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Chemical Kinetics

In a chemical reaction, substances with well defined properties are converted into other substances with different properties. For any chemical change, chemists try to know that –

- 1- The feasibility of a reaction under the given experimental conditions can be predicted on the basis of decrease in Gibb's free energy ($-\Delta G$)
- 2- The extent to which a chemical reaction proceeds can be determined with the help of equilibrium constant of the reaction.
- 3- The third important aspect of the chemical reactions is the speed with which the reactants are converted into products – i.e. how fast the reaction can occur.

All above aspects depend on the experimental conditions like pressure, temperature, concentrations of reacting substances and the presence of any catalyst. The mechanism of the reaction is also helpful to understand the various aspects of a chemical reaction. The chemical reactions proceed with various velocities. Some reactions like acid-base reactions, precipitation reactions like formation of AgCl , BaSO_4 etc. are completed within a fraction of second. These are ionic reactions which are very fast and occur in about 10^{-12} to 10^{-16} seconds. On the other hand, there are certain reactions which occur at an extremely slow speed, for example, rusting of iron, decay of rocks, conversion of fossil fuel, certain radioactive disintegration etc. These occur so slowly that one could be misled into thinking that no reaction is taking place at all. However, there are some

molecular reactions which occur in a conveniently measurable time and their states can be measured easily in the laboratory. Almost all of the organic reactions are of such kind; some examples are hydrolysis of esters, decomposition of hydrogen peroxide, inversion of cane sugar, decomposition of nitrogen penta oxide etc.

The branch of chemistry which deals with the rates of chemical reactions and the factors which influence the rates of reaction is called chemical kinetics. The word kinetics is derived from the Greek word 'kinesis' meaning movement. Thus, thermodynamics tell us only about the rates of reactions.

The kinetic studies not only help us to know the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates may be altered. The study of the rates of reaction also helps us to understand the mechanism of reaction by which the reactants are converted into products. This path is called mechanism of that reaction. Hence the kinetic study is very important to know the mechanism of any reactions.

Rate of Chemical Reaction :

The ionic reactions occur very fast, for example if hydrochloric acid is added to silver nitrate solution; a precipitate of AgCl is obtained quickly. Similarly, the neutralization of an acid by a base occurs as soon as the both of the substances are mixed. These reactions occur in about 10^{-12} to 10^{-16} second. On the other hand the rusting of iron is very slow process. Molecular reactions occur not to very

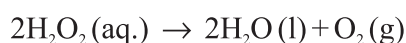
fast and not to very slow. For example nitration of benzene takes about one hour to give nitro benzene. Thus, the molecular reactions are needed to their kinetic study to understand their mechanism of chemical transformation of reaction to products.

Some examples of molecular reactions are :

- 1- Hydrolysis of ester in presence of sodium hydroxide–



- 2- Decomposition of hydrogen peroxide–



- 3- Decomposition of nitrogen penta oxide–



- 4- Inversion of cane sugar to give glucose and fructose–



We know that speed of an automobile is expressed in terms of change in position of distance covered by it in a certain period of time. Similarly, the rate of a chemical reaction is a measure of the speed with which the reactants are converted into products. It may be defined as the change in any one of the reactant or products per unit time.

Consider the following hypothetical reaction:



Here one mole of the reactant ‘R’ produces one mole of the product ‘P’ the rate of reaction may be expressed in either of the following two ways:

- 1- The rate of decrease in concentration of R

$$\text{Rate of reaction} = \frac{\text{Decrease in conc. of R}}{\text{Time taken}}$$

- 2- The rate of increase in concentration of P

$$\text{Rate of reaction} = \frac{\text{Increase in conc. of P}}{\text{Time taken}}$$

If $[\text{R}]_1$ and $[\text{P}]_1$ are the concentration of R and P respectively at time t_1 and $[\text{R}]_2$ and $[\text{P}]_2$ are at time t_2 , then:

$$\Delta t = t_2 - t_1$$

$$\Delta \text{R} = [\text{R}]_2 - [\text{R}]_1$$

$$\Delta \text{P} = [\text{P}]_2 - [\text{P}]_1$$

Where concentrations are represent in the square brackets and ΔR and ΔP represents the changes in the concentrations of R and P respectively in time interval Δt then, the rate of reaction may be expressed as :

$$\text{Rate of reaction} = - \frac{\Delta \text{R}}{\Delta t}$$

$$\text{or Rate of reaction} = + \frac{\Delta \text{P}}{\Delta t}$$

Where negative sign shows the decrease in the concentration of reactant R and positive sign shows the increase in the concentration of product P with time interval Δt . The changes in concentration of reactant and products are shown in the following plot which is drawn between concentration and time.

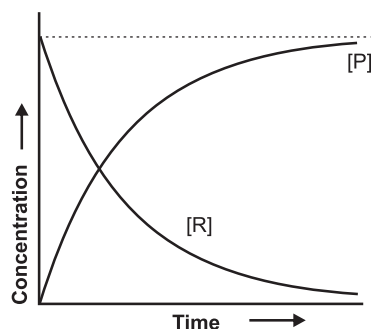


Fig. (1)

As the reaction proceeds the rate of reaction decreases exponentially as shown in the following figure (2). It is to be seen in the plot that initially the rate of reaction is highest and decreases rapidly with time in the beginning and then decreases slowly which becomes negligible at the end but never becomes zero. It means that theoretically a chemical reaction never completes.

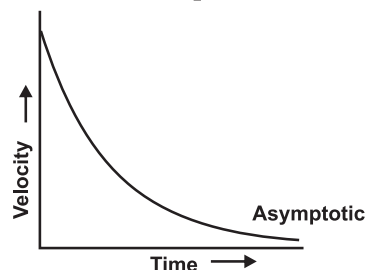


Fig. (2)

Average Velocity :

The rate of reaction decreases rapidly with time in the beginning of the reaction, and then it

decreases slowly and at the end the rate becomes negligible as shown in the above figure (2). Thus, the average rate of a reaction has no significance but we can consider an average velocity for a small interval of time.

Average velocity from t_1 to t_2 time interval may be given as,

$$\bar{V} = \pm \frac{\Delta C}{\Delta t}$$

where C_1 and C_2 are the concentration at t_1 and t_2 respectively. Positive and negative sign show the change in concentrations for products and the reactants respectively.

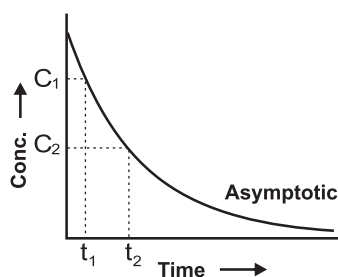


Fig. (3)

Instantaneous Velocity :

The average rate of a reaction cannot be taken as actual rate, as it changes every moment. Thus the rate is significant only for a particular time or a moment.

To determine the actual rate, a tangent is drawn on a curve, at any instant, between concentration and time. The slope of this tangent gives the actual rate at that particular time which is known as instantaneous velocity.

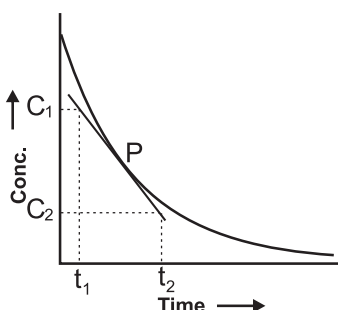


Fig. (4)

The slope of a tangent ($\tan \theta$) at a given point, is the limiting value of $\Delta C/\Delta t$. Thus, the limiting value can be given as in the calculus :

Instantaneous Velocity (V) =

$$\lim_{\Delta t \rightarrow 0} \left(\pm \frac{\Delta c}{\Delta t} \right) = \pm \frac{dc}{dt}$$

Where Δt is infinitesimally small time interval and Δc is similar change in concentration.

The instantaneous velocity is the slope of the tangent. Instantaneous velocity at P is equal to the $\tan \theta$ of the tangent.

$$\tan \theta = - \frac{\Delta c}{\Delta t} \quad \text{or} \quad \tan \theta = \frac{c_2 - c_1}{t_2 - t_1}$$

Rate of Reaction and Stoichiometry :

The rate of reaction can be measured by plotting a graph between the concentrations of any of the reactants or products as function of time. The community measurable properties are volume change, pressure change, change in thermal or electrical conductivities, change in optical rotation, change in color, pH or refractive index etc. To express the rate of reaction by change in concentration with time either of the reactant or product it is essential that the reaction must represent its stoichiometric relations. In other words the reactions are to be balanced in mass relations.

For example in this reaction :



The rate may be expressed in either of the following :

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

It is clear from the above stoichiometric equation that the rate of disappearance of A and B are equal to the rate of formation of C and D. Now consider the following reaction

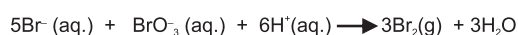


The rate of reaction may be given by any of the following :

$$- \frac{1}{2} \frac{d[A]}{dt} = + \frac{d[C]}{dt} = + \frac{d[D]}{dt}$$

Thus, the rate of disappearance of A is double to the rate of formation of C and D.

Consider the following reaction :



The rate may be given as :

$$= - \frac{1}{5} \frac{\Delta [\text{Br}^-]}{\Delta t} = - \frac{\Delta [\text{BrO}_3^-]}{\Delta t} = - \frac{1}{6} \frac{\Delta [\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta [\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta [\text{H}_2\text{O}]}{\Delta t}$$

Any of the above steps may give the rate of whole reaction; this concept is called "stoichiometric relation and the rate of reaction."

Initial Velocity :

It would be useful to introduce here one more term often used in connection with the rates of

reactions and it is initial rate. In figure (5), the tangent to the rate curve is drawn at zero time, i.e. at the point of initial concentration, the slope of the tangent is known as initial rate.

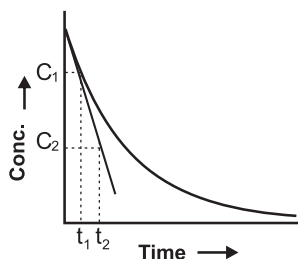


Fig. (5)

$$\text{Initial Velocity} = \tan\theta = - \frac{\Delta C}{\Delta t}$$

Rate Constant and Rate of Reaction :

According to the 'Law of Mass Action' the rate of a chemical reaction is proportional to the molar concentration of the reactant. Consider the following reaction :



If at any instant the concentration of A is equal to C_A , then according to the law of mass action:

$$\begin{aligned} \text{Rate of reaction} &= \frac{dx}{dt} \propto C_A \\ \text{or } \frac{dx}{dt} &= kC_A \end{aligned} \quad \text{.....(i)}$$

Here k is proportionality constant and called 'rate constant', which depends on the nature of reactants, temperature of the reactions. The rate constant is temperature of the reaction etc. The rate constant is also called velocity constant or specific rate of reaction.

Consider a general reaction :



The rate of this reaction :

$$\begin{aligned} \frac{dx}{dt} &\propto [A]^a [B]^b [C]^c \\ \text{or } \frac{dx}{dt} &= K [A]^a [B]^b [C]^c \end{aligned} \quad \text{.....(ii)}$$

This expression (ii) is the rate law or rate equation. "It is the mathematical expression which denotes the rate of a reaction in terms of molar concentrations of reactants with each term raised to some power which may (or may not) be same as the

stoichiometric coefficient of the reacting species in a balanced chemical equation." The power of concentration terms corresponds to experimentally observed rate of reaction.

Now, if the concentrations of all the reactant all taken unity, then,

$$[A]^a = [B]^b = [C]^c = 1$$

The rate of reaction :

$$\frac{dx}{dt} = k \quad \text{..... (iii)}$$

Thus, the specific rate of reaction or rate constant of the reaction (k) is equal to the rate of reaction when concentration of all the reactants is unity. The unit of rate constant depends upon the order of reaction.

Units of Rate Constants :

The units of rate constant of a reaction depend upon the order of reaction. Again consider the following chemical reaction.



As we know that,

$$\begin{aligned} \text{Rate of reaction} &= - \frac{dc}{dt} = \frac{\text{Change of Concentration}}{\text{Time is taken}} \\ &= \text{Concentration} \times \text{time}^{-1} \end{aligned} \quad \text{.....(i)}$$

Again,

$$\begin{aligned} \text{Rate of reaction} &= k [A]^a [B]^b [C]^c \\ &= k [\text{Conc.}]^a [\text{Conc.}]^b [\text{Conc.}]^c \\ &= k [\text{Conc.}]^{a+b+c} \end{aligned} \quad \text{.....(ii)}$$

From (i) and (ii), we get :

$$\begin{aligned} k [\text{Conc.}]^{a+b+c} &= \text{Concentration} \times \text{time}^{-1} \\ \Rightarrow k &= \frac{\text{Conc.}}{\text{Conc.}^n} \text{time}^{-1} \quad \text{where } n = a+b+c \\ \Rightarrow k &= [\text{Conc.}]^{(1-n)} \times \text{time}^{-1} \end{aligned} \quad \text{.....(iii)}$$

If the concentration is taken as gm mal per liter and the time is taken as second, then :

$$\text{Rate constant (k)} = \left[\frac{\text{Mol}}{\text{Lit}} \right]^{1-n} \times \text{sec}^{-1}$$

This is generalized relation, by which we can determine the units of reactions of any order for example :

- (1) For zero order reaction, ($n=0$), the unit of k is given as :

$$k_0 = \left[\frac{\text{Mol}}{\text{Lit}} \right]^{1-0} \text{sec}^{-1}$$

Unit of k_0 is $\text{mol} \cdot \text{Lit}^{-1} \text{sec}^{-1}$

- (2) For first order reaction, $n=1$

$$k_1 = \left[\frac{\text{Mol}}{\text{Lit}} \right]^{(1-1)} \text{sec}^{-1} = \left[\frac{\text{Mol}}{\text{Lit}} \right]^0 \text{sec}^{-1} = \text{sec}^{-1}$$

The unit of k_1 is sec^{-1}

- (3) For second order reaction $n=2$

$$k_2 = \left[\frac{\text{Mol}}{\text{Lit}} \right]^{1-2} \text{sec}^{-1} = \left[\frac{\text{Mol}}{\text{Lit}} \right]^{-1} \text{sec}^{-1}$$

The unit of k_2 is $\text{lit} \cdot \text{mol}^{-1} \text{sec}^{-1}$.

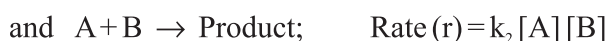
Order of Reaction and Molecularity :

The dependence of the reaction rates on concentrations of reactants may be expressed in terms of order of reactions. To calculate the order of a reaction, we must carry out the experiments to find out the dependence of reaction rate on the concentration of each individual reactant at a given temperature. Thus, the order of reaction is the molecularity of reactants in the rate determining step."

Generally, in the most of simple reactions the numbers of reacting is equal to the rate of reaction but it is not always bus. For example :

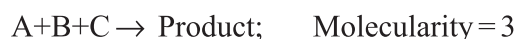


Hence, this first order reaction. Similarity :



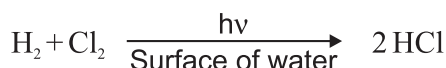
Hence, these both are of second order reactions.

The total numbers including all steps the reacting species (molecules, atoms or ions) which bring about a chemical reaction is called "molecularity of a reaction.' If a reaction involves the decomposition of only a single species, the molecularity is one or it is called 'unimolecular' reaction. Molecularity can be determined by the stoichiometric equation of the chemical reaction. For example:



Thus, the molecularity of first order reaction is one, second order reaction is two and third order of reaction is three but it is not always true because order of reaction cannot be exceeding to three. In other words the maximum order of any reaction may be three but molecularity of any reaction may be more then there. According to the collision theory of reaction, there are maximum three reacting species may collide to each other at any instant, so that, maximum order may be three only. Again the order of a reaction may be zero or a fraction but molecularity is a pure number. It is because the order of reaction is expressed by the sum of powers of the concentration of molecules the rate of deterring step. In zero order reaction does not depends upon the reacting molecules. Molecularity and order of reaction is cleared by the following examples:

- (1) Formations of hydrogen chloride from the reaction between hydrogen and chloride in the presence of sunlight at constant pressure and at the surface of water

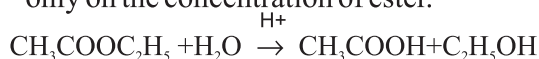


The molecularity of this reaction is two but it is a zero order reaction, because the rate does not depend on the concentrations of H_2 and Cl_2 .

$$\text{Rate} = k_0 [H_2]^0 [Cl_2]^0$$

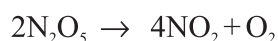
$$\Rightarrow \text{Rate} = k_0$$

- (2) Hydrolysis of ethyl acetate in acidic medium is a first order reaction but its molecularity is two. Actually the rate of this reaction depends only on the concentration of ester.



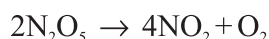
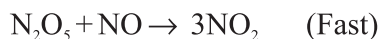
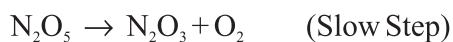
$$\text{Rate} = k_1 [CH_3COOC_2H_5]$$

- (3) The following reaction is also of first order while its molecularity is two :



$$\text{Rate} = k_1 [N_2O_5]$$

It can be explained by its mechanism :



In the mechanism of this reaction, the first step is slow step and this is the rate determining step. Hence the molecularity of the slow step is one and so that it is a first order reaction.

Factors Affecting the Rate of Reaction :

It is observed that the rate of chemical reactions is affected by a number of factors, some of the important factors are :

- (1) Concentration of reactants
- (2) Temperature of the system
- (3) Nature of reactants and products
- (4) Presence of any catalyst
- (5) Surface area of reactants
- (6) Radiation effect.

The explanation of each factor is as follows :

(1) Concentration of reactants :

It has been observed that the rate of a chemical reaction decreases with time. As we know that there is maximum concentration of reactants at the initiation of reaction, and therefore, the rate of change of concentration is also maximum at the start of reaction. As the concentration of the reactants decreases it brings about the corresponding decrease in the rate of the reaction. This means that the rate of reaction is directly proportional to the concentration of the reactants.

(2) Temperature of the system :

Generally, the rate of almost all chemical reactions increases with increase in temperature. On the other hand, a decrease in temperature decreases the rate of reaction. This effect is observed for exothermic as well as for endothermic reactions. A general approximation is made for the effect of temperature on reaction rates is that the reaction rate for most of the chemical reactions becomes almost double or triple, for every 100°C

increase in temperature. This is due to the reason that when the temperature is increased the kinetic energy of reacting molecules is also increased and number collisions of colliding molecules also increased. Hence the rate of transformations of reactant in product increases and the rate of reaction also increases.

(3) The Nature of Reactants and Products :

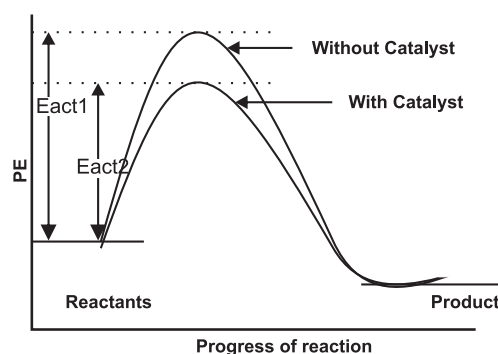
Rates of reaction are influenced by the nature of reacting species (molecules, atom or ions) and the products. A chemical reaction involves the breaking of old bonds and formation of new bonds. The reactivity of a substance can, therefore, be related to the ease with which the specific bonds are broken or formed and the number of such bonds involved. For example, the oxidation of nitric oxide to nitrogen dioxide takes place fairly rapidly while the oxidation of carbon monoxide to carbon dioxide takes place slowly :



In these both of reactions, the reacting species appear to be very similar, still the rate of reactions of these are very different.

(4) Effect of Catalyst :

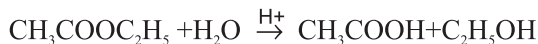
A catalyst is an external substance which increases the rate of chemical reaction without undergoing any permanent chemical change in itself. It has been observed that many of the reactions are made to proceed at an increased rate by the presence of certain catalysts. For example



E_{act1} = Energy of activation without catalyst
 E_{act2} = Energy of activation with catalyst

Fig. (6)

the hydrolysis of an ester is very slow process while it has increased by the presence of dilute acid.



It is believed that the presence of catalyst decrease the energy of activation of a particular reaction. As shown in the figure (6).

(5) Surface of Reactants:

In some heterogeneous reactions, rate of reaction depends on the contact surface area of the reactants. This fact is supported by the general observation that finely divided solids (power form) reacts faster than massive particles of the substances. Surface area for reacting site increases with increase in the divisions of massive particles. For example, a log of wood burns slowly but if it is cut into small wooden chips, the burning process takes place rapidly.

(6) Expose to Radiation:

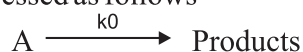
There are many reactions, which are very slow and on absorbing specific radiation photons, they becomes very fast. The photon of these radiations having frequencies (v) sufficient high energy to bring a chemical change in the reactants for example, reaction of hydrogen and chlorine takes place very slowly in the absence of sunlight. However, it becomes at explosive rate in presence of light.



Zero order Reactions :

The reactions in which the rate of reaction does not depend on the concentrations of reacting species are called zero order reactions. The rate of reaction of these reactions depends on the zero power of the concentrations of reacting species. Mathematical study of these reactions is done as follows:

Rate Law : A zero order reaction may be expressed as follows-



$$\text{Rate of reaction} = -\frac{d[\text{A}]}{dt} = \frac{dx}{dt} \propto [\text{A}]^0$$

$$\Rightarrow \frac{dx}{dt} = K_0 [\text{A}]^0$$

$$\Rightarrow \frac{dx}{dt} = K_0 \dots\dots\dots (I)$$

This is differential form of rate law of zero order reaction. The rate is constant; whatever is the concentration of reactants.

Integral Equation :

Equation (i) may be written as :

$$dx = k_0 dt \dots\dots\dots (i)$$

On integrating the equation (ii), we get :

$$\int dx = k_0 \int dt$$

$$\Rightarrow x = k_0 t + c \dots\dots\dots (iii)$$

Where C is integral coefficient and its value can be determine by applying the initial condition of the reaction, i.e.

When $t = 0$, $x = 0$, and $c = 0$

Then, $x = k_0 t$

$$\Rightarrow K_0 = \frac{x}{t} \dots\dots\dots (iv)$$

This is integral equation of zero order reaction and k_0 is rate constant of this reaction.

Units : According to the unit equation, we know that :

$$K_0 = \left(\frac{\text{Mol}}{\text{Lit}} \right)^{1-0} \text{Sec}^{-1}$$

Units of K_0 is $\text{mol lit}^{-1} \text{sec}^{-1}$.

Graphical Representation :

The rate equation for zero order reaction is $x = K_0 t$ which represent a straight line ($y = mx$) having slope ($\tan \theta$) is equal to the rate constant K_0 . As shown if figure (7) :

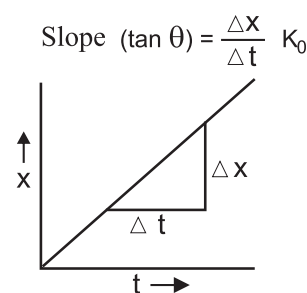


Fig. (17)

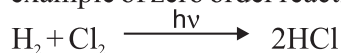
Half Life : Half life is a time period in which, half of the reactants are converted into the products and it is denoted by $t_{1/2}$. If the initial concentration of reactant is a and $t_{1/2}$ the concentration remain $a/2$. Then by equation (IV) we get :

$$t_{1/2} = \frac{a/2}{K_0} \rightarrow \boxed{t_{1/2} = \frac{a}{2K_0}} \dots\dots\dots(v)$$

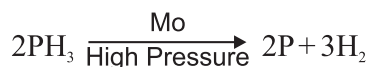
It is clear from the equation (V) that the 'half life of zero order reaction is proportional to the initial concentration of reactants.' ($t_{1/2} \propto a$)

Some examples of zero order reactions are :

- (1) In the presence of sunlight the reaction between H_2 and Cl_2 on the surface of water is example of zero order reaction.



- (2) The decomposition phosphene, in the presence of Mo at high pressure is also a zero order reaction.



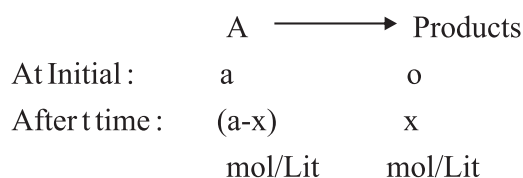
- (3) Decomposition of ammonia at the surface of W



First Order Reactions :

When the rate of reaction is proportional to the first power of the concentration of a reactant, it is a first order reaction.

Rate Law : A first order reaction may expressed as :



The initial concentration a is 'a' at time zero and after 't' time the concentration decreased and become $(a-x)$ mol per litre.

Now, according to law of mass action,

Rate of reaction :

$$\left(\frac{dx}{dt}\right) = - \frac{d(a-x)}{dt} = - \frac{d[A]}{dt} \propto (a-x) \dots\dots(i)$$

$$\text{i.e.} \quad \frac{dx}{dt} = k_1(a-x) \dots\dots\dots(ii)$$

Equation (ii) is the differential equation of rate of reaction of first order where k_1 is the rate constant of this reaction.

Integral Equation : By integrating the equation (ii) –

$$\int \frac{dx}{(a-x)} = K_1 \int dt \quad \text{Formula} \int \frac{dx}{x} = \ln x$$

$$- \ln(a-x) = k_1 t + c \dots\dots\dots(iii)$$

At initial when $t = 0$, the $x = 0$, so that-

$$- \ln a = c \dots\dots\dots(iv)$$

From equation (iii) and (iv) -

$$- \ln(a-x) = k_1 t - \ln a$$

$$\Rightarrow \ln a - \ln(a-x) = k_1 t$$

$$\Rightarrow \ln \frac{a}{a-x} = k_1 t \dots\dots\dots(v)$$

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

$$\Rightarrow K_1 = \frac{2.303}{t} \log \frac{a}{(a-x)} \dots\dots\dots(vi)$$

This equation (vi) is integral form of first order reaction.

Interval Equation :

If the initial concentration is not known, the rate of reaction is then determined by using the interval equation for the first order reaction. Let us suppose that X_1 and X_2 are the dissociated amounts of reactant at time t_1 and t_2 . Then, the equation (vi) may be written as :

$$t_1 = \frac{2.303}{K_1} \log \frac{a}{(a-x_1)} \dots\dots\dots(vii)$$

$$\text{and} \quad t_2 = \frac{2.303}{K_1} \log \frac{a}{(a-x_2)} \dots\dots\dots(viii)$$

By subtracting the equation (vii) from (viii), we get :

$$(t_2 - t_1) = \frac{2.303}{K_1} \left[\log \frac{a}{(a-x_2)} - \log \frac{a}{(a-x_1)} \right]$$

$$\Rightarrow (t_2 - t_1) = \frac{2.303}{K_1} \log \frac{a-x_1}{a-x_2} \dots\dots\dots(ix)$$

Graphical Presentation :

Various types of plot may be drawn for first order reactions. As the kinetic equation for first order reaction :

$$t = \frac{2.303}{K_1} \log \frac{a}{a-x}$$

$$\Rightarrow \log \frac{a}{(a-x)} = \frac{K_1}{2.303} t \dots\dots\dots(x)$$

If plot is drawn between $\log a / (a-x)$ and t , there occur a straight line, which is passes through the origin ($y=mx$) as shown in the figure (8). The slope of the line is :

$$\tan \theta = \frac{K_1}{2.303} \dots\dots\dots(xi)$$

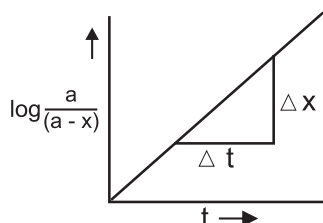


Fig. (8)

We can easily calculate the rate constant from the slope of above straight line.

The equation (x) can be written as :

$$\log a - \log (a-x) = \frac{K_1}{2.303} t$$

But we know that the initial concentration of reactant is a known constant amount, so that $\log a$ is constant.

$$\log (a-x) = - \frac{K_1}{2.303} t + \log a \dots\dots\dots(xii)$$

The equation (vii) also represents a straight if a graph is plotted against $\log(a-x)$ and time t . As shown in figure (9) intercept at y axis like $y=mx+c$ line.

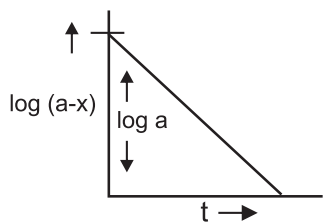


Fig. (9)

We can calculate the rate constant k_1 by the slope of this straight line.

$$\tan \theta = \frac{\Delta y}{\Delta t} = - \frac{K_1}{2.303}$$

Plot can also be drawn by the interval equation

$$\log \frac{a-x_1}{a-x_2} = \frac{K_1}{2.303} (t_2 - t_1) \dots\dots\dots(xiii)$$

Slope of the straight line which is passes through the origin may be given as fig. (10)

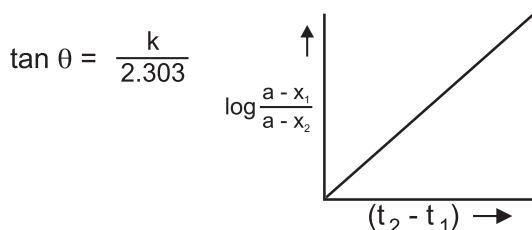


Fig. (10)

Half Life : Let us suppose the initial concentration of reactant is 'a' mol per litre and after $t_{1/2}$ the concentration decrease up to $a/2$ then:

$$\Rightarrow t_{1/2} = \frac{2.303}{K_1} \log \frac{a}{a-a/2}$$

$$\Rightarrow t_{1/2} = \frac{2.303}{K_1} \log (2)$$

$$\Rightarrow t_{1/2} = \frac{2.303 \times 0.3010}{K_1} \quad \because \log 2 = 0.3010$$

$$\therefore t_{1/2} = \frac{0.693}{K_1} \dots\dots\dots(xiv)$$

The above equation shows the half life of first order reaction and it is clear from the equation that the half life of first order reaction does not depend on the initial concentration of reactant:

Units : As we know that for first order reaction;

$$\text{Unit of } k_1 = \left[\frac{\text{Mol}}{\text{Lit}} \right]^{1-n} \text{ sec}^{-1} \quad \therefore n = 1$$

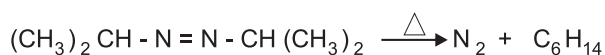
$$\text{Unit of } k_1 = \text{Sec}^{-1}$$

Some examples of first order reactions are as follows :

- (1) Aqueous decomposition of ammonium nitrate



- (2) Thermal decomposition of azo isopropane :



- (3) All the radioactive disintegration reactions are of first order.

Collision Theory :

[No mathematical derivations]

The basis requirement for a reaction to occur is that the reacting species (atom, ion or molecule) must collide with one another. Due to collision, the old bonds break and with the result, new arrangements take place, forming new bonds and giving products. This is the basis of ‘collision theory.’ This theory was put by Max Trautz and William Lewis in 1916-18. It is based on the concept of ‘Kinetic theory of gases.’

According to this theory, the reactant molecules are assumed to be hard spheres and reactions are postulated to occur when molecules collide with each other. ‘The number of collisions that take place per second per unit volume of the reaction mixture is known as collision frequency (z).’ The number of collision frequency is generally very high. For instance, at normal temperature and pressure of a gaseous system, the collision frequency of binary collisions is of the order of 10^{25} to 10^{28} . If all these collisions are effective in forming the products, the reactions must be completed in a very short time. However, in actual practice, most of the chemical reactions are slow and take longer time for their completion.

Thus, all the collisions among the reacting species at a given temperature are not effective in bringing about chemical reaction. “The collisions which actually produce the products and therefore, result in the chemical reactions are called effective collisions.”

They are two important barriers to a chemical reaction:

- (1) Energy barrier
- (2) Orientation barrier.

(1) Energy Barrier :

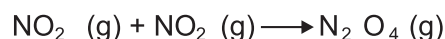
For the reacting species to make effective collisions, they should have sufficient energy to break the chemical bonds in the reacting species. “The required minimum amount of energy possessed by colliding molecules to convert into products is

known as threshold energy.” Thus, have energies greater than threshold energy.

(2) Orientation Barrier :

The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed.

For example, in the following reaction :



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. As shown in figure (11) :

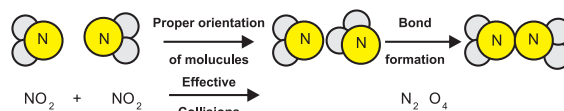


Fig. (11)

On the other hand, the molecules do not have proper orientation at the time of collision as shown in figure (12). These are ineffective collisions which do not form the products.

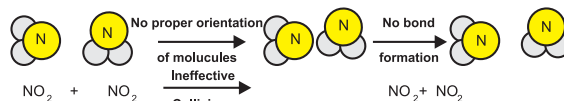


Fig. (12)

Thus, the collisions in which the colliding molecules do not possess the minimum energy for effective collisions (threshold energy) or proper orientation do not form products. Therefore, it follows that only a small fraction of collisions are effective.

Thus, the rate of reaction is proportional to :

- (1) The number of collisions per unit volume per second between the reacting species i.e. the collision frequency (z).
- (2) The fraction of effective collisions i.e. properly oriented and possessing sufficient energy (f) . i.e.,

$$\text{Velocity } \frac{dx}{dt} = f \times z$$

Dependence of Reaction Rates on Temperature :

Most of the chemical reactions are accelerated by increase in temperature. On the other hand, a decrease in temperature decreases the rate of

reactions. This effect is observed for exothermic as well as endothermic reactions. For example, the rate constant for the decomposition of N_2O_5 is $7.87 \times 10^{-7} \text{ sec}^{-1}$ at 273 K but becomes $3.56 \times 10^{-5} \text{ sec}^{-1}$ at 298 K. This means that for a rise of 25°C in temperature, the rate constant is increased by about 45 times.

A general approximate rule for the effect of temperature on reaction rates is that the rate of a reaction or rate constant becomes almost double for every 10°C rise in temperature. This is also called temperature coefficient, which is the ratio of rate constants of the reaction at two temperatures differing by 10°C . Thus,

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } (T + 10)^\circ\text{C}}{\text{Rate constant at } T^\circ\text{C}} = 2 \text{ to } 3$$

According to collision theory of chemical reactions, we know that rate of a chemical reaction depends upon the collision frequency (z) and the fraction of effective collisions (f). Thus, increase in the rate of reaction with temperature can be explained by either of the two or a combination of both these factors.

(i) Increase in Collision Frequency :

With the increase in temperature, the average kinetic energy of the molecules increases which leads to an increase in number of collisions per unit time (z). The average kinetic energy of the molecules is directly proportional to the absolute temperature. This increases only by 3% when the temperature rises from 300 K to 310 K.

This means that if the increase in the collision frequency is the only reason for increase in rate of reaction with temperature, then the reaction rate would have been increased by a factor of only 3%. This is very small in comparison of the actually observed factor of 2 or 3 more in some cases. In other words the rate actually increases 200% to 300% with the increase about 10°C temperature. Therefore, the increase in rate of reaction is not simply due to the increase in collision frequency.

(2) Effective Collisions :

The collision theory states that only a very

small fraction of collisions is effective in bringing about a chemical reaction and rest all the collisions are ineffective. Thus, for effective collision the colliding molecules must have more than to certain minimum required amount of energy called threshold energy. If the energy of colliding molecules is lesser than this threshold energy value, the collisions will be ineffective i.e. no products will occur. Hence, the energy of collisions determines the possibility of a reaction.

According to Ludwig Boltzmann and James Clerk Maxwell the energy distribution between molecules may be explained by statistics. We know that all the molecules do not possess the equal amount of kinetic energy. This is because the collisions between the moving molecules so that their energies are transferred from one molecule to another. Thus, there is a large distribution of kinetic energy among reacting molecules. If the 'energy' of molecules are plotted against the corresponding fraction of molecules at a particular temperature, a curve of the type shown in figure (13), is obtained. This is called Maxwell's distribution of energies.

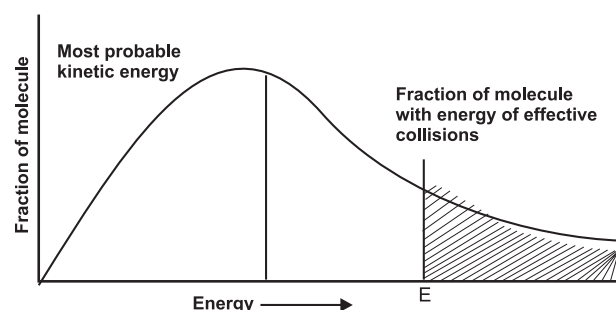


Fig. (13)

It is evident from the curve that the fraction of molecules having very low or very high energies is very small. Most of the molecules have intermediate kinetic energies as shown by the peak in the curve. This peak corresponds to "most probable kinetic energy" i.e. the kinetic energy of maximum numbers (fraction) of molecules. In the figure, E corresponds to minimum or threshold energy required for effective collisions. The molecules having energy equal to or greater than E will result in the formation of products and this fraction of molecules, which are capable to effective collisions, is very small.

It may be seen that for reaction having low values of threshold energy E , there will be larger fraction of colliding molecules which produces effective collisions and hence, the rate of reaction will be high. On the other hand if the value of E for reaction is high, then the number of effective collisions will be low and hence, the reaction rate will also be low.

Let us now consider the effect of increase in the temperature on the number of effective collisions. Figure (14) shows the energy distribution of molecules at two different temperatures T_1 and T_2 , where $T_2 = (T_1 + 10)^\circ\text{C}$.

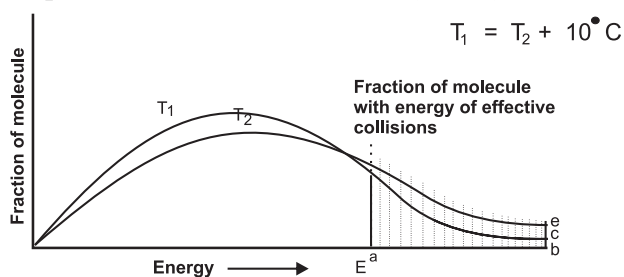


Fig. (14)

It is evident from the figure (14) that the curve at higher temperature gets shifted towards the right which indicates that at higher temperature, the molecules have higher energies. Further, the curve at higher temperature is flatter than that at lower temperature which also indicates that the number of molecules with higher energy content has increased. The number of molecules possessing energies equal to or greater than E , is proportional to area $a b c d$ at temperature T_1 , and area increased up to $a b e f$ at temperature T_2 . Thus the increase in the rate of reaction with temperature is mainly due to the increase in number of effective collisions.

TRANSITION STATE THEORY

Arrhenius Equation and Activation Energy :

According to Arrhenius, only a few molecules of reactant in a reaction mixture take part in the reaction, such molecules are known as active molecules. On increase in temperature, the number of active molecules increases and hence the rate of reaction also increases. Arrhenius proposed a quantitative relationship between rate constant and temperature as

$$K = Ae^{-E_a/RT} \dots\dots\dots(i)$$

This relation is known as Arrhenius equation in which A is known as Arrhenius factor or frequency factor. It is a pre exponential coefficient. This factor is related to number of binary molecular collisions per second per liter. E_a is the 'energy of activation' which represents the minimum energy that the reacting molecules must possess before undergoing reactions.

Both A and E_a are characteristics of the reaction. T is absolute temperature and R is the gas constant.

Taking logarithm, equation (i) may be written as

$$\ln k = \ln A - \frac{E_a}{RT} \dots\dots\dots(ii)$$

Converting the exponential logarithm into common logarithm ($\ln = 2.303 \log$), we get :

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

$$\log k = - \frac{E_a}{2.303 R} \frac{1}{T} + \log A \dots\dots\dots(iii)$$

This is in the form of $y = mx + c$ which represents a straight line. When $\log k$ is plotted against $1/T$, we get a straight line as shown in figure (15). This line is with opposite slope, intercepts the y -axis which is equal to $\log A$.

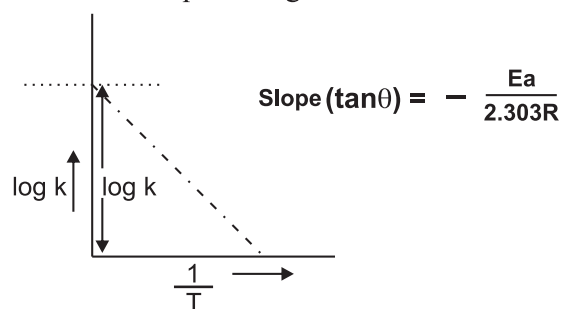


Fig. (15)

It is also clear from the equation that E_a is inversely proportional to the rate of reaction k i.e. the rate of reaction decreases with increase in activation energy E_a . The slope (negative) of the straight line can be calculated easily from the plot i.e.

$$\text{Slope (tan}\theta) = - \frac{E_a}{2.303R} \dots\dots\dots(iv)$$

And Energy of activation (E_a) = $2.303 R \times \text{Slope}$

E_a and A can be determined by measuring the

values of rate constant at two different temperatures. Let k_1 and k_2 are the rate constants for the reaction at two different temperatures T_1 and T_2 respectively. Then :

$$\log k_1 = - \frac{E_a}{2.303 R} \frac{1}{T_1} + \log A \dots\dots\dots(v)$$

$$\log k_2 = - \frac{E_a}{2.303 R} \frac{1}{T_2} + \log A \dots\dots\dots(vi)$$

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

$$\log (k_2 / k_1) = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Energy of Activation and Transition State :

The excess energy which must be supplied to the reactants to undergo chemical reaction is called energy of activation. It is equal to the difference between the threshold energy needed for the reaction to occur and the average kinetic energy of all the reacting molecules. That is,

Activation energy = Threshold energy - Average kinetic energy of reacting molecules

$$E_a = E(\text{threshold}) - E(\text{reactants})$$

Every chemical reaction possesses a definite energy of activation which depends upon the temperature of the reaction. The total fraction of effective collisions may also be energy of activation.

The energy of activation is low for chemical reaction, the number of effective collisions will be more and hence, the rate of reaction will also be more. This is shown in the following figure (16) :

Rate of Reaction $\propto 1 / \text{Energy of Activation}$

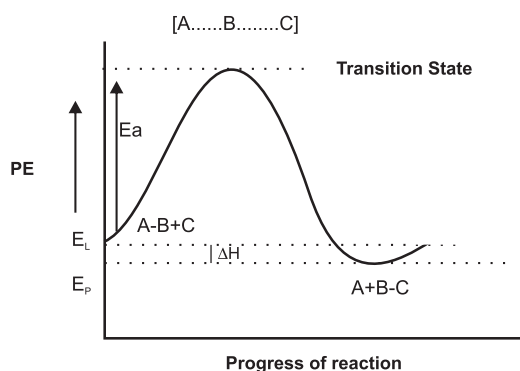


Fig. (16)

Here : E_t = Threshold energy

E_r = Average kinetic energy of reactants

E_a = Energy of activation

ΔH = Enthalpy of reaction

The reaction is as follows, as in the above energy profile diagram. (shown in above figure)



Reactants Transition state Products

When the colliding molecules possess the kinetic energy equal to E_a , the atomic configuration of species formed at this stage is different from the reactants as well as the products. This stage is called the activated state or transition state and specific configuration of this state is called activated complex or intermediate. The energy released from ineffective collisions is lesser than the energy of activation, so that such collisions do not bring the reactants into the products.

Solved Numerical Problems

- (1) Calculate the overall order of a reaction, which has the rate expression :

$$(i) \text{ Rate} = K [A]^{1/2} [B]^{3/2}$$

$$(ii) \text{ Rate} = K [A]^{3/2} [B]^{-1}$$

Solution :

Orders of reaction can be calculated by addition of powers of reactants –

$$(i) \text{ Order} = \frac{1}{2} + \frac{3}{2} = 2$$

$$(ii) \text{ Order} = \frac{3}{2} - 1 = \frac{1}{2}$$

- (2) The decomposition of NH_3 on platinum, surface, gives nitrogen and hydrogen. Rate constant for this zero order reaction is $2.5 \times 10^{-4} \text{ mol.lit}^{-1} \text{ sec}^{-1}$. What are the rate of production of N_2 and H_2 ?

Solution :

Decomposition of ammonia can be shown as :



The rate of decomposition of ammonia-

$$-\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = k = 2.5 \times 10^{-4} \text{ MS}^{-1}$$

Rate of formation of nitrogen

$$\frac{d[N_2]}{dt} = -\frac{1}{2} \frac{d[NH_3]}{dt} = 2.5 \times 10^{-4} \text{ Ms}^{-1}$$

Rate of formation of hydrogen

$$\frac{1}{3} \frac{d[H_2]}{dt} = -\frac{1}{2} \frac{d[NH_3]}{dt} = 2.5 \times 10^{-4} \text{ Ms}^{-1}$$

$$\Rightarrow \frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4} \text{ Ms}^{-1} \\ = 7.5 \times 10^{-4} \text{ Ms}^{-1}$$

- (3) The following data were obtained during the first order thermal decomposition of N_2O_5 (g) at constant volume,

$2N_2O_5(g) \longrightarrow$	$2N_2O_4(g) +$	$O_2(g)$
Time(s):	0	100
Total pressure:	0.500	0.512

Calculate the rate constant.

Solution :

Let the pressure of N_2O_5 decompose to give 2 moles of N_2O_4 and one mole of O_2 , then pressure of N_2O_4 (g) increased by $2x$ atm. and that of O_2 (g) increases by x atm.



At time $t = 0$	0.5 atm	0	0
At time ($t = 100$ s)	$(0.5 - 2x)$ atm	$2x$ atm	x atm

$$\text{Total pressure } (P_t) = 0.5 - 2x + 2x + x = 0.5 + x$$

$$t = 100 \text{ s}, P_t = 0.512 \text{ atm}$$

$$x = P_t - 0.5 = 0.512 - 0.5 = 0.012 \text{ atm}$$

$$\text{Now, } p[N_2O_5]_t = 0.5 - 2x = 0.5 - 2 \times 0.012 = 0.476 \text{ atm}$$

For first order reaction-

$$K_1 = \frac{2.303}{t} \log \frac{P[N_2O_5]_0}{P[N_2O_5]_t}$$

$$= \frac{2.303}{100} \log \frac{0.5 \text{ atm}}{0.476 \text{ atm}}$$

$$= \frac{2.303}{100} \log 1.0504$$

$$= \frac{2.303}{100} \times 0.0214$$

$$K_1 = 4.93 \times 10^{-4} \text{ s}^{-1}$$

- (4) A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction.

Solution : for the first order reaction :

$$k_1 = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\text{Suppose } [A] = a, [A] = \frac{1 \times 20}{100} = 0.80 a \quad t = 10 \text{ min}$$

$$\therefore k_1 = \frac{2.303}{10} \log \frac{a}{0.80 a}$$

$$\Rightarrow k_1 = \frac{2.303}{10} \log 1.25$$

$$\Rightarrow k_1 = \frac{2.303}{10} \times 0.0969$$

$$\Rightarrow K_1 = 0.0223 \text{ min}^{-1}$$

$$\text{In second case } [A]_0 = a - \frac{a \times 75}{100} = 0.25 a, t = ?$$

$$t = \frac{2.303}{K_1} \log \frac{[A]_0}{[A]}$$

$$\therefore t = \frac{2.303}{0.0223} \log \frac{a}{0.25 a}$$

$$\Rightarrow t = \frac{2.303}{0.0223} \times 0.6021$$

$$\Rightarrow t = 62.18 \text{ min.}$$

- (5) Show that in case of a first order reaction, the time taken for completion of 99.9% reaction is 10 times the time required for the change of the reaction.

Solution : When 99.9% reaction is completed, from the first order reaction equation.

$$\Rightarrow k_1 = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{t} \log \frac{[R]_0}{[R]_0 - 0.999 [R]_0}$$

$$\Rightarrow k_1 = \frac{2.303}{t} \log 10^3 = \frac{2.303 \times 3}{t} \log 10$$

$$\Rightarrow k_1 = \frac{6.903}{t} \quad [\because \log x^n = n \log x]$$

$$\Rightarrow t_1 = \frac{6.903}{k_1} \quad [\because \log 10 = 1]$$

$$\text{half life of reaction } t_{1/2} = \frac{6.93}{k_1}$$

$$\text{Now } \frac{t}{t_{1/2}} = \frac{6.903t}{k_1} \times \frac{k_1}{6.93} = 10 \quad \text{Hence proved}$$

- (6) The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the concentration of the reaction to 1/10th of its

initial value?

Solution : For a first order reaction,

$$t = \frac{2.303}{k_1} \log \frac{[A]_0}{[A]}$$

$$K_1 = 60 \text{ S}^{-1}, [A] = [A]_0 / 10$$

$$\text{Now } t = \frac{2.303}{k_1} \log \frac{[A]_0}{[A]_0 / 10}$$

$$\Rightarrow t = \frac{2.303}{60} \log 10$$

$$\Rightarrow t = \frac{2.303}{60} \quad [\because \log 10 = 1]$$

$$\Rightarrow t = 0.0385 \text{ या } 3.8 \times 10^{-2} \text{ S}^{-1}$$

(7) Half life of radioactive decay of ^{14}C is 5730 years. Calculate the rate constant.

Solution :

As we know that all the radioactive disintegration reactions are of first order reactions. So that the half life of first order reaction is –

$$\text{Decay constant } k_1 = \frac{0.693}{t_{1/2}}$$

$$\therefore t_{1/2} = 5730 \text{ Year}$$

$$\text{So, } k_1 = \frac{0.693}{5730 \text{ Year}} = 1.209 \times 10^{-4} \text{ Year}^{-1}$$

(8) The rate of decomposition of N_2O_5 in CCl_4 solution has been measured at 318 K and the following results were obtained :

t (min)	0	135	339	689	1680
C (M)	2.08	1.91	1.67	1.35	0.57

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

Solution :

It is clear that the rate of reaction does not remain constant with time and therefore, it is not a zero order reaction. We try integrated rate equation for first order reaction as :

$$K_1 = \frac{1}{t} \log \frac{C_0}{C}$$

$$\begin{array}{ccc} t & C & K_1 \\ \text{(time)} & \text{(M)} & \end{array} \quad K_1 = \frac{2.303}{t} \log \frac{C_0}{C} \text{ min}^{-1}$$

$$\begin{array}{ccc} 0 & 2.08 & — \end{array}$$

$$135 \quad 1.91 \quad \frac{2.303}{339} \log \frac{2.08}{1.91} = 6.32 \times 10^{-4} \text{ min}^{-1}$$

$$339 \quad 1.67 \quad \frac{2.303}{689} \log \frac{2.08}{1.67} = 6.30 \times 10^{-4} \text{ min}^{-1}$$

$$689 \quad 1.35 \quad \frac{2.303}{1680} \log \frac{2.08}{1.35} = 6.33 \times 10^{-4} \text{ min}^{-1}$$

$$1680 \quad 0.57 \quad \frac{2.303}{1680} \log \frac{2.08}{0.57} = 6.31 \times 10^{-4} \text{ min}^{-1}$$

The values of rate constant are found constant for the first order rate equation, so that this reaction is first order. The average value of constant is as follows :

$$K_1 = 6.315 \times 10^{-4} \text{ min}^{-1}$$

The half life of first order reaction is given by-

$$t_{1/2} = \frac{0.693}{K_1}$$

$$\Rightarrow t_{1/2} = \frac{0.693}{6.315 \times 10^{-4} \text{ min}^{-1}} = 1.097 \times 10^3 \text{ min}$$

(9) The rate constant for the decomposition of ethyl iodide by the reaction:



At 600K is $1.60 \times 10^{-5} \text{ sec}^{-1}$. Its energy of activation is 209 KJ. Mol^{-1} . Calculate the rate constant of the reaction at 700 K.

Solution :

The unit of rate constant is sec^{-1} , so that it is a first order reaction. From Arrhenius equation of interval form.

$$\log K_2 - \log k_1 = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\Rightarrow \log K_2 - \log k_1 + \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

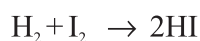
$$= \log (1.60 \times 10^{-5}) + \frac{209000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1}} \left[\frac{1}{600\text{K}} - \frac{1}{700\text{K}} \right]$$

$$= -4.796 + 2.599$$

$$\Rightarrow \log K_2 = -2.197$$

$$\Rightarrow K_2 = 6.36 \times 10^{-3} \text{ S}^{-1}$$

(10) The specific rate constant for the combination of H_2 and I_2 to form HI



is $2.34 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$ at 673K and $7.50 \times 10^{-2} \text{ mol L}^{-1} \text{ sec}^{-1}$ at 773K. Calculate the

activation energy for the reaction.

Solution : The Arrhenius equation is –

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

$$\text{Here, } k_1 = 2.34 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} ; T_1 = 673 \text{ K}$$

$$k_2 = 7.50 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1} ; T_2 = 773 \text{ K}$$

So,

$$\log \frac{7.50 \times 10^{-2}}{2.34 \times 10^{-3}} = \frac{E_a}{2.303} \left[\frac{1}{673} - \frac{1}{773} \right]$$

$$\Rightarrow \log 32.05 = \frac{E_a}{2.303R} \left[\frac{773-673}{673 \times 773} \right]$$

$$\Rightarrow 1.506 = \frac{E_a}{2.303R} \times \frac{100}{673 \times 773}$$

$$\Rightarrow E_a = \frac{1.506 \times 2.303 \times 673 \times 773 \times 8.314}{100}$$

$$\Rightarrow E_a = 1.51 \times 10^4 \text{ J mol}^{-1} = 15.1 \text{ KJ mol}^{-1}$$

Exercise Question

Multiple Choice Questions :

- The unit of zero order rate constant is:
 - $\text{mol L}^{-1} \text{s}^{-1}$
 - $\text{L mol}^{-1} \text{s}^{-1}$
 - s^{-1}
 - $\text{mol}^2 \text{L}^{-2} \text{s}^{-1}$
- Half life of first order reaction is 69.3 s, the rate constant will be :
 - 10^{-2}s^{-1}
 - 10^{-4}s^{-1}
 - 10s^{-1}
 - 10^2s^{-1}
- Rate constant for a reaction is $7.239 \times 10^{-4} \text{ sec}^{-1}$, the order of reaction will be :
 - 0
 - 1
 - 2
 - 3
- Which of the following statement is true for first order reactions –
 - The rate of reaction is proportional to the zero power of concentration of reactant.
 - The unit of rate constant is $\text{mol L}^{-1} \text{s}^{-1}$
 - The half life of reaction does not depend upon the initial concentration of reactants.
 - Nothing is to be said directly.
- A straight line occurs, when $\log k$ is plotted against $1/T$ in first order reaction. The slope of

line is equal to –

$$(a) - \frac{E_a}{2.303} \quad (b) - \frac{E_a}{2.303R}$$

$$(c) - \frac{2.303}{E_a R} \quad (b) - \frac{E_a}{R}$$

- A small increase in temperature of the reacting system, the rate of reaction exceed to large extend. The most appropriate reason for this is–
 - Increase in the number of active reactants.
 - Number of collisions increases
 - The length of free path increases
 - The heat of reaction increases
- Which of the following relation is true for zero order reactions?
 - $t_{3/4} = 2t_{1/2}$
 - $t_{3/4} = 1.5t_{1/2}$
 - $t_{3/4} = 0.25t_{1/2}$
 - $t_{3/4} = t_{1/2}$
- Which of the following is Arrhenius equation –
 - $K = -Ae^{-E_a/RT}$
 - $K = A e^{-E_a/RT}$
 - $K = Ae^{E_a/RT}$
 - $K = e^{-E_a/RT}$
- If half life of first order reaction is 480s, then the rate constant will be :
 - $1.44 \times 10^{-3} \text{s}^{-1}$
 - 1.44s^{-1}
 - $0.72 \times 10^{-3} \text{s}^{-1}$
 - $2.88 \times 10^{-3} \text{s}^{-1}$
- Time for first order reaction to complete 90% reaction will be-
 - 1.1 of half life
 - 2.2 of half life
 - 3.3 of half life
 - 4.4 of half life

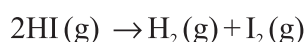
Ans. : 1(a), 2(a), 3(b), 4(c), 5(b),
6(a), 7(b), 8(b), 9(a), 10(c)

Very Short Answer Questions :

- For a reaction -
 $A + B \rightarrow \text{Products}$,
 The rate constant depends on $[A]^{1/2} [B]$; what will be the order of reaction ?
- Transformation of X molecule into Y is a second order kinetics. Now the concentration X exceeded up to three times then what effect will be observed in the formation at Y?

Short Answer Questions :

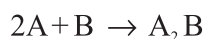
- (1) For reaction $R \rightarrow P$, in 25 minutes the concentration of reactant changed from 0.03 M to 0.02 M. Give the average velocity in seconds and minutes.
- (2) In a reaction $2A \rightarrow \text{Product}$. Initial concentration is 0.5 mol L^{-1} which reduced upto 0.4 mol L^{-1} in 10 minutes. Calculate the rate of reaction for this time period.
- (3) The rate constant for a first order reaction is $1.15 \times 10^{-3} \text{ s}^{-1}$. How much time will be taken to reduce the amount of reactants from 5 gm to 3 gm?
- (4) If 60 minutes time is taken to decompose up to half amount of the initial of SO_2Cl_2 . Calculate the rate constant if it is a first order reaction.
- (5) Discuss the effect of temperature on rate constant.
- (6) The rate of reaction becomes double, if the temperature is increased by 10 K of chemical reaction at 298 K. Calculate the energy of activation E_a , for this reaction.
- (7) The energy of activation is $209.5 \text{ KJ mol}^{-1}$ at 581 K for a reaction.



Calculate the fraction of molecules whose energy will be greater than or equal to the energy of activation.

- (8) Determine the order and units of rate constants from the rate of following reactions –
 - (a) $3\text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g})$ Rate = $k[\text{NO}]^2$
 - (b) $\text{H}_2\text{O}_2(\text{aq}) + 3\text{I}^-(\text{aq}) + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_3^-$ Rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$
 - (c) $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$ Rate = $k[\text{CH}_3\text{CHO}]^{3/2}$
 - (d) $\text{C}_2\text{H}_5\text{Cl}(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + \text{HCl}(\text{g})$ Rate = $k[\text{C}_2\text{H}_5\text{Cl}]$

- (9) For the reaction -



The rate = $k[\text{A}][\text{B}]^2$ with $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2$

s^{-1} . Calculate the initial rate of reaction when $[\text{A}] = 0.1 \text{ mol L}^{-1}$, $[\text{B}] = 0.2 \text{ mol L}^{-1}$. Calculate the rate of reaction after $[\text{A}]$ is reduced to 0.06 mol L^{-1} .

- (10) The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 . If $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ Sec}^{-1}$?
- (11) Discuss the factors that affect the rate of chemical reaction.
- (12) A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is :
 - (i) Doubled
 - (ii) reduced to half?
- (13) In a pseudo first order hydrolysis of ester in water, the following results were obtained :

t/s	0	30	60	90
Ester(mol/Lit)	0.55	0.31	0.17	0.085

- (i) Calculate the average rate of reaction between the time intervals 30 to 60 seconds.
 - (ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.
- (14) In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentration of A and B as given below:

A/ mol L ⁻¹	0.20	0.20	0.40
B/ mol L ⁻¹	0.30	0.10	0.05
$r_0 \text{ mol L}^{-1} \text{ S}^{-1}$	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B?

- (15) The following results have been obtained during the kinetic studies of the reaction:
 $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$

Experiment	[A]/mol L ⁻¹	[B]/mol L ⁻¹	Initial rate of formation of D. mol L ⁻¹ min ⁻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

Determine the rate law and the rate constant for the reaction.

- (16) The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table :

Experiment	[A]/mol L ⁻¹	[B]/mol L ⁻¹	Initial rate / mol L ⁻¹ min ⁻¹
I	0.1	0.1	2.0x10 ⁻²
II	-	0.2	4.0x10 ⁻²
III	0.4	0.4	-
IV	-	0.2	2.0x10 ⁻²

- (17) Calculate the half life of a first order reaction from their rate constants given below:

(i) 200 s⁻¹ (ii) 2 min⁻¹ (iii) 4 year⁻¹

- (18) The half life for radioactive decay of ¹⁴C is 5730 years. An archeological artifact containing wood had only 80% of the ¹⁴C found in a living tree. Estimate the age of the sample.

- (19) The rate constant for a first order reaction is 60 s⁻¹. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

- (20) During nuclear explosion, one of the products is ⁹⁰Sr with half life of 28.1 years. If 1 ug of ⁹⁰Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

- (21) For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

- (22) A first order reaction takes 40 min for 30% decomposition. Calculate the t_{1/2}.

- (23) For the decomposition of azoisopropane to hexane and nitrogen at 543K, the following data are obtained :

t(sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

- (24) The following data were obtained during the first order thermal decomposition of SO₂Cl₂ at a constant volume.



Experiment	Time/s-1	Total Pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

- (25) The rate of constant for the decomposition of N₂O₅ at various temperatures in given below :

T/°C	0	20	40	60	80
10 ⁵ s ⁻¹	0.0787	1.7025.7	25.7	178	2140

Draw a graph between ln k and 1/T and calculate the values of A and Ea. Predict the rate constant at 30°C and 50°C.

- (26) The rate constant for the decomposition of hydrocarbons is 2.418 x 10⁻⁵ s⁻¹ at 546 K. If the energy of activation is 179.9 KJ.mol⁻¹, what will be the value of pre exponential factor.

- (27) Consider a reaction; A→Products, with k=2.0x10⁻² s⁻¹. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L⁻¹.

- (28) Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with t_{1/2}=3.00 hours. What fraction of sample of sucrose remains after 8 hours?

- (29) The decomposition of hydrocarbon follows the equation k=[4.5x10¹¹ s⁻¹] e^{-28000k/T}.

Calculate Ea.

- (30) The rate constant for first order decomposition of H₂O₂ is given by the following equation.

$$\text{Log } k = 14.34 - 1.25 \times 10^4 \text{K/T}$$

Calculate Ea for this reaction and at what temperature will its half period be 256 minutes?

- (31) The decomposition of A into product has value $4.5 \times 10^3 \text{ s}^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1} . At what temperature would k be $1.5 \times 10^4 \text{ s}^{-1}$?
- (32) The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. The value of A is $4 \times 10^{10} \text{ s}^{-1}$. Calculate k at 318 K and E_a .
- (33) The rate of reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Large Answer Questions :

- (1) Decomposition of dimethyl ether gives CH_4 , H_2 and CO and the rate of this reaction is given by –

$$\text{Rate} = k [\text{CH}_3\text{OCH}_3]^{3/2}$$

The rate of reaction is determined by the increase in pressure in a closed vessel. The rate equation of dimethyl ether may also be given as partial pressure term.

$$\text{Rate} = k (P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

If pressure is measured in bar and time in minutes, then what will be rate of reaction and the unit of rate constant?

- (2) What will be the effect on rate constant of a reaction? How the effect of temperature can be expressed quantitatively?
- (3) A reaction w.r.t. A is first order and w.r.t. B is of zero order –
- Write the differential equation of rates.
 - What will be the effect on the rate if the concentration of B increased up to three times?
 - What will be the effect on rate, if the concentrations of A and B are doubled?
- (4) The experimental data for decomposition of N_2O_5 in gas phase at 318 K are given below:
- $$2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$$

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^3 \times [\text{N}_2\text{O}_5] / \text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

- Plot $[\text{N}_2\text{O}_5]$ against t .
- Find the half life period for the reaction
- What is the rate law?
- Calculate the rate constant
- Calculate the half life.