 used as catalyst in granular form for the decomposition of $KClO_3$, is left in powder form at the end of reaction.

(ii) A catalyst never initiate a chemical reaction . It simply influences the rate of reaction. **Exception: combination of H_2 and Cl_2 takes place only when moisture (catalyst) is present.**

(iii) A small quantity of catalyst is sufficient to influence the rate of reaction e.g. 1 g atom of Platinum is sufficient to catalyse 108 litre of H_2O_2 decomposition.

(iv) A catalyst does not influence the equilibrium constant of reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward & backward reactions equally.

(v) A catalyst normally does not alter the nature of products in a reaction. However some exceptions are found to this characteristic.

(a) $HCOOH \xrightarrow{AlCl_3} H_2O + CO,$ $\quad HCOOH \xrightarrow{Cu} H_2 + CO_2$

(b) $CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O,$ $\quad CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$

$CO + H_2 \xrightarrow{Cu} HCHO$

It may therefore be concluded that in some cases nature of products formed depends upon the presence and nature of catalyst used.

(vi) A catalyst does not make reaction more exothermic

(vii) Catalyst's activity is more or less specific : A catalyst for one reaction is not necessary to catalyse the another reaction.

13.2 Types of Catalysis

(i) **Homogeneous catalysis :** The reaction in which catalyst and the reactants have same phase. It includes two types.

(a) **Gaseous phase catalysis :** When reactants and catalyst are in gaseous phase e.g. chamber process for H_2SO_4.

$$2SO_2(g) + O_2(g) \xrightarrow[catalyst]{NO} 2SO_3(g)$$

(b) **Solution phase catalysis :** The reactions in which catalyst and reactants are in solution phase or liquid phase of miscible nature.

$$\underset{ester}{RCOOR'_{(l)}} + H_2O_{(l)} \xrightarrow{H^+} RCOOH + R'OH$$

(ii) **Heterogeneous catalysis :** The reactions in which catalyst and reactants form phase ≥ 2.

(a) **Solid-liquid catalysis :** $\left.\begin{array}{l}\text{Reactant : Liquid}\\ \text{Catalyst : Solid}\end{array}\right\}\text{Immiscible}$

$$2H_2O_{2(l)} \xrightarrow[\text{Catalyst}]{MnO_{2(s)}} 2H_2O + O_2$$

(b) **Liquid-Liquid catalysis :** $\left.\begin{array}{l}\text{Reactant : Liquid}\\ \text{Catalyst : Liquid}\end{array}\right\}\text{Immiscible}$

$$2H_2O_{2(l)} \xrightarrow[\text{catalyst}]{Hg(l)} 2H_2O + O_2$$

(c) **Solid-gas catalysis :** $\left.\begin{array}{l}\text{Reactant : gases}\\ \text{Catalyst : solid}\end{array}\right\}\text{Immiscible}$

Two aspects of solid catalyst are more significant, one is activity and the other is selectivity. Activity is the ability of catalyst to accelerate chemical reactions; the degree of acceleration can be as high as 10^{10} times in certain reactions. Selectivity is the ability of catalyst to direct reaction to yield particular reaction (excluding others). For example , n-heptane selectivity gives toluene in presence of Pt catalyst . Similarly,
$CH_3-CH=CH_2+O_2$ give $CH_2=CHCHO$ selectivity over Bismuth molybdate catalyst.

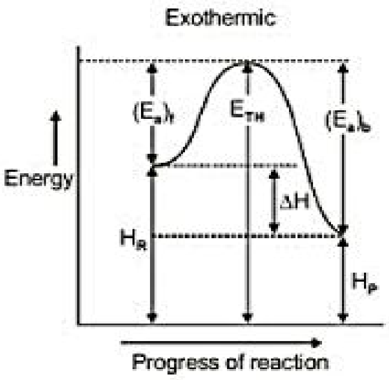
14. ARRHENIUS THEORY

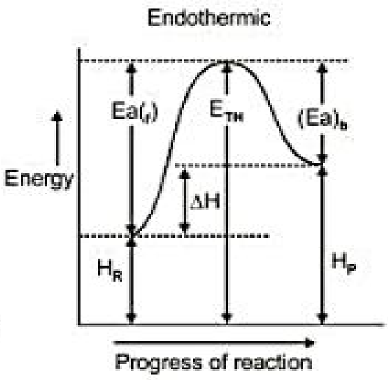
Threshold Energy and Activation Energy :

Threshold energy : For a reaction to take place the reacting molecules must colloid together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy (E_T) or the total minimum energy that reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.

Activation energy : It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to formation of product molecules.

$$E_a = E_{(Threashould\ energy)} - E_{(Reactant)}$$





E_{TH} = Threshold Energy, H_R = Enthalpy or Energy or Potential of reactants.
H_P = Enthalpy or Energy or Potential of product, $(E_a)_f$ = Activation energy for forward reaction.
$(E_a)_b$ = Activation energy for backward reaction.

Activated complex. It is formed between reacting molecules which is highly unstable and readily changes into product.

$$\Delta H_{react.} = (E_a)_f - (E_a)_b$$

Influence of Temperature on reaction rates

Temperature coefficient : The temperature coefficient of a chemical reaction is defined as the ratio of the reaction rates at two temperatures differing by 10°C. Its value usually lies between 2 & 3.

$$\text{Temperature coefficient} = \frac{k_{t+10}}{k_t}.$$

If no temperature is specified in T.C. then it can be taken as 25°C

Arrhenius Equation : A quantitative relationship was proposed by Arrhenius

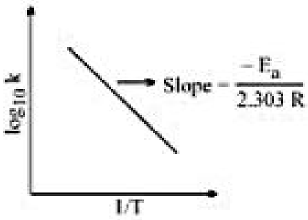
$$k = A.\ e^{-Ea/RT}$$

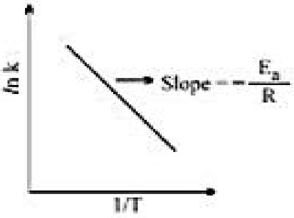
where

k = rate constant ; A = frequency factor (or pre – exponential factor);
R = gas constant ; T = Temperature (kelvin) ; E_a =Activation energy.

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Graphical representations are :





Illustration

1. In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are 4×10^{13} sec^{-1} and 98.6 kJ mol_{-1} respectively. At what temperature, the reaction will have specific rate constant 1.1×10^{-3} sec^{-1} ?

Sol. According to Arrhenius equation

$$k = Ae^{-E_a/RT}$$

or $$\log_e k = \log_e A - \frac{E_a}{RT}\log_e e$$

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

or $$2.303\ \log(1.1 \times 10^{-3}) = 2.303\ \log(4 \times 10^{13}) - \frac{98.6 \times 10^3}{8.314 \times T}$$

$$T = \frac{98.6 \times 10^3}{8.314 \times 2.303 \times 16.56}\ K\ = 311\ K$$

2. The rate constant is given by Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Calculate the ratio of the catalysed and uncatalysed rate constant at 25°C if the energy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 kJ.

Sol. Let k_{ca} and k_{un} be the rate constants for catalysed and uncatalysed reactions.

$$2.303 \log_{10} k_{ca} = 2.303 \log_{10} A - \frac{162 \times 10^3}{RT} \quad ......(i)$$

and $$2.303 \log_{10} k_{un} = 2.303 \log_{10} A - \frac{350 \times 10^3}{RT} \quad ......(ii)$$

Substracting Eq. (ii) from Eq.(i)

$$\log_{10} \frac{k_{ca}}{k_{un}} = \frac{10^3}{2.303RT}(350 - 162)$$

$$= \frac{188 \times 10^3}{2.303 \times 8.314 \times 298} = 32.95$$

$$\frac{k_{ca}}{k_{un}} = 8.88 \times 10^{32}$$

3. At 407 K the rate constant of a chemical reaction is $9.5 \times 10^{-5} s^{-1}$ and at 420 K, the rate constant is $1.9 \times 10^{-4} s^{-1}$. Calculate the frequency factor of the reaction.

Sol. The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Given $k_1 = 9.5 \times 10^{-5}\ s^{-1}$; $k_2 = 1.9 \times 10^{-3}\ s^{-1}$;
$R = 8.314\ J\ mol^{-1}K^{-1}$;
$T_1 = 407$ K and $T_2 = 420$ K
Substituting the values in Arrhenius equation.

$$\log_{10} \frac{1.9 \times 10^{-4}}{9.5 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{420 - 407}{420 \times 407}\right]$$

$$E_a = 75782.3\ J\ mol^{-1}$$

Applying now $\log k_1 = \log A - \frac{E_a}{2.303\ RT_1}$

$$\log 9.5 \times 10^{-5} = \log A - \frac{75782.3}{2.303 \times 8.314 \times 407}$$

or $$\log \frac{A}{9.5 \times 10^{-5}} = \frac{75782.3}{2.303 \times 8.314 \times 407}$$

$$= 9.7246$$

$$A = 5.04 \times 10^5\ s^{-1}$$

4. The energy of activation for a reaction is 100 kJ mol^{-1}. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C, other things being equal ?

Sol. The arrhenius equation is

$$k = Ae^{-E_a/RT}$$

In absence of catalyst, $k_1 = Ae^{-100/RT}$
In presence of catalyst, $k_2 = Ae^{-25/RT}$

$$\text{So} \quad \frac{k_2}{k_1} = e^{75/RT} \quad \text{or} \quad 2.303 \log \frac{k_2}{k_1} = \frac{75}{RT}$$

$$\text{or} \quad 2.303 \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293}$$

$$\text{or} \quad \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293 \times 2.303}$$

$$\text{or} \quad \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

As the things being equal in presence or absence of a catalyst,

$$\frac{k_2}{k_1} = \frac{\text{rate in presence of catalyst}}{\text{rate in absence of catalyst}}$$

$$\text{i.e.,} \quad \frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

Exercise

The rate of a reaction triple when temperature changes from 20°C to 50°C. Calculate energy of activation for the reaction (R = 8.314 JK^{-1} mol^{-1}).

Ans. 28.8118 kJ mol^{-1}

15. COLLISION THEORY

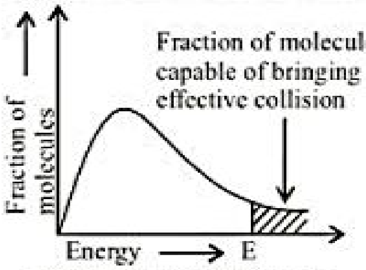
(i) The basic requirement for a reaction to occur is that the reacting species must collide with one another. This is the basis of **collision theory** for reactions.

(ii) The number of collisions that takes place per second per unit volume of the reaction mixture is known as **collision frequency** (Z).

(iii) Every collision does not bring a chemical change. The collisions that actually produce the product are **effective collisions**. The effective collisions, which bring chemical change, are few in comparison to the total number of collisions. The collisions that do not form a product are **ineffective elastic collisions**, i.e., molecules just collide and disperse in different directions with different velocities.

(iv) For a collision to be effective, the following two barriers are to be cleared.

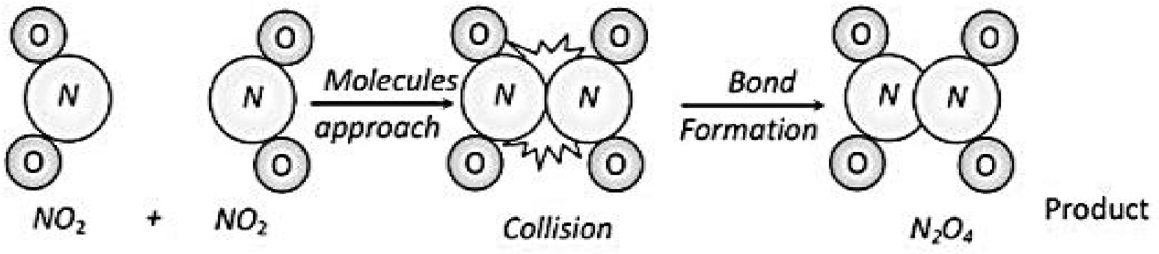
(a) **Energy barrier :** "The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as **threshold energy**".



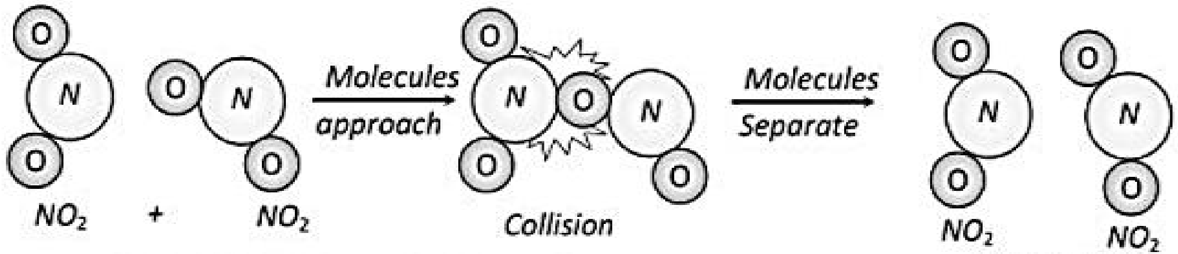
Distribution of energies at a definite temperature

- In the graph 'E' corresponds to minimum or threshold energy for effective collision.
- There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy to cross the energy barrier.

(b) **Orientation barrier :** The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed. For example, $NO_2(g) + NO_2(g) \rightarrow N_2O_4(g)$ During this reaction, the products are formed only when the colliding molecules have proper orientation at the time of collisions. These are called effective collisions.



(a) Properly oriented collisions form products



(b) Collisions not properly oriented

(v) Thus, the main points of collision theory are as follows,
(a) For a reaction to occur, there must be collisions between the reacting species.
(b) Only a certain fraction of the total number of collisions is effective in forming the products.
(c) For effective collisions, the molecules should possess sufficient energy as well as orientation.

(vi) The fraction of effective collisions, under ordinary conditions may vary from nearly zero to about one for ordinary reactions. Thus, the rate of reaction is proportional to :
(a) The number of collisions per unit volume per second (Collision frequency, Z) between the reacting species
(b) The fraction of effective collisions (Properly oriented and possessing sufficient energy), f

i.e., $\text{Rate} = \frac{-dx}{dt} = f \times Z$; Where f is fraction of effective collision and Z is the collision frequency.

(vii) The physical meaning of the activation energy is that it is the minimum relative kinetic energy which the reactant molecules must possess for changing into the products molecules during their collision. This means that the fraction of successful collision is equal to $e^{-E_a/RT}$ called **Boltzmann factor**.

(viii) It may be noted that besides the requirement of sufficient energy, the molecules must be properly oriented in space also for a collision to be successful. Thus, if Z_{AB} is the collision frequency, P is the **orientation factor** (Steric factor) then, $k = PZ_{AB}.e^{-E_a/RT}$. If we compare this equation with Arrhenius equation $k = Ae^{-E_a/RT}$.
We know that pre-exponential form 'A' in Arrhenius equation is, $A = PZ_{AB}$.

SOLVED EXAMPLE

Q.1 In the following reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$
rate of formation of O_2 is 3.6 M min^{-1}.
(a) What is rate of formation of H_2O?
(b) What is rate of disappearance of H_2O_2?

Ans. (i) 7.2 mol $litre^{-1}min^{-1}$, (ii) 7.2 mol $litre^{-1}$ min^{-1}

Sol. $\frac{d}{dt}[H_2O_2] = \frac{d}{dt}[H_2O] = 2 \times \frac{d}{dt}[O_2]$

Q.2 In a catalytic experiment involving the Haber process, $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of formation of Ammonia was measured as

$$\text{Rate} = \frac{\Delta[NH_3]}{\Delta t} = 2 \times 10^{-4} \text{ mol } L^{-1} s^{-1}.$$

If there were no sides reactions, what was the expressed in terms of (a) N_2, (b) H_2?

Ans. (a) 1×10^{-4} mol L^{-1} s^{-1}, (b) 3×10^{-4} mol L^{-1} s^{-1}

Sol. (a) $\frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

$$\therefore r = \frac{d}{dt}[N_2] = \frac{1}{2} \times (2 \times 10^{-4}) = 10^{-4}$$

(b) $\frac{d}{dt}[H_2] = \frac{3}{2} \times (2 \times 10–4) = 3 \times 10^{-4}$

Q.3 For the elementary reaction $2A + B_2 \longrightarrow 2AB$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

Ans. rate increase by 27 times
Sol. Rate = K $[3A]^2 [3B_2]$ = 27 Rate.

Q.4 In the following reaction, rate constant is 1.2×10^{-2} M s^{-1} $A \longrightarrow B$. What is concentration of B after 10 and 20 min., if we start with 10 M of A.

Ans. (i) 7.2 M, (ii) Think

Sol. (a) $K = \frac{1}{t}[A_0 - A] \quad \Rightarrow Kt = [B]$

$$\Rightarrow 1.2 \times 10^{-2} \times 10 \times 60 = [B] = 7.2$$

(b) Same way

Q.5 A first order reaction is 75% completed in 72 min.. How long time will it take for
(i) 50% completion (ii) 87.5% completion

Ans. (i) 36 min., (ii) 108 min.

Sol. $K = \frac{2.303}{72} \log_{10} \frac{100}{25} = 0.19$

(i) $t_{1/2} = \frac{0.693}{.019} = 36$

(ii) $t = \frac{2.303}{.019} \log_{10} \frac{100}{12.5} = 108$

Q.6 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place is ten times that required for half of the reaction.

Sol. $\frac{t_1}{t_2} = \frac{3}{0.3}$ Calculate t1 & t2 separately

$\therefore t_1 = 10\,t_2$

Q.7 The half life of the unimolecular elementary reaction $A(g) \longrightarrow B(g) + C(g)$ is 6.93 min. How long will it take for the concentration of A to be reduced to 10 % of the initial value?

(A) 10.053 min (B) 4.6 min (C) 46 min (D) 23.03 min

Ans. **(D)**

Sol. $\frac{0.693}{6.93} \times t = 2.303 \log \frac{[A]_0}{0.1[A]_0} \quad \Rightarrow \quad t = 23.03 \text{ min}$

Q.8 A 1 L reaction vessel which is equipped with a movable piston is filled completely with a 1M aqueous solution of H_2O_2. The H_2O_2 decomposes to $H_2O\,(l)$ and $O_2(g)$ in a first order process with half life 5 hrs at 300 K. As gas formed, the piston moves up against constant external pressure of 1 atm. What is the net work done by the gas from the start of sixth hour till the end of 10 hrs?

(A) 25 Cal (B) 150 Cal (C) 75 Cal (D) 100 Cal

Ans. **(C)**

Sol. At the end of 5 hours

$$A_{t,1} = \frac{A_0}{2}$$

at the end of 10th hours

$$A_{t,2} = \frac{A_0}{4}$$

$A_{t,2} - A_{t,1} = \frac{A_0}{2} - \frac{A_0}{4} = \frac{A_0}{4} = 0.25\,A_0$

amount decayed = 0.25 mol

moles of O_2 formed = 0.25/2 = 1/8

$W = -P\Delta V = -nRT = -(1/8) \times 300 \times 2 \text{ Cal} = 75 \text{ Cal}$

Q.9 At a certain temperature the following data were collected for the reaction

$$2ICl + H_2 \rightarrow I_2 + 2HCl$$

Initial Concentrations (M)		Initial Rate of formation of I_2 (Ms^{-1})
[ICl]	$[H_2]$	
0.10	0.10	0.0015
0.20	0.10	0.0030
0.10	0.05	0.00075

Determine overall order of reaction

(A) 0 (B) 1 (C) 2 (D) 3

Ans. (C)

Sol. From 1st and 2nd data order of reaction w.r.t. ICl is 1, from 1st and 3rd data order of reaction w.r.t. H_2 is 1, so overall order of reaction is 2.

Q.10 For the reaction

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + H^+ + Br^-$$

the following data was collected

[Acetone]	$[Br_2]$	$[H^+]$	Rate of reaction (Ms^{-1})
0.15	0.025	0.025	6×10^{-4}
0.15	0.050	0.025	6×10^{-4}
0.15	0.025	0.050	12×10^{-4}
0.20	0.025	0.025	8.0×10^{-4}

The order of the reaction w.r.t. CH_3COCH_3 and Br_2 respectively are :

(A) 0,1 (B) 1,0 (C) 1,1 (D) 1,2

Ans. (B)

Sol. Rate = k . [Acetone]^x . $[Br_2]^y$. $[H]^z$

$6 \times 10^{-4} = k . (0.15)^x (0.025)^y (0.025)^z$ ... (i)

$6 \times 10^{-4} = k . (0.15)^x (0.050)^y (0.025)^z$ ... (ii)

$12 \times 10^{-4} = k . (0.15)^x (0.025)^y (0.050)^z$ ... (iii)

$8 \times 10^{-4} = k . (0.20)^x (0.025)^y (0.025)^z$ ... (iv)

(i) ÷ (ii), $1 = \left(\frac{0.025}{0.050}\right)^y$

y = 0, hence rate does not depend upon the concentration of Br_2.

(i) ÷ (iii), $\frac{6}{12} = \left(\frac{0.025}{0.050}\right)^z$; $\frac{1}{2} = \left(\frac{1}{2}\right)^z$

$\therefore \quad z = 1$

(i) ÷ (iv), $\frac{3}{4} = \left(\frac{3}{4}\right)^x$

$\therefore \quad x = 1$

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Direction for Q.11 and Q.12 (2 questions) : Read the following passage carefully and answer the questions given after the passage.

Dinitrogen pentroxide decomposes on heating to nitrogen dioxide and oxygen following first order kinetics.

$$2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$$

0.2 mole of N_2O_5 was taken in a vessel of capacity 1 L and heating to a certain temperature of T Kelvin at which the reaction begins. The concentration of N_2O_5 is measured at different intervals of time by withdrawing samples of reaction mixture. A plot of $\text{In}[N_2O_5]$ v/s time is shown in figure-1. The value of rate constant (k) of the reaction is determined from the slope of the linear plot. The same experiment is repeated at five different temperatures and the value of the rate constants are calculated at each temperature. A plot of In k v/s $(\text{temperature})^{-1}$ is shown in figure-2.

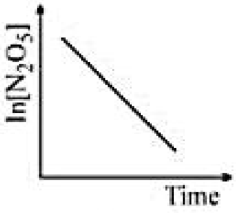


Fig-1

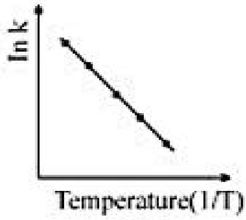


Fig-2

Q.11 Slope of straight line in figure-2 is -1.2×10^4 K. What is the activation energy of the reaction? (J/mole)
(A) 1.0×10^5 J mole^{-1} (B) 2.303×10^5 mole^{-1} (C) 1.2×10^5 mole^{-1} (D) 2.5×10^5 mole^{-1}

Ans. **(A)**

Sol. $\ln k = \frac{-E_a}{RT} + \ln A$

$$\text{slope} = \frac{-E_a}{R} = -1.2 \times 10^{-4}$$

$E_a = 1.2 \times 10^4 \times 8.314 = 9.97 \times 10^4$ Joule

Q.12 Slope of straight line in figure-1 is -1×10^{-1} sec^{-1}. What is the half-life of the reaction?
(A) 15.96 sec (B) 6.93 sec (C) 693 sec (D) 31.92 sec

Ans. **(B)**

Sol. $Kt = \ln A_0 - \ln A_E$
$\ln A_t = \ln A_0 - Kt$
$\text{slope} = -K = -(1 \times 10^{-1})$

$$t_{\frac{1}{2}} = \frac{0.693}{10^{-1}} = 6.93 \text{ sec}$$

Q.13 The rate constant for an isomerisation reaction $A \rightarrow B$ is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h.

Ans. 3.435×10^{-3} M/min

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

$$4.5 \times 10^{-3} = \frac{2.303}{60} \log \frac{1}{(a-x)} \Rightarrow (a-x) = 0.7633$$

Rate = k [a – x]
$= 4.5 \times 10^{-3} \times 0.7633 = 3.43 \times 10^{-3}$

Q.14 A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJmol^{-1}.

Ans. 100 kJmol^{-1}

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

Given that two rate are same

$$e^{-Ea'/RT} = e^{-Ea'/RT'}$$

$$\frac{Ea}{T} = \frac{Ea - 20}{T'}$$

$$\frac{Ea}{500} = \frac{Ea - 20}{400} \text{ or } Ea = 100 \text{ kJ}$$

Q.15 The energy of activation of a first order reaction is 104.5 kJ mole^{-1} and pre – exponential factor (A) is 5×10^{13} sec^{-1}. At what temperature, will the reaction have a half life of 1 minute?

Ans. 349.1 k

Sol. $k = A.e^{-Ea/RT}$

$$\log k = \log A - \frac{Ea}{RT}$$

$$\log \frac{0.693}{t_{1/2}} = \log A - \frac{Ea}{2.303RT}$$

$$\log \frac{0.693}{60} = \log 5 \times 10^{13} - \frac{104.5}{2.303 \times 8.314 \times 10^{-3} \times T}$$

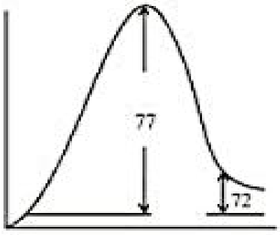
$$-1.9412 = 13.699 - \frac{104.5}{0.019147T}$$

$T = 348.95$

Q.16 In gaseous reactions important for understanding the upper atmosphere, H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and $E_a = 77$ kJ mol^{-1}, then calculate E_a for the biomolecular recombination of 2OH radicals to form H_2O & O at 500 K

Ans. 5 kJ mol^{-1}

Sol.



$Ea_1b = 77 - 72 = 5$