

# UNIT

## 1

# Chemical Kinetics

### 1.1 Introduction

The chemist tries to find out the following things for any chemical reaction : (i) The feasibility of the reaction which can be predicted on the basis of thermodynamics (As you know that the value of change in free energy must be less than zero i.e. it should be negative and the change in total entropy of the system and surrounding should be positive). (ii) It is necessary for him or her to study the equilibrium of the reaction so as to know to which extent the reaction will be completed (As you know the value of the equilibrium constant  $K$  should be more than 1). (iii) the rate of chemical reaction i.e. the time required for the reaction to reach to equilibrium (As you know that the reaction can be very slow, slow or fast).

We shall study chemical kinetics in this unit, taking into consideration all these three points. The word kinetics is derived from original Greek word '**Kinesis**' which means velocity or movement.

In industrial field as well as in everyday life, attempts have been made so that the reaction may result. The limitation of thermodynamics is that it does not provide information about the time in which the reaction will be completed. Spontaneous or reaction occurring on its own are completed in as less as possible time. And the equilibrium constants of such reactions are very high as well as the values of change in free energy is as high as possible but negative. Nitrogen and oxygen are present together in the air, from a very long time, even then they do not react. But, under certain circumstances, viz. during the lightening in the sky, both of them combine and form nitric oxide. Thus, the reaction is extremely slow under normal condition. Milk kept in the refrigerator at low temperature does not get spoiled because the biological reaction in it becomes very slow. Thus the rate of reaction like spoilage of milk can be decreased by decreasing temperature and so more time will be required to complete the reaction that is, the milk remains fresh for long time. The liquid or gaseous fuel burns faster than the solid fuel. To cook food, high temperature is required i.e. chemical phenomenon or a reaction is slow

at lower temperature but with increase in temperature it becomes very fast. The reactions can be divided into three parts regarding the completion of reaction : (1) very slow reaction, e.g. the radiations emitted from uranium, (2) slow reaction e.g., to carry out reaction by combining dinitrogen and dihydrogen under certain conditions, (3) very fast reaction e.g., the reaction between sodium hydroxide and hydrochloric acid which is completed in only 1 nanosecond ( $10^{-9}$  sec.). It is difficult to study very slow reactions. Similarly the human being and the apparatus become incapable to measure very fast or instantaneous reaction. Hence, we shall study only slow reactions in this unit.

As studied in chemical equilibrium the reaction occurs both in forward and reverse directions. Suppose, the rate of forward reaction is shown as  $V_f$  and the rate of reverse reaction as  $V_r$ , then there are three possibilities (1)  $V_f > V_r$ , i.e. the rate of forward reaction is more than that of reverse reaction. Hence more product will be obtained i.e. more reactant will react. (2)  $V_f < V_r$  i.e. the rate of forward reaction is less than that of reverse reaction, less product will be obtained and less amount of reactant will undergo reaction. (3)  $V_f = V_r$ . If the rates of forward and reverse reactions are same the concentrations of products and reactants will be constant, i.e. equilibrium will be obtained. Thus the rate of reaction shows in which direction the reaction will occur but what will be the proportion (quantity) of the product can not be known. For this, thermodynamics is required. Thus chemical kinetics is completely separate from thermodynamics but both of them are supplementary to each other. In industrial field, the combination of these two is essential and useful.

**In chemical kinetics, the rate of reaction and the factors affecting them are studied.** The knowledge of chemical kinetics is very important in understanding the factors affecting the rate of reaction and the mechanism of the reaction. If the reaction occurs in more than one steps then the slowest step determines the rate of integrated reaction. Generally the rates of reaction are determined from the changes in concentration of reactants or products in unit time.

## 1.2 Factors Affecting The Rate of Chemical Reaction

The factors affecting rate of chemical reaction are as follows :

**(1) The state of substance and the area of surface :** If the reactant is in powder form instead of its solid block form the rate of reaction becomes faster. The surface area of contact increases by changing to powder form and so the reaction becomes fast. e.g. iron powder instead of a piece of iron is a better catalyst and so the reaction becomes faster. The area of the surface becomes more by changing to powder form.

**(2) Concentration of solution :** If the reaction takes place in solution state the rate of forward reaction increases with increase in concentration of reactants. For practical purpose, it is advisable to keep higher concentration of reactants. This is obvious from **LeChatelier's principle**. In industry, the reactant which is cheaper is taken in more proportion. The stoichiometry plays an important role.

**(3) Temperature of system :** Generally if the temperature is increased, the rate of reaction increases because kinetic energy and the collision of molecules increase with increase in temperature which becomes helpful in increasing the rate, e.g., sugar added in cold water dissolves faster if the temperature of solution is increased and dissolves completely. At equilibrium stage the increase in temperature is advantageous for an endothermic reaction while for exothermic reaction, decrease in temperature is advantageous. The reason for this is that heat reacts as reactant or product.

**(4) Pressure of system :** If the reaction is in gaseous phase or state, then the rate of reaction will increase or decrease by change in pressure. The increase in pressure will result in increase or decrease of rate depending on the nature of the reactant and stoichiometry. As studied in chemical

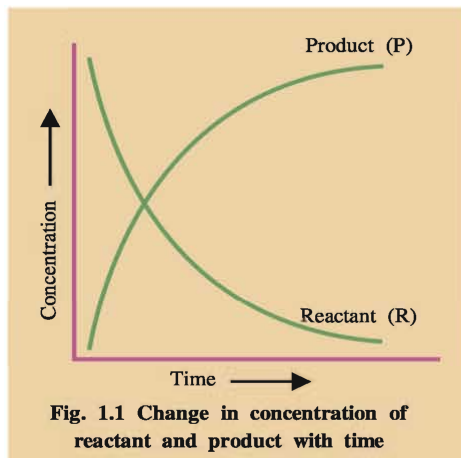
equilibrium the increase of pressure in certain reactions decreases the rate, while in certain reactions decrease in pressure increases the rate. It is necessary to note that for a gaseous reaction pressure is considered as concentration of gas. Because the pressure and concentration both are associated with the number of molecules of substance. In the reaction, if the number of moles of gaseous products is more than that of gaseous reactants, the decrease in pressure of system is advantageous i.e. more product will be obtained. But if the number of moles of gaseous products is less than that of gaseous reactants then increase of pressure on the system is advantageous and so more product will be obtained.

**(5) Effect of Catalyst :** With the use of suitable catalyst, the reaction can be made faster i.e. its rate can be increased. The use of catalyst cannot bring change in the proportion (amount) of products. As it increases the rate of reaction, the reaction will be completed in less time. The reason for this is that the energy of activation decreases. We shall study about this later on in this unit. There is no effect of catalyst on equilibrium because it increases uniformly both the rate of forward reaction as well as rate of reverse reaction. If there is any impurity which tries to decrease the rate of reaction then it is called **catalytic poison**. We shall study this in catalysis.

### 1.3 Rate of Chemical Reaction

The progress of chemical reaction is studied as a function of measuring concentration of reactants / or products and for gaseous reactions measuring pressure instead of concentration i.e. at some definite intervals of time the concentration of any one of the reactants or products can be measured. It can be assumed from the study of general reactions, the proportion (volume) of reactant or product is taken then there is not much change in the total proportion or the concentration remains almost same or remains constant. For this volume of reactant is taken. During the progress of the reaction it is noted that with increase in time the concentration of reactants will decrease and the concentrations of products will increase. Hence the concentration of reactant or product is determined with suitable method of measurement at definite intervals of time.

Suppose, in a reaction one mole of reactant (R) produces one mole of product (P). In the initial concentration of R and P, the decrease and increase remain same respectively. Only the magnitude will change. If the graph of concentration versus time is plotted then, the graph obtained will be as shown in fig. 1.1



Suppose, at time  $t_1$ , the concentrations of reactant and product are  $[R]_1$  and  $[P]_1$  respectively and at any other time  $t_2$ , their concentrations are  $[R]_2$  and  $[P]_2$  respectively, then  $\Delta t = t_2 - t_1$  and  $\Delta[R] = [R]_2 - [R]_1$  and  $\Delta[P] = [P]_2 - [P]_1$  where  $\Delta[P]$  and  $\Delta[R]$  are the changes in concentration of product and reactant respectively. The **average rate** of reaction  $r_{av}$  can be expressed as follows :

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t} \quad \dots (1.1)$$

There is decrease in concentration of reactant and so it is expressed with negative (–) sign and there is increase in concentration of product and so it possesses positive (+) sign which is generally not mentioned. The negative sign is

only for mathematical significance. It is apparent from the equation 1.1 that the unit of average rate is concentration  $\text{time}^{-1}$ , viz. molar  $\text{second}^{-1}$ , molar  $\text{minute}^{-1}$ , molar  $\text{day}^{-1}$ , molar  $\text{year}^{-1}$ .

To determine the speed of any vehicle, average speed is considered because there is increase and decrease in the speed of the vehicle,. Hence the values determined at any definite time will be different viz. if there is disturbance of traffic then it will be slow and the speed will decrease, but if the road is without traffic, the vehicle will go faster. This is difficult to determine. Hence, all these are integrated and the average is determined and we use it in practice.

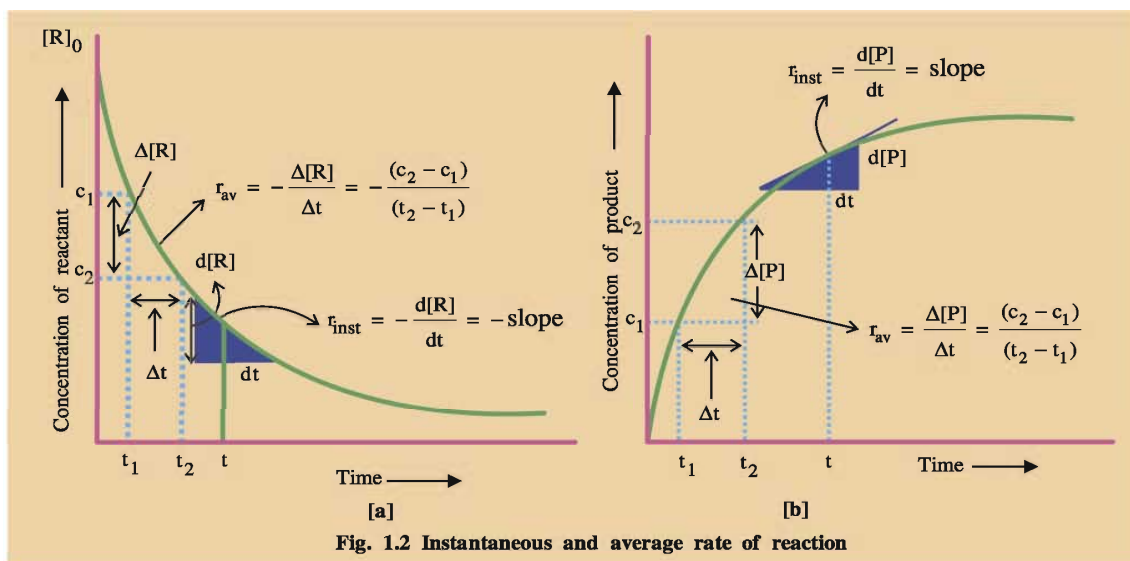


Fig. 1.2 Instantaneous and average rate of reaction

It is clear from the fig 1.2(a) that the rate of reaction decreases rapidly in the beginning and becomes less with the increase in time. The instantaneous rate ( $r_{inst}$ ) changes with the change in instantaneous speed so the instantaneous rate ( $r_{inst}$ ) is changing. The instantaneous rate ( $r_{inst}$ ) at any instant of time ( $t$ ) has definite value. The **instantaneous rate** can be expressed mathematically as follows :

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \quad \text{OR} \quad r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt} \quad (\text{when } \Delta t \rightarrow 0) \quad \dots (1.2)$$

To determine **instantaneous rate**, at any time ( $t$ ) in the graph showing concentration of reactant versus time a tangent (Fig. 1.2) is drawn. The slope of the tangent of the curve is equal to the instantaneous rate at that time.

$$r_{inst} = -\text{slope (for R)} = -\frac{d[R]}{dt}$$

$$r_{inst} = +\text{slope (for P)} = \frac{d[P]}{dt}$$

**Example 1 :** The following results are obtained in the hydrolysis of chlorobutane ( $C_4H_9Cl$ ) :

Time (Sec)	0	100	200	300	400	700	800
Concentration of chlorobutane ( $\text{mol lit}^{-1}$ )	0.100	0.082	0.067	0.055	0.044	0.021	0.017

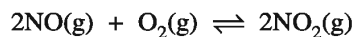
Find out average rate  $r_{av}$  of the reaction during different intervals of time.

**Solution :** From the given results a table as below can be prepared :

No.	Time ( $t_1$ ) second	Time( $t_2$ ) second	Concentration at time $t_1$ $R_1$ (mol lit <sup>-1</sup> )	Concentration at time $t_2$ $R_2$ (mol lit <sup>-1</sup> )	$t_2 - t_1$ = $\Delta t$	$[R]_2 - [R]_1$ = $\Delta[R]$	Average $r_{av} = \frac{-\Delta[R]}{\Delta t}$ (mol lit <sup>-1</sup> sec <sup>-1</sup> )
1.	0	100	0.100	0.082	100	-0.018	$1.8 \times 10^{-4}$
2.	100	200	0.082	0.067	100	-0.015	$1.5 \times 10^{-4}$
3.	200	300	0.067	0.055	100	-0.012	$1.2 \times 10^{-4}$
4.	300	400	0.055	0.044	100	-0.011	$1.1 \times 10^{-4}$
5.	400	700	0.044	0.021	300	-0.023	$7.7 \times 10^{-5}$
6	700	800	0.021	0.017	100	-0.004	$4.0 \times 10^{-5}$

It is apparent from the results that the average rate  $r_{av}$  decreases from  $1.8 \times 10^{-4}$  to  $4.0 \times 10^{-5}$  mol lit<sup>-1</sup> sec<sup>-1</sup>. It is difficult to show instantaneous rate of reaction. To determine reaction rate at any time, the instantaneous rate is to be determined. For which a graph of concentration of reactant versus time is drawn.

The reaction above was resulting from 1mole reactant to one mole product. Thus, the stoichiometric coefficients were 1. In all the reactions it may not happen like this and so, the stoichiometric coefficients may be different viz. in the following reaction.



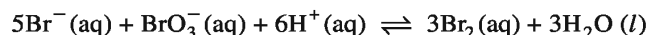
Two moles of one reactant NO and one mole of other reactant O<sub>2</sub> react and 2 moles of product NO<sub>2</sub>, are obtained. Thus, coefficient becoming different, to calculate the change in concentration they are to be taken into consideration. There will be two times decrease in concentration of NO in comparison to concentration of O<sub>2</sub> which will be equal to the change in concentration of NO<sub>2</sub> but will be opposite. As seen earlier the rate of reaction can be determined by determining concentration of reactant or product but the determination must be consistent. In chemical kinetics, the following method (convention) is accepted.

$$\begin{aligned} \text{Rate of reaction} &= -\frac{1}{\nu_R} \left( \frac{d[R]}{dt} \right) \\ &= +\frac{1}{\nu_P} \left( \frac{d[P]}{dt} \right) \end{aligned} \quad \dots (1.3)$$

where R is reactant and its stoichiometric coefficient is  $\nu_R$  and P is any product whose stoichiometric coefficient is  $\nu_P$ . If we write the above equation in this convention, then

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{-d[\text{O}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NO}_2]}{dt} \quad \dots (1.4)$$

Suppose the reaction is as follows :



$$\text{Then rate} = -\frac{1}{5} \frac{d[\text{Br}^-]}{dt} = -\frac{d[\text{BrO}_3^-]}{dt} = -\frac{1}{6} \frac{d[\text{H}^+]}{dt} = \frac{1}{3} \frac{d[\text{Br}_2]}{dt} \quad \dots (1.5)$$

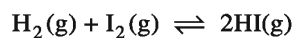
In aqueous solution, there is negligible change in concentration of water and so the change in its concentration is not expressed.

From the above discussion, for any reaction  $n_1\text{A} + n_2\text{B} = n_3\text{C} + n_4\text{D}$

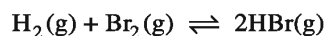
$$\text{Rate} = -\frac{1}{n_1} \frac{d[\text{A}]}{dt} = -\frac{1}{n_2} \frac{d[\text{B}]}{dt} = +\frac{1}{n_3} \frac{d[\text{C}]}{dt} = +\frac{1}{n_4} \frac{d[\text{D}]}{dt} \quad \dots (1.6)$$

For gaseous reaction the rate at given temperature will depend on the pressure of reactant or product. Sometime there is effect of external foreign material present, on the concentration.

The presentation of rate of reaction with reference to concentration of reactants is called **rate law**. This rate law in the wide range of concentrations of reactant or product is studied and the law that is established is called differential rate equation or rate expression. This presentation of rate is not easy, because if the same reaction is carried out in different conditions, it changes viz.



Rate =  $K [\text{H}_2][\text{I}_2]$  where  $K$  is constant but other reaction of the same type for



$$\text{rate} = \frac{K_1[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{1 + K_2 [\text{HBr}/\text{Br}_2]} \quad \dots (1.7)$$

where  $K_1$  and  $K_2$  are constants

These constants depend on the temperature. In the absence of  $\text{HBr}$ , the rate of above reaction will be as follows :

$$\text{Rate} = K[\text{H}_2][\text{Br}_2]^{\frac{1}{2}} \quad \dots (1.8)$$

If the reaction instead of being simple, parallel reactions are occurring then, the terms on the right side will be more than one.

**Example 2 :** The study of decomposition of  $\text{N}_2\text{O}_5$  prepared in  $\text{CCl}_4$  at 318 K. was carried out. In the beginning the concentration of  $\text{N}_2\text{O}_5$  was  $2.33 \text{ mol lit}^{-1}$ . After 184 minute it decreases and became  $2.08 \text{ mol lit}^{-1}$ . The reaction occurs as below :



Find average rate of reaction.

**Solution :**

**Reaction occurs as :**  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

$$\begin{aligned} \text{Average rate} &= -\frac{1}{2} \left\{ \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \right\} \\ &= -\frac{1}{2} \left\{ \frac{(2.08 - 2.33) \text{ mol lit}^{-1}}{184 \text{ min}} \right\} \\ &= 6.79 \times 10^{-4} \text{ mol lit}^{-1} \text{ min}^{-1} \end{aligned}$$



#### 1.4 Rate Constant and Order of Reaction

In most of the reactions carried out by taking pure reactant, the simple rate equation can be obtained in which rate is proportional to exponent of the concentration of reactant. In one of the reactions seen above  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  the rate is directly proportional to concentration of reactants hydrogen and iodine. While in other reaction it is directly proportional to concentration of hydrogen and square root of concentration of bromine.

Reaction rate  $\propto [\text{H}_2][\text{I}_2]$  and

Reaction rate  $\propto [\text{H}_2][\text{Br}_2]^{\frac{1}{2}}$

Suppose we take reaction of decomposition of  $\text{N}_2\text{O}_5(\text{g})$ , then,

Reaction rate  $= -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} \propto [\text{N}_2\text{O}_5]$  OR

$$-\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = K [\text{N}_2\text{O}_5] \quad \dots (1.9)$$

where K is **rate constant** and it is called **specific rate constant** when concentration of reactant is 1M. Thus the rate of reaction is proportional to exponent 1 of concentration of  $\text{N}_2\text{O}_5$ . This exponent is called order of reaction in relation to reactant. In this reaction its value is 1. It is necessary to note that the order of reaction has no relation with the stoichiometric coefficient of reactant viz. The stoichiometric coefficient of  $\text{N}_2\text{O}_5$  is 2 even then the order of reaction is 1.

If we write in a general form, for the reaction  $n_1\text{A} + n_2\text{B} = n_3\text{C} + n_4\text{D}$

$$\text{Reaction rate} = K [\text{A}]^x[\text{B}]^y \quad \dots (1.10)$$

The meaning of this is that the order of reaction with reference to reactant A is x and with that of reaction B is y. Hence the total order of reaction is the sum of exponents equal to (x + y), for the reaction as seen earlier

$5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightleftharpoons 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$  the reaction rate on the basis of experimental results can be written as follows :

$$\text{Reaction rate} = K[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2 \quad \dots (1.11)$$

i.e. in the above reaction with reference to  $[\text{Br}^-]$  and  $[\text{BrO}_3^-]$  it is first order and with reference to  $[\text{H}^+]$  it is of second order. The total order of reaction will be  $1 + 1 + 2 = 4$ . The total order of reaction can be positive integer, zero or even a fraction.

Thus the **total order of reaction** is equal to the sum of exponents of concentration of all reactants.

As studied earlier, the dimensions of rate is **concentration time<sup>-1</sup>**. In SI units concentration can be mentioned by  $\text{mol m}^{-3}$  or  $\text{mol cm}^{-3}$  but  $\text{mol lit}^{-1}$  unit is in general use. Generally time is taken in second but it can be in minute, hour, day, year etc. Time is taken in years because of very slow reaction e.g. nuclear reaction of uranium. While many reactions are very fast (neutralisation of strong acid and strong base) and so nanosecond ( $10^{-9}$  sec.) or picosecond ( $10^{-12}$  sec.) are taken.

As studied earlier.

$$\text{Rate of reaction} = K [A]^x[B]^y \quad \dots (1.12)$$

$$K = \frac{\text{Reaction rate}}{[A]^x[B]^y} \quad \dots (1.13)$$

where,  $x + y$  will be the total order of reaction. Thus dimension of rate constant depends on order of reaction. The dimensions of  $K = \frac{(\text{Concentration})}{(\text{Time})(\text{Concentration})^n} = (\text{Time}^{-1})(\text{Concentration}^{1-n})$ . The units of  $K$  for reactions of different orders are shown in table 1.1

Table 1.1

Order	Type of reaction	Unit of K (in sec.)	Unit of K (general)
0	Zero order reaction	$\text{mol lit}^{-1} \text{sec}^{-1}$	$\text{mol lit}^{-1} \text{time}^{-1}$
1	First order reaction	$\text{sec}^{-1}$	$\text{time}^{-1}$
2	Second order reaction	$(\text{mol lit}^{-1})^{-1} \text{sec}^{-1}$	$(\text{mol lit}^{-1})^{-1} \text{time}^{-1}$
n	n order reaction	$(\text{mol lit}^{-1})^{1-n} \text{sec}^{-1}$	$(\text{mol lit}^{-1})^{1-n} \text{time}^{-1}$

The order of reaction can be determined experimentally. The methods for this will be studied later on in this unit.

### 1.5 Molecularity

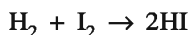
The second important term in addition to order of reaction is the **molecularity**. It can be defined for an elementary reaction. There is no meaning of molecularity for complex reaction. The definition of molecularity for an elementary reaction can be given as below :

**“The number of atoms, ions or molecules of the reactant that take part in the reaction and which experience collision with each other so that the reaction results, it is called molecularity of the reaction.”** If one molecule is associated in the reaction it is called monomolecular (unimolecular) reaction. e.g. Decomposition of ammonium nitrite  $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ . In bimolecular reaction two molecules have collision with each other e.g. decomposition of hydrogen iodide  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ .

In termolecular reaction three molecules collide with one another e.g. reaction of nitric oxide with dioxygen  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ .

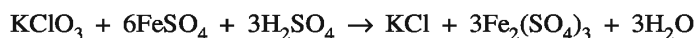
The possibility of collision of three or more molecules with one another and to result in the reaction is less. The molecularity more than three is not seen. Hence, the orders of reactions and molecularities of bimolecular, trimolecular elementary reaction are same.

$\text{H}_2$  and  $\text{I}_2$  combine and form HI.



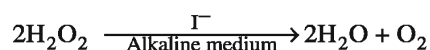
In this, one molecule of hydrogen and one molecule of iodine is used and so its molecularity is  $1 + 1 = 2$ , i.e. it is a bimolecular reaction. Looking to the order of the reaction, the exponents of  $\text{H}_2$  and  $\text{I}_2$  are 1 and 1. Hence the order of reaction will be  $1 + 1 = 2$ . Thus the order of reaction and molecularity are same i.e. 2. For monomolecular reaction, the order of reaction will be one at high pressure or concentration but at lower pressure or concentration the order will be 2. Under those circumstances, it does not remain elementary reaction. The order of reaction of the following reaction will be 10.



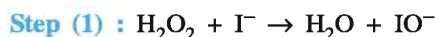


but, in fact its order of reaction is 2. The reason for this is that in a reaction occurring in more than one steps, the slowest step in the reaction determines order of reaction and so it becomes rate determining step.

The reaction of decomposition of hydrogen peroxide in presence of iodide ion catalyst occurs as follows :



In this reaction, it is first order reaction with reference to both  $\text{H}_2\text{O}_2$  and  $\text{I}^-$  but this reaction occurs in following two steps.



Both the steps are bimolecular elementary reactions;  $\text{IO}^-$  is called intermediate. It is formed during the reaction but is not found in overall reaction. First step is slow and hence it is rate determining step. Hence the formation of intermediate  $\text{IO}^-$  decides the rate of reaction. From this type of study following can be concluded.

- (1) The order of reaction is an experimental quantity. It can be zero or even a fraction, while molecularity of a reaction cannot be zero or fraction.
- (2) The order of reaction can be applied to elementary as well as complex reaction, while molecularity is applicable only to elementary reaction. Hence there is no meaning of molecularity for a complex reaction.
- (3) For complex reaction the slowest step shows the order of reaction and generally the molecularity of the slowest step is equal to the order of the total reaction.

**Example 3 :** The following are the results of the three experiments carried for determination of differential rate of reaction  $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$  at definite temperature. (1) Deduce the differential rate law (2) Calculate order of reaction and (3) Find out value of rate constant.

No	Initial concentration of reactants mol lit <sup>-1</sup>		Initial rate of reaction $-\frac{d[\text{Cl}_2]}{dt}$ mol lit <sup>-1</sup> sec <sup>-1</sup>
	[NO]	[Cl <sub>2</sub> ]	
1	0.01	0.02	$3.50 \times 10^{-4}$
2	0.02	0.02	$1.40 \times 10^{-3}$
3	0.01	0.04	$7.00 \times 10^{-4}$

**Solution :**  $-\frac{d[\text{Cl}_2]}{dt} = \text{K}[\text{NO}]^a [\text{Cl}_2]^b$

Putting the experimental values in the equation.

(i)  $3.50 \times 10^{-4} = \text{K}(0.01)^a (0.02)^b$     (ii)  $1.40 \times 10^{-3} = \text{K}(0.02)^a (0.02)^b$

(iii)  $7.00 \times 10^{-4} = \text{K}(0.01)^a (0.04)^b$

Dividing equation (ii) by equation (i),

$$\frac{1.40 \times 10^{-3}}{3.50 \times 10^{-4}} = \left(\frac{0.02}{0.01}\right)^a$$

$$\therefore 4 = (2)^a \therefore a = 2$$

Dividing equation (iii) by equation (i),

$$\frac{7.00 \times 10^{-4}}{3.50 \times 10^{-4}} = \left(\frac{0.04}{0.02}\right)^b$$

$$\therefore 2 = (2)^b \therefore b = 1$$

$$\therefore -\frac{d[\text{Cl}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = K[\text{NO}]^2[\text{Cl}_2]^1$$

$$\therefore \text{Total order of reaction} : 2 + 1 = 3$$

$$\text{Now, Rate constant } K = -\frac{d[\text{Cl}_2]/dt}{[\text{NO}]^2[\text{Cl}_2]^1}$$

Putting any of the experimental results in the equation, the value of K can be calculated.

$$K = \frac{3.50 \times 10^{-4} \text{ mol lit}^{-1} \text{ sec}^{-1}}{(0.01)^2 \text{ mol}^2 \text{ lit}^{-2} \times 0.02 \text{ mol lit}^{-1}} = 175 \text{ lit}^2 \text{ mol}^{-2} \text{ sec}^{-1}$$

## 1.6 Integrated Rate Law

We have seen that the change in concentration on rate is the differential rate equation. Always it is not easy to determine instantaneous rate as we have seen for the measurement of instantaneous rate. Thus it is a difficult work to determine rate of reaction from differential rate. Hence, the use of integrated rate law can be made. This law simplifies the determination of concentration at different times. It is also practical in chemical kinetics. We shall understand this integrated rate for zero and first order reaction.

## 1.7 Zero Order Reaction

The meaning of zero order reaction is that **the rate of the reaction is proportional to zero exponent of the concentration of reactant**. Exponent zero means, the value of term will be 1, that is will be constant. Hence for zero order reaction  $R \rightarrow P$  (R = Reactant and P = Product) :

$$\text{rate} = -\frac{d[\text{R}]}{dt} = K [\text{R}]^0 = K (1) = K \quad \dots (1.14)$$

$$\therefore -d[\text{R}] = Kdt \quad \dots (1.15)$$

On intergration,

$$[\text{R}] = -Kt + C \quad \dots (1.16)$$

where C is the integration constant and its value can be determined for the concentration at time  $t = 0$  or  $[\text{R}]_0 = C$

$$\therefore [\text{R}]_0 = -K \times 0 + C = C \text{ OR } [\text{R}]_0 = C \quad \dots (1.17)$$

Putting this in equation (1.16)

$$[R] = -Kt + [R]_0 \quad \dots (1.18)$$

Now, if we draw graph of concentration  $[R]$  versus time  $(t)$  then straight line will be obtained. (Fig 1.3) and the value of the slope will be equal to the negative value of  $K$  i.e.  $-K$  and the value of the intercept will be  $[R]_0$  that is the concentration at zero time or equal to initial concentration  $[R]_0$ .

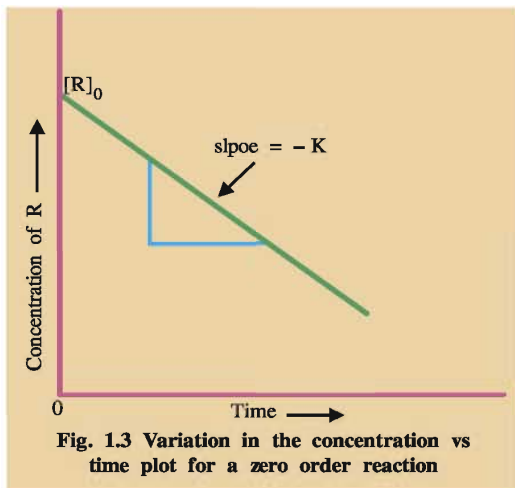


Fig. 1.3 Variation in the concentration vs time plot for a zero order reaction

Equation 1.18 can be written in this form

$$[R] = -Kt + [R]_0$$

$$-Kt = [R] - [R]_0 \quad \dots (1.19)$$

$$\therefore Kt = [R]_0 - [R] \quad \dots (1.20)$$

$$\therefore K = \frac{[R]_0 - [R]}{t} \quad \dots (1.21)$$

Now, if we write the values of reactant at different times  $(t)$  as  $[R]_t$  then equation 1.21 can be written as follows :

$$K = \frac{[R]_0 - [R]_t}{t} \quad \dots (1.22)$$

**Half life period of reaction :** Half life period of reaction means the time required for the concentration of the reactant in the reaction to be half. The half life period of radioactive elements is definite and it is expressed as  $t_{1/2}$ . If we put the value of concentration at time  $t_{1/2}$  in equation 1.22 then,

$$[R]_t = \frac{1}{2}[R]_0 \quad \text{so}$$

$$t_{1/2} = \frac{[R]_0 - \frac{1}{2}[R]_0}{K} = \frac{[R]_0}{2K} \quad \dots (1.23)$$

It is apparent from above that the **half life period ( $t_{1/2}$ ) of a zero order reaction is directly proportional to initial concentration  $[R]_0$  and inversely proportional to rate constant.**

Zero order reactions are mostly found in heterogeneous reactions viz. adsorption of adsorbent on the surface of the adsorbate. In adsorption reaction the fraction of the surface of the catalyst occupied is proportional to concentration and so it becomes first order reaction but the situation does not change with more and more adsorption and so rate becomes independent of concentration that is it becomes zero order reaction.

The adsorption of ammonia gas on the surface of the finely divided nickel catalyst is proportional to pressure (concentration) of ammonia gas but at high pressure (more concentration) the surface is completely covered and so it becomes zero order reaction. The rate of this reaction can be shown by following equation,

$$\text{rate} = K_1 \cdot \frac{[\text{NH}_3]}{1 + K_2[\text{NH}_3]}$$

$K_1$  and  $K_2$  are constants and  $[\text{NH}_3]$  is concentration of ammonia. If  $[\text{NH}_3]$  is less than  $K_2[\text{NH}_3]$  can be neglected in comparison to 1 and so rate =  $K_1[\text{NH}_3]$  and the reaction will be first order reaction. At high concentrations of  $\text{NH}_3$ , 1 can be neglected in comparison to  $[\text{NH}_3]$ .

$$\text{Hence, rate} = \frac{K_1[\text{NH}_3]}{K_2[\text{NH}_3]} = \frac{K_1}{K_2} = K$$

That is the reaction will be of zero order and the specific rate constant  $K$  for the reaction can be obtained.

### 1.8 Rate Equation For First Order Reaction

In the first order reaction **the rate of reaction is proportional to exponent one of concentration of reactant** e.g., For reaction  $\text{R} \rightarrow \text{P}$

$$\text{Rate of reaction} = -\frac{d[\text{R}]}{dt} = K[\text{R}] \quad \dots (1.24)$$

OR

$$= -\frac{d[\text{R}]}{[\text{R}]} = Kdt \quad \dots (1.25)$$

Integrating equation (1.25)

$$\ln[\text{R}] = -Kt + C \quad \dots (1.26)$$

where  $C$  is integration constant. Its value can be obtained from the concentration of reactant  $[\text{R}]_0$  at zero time ( $t_0$ ). When  $t = 0$  then  $[\text{R}] = [\text{R}]_0$ . Putting this value in equation (1.26).

$$\ln[\text{R}]_0 = -K \times 0 + C = 0 + C$$

Putting this value in equation (1.26),

$$\ln[\text{R}] = -Kt + \ln[\text{R}]_0 \quad \dots (1.27)$$

$$\therefore Kt = \ln[\text{R}]_0 - \ln[\text{R}] \quad \dots (1.28)$$

$$\therefore K = \frac{1}{t} \ln \frac{[\text{R}]_0}{[\text{R}]} \quad \therefore K = \frac{2.303}{t} \log_{10} \frac{[\text{R}]_0}{[\text{R}]_t} \quad (\text{Where } [\text{R}]_t = \text{Concentration at time 't'}) \quad \dots (1.29)$$

Suppose the concentration  $[\text{R}]_1$  and  $[\text{R}]_2$  of the reactants are determined at times  $t_1$  and  $t_2$  and put in the equation (1.29) then,

$$K = \frac{1}{(t_2 - t_1)} \ln \frac{[\text{R}]_1}{[\text{R}]_2} \quad \dots (1.30)$$

If equation (1.27) is rewritten in the exponential form, it can be written as  $[\text{R}] = [\text{R}]_0 e^{-Kt}$

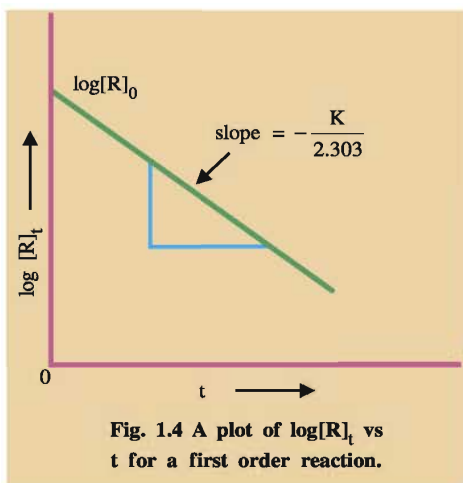
If we think of equation  $\ln [\text{R}]_t = -Kt + \ln[\text{R}]_0$ , then if a graph of values of  $\ln[\text{R}]_t$  obtained is plotted against different times ( $t$ ) then a straight line is obtained and the value of slope will be equal to  $-K$  and the value of intercept will be equal to  $\ln [\text{R}]_0$ . Writing the above equation to the base 10 of logarithm the above equation  $\ln [\text{R}]_t = -Kt + \ln[\text{R}]_0$  can be written as.

$$2.303 \log [\text{R}]_t = -Kt + 2.303 \log [\text{R}]_0 \quad \dots (1.31)$$

Dividing equation 1.31 by 2.303,

$$\log_{10}[R]_t = -\frac{K}{2.303}t + \log_{10}[R]_0 \quad \dots (1.32)$$

Hence, if a graph of  $\log_{10} [R]_t$  against  $t$  is plotted a straight line will be obtained and the value of slope will be equal to  $-\frac{K}{2.303}$  and the value of intercept will be equal to  $\log_{10} [R]_0$  (fig 1.4).



As seen earlier, if time  $t$  is taken such that the initial concentration of the reactant becomes half. i.e.  $[R]_t = \frac{1}{2}[R]_0$ . This time is called half life period. Putting these values in equation 1.32.

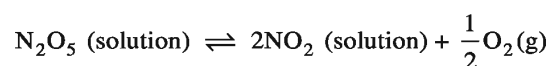
$$\log \frac{1}{2}[R]_0 = -\frac{K}{2.303}t_{1/2} + \log[R]_0 \quad \dots (1.33)$$

$$\therefore \frac{K}{2.303}t_{1/2} = \frac{\log[R]_0}{\log \frac{1}{2}[R]_0} = \log 2 \quad \dots (1.34)$$

$$\therefore t_{1/2} = \log 2 \times \frac{2.303}{K} = \frac{0.3010 \times 2.303}{K} = \frac{0.693}{K} \quad \dots (1.35)$$

$t_{1/2}$  will be constant because 0.693 and  $K$  both are constants. **Thus, the half life period of first order reaction is independent of initial concentration of reactant and is inversely proportional to rate constant  $K$ .** The study of this is included in subject of nuclear chemistry, where reactions are of first order.

**Example 4 :** The decomposition of  $N_2O_5$  dissolved in carbon tetrachloride, occurs as follows :



This reaction is of first order and its rate constant is  $5.0 \times 10^{-4} \text{ sec}^{-1}$ . If initial concentration of  $N_2O_5$  for this reaction is 0.30 mole, then (i) What will be the initial reaction rate ? (2) What will be half life period of this reaction ? (iii) What time will it take to complete 80% reaction and what will be concentrations of  $N_2O_5$  and  $NO_2$  at the end of 40 minutes after the starting of reaction ?

**Solution :**

$$(1) \text{ Reaction rate } -\frac{d[N_2O_5]}{dt} = KC_O = 5.0 \times 10^{-4} \text{ sec}^{-1} \times 0.30 \text{ mol lit}^{-1} \\ = 1.5 \times 10^{-4} \text{ mol lit}^{-1} \text{ sec}^{-1}$$

$$(2) \text{ Half life period } t_{1/2} = \frac{0.693}{K} = \frac{0.693}{5.0 \times 10^{-4} \text{ sec}^{-1}} = 1386 \text{ sec}$$

$$(3) \text{ When reaction is 80\% completed, the concentration of remaining } N_2O_5 = \frac{(100 - 80)}{100} \times 0.30 \\ = 6 \times 10^{-2} \text{ mol lit}^{-1}$$

$$K = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\begin{aligned} \therefore t &= \frac{2.303}{5 \times 10^{-4}} \log \frac{0.30}{6 \times 10^{-2}} \\ &= 3219 \text{ second} = 3.219 \times 10^3 \text{ sec} \end{aligned}$$

$$\begin{aligned} (4) \text{ The concentration of } N_2O_5 \text{ at the end of 40 minutes} &: 5 \times 10^{-4} = \frac{2.303}{40 \times 60} \log \frac{0.30}{C} \\ &= 0.0903 \text{ mol lit}^{-1} \approx 0.09 \text{ mol lit}^{-1} \end{aligned}$$

At the end of 40 minutes decrease in concentration of  $N_2O_5$  will be decreased by =  $0.30 - 0.09$   
 $= 0.21 \text{ mol lit}^{-1}$

2 moles  $N_2O_5$  are obtained by decomposition of 1 mole of  $N_2O_5$  and so at the end of 40 minutes concentration of  $NO_2 = 2.0 \times 0.21 = 0.42 \text{ mol lit}^{-1}$ .

**Example 5 :** In a first order reaction, the concentration of reactant decreases from  $0.060$  to  $0.040 \text{ mol lit}^{-1}$  and this requires 45 minutes, what will be the half life period of this reaction?

**Solution :**  $K = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]_t}$

$$K = \frac{2.303}{45} \log_{10} \frac{0.06}{0.04}$$

$$K = 9.01 \times 10^{-3} \text{ min}^{-1}$$

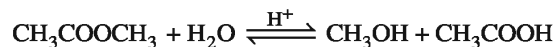
Now, half life period

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{9.01 \times 10^{-3}}$$

$$= 7.69 \times 10^1 = 76.9 \text{ min}$$

### 1.9 Pseudo First Order Reaction

Some reactions are of first order with reference to two different reactants e.g. the rate of a reaction =  $K [A][B]$ ; suppose the concentration of reactant A is less in comparison to concentration of reactant B; viz.  $[A] = 0.01 \text{ M}$  and  $[B] = 55.55 \text{ M}$ . (molarity of water), then concentration of water during the reaction decreases to  $55.55 - 0.01 = 55.54 \text{ M}$ , which can be taken almost as  $55.5 \text{ M}$ . because  $0.01 \text{ M}$  can be neglected. Thus, even when the reaction is completed, the concentration of water does not change appreciably. That is if it can be taken as constant then the rate =  $K_0[A]$  can be written where  $K_0 = K[B]$  will be constant. Now, this reaction will act as first order reaction. Such reactions are called pseudo first order reactions. The hydrolysis of methyl acetate in presence of  $H^+$  gives methanol and ethanoic acid respectively.



In this reaction as seen above, the concentration of water remains almost constant and so this reaction will be considered of first order but this reaction is not really first order reaction, because both



the reactants are consumed in this reaction and the exponents of their concentration are 1. Hence this reaction should be  $1 + 1 = 2$ , second order reaction. But considering concentration of water as constant, it becomes first order reaction and it is experimentally proved. **Such reaction is called pseudo first order reaction.** In your practical book this type of experiment is presented as demonstration experiment. If you record the results carefully during the demonstration experiment you will have more information about chemical kinetics, real reaction and pseudo reaction and will be able to understand more about determination of rate constant and the determination of order of reaction experimentally.

**Example 6 :** Acetic acid obtained by hydrolysis reaction of methyl acetate in presence of HCl is determined by titrating with sodium hydroxide. The concentration of ester (C) at different time (t) were obtained as below :

Time(t) in minutes	0	30	60	90
Concentration (C) of ester M	0.850	0.800	0.754	0.710

The above results show that this reaction is pseudo first order reaction. The concentration of water during the experiment remains constant as 54.2M. Calculate the value of rate constant K

**Solution :** As the concentration of water remains constant during pseudo first reaction this reaction will be first order reaction in relation to ester. The calculation values can be shown as follows in the table given below :

Time (t) in minutes	Concentration of ester (C) M	$K[\text{H}_2\text{O}] = \frac{2.303}{t} \log_{10} \frac{C_0}{C}$
0	0.850	–
30	0.800	$2.016 \times 10^{-3}$
60	0.754	$1.996 \times 10^{-3}$
90	0.710	$1.996 \times 10^{-3}$

It is apparent from the table that the value of K [H<sub>2</sub>O] is constant and the approximate value obtained is  $1.996 \times 10^{-3} \text{ min}^{-1}$ . In the calculation of rate constant the equation used is for first order reaction. We got value of K as constant and so this reaction is of first order,

$$\text{Now } K [\text{H}_2\text{O}] = 1.996 \times 10^{-3}$$

$$\therefore K \times (54.2) = 1.996 \times 10^{-3}$$

$$\therefore K = \frac{1.996 \times 10^{-3}}{54.2}$$

$$= 3.683 \times 10^{-5} \text{ mol}^{-1} \text{ lit min}^{-1}$$

The unit of K is for second order reaction. Hence, the hydrolysis reaction of ester is of pseudo first order reaction.

The integrated rate law can be expressed for zero and first order reaction as follows :

Order of reaction	Type of Reaction	Differential rate law	Integrated rate law	Straight line graph	Half life period	Unit of K
0	R → P	-d[R] / dt = K	Kt = [R] <sub>0</sub> - [R] <sub>t</sub>	[R] vs t	[R] <sub>0</sub> / 2K	con. time <sup>-1</sup> or mol lit <sup>-1</sup> sec <sup>-1</sup>
1	R → P	-d[R] / dt = K[R]	Kt = ln[R] <sub>0</sub> / [R] <sub>t</sub>	ln [R] vs t	ln 2 / K	time <sup>-1</sup> or sec <sup>-1</sup>

### 1.10 Determination of Order of Reaction

The methods used for determination of order of reaction are as follows :

(1) Initial rate method (2) Use of Integrated rate equation method or Graphical method (3) Half life (reaction time) method and (4) Ostwald's isolation method. From the above methods we shall study only three methods-Integrated rate equation or graphical method, Ostwald's isolation method and half life method in detail.

**(1) Integrated Rate Equation Method :** The following equations are used for determination of reaction rate constant for zero and first order reactions

$$\text{For zero order reaction : } K = \frac{[R]_0 - [R]_t}{t}$$

$$\text{For first order reaction : } K = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]_t}$$

Thus the concentration of reactant [R]<sub>t</sub> is determined experimentally at different time (t) and calculated the values of K by substituting the experimental values in the above equation for zero or first order reaction, and values of K can be found out. If the calculation of value of K, is carried out using

$K = \frac{[R]_0 - [R]_t}{t}$  and the value of K remains almost constant, then the reaction should be of zero order

reaction. If the value of K is calculated by putting the values in equation  $K = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]_t}$  and the

values of K obtained are constant then the reaction should be of first order. In this way for zero and first order reaction, trial and error method for calculation of K is carried out to find whether K obtained is constant or not and from that the order of reaction can be determined.

In addition to calculating as earlier the **graphical method** can also be used. For this the above equation can be transformed to Y = mX + C type straight line graph and graph can be plotted viz.

$$\text{For zero order reaction } K = \frac{[R]_0 - [R]_t}{t}$$

This equation can be changed as Kt = [R]<sub>0</sub> - [R]<sub>t</sub> or [R]<sub>t</sub> = [R]<sub>0</sub> - Kt

Now, if concentration [R]<sub>t</sub> is plotted on Y-axis and time (t) on X-axis and the graph is drawn for experimental results, the graph obtained will be straight line which proves that the reaction should be of zero order. The value of K can be obtained from the slope and [R]<sub>0</sub> from the value of intercept of graph.

For first order reaction,  $K = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]_t}$

can be changed as :  $\frac{Kt}{2.303} = \log_{10} [R]_0 - \log_{10} [R]_t$  or  $\log_{10} [R]_t = \log_{10} [R]_0 - \frac{K}{2.303} t$

Now if  $\log_{10}[R]_t$  on Y-axis and time (t) on X-axis is taken and graph is plotted of the experimental results, then a straight line will be obtained which proves that the reaction is of first order. The value of K can be obtained from the slope of the graph. The value of slope =  $-\frac{K}{2.303}$  or  $-\text{slope} \times 2.303 = K$  and the value of  $\log_{10}[R]$  as the intercept of the graph.

**(2) Ostwald's Isolation method :** In certain reactions there is involvement of more than one reactants. To determine the order of reaction of such reactions, Ostwald gave a method which is known as Ostwald's isolation method. In this method, the concentration of other reactants in comparison to one reactant is taken in very large proportion. The reaction rate will be indicative with respect to reactant with less concentration because the concentration of other reactants remain almost constant. Including the constant terms, we can write the equation for rate of reaction.

$$\text{Rate} = K[A]^a [B]^b [C]^c = K_0[A]^a \text{ (where } K_0 = [B]^b [C]^c \text{)}$$

As [B] and [C] are in very large proportion they are accepted as constant which are included in  $K_0$ . The value "a" that is the order of reaction with reference to A can be determined. Thus the order of reaction with reference to B and C can be determined by changing (by increasing) concentrations of A, B and C. The above method will be clear from the example given below :

**Example 7 :** The reaction  $\text{CH}_3\text{COF} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{HF}$  was studied under following conditions :

Condition-I	Condition-II
$[\text{H}_2\text{O}]_0 = 1.00 \text{ M}$	$[\text{H}_2\text{O}]_0 = 0.02 \text{ M}$
$[\text{CH}_3\text{COF}]_0 = 0.01 \text{ M}$	$[\text{CH}_3\text{COF}]_0 = 0.80 \text{ M}$

Condition-I		Condition-II	
Time (t) min.	$[\text{CH}_3\text{COF}] \text{ M}$	Time (t) in min.	$[\text{H}_2\text{O}] \text{ M}$
0	0.01000	0	0.0200
10	0.00867	10	0.0176
20	0.00735	20	0.0156
40	0.00540	40	0.0122

Determine the order of reaction and calculate rate constant.

**Solution :** Suppose, Reaction rate =  $K[\text{CH}_3\text{COF}]^a [\text{H}_2\text{O}]^b$ . Ostwalds' method can be used. In condition-I  $[\text{H}_2\text{O}]_0 \gg [\text{CH}_3\text{COF}]_0$  and in condition-II  $[\text{H}_2\text{O}]_0 \ll [\text{CH}_3\text{COF}]_0$ .

Hence, in condition-I the order of reaction can be determined relative to  $\text{CH}_3\text{COF}$ . The reaction is not of zero order because reaction rate changes with time. Hence, the equation for first order can be applied and if we calculate; results as shown below are obtained.

Time (t) min.	M	$\text{K}[\text{H}_2\text{O}]^b = \frac{\ln \frac{[\text{CH}_3\text{COF}]_0}{[\text{CH}_3\text{COF}]_t}}{t}$
0	0.0100	–
10	0.00857	0.0154
20	0.00735	0.0154
40	0.00540	0.0154

Thus,  $\text{K}[\text{H}_2\text{O}] = 0.0154$  minute is obtained as constant. Hence the order of reaction relative to  $\text{CH}_3\text{COF}$  is 1. Now, applying the equation for first order, for water following values will be obtained.

Time (t) min.	$[\text{H}_2\text{O}]$ M	$\text{K}[\text{CH}_3\text{COF}]^a = \frac{\ln \frac{[\text{H}_2\text{O}]_0}{[\text{H}_2\text{O}]_t}}{t}$
0	0.0200	–
10	0.0176	0.0128
20	0.0156	0.0124
40	0.0122	0.0124

$\text{K}[\text{CH}_3\text{COF}] = 0.0124$  is constant Hence, order of reaction with reference to  $\text{H}_2\text{O}$  will be 1.

$$\begin{aligned} \text{In condition (I)} \quad \text{K} &= 0.0154 \text{ min}^{-1} / 1.0 \text{ M} \\ &= 0.0154 \text{ min}^{-1} \text{ M}^{-1} \end{aligned}$$

$$\begin{aligned} \text{In condition (II)} \quad \text{K} &= 0.0124 \text{ min}^{-1} / 0.800 \\ &= 0.0150 \text{ min}^{-1} \text{ M}^{-1} \end{aligned}$$

The order of reaction with reference to both the reactants obtained is 1. Hence, total number of order of reaction will be  $1 + 1 = 2$ .

**(3) Half life (Half reaction time) method :** In addition to the above two methods, the half life or half reaction time method is very simple. As studied earlier the time required to have initial concentration  $[\text{R}]_0$  to be exactly half i.e.  $\frac{1}{2}[\text{R}]_0$  is called half life period and it can be determined. The order of reaction can be obtained from following relations.

$$\text{For zero order reaction } t_{1/2} \propto [\text{R}]_0$$

$$\text{For first order reaction } t_{1/2} \text{ is independent of initial concentration.}$$

$$\text{For second order reaction } t_{1/2} \propto \frac{1}{[\text{R}]_0}$$

Hence, for  $n^{\text{th}}$  order reaction  $t_{1/2} \propto \frac{1}{[R]_0^{n-1}}$

Two theories are known for the study of chemical kinetics (1) Transition state theory and (2) Theory of collision. We shall study these theories later on.

### 1.11 Effect of Temperature on Rate Constant

Mostly the rate constant increases with increase in temperature. It is noted that if the graph (fig. 1.6) of rate constant  $\ln K$  or  $\log_{10} K$  is plotted against inverse of temperature, ( $T$  = temperature in Kelvin units) a straight line is obtained. This result is derived from Arrhenius equation.

#### Arrhenius equation :

Arrhenius equation can be expressed in the following form :

$$K = Ae^{-E_a/RT} \quad \dots (1.36)$$

where  $K$  = rate constant,  $A$  = Arrhenius constant,  $R$  = Gas constant,

$T$  = Temperature (absolute),  $E_a$  = Energy of activation.

Taking logarithm of equation 1.36.

$$\ln K = \ln A - \frac{E_a}{RT} \quad \text{or}$$

$$\ln K = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad \dots (1.37)$$

The values of rate constant  $K$  are determined at different temperatures, and a graph of  $\ln K$  versus  $\frac{1}{T}$  is plotted. Thus straight line will be obtained. By changing the equation (1.37) it can be written as

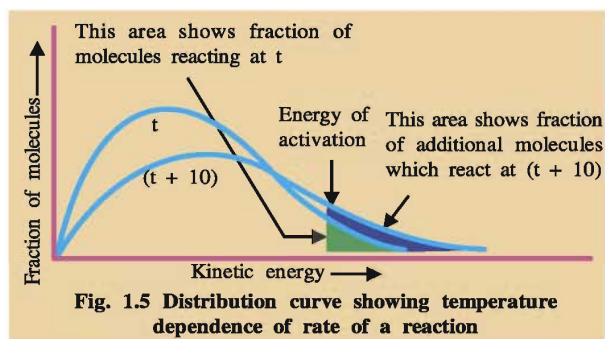
$$2.303 \log_{10} K = 2.303 \log_{10} A - \frac{E_a}{RT} \quad \text{or}$$

$$\log_{10} K = \log_{10} A - \frac{E_a}{2.303 R} \cdot \frac{1}{T} \quad \dots (1.38)$$

The energy of activation for a reaction being constant,  $R$  is gas constant, the above equation can be of straight line type. Hence, if a graph of  $\log K$  versus  $\frac{1}{T}$  is plotted, the value of slope will be  $-\frac{E_a}{2.303 R}$ . If the value of  $R$  is taken in k cal or k joule then the value of  $E_a$  will be also in k cal or k joule. From the value of intercept, the value of  $\log A$  will be obtained and constant  $A$  can be determined.

Arrhenius equation shows that rate constant increases exponentially with temperature. How can this exponential variation be studied? Is it due to increase in average kinetic energy of molecules? It is also noted in addition to this that by increasing temperature from 300 to 310 K, the kinetic energy increases only by 3 % because it is proportional to temperature. In addition to this, for most of the reactions the rates have almost **doubled by** increase in temperature by **10 K**. The explanation for this

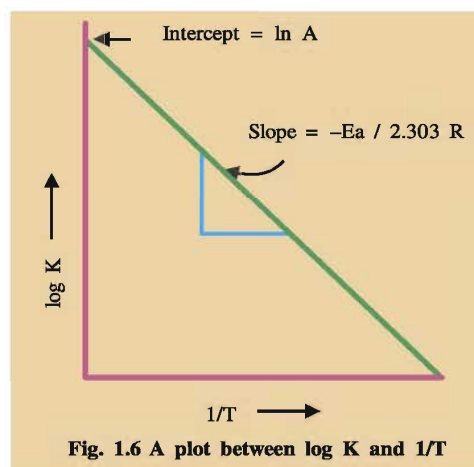
can be given that there must be some pushing energy or threshold energy required for the reaction of molecules. In the fig 1.5 this is shown,



$$E_a = N_A E^* \text{ where } N_A = \text{Avogadro number.}$$

In Arrhenius equation the parameter A is called pre-exponential factor or frequency factor.  $E_a$  is called energy of activation. Both of these factors are known as Arrhenius factors. To determine their values a graph of  $\log K$  versus  $\frac{1}{T}$  is plotted and from the value of the slope,  $E_a$  can be determined (fig 1.6). But for intercept  $\frac{1}{T} = 0$  taken then the value of T should be  $\infty$ . The rate constant of a reaction is determined from the change in the limited temperature range and so  $\frac{1}{T} = 0$  cannot

The graph of the fraction of the molecules which experience collision possessing different kinetic energy is plotted. It is apparent from this that the average relative kinetic energy increases as expected but the number of molecules (fig. 1.5 portion shown shaded) which possesses threshold relative kinetic energy. It shows increase of  $E^*$ . Thus the activation energy  $E_a$  and such kinetic energy ( $E^*$ ) can be shown by following relation.



be taken. Hence, by obtaining value of  $E_a$  all the values except A in the equation  $\log K = \log A - \frac{E_a}{2.303 R} \cdot \frac{1}{T}$  are substituted from any result (K and T) and the value of  $\log A$  will be obtained from which the Arrhenius constant or frequency factor can be determined. In physical chemistry, generally if a graph can be obtained then the results can be transformed in to equation of a straight line and graph is plotted. The values of slope and intercept are determined from the graph. Suppose the Arrhenius equation mentioned earlier is written corresponding to two different temperatures  $T_1$  and  $T_2$ , then we can write

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \quad \dots (1.39)$$

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \quad \dots (1.40)$$

$$\therefore \ln K_2 - \ln K_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2} \text{ or}$$

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \text{ or} \quad \dots (1.41)$$



$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots (1.42)$$

When the number of results is less than instead of drawing the graph values of  $K_1$  and  $K_2$  can be determined experimentally at temperatures  $T_1$  and  $T_2$  and by putting the values in equation 1.42, the value of  $E_a$  can be obtained. In any one of the equations, the values of  $E_a$ ,  $K$  and  $T$  are substituted and the value of,  $\log A$  or  $A$  can be obtained. In addition the value of  $E_a$  for any reaction is definite and so the rate constant ( $K$ ) at any other temperature ( $T$ ) can be evaluated from the value of  $E_a$ . This will be clear from the following example :

**Example 8 :** The rate constant of a reaction at  $27^\circ \text{C}$  is  $2 \times 10^{-3} \text{ minute}^{-1}$ . The temperature was increased by  $20^\circ \text{C}$  and the value of rate constant  $K$  increased three times. Calculate the energy of activation of the reaction. What will be value of rate constant at  $37^\circ \text{C}$  ?

**Solution :** The value of  $K$  at  $20^\circ \text{C}$  is  $2 \times 10^{-3} \text{ minute}^{-1}$ . If we increase temperature by  $20^\circ \text{C}$ ,  $K$  will be three times. i.e.  $3 \times 2 \times 10^{-3} = 6 \times 10^{-3} \text{ min}^{-1}$ . Now

$$T_1 = 27 + 273 = 300 \text{ K}, T_2 = 47 + 273 = 320 \text{ K},$$

$$K_1 = 2 \times 10^{-3} \text{ min}^{-1}, K_2 = 6 \times 10^{-3} \text{ min}^{-1}$$

$$R = 1.987 \times 10^{-3} \text{ kcal.}$$

Putting the above values in the following equation,

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\log \frac{6 \times 10^{-2}}{2 \times 10^{-2}} = \frac{E_a}{2.303 \times 1.987 \times 10^{-3}} \left( \frac{1}{300} - \frac{1}{320} \right)$$

$$\therefore \log 3 = \frac{E_a}{2.303 \times 1.987 \times 10^{-3}} \left( \frac{320 - 300}{300 \times 320} \right)$$

$$\therefore 0.4771 = \frac{E_a}{2.303 \times 1.987 \times 10^{-3}} \left( \frac{20}{300 \times 320} \right)$$

$$\therefore E_a = \frac{0.4771 \times 2.303 \times 1.987 \times 10^{-3} \times 300 \times 320}{20}$$

$$= 10.480 \text{ k cal}$$

Now we want to find out the value of  $K$  at  $37^\circ \text{C}$  then value of  $E_a = 10.480 \text{ k cal}$  can be used and any value of  $K$  and corresponding  $T$  will have to be taken.

$$\therefore \log \frac{K_{37}}{2 \times 10^{-3}} = \frac{10.480}{2.303 \times 1.987 \times 10^{-3}} \left( \frac{310 - 300}{310 \times 300} \right)$$

$$\therefore \log K_{37} - \log 2 \times 10^{-3} = \frac{10.480 \times 10}{2.303 \times 1.987 \times 10^{-3} \times 310 \times 300}$$

$$\therefore \log K_{37} - (-2.6990) = \frac{10.480 \times 10}{2.303 \times 1.987 \times 10^{-3} \times 310 \times 300}$$

$$\therefore \log K_{37} = -2.6990 + \frac{10.480 \times 10}{2.303 \times 1.987 \times 10^{-3} \times 310 \times 300}$$

$$= -2.6990 + 0.2463$$

$$= -2.4527$$

Changing before taking the antilogarithm  $-2.4537 = \bar{3}.5473$

$$\text{Antilog } \bar{3}.5473 = 3.526 \times 10^{-3}$$

$$\therefore K = 3.526 \times 10^{-3} \text{ min}^{-1}$$

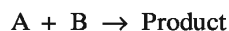
### 1.13 Theory of Collision

The theory of collision for chemical reaction was developed by Max Trauz and William Lewis in 1916-18. This principle deals with the energetic and mechanistic matter of the reaction. It is based on the theory of kinetic energy of gases.

According to this theory, it is supposed that the molecules are hard spheres and the reaction occurs only when these molecules collide with each other. In chemical reaction, the number of collision per second per unit volume is called collision frequency ( $Z$ ).

The other factor affecting rate of chemical reaction is the energy of activation about which you have studied in the Arrhenius equation.

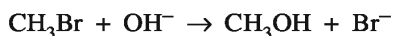
Suppose any bimolecular reaction is as follows

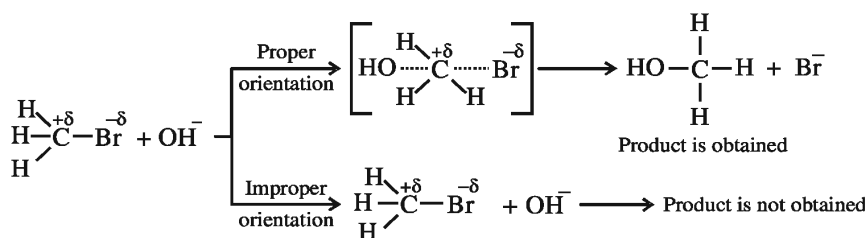


The rate of reaction can be shown as below :

$$\text{Rate} = Z_{AB} e^{-E_a/RT} \quad \dots (1.43)$$

where  $Z_{AB}$  is the **collision frequency** of reactants, A and B whose energy is equal to or more than  $e^{-E_a/RT}$  activation energy. This equation when compared with Arrhenius equation  $K = Ae^{-E_a/RT}$  it can be said that Arrhenius constant A is related to collision frequency  $Z_{AB}$ . The values of rate constants of reactions having atomic species or simple molecules can be determined accurately using equation (1.43), but there is notable deviation for complex molecules. The reason for this is that all the collisions, do not result into products. Those collisions in which molecules collide with sufficient kinetic energy (which is called threshold energy) and proper direction, then bonds of the reactants break and new bonds are formed resulting into products. Such collisions are called **effective or fruitful collisions**. If we take as an example the preparation of methanol from bromomethane the molecules are oriented as shown below. The reactant molecules having proper orientation lead to bond formation, where as improper direction makes them collide but do not result into product. We shall study the reaction :





For effective collision, another parameter is added which is called **steric factor or probability factor** which takes into consideration the collision from proper direction. Hence ,

$$\text{Rate} = PZ_{AB}e^{-E_a/RT} \quad \dots (1.44)$$

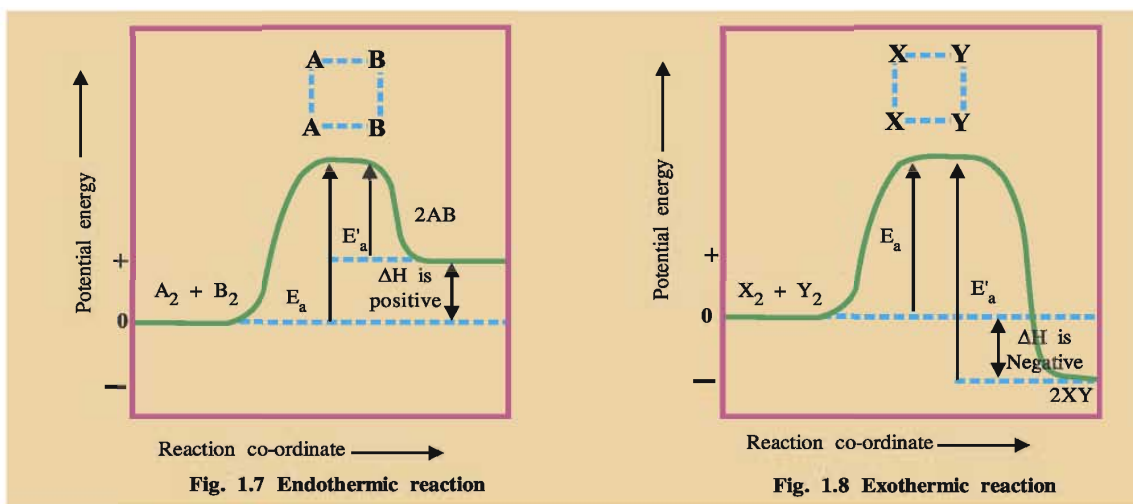
where, P = probability factor

Thus according to the collision theory, the combinations of activation energy and collision of molecules from proper direction are required for effective collision. Hence, the following points can be concluded :

- (1) The collisions between the reactants is essential
- (2) There must be certain minimum energy( threshold energy) for the reactant experiencing collision.
- (3) The collision of the reactant molecules should be in proper direction(orientations)
- (4) The reactants experiencing fruitful collision are converted to products

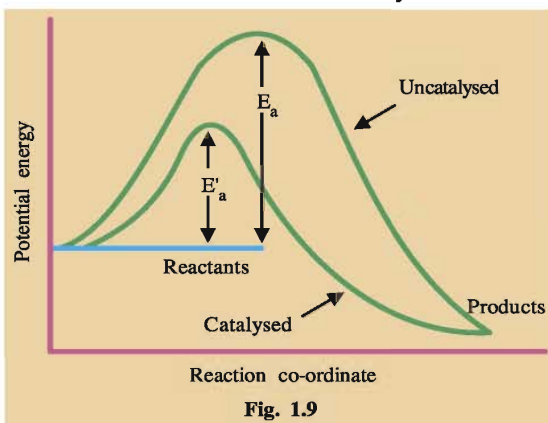
Many advantages of the phenomenon are found. Had there been no requirements mentioned as above the oxygen of the air will be reacting experiencing fruitful collision with carbon and would burn. The nitrogen and oxygen of the air would have reacted and the oxygen required for life would not have been available. There are certain demerits of collision theory viz. the atoms are assumed to be hard spheres and their structural aspects are not taken into consideration.

**Endothermic and Exothermic reactions :** To understand the above phenomenon when molecules come nearer to each other, the changes in energy that take place can be studied. When the molecules come nearer to each other, the distance between them is decreasing and their potential energy increases. Such molecules combine with each other and a short lived complex molecule is produced. It possesses maximum potential energy. This short lived molecule is known as **activated complex**. This activated complex possesses very weak bonds. They break due to their oscillation motion. Hence product or original reactant is obtained. As the molecules of resultant product go away from each other, their potential energy decreases. There can be two options for this : (1) If the minimum potential energy of reactant is less than that of product then the reaction will be endothermic (2) If the minimum potential energy of reactants is more than the potential energy of product then the reaction will be exothermic. Thus, in endothermic reaction, the potential energy of products is more than potential energy of reactants. Hence,  $H_p - H_r = \Delta H$  will have positive value. In exothermic reaction the potential energy of product is less than the total potential energy of reactants. Hence, the value of  $H_p - H_r = \Delta H$  will be negative which can be shown by following fig. 1.7 and 1.8.



The **energy of activation** is the difference between potential energy of reactant molecules and activated complex. In the above figure if the activation energy of reverse reaction is  $E'_a$  and activation energy of forward reaction is  $E_a$ , then,  $\Delta H = E_a - E'_a$ .

Now, if  $E_a > E'_a$  the value of  $\Delta H$  obtained will be positive and so the reaction will be endothermic. If  $E_a < E'_a$  then the value of  $\Delta H$  obtained will be negative and the reaction will be exothermic. It is clear from the above reactions, that there exists an **energy barrier** between molecules of reactant and products. The height of this barrier is the important factor in determining the rate of reaction. If the energy barrier is high, the reaction rate will be low and if the energy barrier is low, the reaction rate will be high. By using proper catalyst the value of reaction rate can be increased. The function of the catalyst is to bring energy barrier down and to decrease the energy of activation so that the path for the reaction to result becomes easy.



#### Effect of catalyst on the rate of reaction :

You have studied earlier that oxygen can be obtained by decomposing potassium chlorate ( $\text{KClO}_3$ ) by supplying heat. But as the rate of reaction is slow; time required for obtaining oxygen is more; But if manganese dioxide ( $\text{MnO}_2$ ) powder is added and then heated, decomposition becomes fast. Here  $\text{MnO}_2$  does not react but increases the rate of reaction. Hence it is called catalyst. We shall study in detail about catalyst in unit 2. The function of catalyst is to combine with the reactant and to form an intermediate complex. This transition state does not

last for a longer period and so it decomposes and gives the product as well as the original catalyst is obtained back. The catalyst tries to find out the alternate way so that the activation energy decreases and the height of energy barrier decreases and brings the reaction towards the result. Thus the main function of catalyst is to decrease the activation energy. This phenomenon can be shown in the following fig. 1.9.

It is necessary to remember that the catalyst does not affect the equilibrium constant ( $K$ ) or free energy change ( $\Delta G$ ). It catalyses the spontaneous reaction. Thus the catalyst has the same impact

on the forward and the reverse reaction, with effect that the value of equilibrium constant ( $K$ ) is not changed but the value of rate of reaction changes, with an increase.

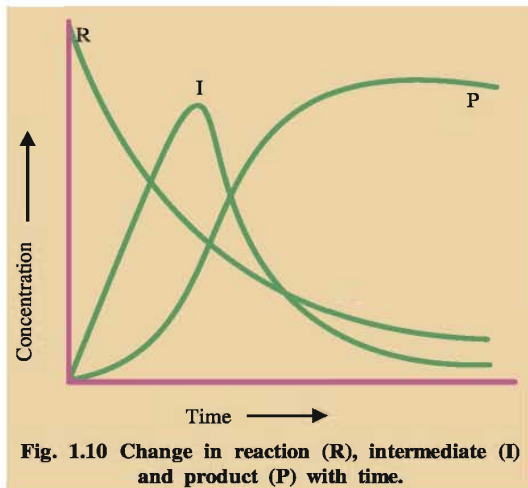
**Mechanism of chemical reaction :** To understand the mechanism of any complex reaction it is necessary to know its stoichiometry that is the number of moles of each reactant and number of moles of each product.

In certain reactions, so the molecule of intermediate compound is formed in substantial amount in the beginning which then react to give the final product. To determine the mechanism of a reaction is not a simple task. It depends on the experience and expertise of a scientist. The necessary condition for the study of mechanism is that it leads to correct rate law. Even with this it is not sure that we will be able to know correct mechanism. To include in mechanism some methods are necessary to test this study of several steps. We shall study some simple or easy reactions.

**(1) Reaction involving two successive first order steps :** This type of reaction occurs in two steps in which both the steps are first order reaction viz.



In the above reaction in first step : (i) Intermediate compound (I) is formed. (I) Is being collected and becomes maximum as mentioned earlier, then it decomposes and reaches zero concentration and changes in to product. In the fig 1.10 this is shown.



With the time, the concentration of R decreases and that of I goes towards maximum. After being maximum, at certain time concentration of I decreases and concentration of P increases.

**(2) Reaction involving slow step :** Suppose any reaction occurs in more than one steps, then the **slowest step becomes rate determining step**. As the rate of this step is slow because the value of its rate constant is low or the concentration of one or more species may be low in elementary reaction. We shall study the following reaction.



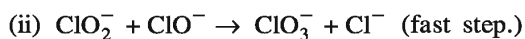
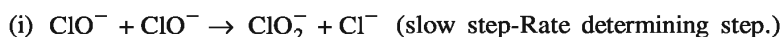
In the above reaction if  $K_1 \ll K_2$  then the conversion of I into product will be as soon as I is formed. Hence, we can write.

$$\frac{-d[R]}{dt} = \frac{d[P]}{dt} = K_1[R]$$

To understand this phenomenon, we shall take following illustration. Suppose a message is to be sent from New York to New Delhi. There are two alternatives. In the first alternative the person sending the message (writer) writes a letter in New York and sends it by post. The postman delivers the message to the other person (receiver) in New Delhi. It is clear from the illustration that the time required for the post to reach from New York to New Delhi will be more. Hence, this first step is the slow step.

Hence, the time required in receiving the post, the first step is slow and so more time will be required and so the rate determination for delivery of the post will become rate determining step. Second alternative is that the writer of the message sends the message from New York to New Delhi by telegram and the postman delivers the post to the receiver of the message. In this alternative, the first step is fast but second step will be slow. Hence, the time required for receiving the message will be determined by this step or will become the rate determining step.

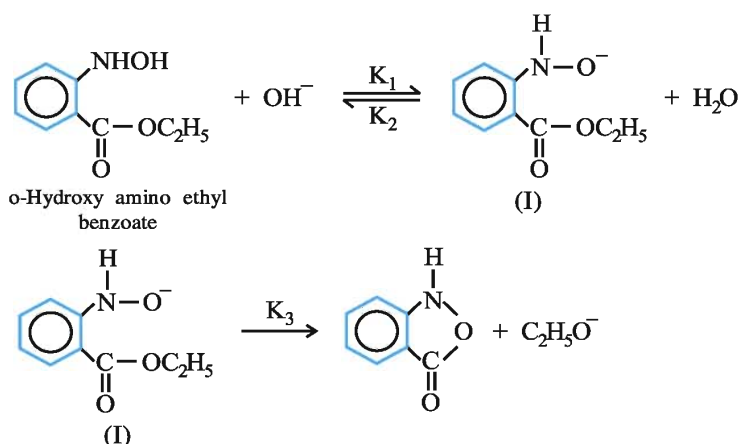
The chemical reaction :  $3\text{ClO}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^-$  occurring in certain following steps.



Hence, rate of reaction =  $K_1[\text{ClO}^-]^2$

**(3) The reaction for which steady state hypothesis is valid :** Suppose a chemical reaction occurs in more than one steps and certain intermediate compounds of it are possible. In the hypothesis of steady state, we assume that the intermediate compounds carry out reaction in such a way that in the short time at the beginning (which is called induction time) their concentration decreases to some higher value than zero and remains almost constant during the time period of that reaction. Hence, it can be accepted that the concentration of such intermediate compounds (active) which can react is zero. By this hypothesis the equations for the rates of complex reactions can be derived.

**(4) Reaction involving intermediate compounds in equilibrium with reactants :** Especially in the reactions  $\text{H}^+$  and  $\text{OH}^-$  the rate constants of forward and reverse reactions are very high between them. The intermediate compound that is formed in this way, reacts so slow that there is little change in concentration of intermediate. If we take as an example, the ion  $\text{C}_2\text{H}_5\text{O}^-$  obtained from o-hydroxyaminoethylbenzoate, is catalyzed by  $\text{OH}^-$  ion. The mechanism suggested is as follows :



The value of  $K_3$  is less than the values of  $K_1$  and  $K_2$ . Hence, writing the concentration of intermediate compound (I) at equilibrium :

$$[\text{I}] = K_1 \frac{[\text{Ester}] [\text{OH}^-]}{K_2}$$



$$\begin{aligned}\text{Reaction rate} &= K_3[I] = \frac{K_3K_1}{K_2} [\text{Ester}] [\text{OH}^-] \\ &= K_0 [\text{Ester}] [\text{OH}^-]\end{aligned}$$

This is a second order reaction but the overall or the total reaction rate constant includes all the three rate constants. Hence  $K_0 = \frac{K_3K_1}{K_2}$

Here,  $K_0$  is called overall or total reaction rate constant. Its value depends on the values of all the three rate constants  $K_1$ ,  $K_2$  and  $K_3$

#### SUMMARY

- The study of rate of chemical reaction is called chemical kinetics. It is independent of thermodynamics, equilibrium etc. but all the three are associated for the result of the product. Many reactions occur in our every day life in which some of them are very slow viz. Radioactivity of uranium, some medium viz. combination of dinitrogen and dihydrogen and formation of ammonia gas and very fast reaction viz. neutralization reaction between strong acid and strong base. The spoilage of milk, formation of amino acid from urea, etc. are the enzyme catalyzed reactions in everyday life.
- The rate of reaction depends on the rates of their forward and reverse reactions i.e.  $V_f$  and  $V_r$ . If  $V_f > V_r$  then forward reaction (more product) and if  $V_f < V_r$  then reverse reaction (less product) and if  $V_f = V_r$  then the reactions results in equilibrium.
- Amongst the factors affecting the rate of chemical reaction are (1) state of substance and area of surface (2) concentration of solution (3) pressure of system (for gaseous reactions) (4) Temperature (5) Effect of catalyst.
- The average rate of reaction  $r_{av} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$  and its unit is molar  $\text{sec}^{-1}$ , molar  $\text{min}^{-1}$  or molar  $\text{time}^{-1}$ . In addition, to this the instantaneous rate determination is difficult. To determine average rate, differential or integration method is used. For the reaction like  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ ,

$$\text{the rate of reaction} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

For a general reaction  $n_1\text{A} + n_2\text{B} = n_3\text{C} + n_4\text{D}$

$$\text{Average rate} = -\frac{1}{n_1} \frac{d[\text{A}]}{dt} = -\frac{1}{n_2} \frac{d[\text{B}]}{dt} = +\frac{1}{n_3} \frac{d[\text{C}]}{dt} = +\frac{1}{n_4} \frac{d[\text{D}]}{dt}$$

- The order of reaction is the exponent of the concentration which determines the rate of any reaction in relation to concentration of reactant. It can be zero, first, second and third order reaction. Reactions having three and more order of reactions are complex and so not included in the study. The second term is molecularity. The number of atoms, ions or molecules of a reactant which takes part in elementary reaction, and experience collision simultaneously

and due to which the reaction result is called molecularity. The order of reaction and their rate constants (K) can be shown as below :

Order of reaction (n)	Unit of rate constant (K)
0	mol lit <sup>-1</sup> sec <sup>-1</sup>
1	sec <sup>-1</sup>
2	(mol lit <sup>-1</sup> ) <sup>-1</sup> sec <sup>-1</sup>
n	(mol lit <sup>-1</sup> ) <sup>1-n</sup> sec <sup>-1</sup>

- The integrated rate law is very simple and useful from experimental study point of view. For zero order reaction rate constant  $K = \frac{[R]_0 - [R]_t}{t}$ . For first order reaction

$K = \frac{2.303}{t} \log_{10} \frac{[R]_0}{[R]_t}$ . The equations of the rate constants of both these orders can be derived as shown in the unit.

- Pseudo first order reaction is such a reaction in which the concentration of two molecules might change and so it becomes bimolecular but the experimental results satisfy the first order reaction, hence they are called pseudo first order reaction. e.g., the hydrolysis reaction of methyl acetate with water in which methanol and ethanoic acid are obtained. Some characteristics of first and zero order reactions are shown in the following table :

Order	Type of Reaction	Differential rate law	Integrated rate law	Straight line graph	Half life period	Unit of K
0	R → P	-d[R]/dt = K	Kt = [R] <sub>0</sub> - [R]	R Vs. t	[R] <sub>0</sub> / 2K	Concentration time <sup>-1</sup> or molar sec. <sup>-1</sup>
1	R → P	-d[R]/dt = K[R]	[R] = [R] <sub>0</sub> e <sup>-Kt</sup> or -Kt = ln[R] <sub>0</sub> / [R]	ln[R] Vs. t	ln 2/K	Time <sup>-1</sup> or sec. <sup>-1</sup>

- The methods for determination of order of reaction are (1) Integrated rate equation method or Graphical method (2) Ostwald's isolation method and (3) Half life (reaction time) etc.
- Arrhenius equation combining energy of activation and rate constant is  $K = Ae^{-E_a/RT}$  or  $\log_{10} K = \log_{10} A - \frac{E_a}{2.303 R} \cdot \frac{1}{T}$
- In the above equation K = rate constant, A = Arrhenius constant, E<sub>a</sub> = energy of activation and T is temperature in Kelvin. According to this equation if a graph of  $\log K \rightarrow \frac{1}{T}$  is plotted then the value of E<sub>a</sub> from the slope and the value of A from the intercept can be determined. Generally the rate of reaction is doubled during the temperature range 300 to 310 K temperatures.
- According to Arrhenius theory, when the reaction after obtaining sufficient energy increases the value of potential energy, the energy barrier can be crossed and the reaction results into

products. To become active, these molecules require the threshold energy and reach the activated state. As it is unstable, it is converted to product.

- In addition to this, there is another theory called the collision theory. In it, the molecules are assumed to be hard spheres. For any molecules to collide and to result in the reaction, the following conditions are necessary :
  - (1) There must be collision between reactant molecules.
  - (2) Each molecule experiencing collision must have proper energy which is called threshold energy.
  - (3) The collision of reactant molecules must be in proper direction (oriented).
  - (4) The molecules experiencing fruitful collision change into product molecule.
- In endothermic reaction total potential energy of the reactant molecules is less than the total potential energy of the product molecules and so the value of  $\Delta H$  obtained is positive. In exothermic reaction, the total potential energy of reactant molecules is more than the total potential energy of product and so the value of  $\Delta H$  obtained is negative or the heat is released. The collision theory can be expressed as,  $\text{Rate} = PZ_{AB} e^{-E_a/RT}$  where,  $Z$  = collision frequency factor and  $P$  is the probability of collision. Frequency factor  $Z$  and Arrhenius constant  $A$  have same meaning. The rate of reaction increases due to the presence of catalyst which can be understood by the principle of adsorption.
- To explain the order of reaction, different alternatives are possible, viz., Intermediate compound,  $I$  is formed from reagent  $A$  and then product  $B$  is formed. Such reaction occurs in more than one-step and so the slowest step becomes rate determining step for the reaction. In addition to this, steady state hypothesis is used in which the reactant in the short time of the beginning of the reaction i.e. in induction period the concentration of product becomes highest. On the basis of such types of explanations the mechanism of reactions can be explained. The examples of which are included in the unit.

### EXERCISE

#### 1. Select the proper choice from the given multiple choices :

- (1) Which unit of time is selected for fast reactions ?  
(A) Day                      (B) Second                      (C) Year                      (D) Nanosecond.
- (2) The reaction rate increases with increase in temperature, because .....  
(A) Energy barrier decreases  
(B) Threshold energy increases  
(C) Activation energy increases  
(D) The number of molecules undergoing effective collision increases.
- (3) For the reaction  $n_1A + n_2B \rightarrow \text{Products}$ ;  $\text{rate} = K[A]^3[B]^0$  if concentration of  $A$  is doubled and concentration of  $B$  is halved, then reaction rate....  
(A) Increases by four times                      (B) Increases by eight times  
(C) Is doubled                      (D) Becomes ten times.

- (4) Which of the following is indicated by the stoichiometry of the reaction ?
- (A) Order of reaction  
 (B) Mechanism of reaction  
 (C) The number of intermediate compound  
 (D) The relative mole number of reactants and products.
- (5) What is the SI unit of reaction rate ?
- (A) mol sec<sup>-1</sup>      (B) mol m<sup>-3</sup>sec<sup>-1</sup>      (C) mol dm sec<sup>-1</sup>      (D) mol lit<sup>-1</sup>
- (6) If the order of reaction is 'n', then what will be the unit of its rate constant ?
- (A) lit<sup>n</sup> mol<sup>-n<sup>2</sup></sup> sec<sup>-1</sup>      (B) (mol lit<sup>-1</sup>)<sup>n-1</sup> sec<sup>-1</sup>  
 (C)  $\left(\frac{\text{lit}}{\text{mol}}\right)^{n-1} \text{Sec}^{\frac{-1}{n}}$       (D) mol<sup>n</sup> lit<sup>-n</sup> sec<sup>-1</sup>
- (7) If the relation between half reaction time and [R]<sub>0</sub>, is  $t_{1/2} \propto \frac{1}{[\text{R}]_0^{n-1}}$  then what will be the order of reaction ?
- (A)  $\frac{n-2}{2}$       (B) n-1      (C)  $\frac{1}{n-2}$       (D) n
- (8) The order of following reactions are respectively .....
- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \xrightarrow{h\nu} 2\text{HCl}(\text{g})$   
 $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$   
 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$
- (A) 2, 2, 2      (B) 0, 2, 2      (C) 0, 1.5, 2      (D) 2, 1.5, 2
- (9) If two reactants are taking part in the reaction, then the reaction will never be
- (A) First order      (B) Second order      (C) Monomolecular      (D) Bimolecular.
- (10) Of which of the following factors, the rate of reaction depends on
- (A) Molecular mass of reactant      (B) Atomic mass of reactant  
 (C) Equivalent weight of reactant      (D) Active mass of reactant.
- (11) What is indicated by  $-\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt}$  term ?
- (A) Rate of introduction of N<sub>2</sub>O<sub>5</sub>      (B) Decomposition rate of N<sub>2</sub>O<sub>5</sub>  
 (C) Order of reaction      (D) Molecularity of reaction.

- (12) Which of the following statements is incorrect for Arrhenius rate constant equation ?
- (A) It gives quantitative idea about K and T
  - (B) As T increases K is increasing and A is decreasing
  - (C) As  $E_a$  increases K is increasing
  - (D) If  $E_a = 0$  then  $K = A$ .
- (13) Which of the following statements is incorrect regarding order of reaction and molecularity ?
- (A) Molecularity is the theoretical conclusion while order of reaction is experimental conclusion.
  - (B) The value of molecularity is positive integer while the value of reaction order may be positive, negative or zero.
  - (C) Molecularity explains the reaction mechanism while reaction order does not give any information about reaction mechanism.
  - (D) For elementary reactions, the order of reaction and molecularity are same.
- (14) For which elementary reactions, the order of reaction and molecularity will be same ?
- (A) Monomolecular and bimolecular
  - (B) Bimolecular and termolecular
  - (C) Monomolecular and termolecular
  - (D) All the molecular reactions.
- (15) Which of the following mathematical relations is correct ?
- (A) For zero order  $\left(t_{1/2} \times K\right) = \frac{[R]_0}{2}$
  - (B) For 0.5 order  $\left(t_{1/2} \times K\right) \propto \sqrt{[R]_0}$
  - (C) For first order  $\left(t_{1/2} \times K\right) = 0.693$
  - (D) All the three relations given here are correct.
- (16) What is indicated by negative sign before the term of reaction rate ?
- (A) The kinetic energy of the reaction decreases with time
  - (B) The energy barrier of reaction decreases with time
  - (C) The energy of activation of reaction decreases with time
  - (D) The concentration of reactants decreases with time.
- (17) If temperature of the reaction is increased from 300 to 310 K, the value of rate constant is almost doubled because.....
- (A) Kinetic energy is doubled
  - (B) The fraction of effective collision of molecules is almost doubled
  - (C) The number of molecular collision increases
  - (D) Energy of activation decreases.





- (27) According to transition state theory, the reaction can be shown passing through which of the following steps ?
- (A) Reactants  $\rightarrow$  Products  $\rightarrow$  Activated complex  
(B) Reactants  $\rightarrow$  Products  
(C) Reactants  $\rightarrow$  Activated complex  $\rightarrow$  Products  
(D) Reactants  $\rightarrow$  Activated complex products  $\rightarrow$  Activated complex  $\rightarrow$  Products
- (28) For elementary reaction, which of the following is correct ?
- (A) Order of reaction  $>$  molecularity (B) Order of reaction  $\neq$  molecularity  
(C) Order of reaction = molecularity (D) Order of reaction  $<$  molecularity.
- (29) According to molecular collision theory, the reaction is subjected to .....
- (A) Number of molecular collisions of reactant  
(B) Number of collisions between reactants and activated complex  
(C) The collision rate between reactants and product molecules  
(D) Number of effective molecular collisions of reactants
- (30) Which scientist explained the effect of temperature on the reaction rate constant ?
- (A) Faraday (B) Waag and Guldberg  
(C) Le-Chatelier (D) Arrhenius

**2. Answer the following questions in brief :**

- (1) Mention limitation of thermodynamics.
- (2) Why does the rate of reaction increase with increase in temperature ?
- (3) The charcoal powder burns faster than the piece of charcoal. Why ?
- (4) What is called chemical reaction rate ?
- (5) Mention the mathematical form of instantaneous rate for the reaction  $R \rightarrow P$ .
- (6) What is called specific rate constant ?
- (7) Write definition of order of reaction.
- (8) The reaction becomes fast by the use of suitable catalyst. Why ?
- (9) Write unit of rate constant for zero order reaction.
- (10) Write equation of rate constant for first order reaction.
- (11) What is called molecularity ?
- (12) Write Arrhenius equation.
- (13) Mention the value of slope in the graph of  $\log K$  versus  $\frac{1}{T}$ .

- (14) What is meant by collision theory ? Explain.
- (15) Explain half reaction time : Mention its relation with K for the first order reaction.
- (16) Write definition of energy of activation.
- (17) What is meant by threshold energy ? Why is it required ?
- (18) How many times the reaction rate constant increases when temperature of reaction is increased by  $10^0$  ?
- (19) Give examples of very slow and very fast reactions.
- (20) For the reaction  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$ . write the equation for reaction rate.

**3. Answer the following questions in detail :**

- (1) Mention the factors affecting rate of chemical reaction.
- (2) A second order reaction is in respect to some reactant. If the concentration of reactant is (1) doubled and (2) halved, then how will the rate constant be changed ?
- (3) Explain the effect of temperature, on the rate of chemical reaction.
- (4) Mention Arrhenius equation. Explain the terms involved in it.
- (5) Write important points of collision theory.
- (6) Give definitions : (i) Reaction order (ii) Molecularity.
- (7) Derive the equation of rate constant for the first order reaction.
- (8) Explain graphical method to determine the order of reaction.
- (9) Give information about energy barrier of chemical reaction and explain its importance.
- (10) Describe Ostwald's isolation method for determination of order of reaction.
- (11) Explain the terms : Half reaction time and energy of activation.
- (12) Explain the effect of concentration of reactant on the rate of reaction.
- (13) Explain the effect of catalyst on rate of reaction.
- (14) Describe the method to determine instantaneous rate.
- (15) What is meant by steady state and intermediate compound ?

**4. Calculate the following examples :**

- (1) The initial concentration of  $\text{N}_2\text{O}_5$  in the first order reaction  $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$  is  $1.24 \times 10^{-2} \text{ mol lit}^{-1}$  at 318 K temperature. The concentration of  $\text{N}_2\text{O}_5$  decreases to  $0.20 \times 10^{-2} \text{ mol lit}^{-1}$  after 1 hour. Calculate the rate constant of this reaction at this temperature.
- (2) The rate constant of a first order reaction is  $1.20 \times 10^{-3} \text{ s}^{-1}$ . What time it will take to have reactant 3 gram from 5 gram ?
- (3) During decomposition of  $\text{SO}_2\text{Cl}_2$ , its concentration becomes half of its initial concentration in 60 minutes. What will be the rate constant of this reaction ?

- (4) The following results are obtained in one pseudo first order reaction :

<b>Time (second)</b>	0	30	60	90
<b>Concentration of reactant mol lit<sup>-1</sup></b>	0.551	0.312	0.173	0.085

- (i) Calculate average rate of reaction between 30 and 60 seconds (ii) Calculate the rate constant of this first order reaction.
- (5) Prove for the first order reaction that the time required for completion of 99% reaction is double than the time required for completion of 90% reaction.
- (6) Sucrose is converted to glucose and fructose in presence of acidic solution which is first order reaction. The half reaction time of this reaction is  $t_{1/2} = 3.0$  hours. How many times the initial concentration becomes less after 9 hours ?
- (7) The decomposition of  $\text{NH}_3$  on the platinum surface is zero order reaction. If  $K = 2.5 \times 10^{-4} \text{ Ms}^{-1}$ , what will be the rate of introduction of  $\text{N}_2$  and  $\text{H}_2$  ?
- (8) If the rate of reaction is doubled by increasing the temperature from 298 K to 308 K, then calculate the energy of activation of the reaction.
- (9) The half life period of  $^{14}\text{C}$  is 5370 years. In a sample of dead tree, the proportion of  $^{14}\text{C}$  is found to be 60% in comparison to living tree. Calculate the age of the sample.
- (10) The radioactive  $^{90}\text{Sr}$  that is formed due to nuclear explosion has half life period of 28.1 years. In the body of a child born at this time  $^{90}\text{Sr}$  is found to be  $1\mu\text{g}$  ( $10^{-6}$  gram), then what will be  $^{90}\text{Sr}$  left in the body of the child when (a) the age of the child will be 20 years and (b) when the age of child will be 70 years. ( $^{90}\text{Sr}$  is not lost in any other way).
- (11) The rate constant of a reaction is  $2 \times 10^{-3} \text{ min}^{-1}$  at 300 K temperature. By increase in temperature by 20 K, its value becomes three time; then calculate the energy of activation of the reaction. What will be its rate constant at 310 K temperature ?
- (12) In a reaction  $\text{R} \rightarrow \text{P}$  the concentration  $[\text{M}]$  obtained at different times (t) are shown in the following table, calculate the average rate  $r_{\text{av}}$  of the reaction.
- |  |                      |                     |                     |                     |                      |
|--|----------------------|---------------------|---------------------|---------------------|----------------------|
| <b>Time (t) (second)</b>                     | 0                    | 5                   | 10                  | 20                  | 30                   |
| <b>Concentration <math>[\text{M}]</math></b> | $160 \times 10^{-3}$ | $80 \times 10^{-3}$ | $40 \times 10^{-3}$ | $10 \times 10^{-3}$ | $3.5 \times 10^{-3}$ |
- (13) The rate constant of a reaction of first order is  $70 \text{ sec}^{-1}$ . What time will be taken to have the concentration  $\frac{1}{18}$  part of the initial concentration ?
- (14) The decomposition rate constant of hydrocarbon is  $2.428 \times 10^{-5} \text{ sec}^{-1}$  at 550 K and activation energy is  $197.7 \text{ k joule mol}^{-1}$ , then calculate Arrhenius constant.
- (15) In the reaction of decomposition of reactant A into product, the rate constant is  $4.5 \times 10^3 \text{ sec}^{-1}$  at 283 K temperature and energy of activation is  $60 \text{ k joule mol}^{-1}$ . At which temperature, the value of rate constant K will be  $3 \times 10^4 \text{ sec}^{-1}$  ?