

## 6. CHEMICAL KINETICS

### Can you recall ?

- What is the influence of particle size of reacting solid on rate of a chemical reaction ?
- Why is finely divided nickel used in hydrogenation of oil ?
- What is effect of change of temperature on the rate of a chemical reaction ?



**6.1 Introduction :** Three important characteristics of chemical reactions include : extent of reaction, feasibility and its rate. In standard XI, we learnt how equilibrium constants predict the extent of reaction. In unit 3 of this text, we learnt how thermodynamic properties such as change in entropy or enthalpy tell us whether under the given set of conditions chemical reaction represented by chemical equation occurs or not. Chemical kinetics is a branch of chemistry which deals with the rate of chemical reactions and the factors those affect them.

A chemist wants to know the rates of reactions for different reasons. One the study of reaction rates help us to predict how rapidly the reaction approaches equilibrium. Secondly it gives information on the mechanism of chemical reactions.

A number of reactions occur as a sequence of elementary steps constituting the mechanism of reaction.

**6.2 Rate of reactions :** The rate of reaction describes how rapidly the reactants are consumed or the products are formed.

**6.2.1 Average rate of chemical reaction :** The average rate of a reaction can be described by knowing change in concentration of reactant or product divided by time interval over which the change occurs. Thus,

$$\text{Average rate} = \frac{\text{change in concentration of a species}}{\text{change in time}} = \frac{\Delta c}{\Delta t}$$

Consider the reaction  $A \longrightarrow B$  in which A is consumed and B is produced.

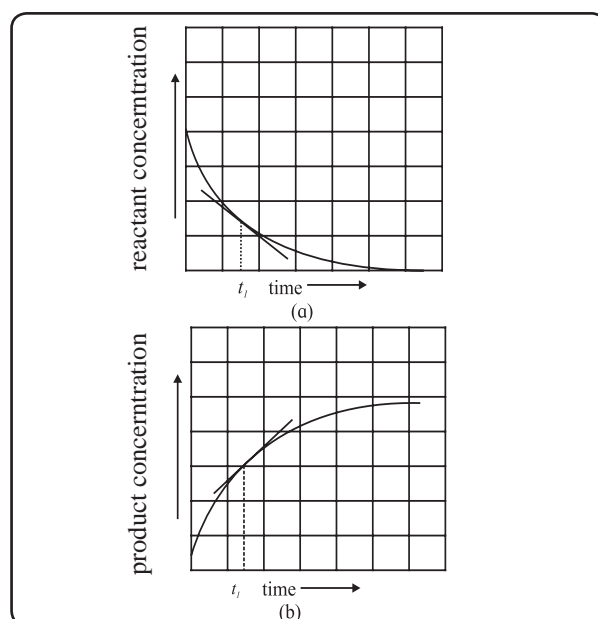
$$\text{average rate of consumption of A} = - \frac{\Delta[A]}{\Delta t}$$

$$\text{Average rate of formation of B} = + \frac{\Delta[B]}{\Delta t}$$

$$\begin{aligned} \text{Therefore, average rate of reaction} &= - \frac{\Delta[A]}{\Delta t} \\ &= + \frac{\Delta[B]}{\Delta t} \end{aligned}$$

The rate of reaction represents a decrease in concentration of the reactant per unit time or increase in concentration of product per unit time. The dimensions of rate are concentration divided by time, that is,  $\text{mol dm}^{-3} \text{sec}^{-1}$ .

**6.2.2 Instantaneous rate of :** To determine the instantaneous rate of a reaction the progress of a reaction is followed by measuring the concentrations of reactant or product for different time intervals. The changes in concentration are relatively fast in the



**Fig. 6.1 : Determination of instantaneous rate**

beginning which later become slow. The concentration of a reactant or a product plotted against time are shown in Fig. 6.1 (a) and 6.1 (b). A tangent drawn to the curve at time  $t_i$  gives the rate of the reaction. The slope thus obtained gives the instantaneous rate of the reaction at time  $t_i$ . The instantaneous rate  $dc/dt$ , is represented by replacing  $\Delta$  by derivative  $dc/dt$  in the expression of average rate. In chemical kinetics we are concerned with instantaneous rates.

For the reaction,  $A \longrightarrow B$ ,

Rate of consumption of A at any time  $t = -\frac{d[A]}{dt}$

Rate of formation of B at any time  $t = \frac{d[B]}{dt}$

Rate of reaction at time  $t = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$

For the reaction involving one mole of A and B each, the rate of consumption of A equals the rate of formation of B. This is not true for the reactions involving different stoichiometries. Consider, for example, a reaction :



When one mole of A is consumed three moles of B are consumed and two moles of C are formed. The stoichiometric coefficients of the three species are different. Thus the rate of consumption of B is three times the rate of consumption of A. Likewise the rate of formation of C is twice the rate of consumption of A. We write,

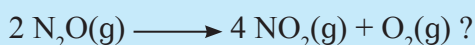
$$-\frac{d[B]}{dt} = -3 \frac{d[A]}{dt} \text{ and } \frac{d[C]}{dt} = -2 \frac{d[A]}{dt}$$

With this

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

$$\begin{aligned} \text{or rate of reaction} &= -\frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} \\ &= \frac{1}{2} \frac{d[C]}{dt} \end{aligned}$$

Write the expression for:



In general, For



$$\begin{aligned} \text{rate} &= -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} \\ &= \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \end{aligned}$$

**Problem 6.1 :** For the reaction

$2 \text{N}_2\text{O}_5\text{(g)} \longrightarrow 4 \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$  in liquid bromine,  $\text{N}_2\text{O}_5$  disappears at a rate of  $0.02 \text{ moles dm}^{-3} \text{ sec}^{-1}$ . At what rate  $\text{NO}_2$  and  $\text{O}_2$  are formed? What would be the rate of reaction?

**Solution :**

$$\begin{aligned} \text{Given : } \frac{d[\text{N}_2\text{O}_5]}{dt} &= 0.02 & \frac{1}{4} \frac{d[\text{NO}_2]}{dt} \\ &= \frac{d[\text{O}_2]}{dt} \end{aligned}$$

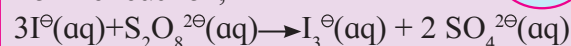
$$\begin{aligned} \text{Rate of reaction} &= -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} \\ &= \frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} \end{aligned}$$

$$\begin{aligned} \text{Rate of formation of } \text{O}_2 &= \frac{d[\text{O}_2]}{dt} \\ &= \frac{1}{2} \times 0.02 \\ &= \frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \times 0.02 \text{ moles dm}^{-3} \text{ sec}^{-1} \\ &= 0.01 \text{ moles dm}^{-3} \text{ sec}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Rate of formation of } \text{NO}_2 &= \frac{d[\text{NO}_2]}{dt} \\ &= \frac{4}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} \\ &= 2 \times \text{moles dm}^{-3} \text{ sec}^{-1} \\ &= 0.04 \text{ moles dm}^{-3} \text{ sec}^{-1} \end{aligned}$$

**Try this...**

For the reaction,



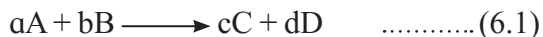
Calculate the rate of formation of  $\text{I}_3^{\ominus}$ , the rates of consumption of  $\text{I}^{\ominus}$  and  $\text{S}_2\text{O}_8^{2\ominus}$  and the overall rate of reaction if the rate of formation of  $\text{SO}_4^{2\ominus}$  is  $0.022 \text{ moles dm}^{-3} \text{ sec}^{-1}$



### 6.3 Rate of reaction and reactant concentration

**6.3 Rate of reaction and reactant concentration :** The rate of a reaction at a given temperature for a given time instant depends on the concentration of reactant. Such rate-concentration relation is the rate law.

**6.3.1 Rate law :** Consider the general reaction,



The rate of reaction at a given time is proportional to its molar concentration at that time raised to simple powers or

Rate of reaction  $\propto [A]^x [B]^y$  or

$$\text{rate} = k [A]^x [B]^y \quad \dots\dots\dots (6.2)$$

where  $k$  the proportionality constant is called the rate constant, which is independent of concentration and varies with temperature. For unit concentrations of A and B,  $k$  is equal to the rate of reaction. Equation (6.2) is called *differential rate law*.

The powers  $x$  and  $y$  of the concentration terms A and B in the rate law not necessarily equal to stoichiometric coefficients ( $a$  and  $b$ ) appearing in Eq. (6.1). Thus  $x$  and  $y$  may be simple whole numbers, zero or fraction. Realize that  $x$  and  $y$  are experimentally determined. The rate law in Eq. (6.2) is determined experimentally and expresses the rate of a chemical reaction in terms of molar concentrations of the reactants and not predicted from the stoichiometries of the reactants.

The exponents  $x$  and  $y$  appearing in the rate law tell us how the concentration change affects the rate of the reaction.

(i) For  $x = y = 1$ , Eq. (6.2) gives

$$\text{rate} = k[A][B]$$

The equation implies that the rate of a reaction depends linearly on concentrations of A and B. If either of concentration of A or B is doubled, the rate would be doubled.

(ii) For  $x = 2$  and  $y = 1$ . The Eq. (6.2) then leads to  $\text{rate} = k[A]^2[B]$ . If concentration of A is doubled keeping that of B constant, the rate of reaction will increase by a factor of 4.

(iii) If  $x=0$ , the rate is independent of concentration of A.

(iv) If  $x < 0$  the rate decreases as  $[A]$  increases.

#### 6.3.2 Writing the rate law

Consider the reaction,



If the rate of the reaction is proportional to concentration of  $\text{H}_2\text{O}_2$ . The rate law is given by

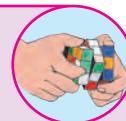
$$\text{rate} = k[\text{H}_2\text{O}_2]$$

#### Try this...

For the reaction,



the rate of reaction is experimentally found to be proportional to the square of the concentration of  $\text{NO}_2$  and independent that of CO. Write the rate law.



**Problem 6.2 :** Write the rate law for the reaction,  $A + B \longrightarrow P$  from the following data :

[A] moles $\text{dm}^{-3} \text{ sec}^{-1}$ (Initial)	[B] moles $\text{dm}^{-3} \text{ sec}^{-1}$ (Initial)	Initial rate/ $\text{moles dm}^{-3} \text{ sec}^{-1}$
(i) 0.4	0.2	$4.0 \times 10^{-5}$
(ii) 0.6	0.2	$6.0 \times 10^{-5}$
(iii) 0.8	0.4	$3.2 \times 10^{-4}$

#### Solution :

- From above data (i) and (ii), when  $[A]$  increases by a factor 1.5 keeping  $[B]$  as constant, the rate increases by a factor 1.5. It means  $\text{rate} \propto [A]$  and  $x = 1$
- From observations (i) and (iii), it can be seen that when concentrations of A and B are doubled, the rate increases by a factor 8. Due to doubling of  $[A]$  the rate is doubled (because  $x = 1$ ) that is rate increases by a factor 2.

This implies that doubling  $[B]$ , the rate increases by a factor 4. or  $\text{rate} \propto [B]^2$  and  $y = 2$ . Therefore,  $\text{rate} = k[A][B]^2$

contd....

**Problem 6.2 contd....****Alternatively**

The rate law gives  $\text{rate} = k[A]^x[B]^y$ .

a. From above observations (i) and (ii)

$$(i) 4 \times 10^{-5} = (0.4)^x(0.2)^y$$

$$(ii) 6 \times 10^{-5} = (0.6)^x(0.2)^y$$

Dividing (ii) by (i), we have

$$\frac{6 \times 10^{-5}}{4 \times 10^{-5}} = 1.5 = \frac{(0.6)^x(0.2)^y}{(0.4)^x(0.2)^y} = \left(\frac{0.6}{0.4}\right)^x$$

$$= (1.5)^x$$

Hence  $x = 1$

b. From observations (i) and (iii) separately in the rate law gives

$$(iii) 4 \times 10^{-5} = (0.4) \times (0.2)^y \quad \text{since } x = 1$$

$$(iv) 3.2 \times 10^{-4} = 0.8 \times (0.4)^y$$

Dividing (iv) by (iii) we write

$$\frac{3.2 \times 10^{-4}}{4 \times 10^{-5}} = \frac{0.8 (0.4)^y}{0.4 (0.2)^y}$$

$$\text{or } 8 = 2 \times \left(\frac{0.6}{0.2}\right)^y$$

$$\text{or } 4 = 2^2 = 2^y$$

Therefore  $y = 2$ .

The rate law is then  $\text{rate} = k[A][B]^2$ .

**Problem 6.3 :** For the reaction,

the rate law is  $\text{rate} = k[\text{NOBr}]^2$ . If the rate of the reaction is  $6.5 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$  when the concentration of NOBr is  $2 \times 10^{-3} \text{ mol L}^{-1}$ . What would be the rate constant for the reaction?

**Solution :**

$$\begin{aligned} \text{rate} &= k[\text{NOBr}]^2 \quad \text{or} \quad k = \frac{\text{rate}}{[\text{NOBr}]^2} \\ &= \frac{6.5 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}{(2 \times 10^{-3} \text{ mol L}^{-1})^2} \\ &= 1.625 \text{ mol}^{-1} \text{ L}^1 \text{ s}^{-1} \end{aligned}$$

**Try this...**

- For the reaction

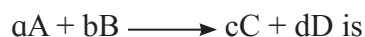
$2A + 2B \longrightarrow 2C + D$ , if concentration of A is doubled at constant [B] the rate increases by a factor of 4. If the concentration of B is doubled with [A] being constant the rate is doubled. Write the rate law of the reaction.

- The rate law for the reaction

$A + B \longrightarrow C$  is found to be

$$\text{rate} = k[A]^2[B].$$

The rate constant of the reaction at  $25^\circ\text{C}$  is  $6.25 \text{ M}^{-2}\text{s}^{-1}$ . What is the rate of reaction when  $[A] = 1.0 \text{ moles dm}^{-3} \text{ sec}^{-1}$  and  $[B] = 0.2 \text{ moles dm}^{-3} \text{ sec}^{-1}$ ?

**6.3.3 Order of the reaction :** For the reaction,

If the rate of the reaction is given as

$$\text{rate} = k[A]^x[B]^y.$$

Then the sum  $x + y$  gives overall order of the reaction. Thus overall order of the chemical reaction is given as the sum of powers of the concentration terms in the rate law expression. For example :

i. For the reaction,



experimentally determined rate law is

$$\text{rate} = k[\text{H}_2\text{O}_2].$$

The reaction is of first order.

ii. If the experimentally determined rate law for the reaction



$$\text{rate} = k[\text{H}_2][\text{I}_2].$$

The reaction is of first order in  $\text{H}_2$  and  $\text{I}_2$  each and hence overall of second order.

### Key points about the order of reaction

a. The order of chemical reaction is experimentally determined.

b. The order can be integer or fractional.

Look at the reaction,

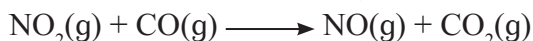


The rate law for the reaction was found to be

$$\text{rate} = k[\text{CH}_3\text{CHO}]^{3/2}.$$

Here the order of the reaction is 3/2.

c. The order of the reaction, can be zero for :



The rate expression for this is :  $\text{rate} = k[\text{NO}_2]^2$ .

This shows that order of reaction with respect to  $\text{NO}_2$  is 2 and with CO is zero or the rate is independent of concentration of CO. The overall order of reaction is 2.

d. Only a few reactions of third order are known. Reactions with the orders higher than three are scanty.

#### Problem 6.4 : For the reaction

$2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ ,  
the rate law is  $\text{rate} = k[\text{NO}]^2 [\text{H}_2]$ . What is the order with respect to NO and  $\text{H}_2$ ? What is the overall order of the reaction?

**Solution :** In the rate law expression, the exponent of  $[\text{NO}]$  is 2 and that of  $[\text{H}_2]$  is 1. Hence, reaction is second order in NO, first order in  $\text{H}_2$  and the reaction is third order.

#### Try this...

The reaction,  $\text{CHCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CCl}_4(\text{g}) + \text{HCl}(\text{g})$  is first order in  $\text{CHCl}_3$  and 1/2 order in  $\text{Cl}_2$ . Write the rate law and overall order of reaction.

#### Problem 6.5 : The rate of the reaction,

$\text{A} + \text{B} \longrightarrow \text{P}$  is  $3.6 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$  when  $[\text{A}] = 0.2 \text{ mol dm}^{-3}$  and  $[\text{B}] = 0.1 \text{ mol dm}^{-3}$ . Calculate the rate constant if the reaction is first order in A and second order in B.

**Solution :** The reaction is first order in A and second order in B. Hence, the rate law gives

$$\text{rate} = k[\text{A}][\text{B}]^2$$

$$\text{or } k = \frac{\text{rate}}{[\text{A}][\text{B}]^2}$$

$$\text{rate} = 3.6 \times 10^{-2} \text{ mol/s},$$

$$[\text{A}] = 0.2 \text{ mol dm}^{-3} \text{ and } [\text{B}] = 0.1 \text{ mol dm}^{-3}$$

Substitution gives

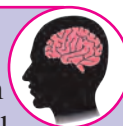
$$k = \frac{3.6 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}}{0.2 \text{ mol dm}^{-3} \times (0.1 \text{ mol dm}^{-3})^2}$$

$$= \frac{3.6 \times 10^{-2} \text{ s}^{-1}}{0.2 \times 0.01 \text{ mol}^2 \text{ dm}^{-6} \text{ sec}^{-1}}$$

$$= 18 \text{ mol}^{-2} \text{ dm}^{-6} \text{ sec}^{-1}$$

#### Use your brain power

The rate of the reaction  $2\text{A} + \text{B} \longrightarrow 2\text{C} + \text{D}$  is  $6 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$  when  $[\text{A}] = [\text{B}] = 0.3 \text{ mol dm}^{-3}$ . If the reaction is of first order in A and zeroth order in B, what is the rate constant?



#### Problem 6.6 : Consider,

$\text{A} + \text{B} \longrightarrow \text{P}$ . If the concentration of A is doubled with  $[\text{B}]$  being constant, the rate of the reaction doubles. If the concentration of A is tripled and that of B is doubled, the rate increases by a factor 6. What is order of the reaction with respect to each reactant? Determine the overall order of the reaction.

#### Solution :

The rate law of the reaction :

$$\text{rate} = k[\text{A}]^x[\text{B}]^y \quad \dots\dots\dots \text{(i)}$$

If  $[\text{A}]$  is doubled, the rate doubles.

$$\text{Hence } 2 \times \text{rate} = k [2\text{A}]^x[\text{B}]^y \\ = k 2^x [\text{A}]^x[\text{B}]^y \quad \dots\dots\dots \text{(ii)}$$

$$6 \times \text{rate} = k [3\text{A}]^x[2\text{B}]^y \quad \dots\dots\dots \text{(iii)}$$

$$\frac{\text{(iii)}}{\text{(i)}} \text{ gives } \frac{6 \times \text{rate}}{\text{rate}} = \frac{3 k [\text{A}]^x 2^y [\text{B}]^y}{k [\text{A}]^x [\text{B}]^y}$$

$$\text{or } 6 = 3 \times 2^y \text{ or } 2 = 2^y \text{ and } y = 1$$

The reaction is first order in A and first order in B. The overall reaction is of the second order.

## 6.4 Molecularity of elementary reactions :

Complex reactions are those which constitute a series of elementary reactions.

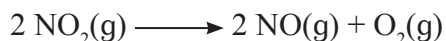
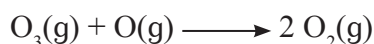
### 6.4.1 Elementary reaction

Consider,



These reactions occur in a single step and cannot be broken down further into simpler reactions. These are elementary reactions.

**6.4.2 Molecularity of reaction :** The molecularity refers to how many reactant molecules are involved in reactions. In the above reactions there is only one reactant molecule. These are unimolecular reactions or their molecularity is one.



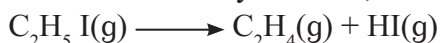
The elementary reactions involving two reactant molecules are bimolecular reactions or they have molecularity as two.

The molecularity of an elementary reaction is the number of reactant molecules taking part in it.

### 6.4.3 Order and molecularity of elementary reactions:

The rate law for the elementary reaction  $2\text{NO}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$  is found to be  $\text{rate} = k[\text{NO}_2]^2$ . The reaction is second order and bimolecular. The order of reaction is 2 and its molecularity is also 2.

For the elementary reaction,



$$\text{rate} = k[\text{C}_2\text{H}_5\text{I}]$$

It is unimolecular and first order. However the order and molecularity of the reaction may or may not be the same.

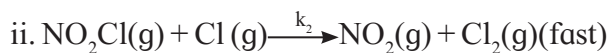
**6.4.4 Rate determining step :** A number of chemical reactions are complex. They take place as a series of elementary steps. One of

these steps is slower than others. The slowest step is the rate determining step.

The slowest step determines the rate of overall reaction.



The reaction takes place in two steps:



The first step being slower than the second it is the rate determining step.

The rate law is

$$\text{rate} = k[\text{NO}_2\text{Cl}]$$

This also represents the rate law of the overall reaction. The reaction thus is of the first order.

### Reaction intermediate:

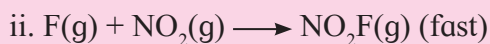
In the above reaction Cl is formed in the first step and consumed in the second. Such species represents the reaction intermediate. The concentration of reaction intermediate does not appear in the rate law.

### Distinction between order and molecularity of a reaction :

Order	Molecularity
1. It is experimentally determined property.	i. It is theoretical entity.
2. It is the sum of powers of the concentration terms of reactants those appear in the rate equation.	ii. It is the number of reactant molecules taking part in an elementary reaction.
3. It may be an integer, fraction or zero.	iii. It is integer.



**Problem 6.7 :** A reaction occurs in the following steps



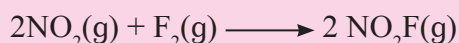
a. Write the equation of overall reaction.

b. Write down rate law.

c. Identify the reaction intermediate.

**Solution :**

a. The addition of two steps gives the overall reaction as



b. Step (i) is slow. The rate law of the reaction is predicted from its stoichiometry. Thus,

$$\text{rate} = k[\text{NO}_2]^2 [\text{F}_2]$$

c. F is produced in step (i) and consumed in step (ii) or F is the reaction intermediate.

**Try this...**

A complex reaction takes place in two steps:



The predicted rate law is  $\text{rate} = k[\text{NO}][\text{O}_3]$ .

Identify the rate determining step. Write the overall reaction. Which is the reaction intermediate? Why?

**6.5 Integrated rate law :** We introduced the differential rate law earlier. It describes how rate of a reaction depends on the concentration of reactants in terms of derivatives.

The differential rate laws are converted into integrated rate laws. These tell us the concentrations of reactants for different times.

**6.5.1 Integrated rate law for the first order reactions in solution :** Consider first order reaction,



The differential rate law is given by

$$\text{rate} = -\frac{d[\text{A}]}{dt} = k[\text{A}] \quad \dots\dots\dots (6.4)$$

where  $[\text{A}]$  is the concentration of reactant at time  $t$ .

Rearranging Eq. (6.4),

$$\frac{d[\text{A}]}{[\text{A}]} = -k dt \quad \dots\dots\dots (6.5)$$

Let  $[\text{A}]_0$  be the initial concentration of the reactant A at time  $t = 0$ . Suppose  $[\text{A}]_t$  is the concentration of A at time  $t$ .

The equation (6.5) is integrated between limits

$[\text{A}] = [\text{A}]_0$  at  $t = 0$  and  $[\text{A}] = [\text{A}]_t$  at  $t = t$

$$\int_{[\text{A}]_0}^{[\text{A}]_t} \frac{d[\text{A}]}{[\text{A}]} = -k \int_0^t dt$$

On integration,

$$[\ln[\text{A}]]_{[\text{A}]_0}^{[\text{A}]_t} = -k(t)_0^t$$

Substitution of limits gives

$$\ln [\text{A}]_t - \ln [\text{A}]_0 = -k t$$

$$\text{or} \quad \ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt \quad \dots\dots\dots (6.6)$$

$$\text{or} \quad k = \frac{1}{t} \ln \frac{[\text{A}]_0}{[\text{A}]_t}$$

Converting  $\ln$  to  $\log_{10}$ , we write

$$k = \frac{2.303}{t} \log_{10} \frac{[\text{A}]_0}{[\text{A}]_t} \quad \dots\dots\dots (6.7)$$

Eq. (6.7) gives the integrated rate law for the first order reactions.

The rate law can be written in the following forms

i. Eq. (6.6) is  $\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$

By taking antilog of both sides we get

$$\frac{[\text{A}]_t}{[\text{A}]_0} = e^{-kt} \text{ or } [\text{A}]_t = [\text{A}]_0 e^{-kt} \quad \dots\dots\dots (6.8)$$

ii. Let 'a'  $\text{mol dm}^{-3}$  be the initial concentration of A at  $t = 0$

Let x  $\text{mol dm}^{-3}$  be the concentration of A that decreases (reacts) during time t. The

concentration of A that remains unreacted at time  $t$  would be  $(a - x)$  mol/dm<sup>3</sup>

Substitution of  $[A]_0$  and  $[A]_t = (a - x)$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \quad \dots\dots\dots (6.9)$$

Equations (6.7), (6.8) and (6.9) represent the integrated rate law of first order reactions.

### 6.5.2 Units of rate constant for the first order reaction:

The integrated rate law is

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

Because  $\log_{10} \frac{[A]_0}{[A]_t}$  is unitless quantity, the dimensions of  $k$  will be (time)<sup>-1</sup>. The units of  $k$  will be s<sup>-1</sup>, min<sup>-1</sup> or (hour)<sup>-1</sup>

### 6.5.3 Half life of the first order reactions ( $t_{1/2}$ )

Radioactive processes follow the first order kinetics. The half life of reaction is time required for the reactant concentration to fall to one half of its initial value.

### 6.5.4 Half life and rate constant of the first order reaction :

The integrated rate law for the first order reaction is

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

where  $[A]_0$  is the initial concentration of reactant at  $t = 0$ . It falls to  $[A]_t$  at time  $t$  after the start of the reaction. The time required for  $[A]_0$  to become  $[A]_0/2$  is denoted as  $t_{1/2}$

or

$$[A]_t = [A]_0/2 \quad \text{at } t = t_{1/2}$$

Putting this condition in the integrated rate

$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{[A]_0}{[A]_0/2}$$

$$= \frac{2.303}{t_{1/2}} \log_{10} 2$$

$$= \frac{2.303}{t_{1/2}} \times 0.3010$$

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

$$t_{1/2} = \frac{0.693}{k_{1/2}} \quad \dots\dots\dots (6.10)$$

Eq. (6.10) shows that half life of the first order reaction is independent of initial reactant concentration. This is shown in Fig (6.2) as a plot of  $[A]_t$  versus  $t$ .

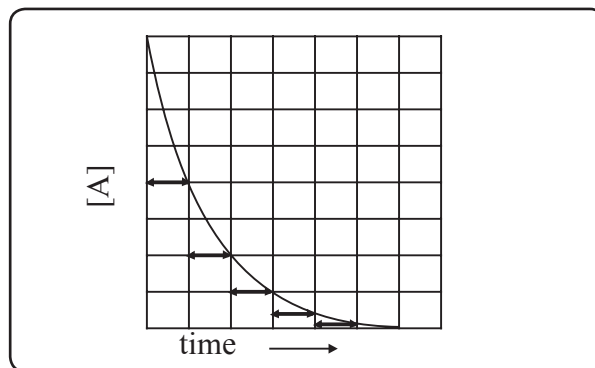


Fig. 6.2 : Half life period of first order reaction

### 6.5.5 Graphical representation of the first order reactions

i. The differential rate law for the first order reaction  $A \longrightarrow P$  is

$$\text{rate} = - \frac{d[A]}{dt} = k [A]_t + 0$$

$\updownarrow$   
y

$\updownarrow$   
m

$\updownarrow$   
x

$\updownarrow$   
c

The equation is of the form  $y = mx + c$ . A plot of rate versus  $[A]_t$  is a straight line passing through origin. This is shown in Fig. 6.3. The slope of straight line =  $k$ .

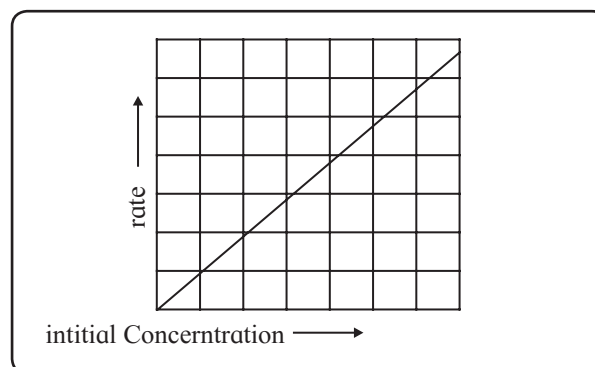


Fig. 6.3 : Variation of rate with  $[A]$



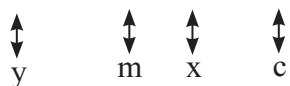
ii. From Eq. (6.7) the integrated rate law is

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

On rearrangement, the equation becomes

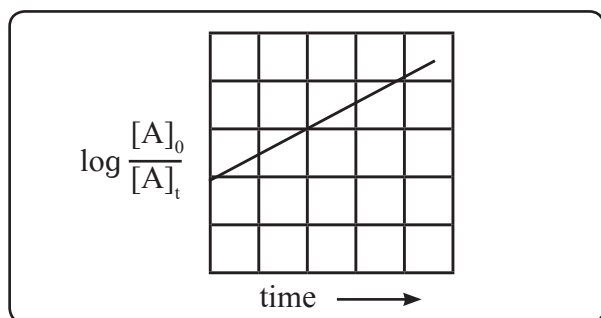
$$\frac{kt}{2.303} = \log_{10} [A]_0 - \log_{10} [A]_t$$

$$\text{Hence, } \log_{10} [A]_t = -\frac{k}{2.303} t + \log_{10} [A]_0$$



The equation is of the straight line. A graph of  $\log_{10} \frac{[A]_0}{[A]_t}$  versus  $t$  yields a straight line with slope  $-k/2.303$  and y-axis intercept as  $\log_{10} [A]_0$

This is shown in Fig. 6.4



**Fig. 6.4 : A plot showing  $\log [A]_0/[A]_t$  vs time**

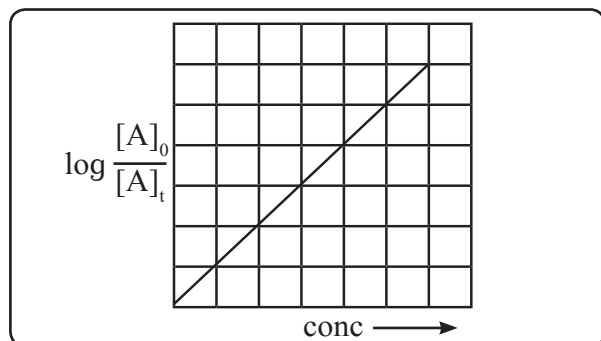
iii. Eq. (6.7) gives

$$\log_{10} \frac{[A]_0}{[A]_t} = \frac{k}{2.303} t$$



The equation has a straight line form  $y = mx$ .

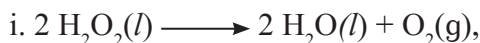
Hence, the graph of  $\log_{10} \frac{[A]_0}{[A]_t}$  versus  $t$  is straight line passing through origin as shown in Fig. 6.5.



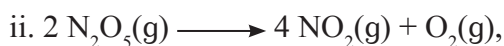
**Fig. 6.5 :**

## 6.5.6 Examples of first order reactions

Some examples of reactions of first order are :



$$\text{rate} = k[\text{H}_2\text{O}_2]$$



$$\text{rate} = k[\text{N}_2\text{O}_5]$$

## 6.5.7 Integrated rate law for gas phase reactions

For the gas phase reaction,



Let initial pressure of A be  $P_i$  that decreases by  $x$  within time  $t$ .

Pressure of reactant A at time  $t$

$$P_A = P_i - x$$

..... (6.11)

The pressures of the products B and C at time  $t$  are

$$P_B = P_C = x$$

The total pressure at time  $t$  is then

$$P = P_i - x + x + x = P_i + x$$

Hence,  $x = P - P_i$  ..... (6.12)

Pressure of A at time  $t$  is obtained by substitution of Eq. (6.12) into Eq. (6.11). Thus

$$P_A = P_i - (P - P_i) = P_i - P + P_i = 2P_i - P$$

The integrated rate law turns out to be

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

The concentration now expressed in terms of pressures.

$$\text{Thus, } [A]_0 = P_i \text{ and } [A]_t = P_A = 2P_i - P$$

Substitution gives in above

$$k = \frac{2.303}{t} \log_{10} \frac{P_i}{2P_i - P} \quad \text{..... (6.13)}$$

$P$  is the total pressure of the reaction mixture at time  $t$ .

**Problem 6.8 :** The half life of first order reaction is 990 s. If the initial concentration of the reactant is  $0.08 \text{ mol dm}^{-3}$ , what concentration would remain after 35 minutes?

**Solution :**

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{990 \text{ s}} = 7 \times 10^{-4} \text{ s}^{-1}$$

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

$[A]_0 = 0.08 \text{ mol dm}^{-3}$ ,  $t = 35 \text{ min}$  or  $2100 \text{ s}$ ,  
 $[A]_t = ?$

$$\log_{10} \frac{[A]_0}{[A]_t} = \frac{k t}{2.303} = \frac{7 \times 10^{-4} \text{ s}^{-1} \times 2100 \text{ s}}{2.303}$$

$$= 0.6383$$

$$\frac{[A]_0}{[A]_t} = \text{antilog } 0.6383 = 4.35$$

$$\text{Hence, } [A]_t = \frac{[A]_0}{4.35} = \frac{0.08}{4.35}$$

$$= 0.0184 \text{ mol dm}^{-3}$$

**Problem 6.9 :** In a first order reaction 60% of the reactant decomposes in 45 minutes. Calculate the half life for the reaction

**Solution :**

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

$[A]_0 = 100$ ,  $[A]_t = 100 - 60 = 40$ ,  $t = 45 \text{ min}$

Substitution of these in above

$$k = \frac{2.303}{t} \log_{10} \frac{100}{40}$$

$$= \frac{2.303}{45} \log_{10} 2.5$$

$$= \frac{2.303}{45} \times 0.3979 = 0.0204 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0204 \text{ min}^{-1}} = 34 \text{ min}$$

**Try this...**

The half life of a first order reaction is 0.5 min. Calculate time needed for the reactant to reduce to 20% and the amount decomposed in 55 s.



**Problem 6.10 :** Following data were obtained during the first order decomposition of  $\text{SO}_2\text{Cl}_2$  at the constant volume.



Times/s	Total pressure/bar
0	0.5
100	0.6

Calculate the rate constant of the reaction.

**Solution :**

$$k = \frac{2.303}{t} \log_{10} \frac{P_i}{2 P_i - P}$$

$P_i = 0.5 \text{ bar}$ ,  $P = 0.6 \text{ bar}$ ,  $t = 100 \text{ s}$

$$k = \frac{2.303}{100} \log_{10} \left( \frac{0.5 \text{ bar}}{2 \times 0.5 \text{ bar} - 0.6 \text{ bar}} \right)$$

$$= \frac{2.303}{100} \log_{10} \left( \frac{0.5}{0.4} \right) = 2.23 \times 10^{-3} \text{ s}^{-1}$$

**6.5.8 Zero order reactions:** The rate of zero order reaction is independent of the reactant concentration.

**Integrated rate law for zero order reactions :** For zero order reaction,



the differential rate law is given by

$$\text{rate} = - \frac{d[A]}{dt} = k [A]^0 = k \quad \dots (6.14)$$

Rearrangement of Eq. (6.14) gives

$$d[A] = -k dt$$

Integration between the limits

$[A] = [A]_0$  at  $t = 0$  and  $[A] = [A]_t$  at  $t = t$  gives

$$\int_{[A]_0}^{[A]_t} d[A] = -k \int_0^t dt$$

$$\text{or } [A]_t - [A]_0 = -kt$$

$$\text{Hence, } kt = [A]_0 - [A]_t \quad \dots (6.15)$$

**Units of rate constant of zero order reactions**

$$k = \frac{[A]_0 - [A]_t}{t} = \frac{\text{mol L}^{-1}}{t} = \text{mol dm}^{-3} \text{ t}^{-1}$$

The units of rate constant of zero order reaction are the same as the rate.

(6.15)

$$k = \frac{[A]_0 - [A]_t}{t}$$

Using the conditions  $t = t_{1/2}$ ,  $[A]_t = [A]_{1/2}$ ,

Eq. (6.15) becomes

$$k = \frac{[A]_0 - [A]_{0/2}}{t_{1/2}} = \frac{[A]_0}{2 t_{1/2}}$$

Hence,  $t_{1/2} = \frac{[A]_0}{2k}$  ..... 6.16

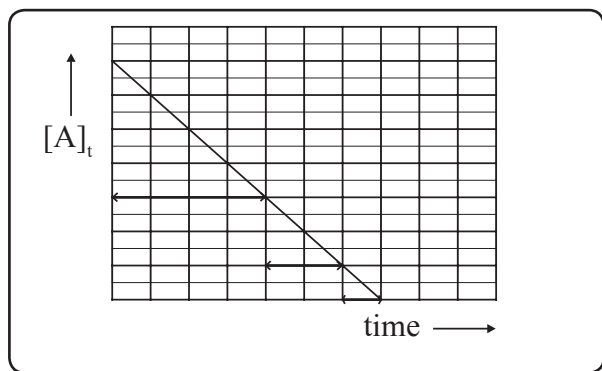
The half life of zero order reactions is proportional to the initial concentration of reactant.

**Graphical representation of zero order reactions :** The rate law in Eq. (6.15) gives

$$[A]_t = -k t + [A]_0 \quad \dots\dots\dots 6.17$$

Which is straight line given by  $y = mx + c$ .

A plot of  $[A]_t$  versus  $t$  is a straight line as shown in Fig 6.6.



**Fig. 6.6 :  $[A]_t$  vs  $t$  for zero order reaction**

The slope of straight line is  $-k$  and its intercept on y-axis is  $[A]_0$ .

The  $t_{1/2}$  of zero order reaction is directly proportional to the initial concentration.

### Examples of zero order reactions :

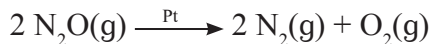
Here follow some examples

## Decomposition of $\text{NH}_3$ on platinum metal



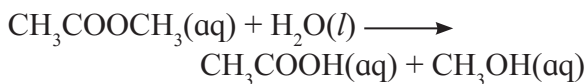
The metals surface gets completely covered by a layer of  $\text{NH}_3$  molecules. A number of  $\text{NH}_3$  molecules attached on platinum surface is small compared to ammonia. A large number of the  $\text{NH}_3$  molecules tend to remain as gas which do not react. The molecules present on the metal surface only react. The rate of a reaction was thus independent of the total concentration of  $\text{NH}_3$  and remains constant.

ii. Decomposition of nitrous oxide in the presence of Pt catalyst.



iii. The catalytic decomposition of  $\text{PH}_3$  on hot tungsten at high pressure.

**6.5.9 Pseudo-first order reactions :** Certain reactions which are expected to be of higher order follow the first order kinetics. Consider hydrolysis of methyl acetate.



The rate law is

$$\text{rate} = k' [\text{CH}_3\text{COOCH}_3] [\text{H}_2\text{O}]$$

The reaction was expected to follow the second order kinetics, however, obeys the first order.

The reason is that solvent water is present in such large excess that the change in its concentration is negligible compared to initial one or its concentration remains constant.

Thus  $[\text{H}_2\text{O}] = \text{constant} = k''$ . The rate law becomes

$$\begin{aligned} \text{rate} &= k' [\text{CH}_3\text{COOCH}_3] k'' \\ &= k [\text{CH}_3\text{COOCH}_3] \end{aligned}$$

where  $k = k'k''$

The reaction is thus of first order.

The reaction  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq}) + \text{H}_2\text{O}(l)$  (excess)  
 $\longrightarrow$   $\underset{\text{glucose}}{\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})} + \underset{\text{fructose}}{\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})}$   
 Can it be of pseudo-first order type ?

## 6.6 Collision theory of bimolecular reactions

### 6.6.1 Collision between reactant molecules

Chemical reactions occur as a result of collisions between the reactant species. It may be expected that the rate of the reaction is equal to the rate of collision. For the gas-phase reactions the number of collisions is far more and typically many powers of tens compared to the observed rate.

**6.6.2 Activation :** For the reaction to occur the colliding reactant molecules must possess the minimum kinetic energy. This minimum kinetic energy is the activation energy. The reaction would occur only if colliding molecules possess kinetic energies equal to or greater than the activation energy.

### 6.6.3 Orientation of reactant molecules

The requirement for successful collision described above is sufficient for reactions involving simple molecules (or ions) however not for those involving complex molecules.

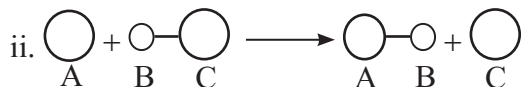
Besides the above considerations the colliding molecules must have proper orientation. The molecules need to be so oriented relative to each other that the reacting groups approach closely.

Consider,  $A + C - B \longrightarrow A - B + C$

i. The collision of A with C approaching toward A would not lead to reaction.



No reaction will take place. The reactant molecules would collide and separate owing to the improper orientation of C - B.



The reaction is successful as a result of proper orientation of C - B. A fraction of such collisions bring forth conversion of reactants to products.

### 6.6.4 Potential energy barrier

Consider again the reaction



During a course of collision, new bond A - B develops. At the same time bond C - B breaks. A configuration in which all the three atoms are weakly connected together is called activated complex.



To attain the configuration  $A \cdots B \cdots C$  atoms need to gain energy, which comes from the kinetic energy of colliding molecules.

The energy barrier between reactants and products is shown in Fig. 6.7. The reactant molecules need to climb up and overcome this before they get converted to products. The height of the barrier is called as activation energy ( $E_a$ ). Thus the reactant molecules transform to products only if they possess energy equal to or greater than such activation energy. A fraction of molecules those possess energy greater than  $E_a$  is given by  $f = e^{-E_a/RT}$ .

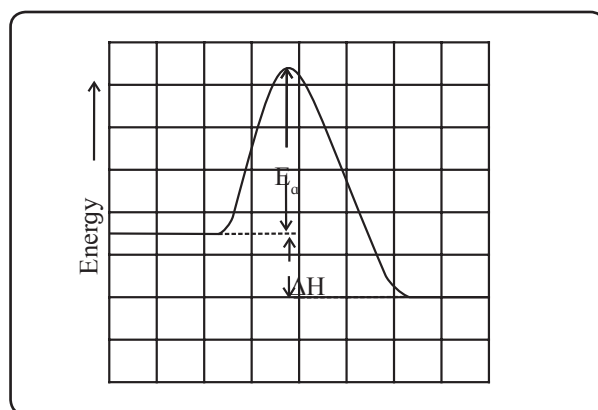


Fig. 6.7 : Potential energy barrier

As a result only a few collisions lead to products. The number of successful collisions are further reduced by the orientation requirement already discussed.

### Do you know ?

For a gaseous reaction at 298 K,  $E_a = 75 \text{ kJ/mol}$ . The fraction of successful collisions is given by  $f = e^{-E_a/RT} = e^{-75000/8.314 \times 298} = 7 \times 10^{-14}$  or only 7 collisions in  $10^{14}$  collisions are sufficiently energetic to lead to the reaction.



### Remember...

All collisions of reactant molecules do not lead to a chemical reaction. The colliding molecules need to possess certain energy which is greater than the activation energy  $E_a$  and proper orientation.



## 6.7 Temperature dependence of reaction rates

### Do you know ?

It has been observed that the rates of most of the chemical reactions usually increase with temperature. In everyday life we see that the fuels such as oil, coal are inert at room temperature but burn rapidly at higher temperatures. Many foods spoil rapidly at room temperature and lasts longer in freezer.



The concentrations change only a little with temperature. The rate constant shows a strong dependence on the temperature.

**6.7.1 Arrhenius equation:** Arrhenius suggested that the rate of reactions varies with temperature as

$$k = A e^{-E_a/RT} \quad \dots\dots\dots 6.18$$

where  $k$  is the rate constant,  $E_a$  is the activation energy,  $R$  molar gas constant,  $T$  temperature in kelvin, and  $A$  is the pre-exponential factor. Eq. (6.18) is called as the Arrhenius equation.

The pre exponential factor  $A$  and the rate constant have same unit in case of the first order reactions. Besides  $A$  is found to be related to frequency of collisions.

### 6.7.2 Graphical determination of activation energy :

Taking logarithm of both sides of eqn (6.18) we obtain

$$\ln k = -\frac{E_a}{RT} + \ln A \quad \dots\dots\dots (6.19)$$

Converting natural base to base 10 we write

$$\log_{10} k = -\frac{E_a}{2.303 R} \frac{1}{T} + \log_{10} A \quad \dots\dots\dots (6.20)$$

$$\begin{array}{cccc} \updownarrow & \updownarrow & \updownarrow & \updownarrow \\ y & m & x & c \end{array}$$

This equation is of the form of straight line  $y = mx + c$ .

The Arrhenius plot of  $\log_{10} k$  versus  $1/T$  giving a straight line is shown in fig. (6.8). A slope of the line is  $-E_a/2.303R$  with its intercept being  $\log_{10} A$ .

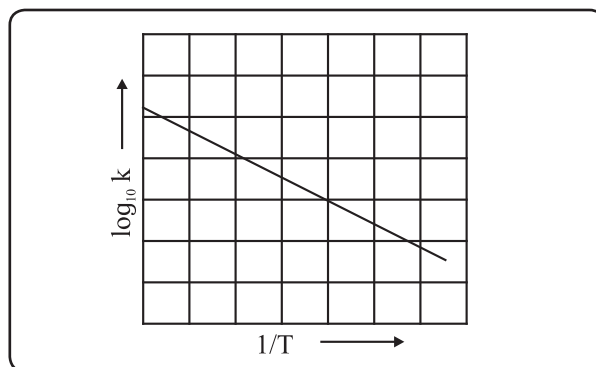


Fig. 6.8 : Variation of  $\log_{10} k$  with  $1/T$

From a slope of the line the activation energy can be determined. Eq. (6.18) shows that with an increase of temperature,  $-E_a/RT$  and in turn, the rate of reaction would increase.

### 6.7.3 Determination of activation energy :

For two different temperatures  $T_1$  and  $T_2$

$$\log_{10} k_1 = \log_{10} A - \frac{E_a}{2.303 RT_1} \quad \dots\dots\dots (6.21)$$

$$\log_{10} k_2 = \log_{10} A - \frac{E_a}{2.303 RT_2} \quad \dots\dots\dots (6.22)$$

where  $k_1$  and  $k_2$  are the rate constants at temperatures  $T_1$  and  $T_2$  respectively. Subtracting Eq. (6.21) from Eq. (6.22),

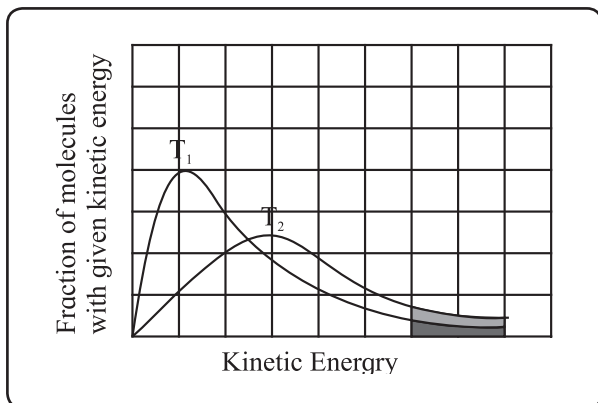
$$\log_{10} k_2 - \log_{10} k_1 = -\frac{E_a}{2.303 R} \frac{1}{T_2} + \frac{E_a}{2.303 R} \frac{1}{T_1}$$

$$\text{Hence, } \log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$= \frac{E_a}{2.303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \quad \dots\dots\dots(6.23)$$

**6.7.4 Graphical description of effect of temperature :** It has been realized that average kinetic energy of molecules is proportional to temperature. The collision theory suggested a bimolecular reaction occurs only if the reacting molecules have sufficient kinetic energies (at least  $E_a$ ) and proper orientation when they collide.

At a given temperature, the fraction of molecules with their kinetic energy equal to or greater than  $E_a$  may lead to the product. With an increase of temperature the fraction of molecules having their energies ( $E_a$ ) would increase. The rate of the reaction thus would increase. This is depicted by plotting a fraction of molecules with given kinetic energy versus kinetic energy for two different temperatures  $T_1$  and  $T_2$  ( $T_2$  being  $> T_1$ ) in Fig. 6.9.



**Fig. 6.9 : Comparison of fraction of molecules activated at  $T_1$  and  $T_2$**

The shaded areas is proportional to total number of molecules. The total area is the same at  $T_1$  and  $T_2$ . The area (a + b) represents a fraction of molecules with kinetic energy exceeding  $E_a$  is larger at  $T_2$  than at  $T_1$  (since  $T_2 > T_1$ ). This indicates that a fraction of molecules possessing energies larger than  $E_a$

increase with temperature. The rate of reaction increases accordingly.

**Problem 6.12 :** The rate constants for a first order reaction are  $0.6 \text{ s}^{-1}$  at  $313 \text{ K}$  and  $0.045 \text{ s}^{-1}$  at  $293 \text{ K}$ . What is the activation energy?

**Solution -**

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

$$k_1 = 0.045 \text{ s}^{-1}, k_2 = 0.6 \text{ s}^{-1}, T_1 = 293 \text{ K}, T_2 = 313 \text{ K}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Substituting

$$\log_{10} \frac{0.6}{0.045} = \frac{E_a}{2.303 \times 8.314} \times \left[ \frac{313 - 293}{293 \times 313} \right]$$

$$\log_{10} 13.33 = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{293 \times 313}$$

$$1.1248 = \frac{E_a}{19.15} \times 2.18 \times 10^{-4}$$

$$E_a = 1.1248 \times 19.15 \text{ J mol}^{-1} / 2.18 \times 10^{-4}$$

$$= 98810 \text{ J/mol}^{-1} = 98.8 \text{ kJ/mol}^{-1}$$

**Problem 6.13 :** A first order gas phase reaction has activation energy of  $240 \text{ kJ mol}^{-1}$ . If the pre-exponential factor is  $1.6 \times 10^{13} \text{ s}^{-1}$ . what is the rate constant of the reaction at  $600 \text{ K}$ ?

**Solution :** Arrhenius equation

$k = A e^{-E_a/RT}$  is written as

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

$$E_a = 240 \text{ kJ mol}^{-1} = 240 \times 10^3 \text{ J mol}^{-1},$$

$$T = 600 \text{ K}, A = 1.6 \times 10^{13} \text{ s}^{-1}$$

$$\text{Hence } \log_{10} \frac{A}{k} =$$

$$\frac{240 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 600 \text{ K}} = 20.89$$

contd....



$$\begin{aligned}\frac{A}{k} &= \text{antilog } 20.89 \\ &= 7.78 \times 10^{20} \\ \text{and } k &= \frac{A}{7.78 \times 10^{20}} \\ &= \frac{1.6 \times 10^{13} \text{ s}^{-1}}{7.78 \times 10^{20}} \\ &= 2.055 \times 10^{-8} \text{ s}^{-1}\end{aligned}$$

**Problem 6.14 :** The half life of a first order reaction is 900 min at 820 K. Estimate its half life at 720 K if the activation energy is 250 kJ mol<sup>-1</sup>.

**Solution :**

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

Rate constants at two different temperatures,  $T_1$  and  $T_2$  are  $k_1$  and  $k_2$  respectively, and the corresponding half lives  $(t_{1/2})_1$  and  $(t_{1/2})_2$ .

$$(t_{1/2})_1 = \frac{0.693}{k_1} \text{ and } (t_{1/2})_2 = \frac{0.693}{k_2}$$

$$\text{Hence, } \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{k_2}{k_1}$$

$$\text{The equation, } \log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 RT} \times \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log_{10} \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{E_a}{2.303 RT} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$E_a = 250 \text{ kJ mol}^{-1}, T_1 = 720 \text{ K},$$

$$T_2 = 820 \text{ K}, (t_{1/2})_2 = 900 \text{ min}$$

$$\text{Thus, } \log_{10} \frac{(t_{1/2})_1}{(t_{1/2})_2} =$$

$$\begin{aligned}& \frac{250 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left[ \frac{820 \text{ K} - 720 \text{ K}}{820 \text{ K} \times 720 \text{ K}} \right] \\ &= 2.212\end{aligned}$$

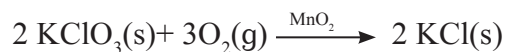
$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \text{antilog } 2.212 = 162.7$$

$$\begin{aligned}(t_{1/2})_1 &= (t_{1/2})_2 \times 162.7 = 900 \times 162.7 \\ &= 1.464 \times 10^5 \text{ min}\end{aligned}$$

## 6.8 Effect of a catalyst on the rate of reaction

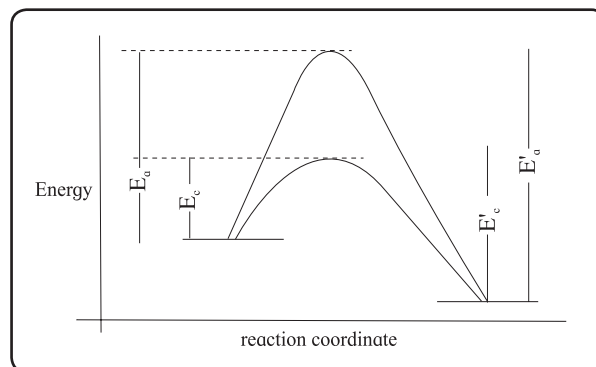
A catalyst is a substance added to the reactants that increases the rate of the reaction without itself being consumed in the reaction.

Consider



Here  $\text{MnO}_2$  is the catalyst. It has been observed that the decomposition rate increases with the addition of catalyst. A catalyst provides alternative pathway associated with lower activation energy.

Fig. 6.10 compares the potential energy barriers for the catalysed and uncatalysed reactions. The barrier for uncatalysed reaction ( $E_u$ ) is larger than that for the same reaction in the presence of a catalyst  $E_c$ .

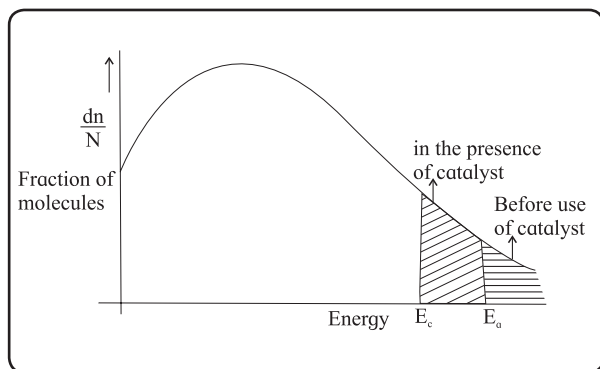


**Fig. 6.10 : Potential energy barriers for catalyzed and uncatalyzed reactions**

Consider the decomposition of  $\text{H}_2\text{O}_2$  in aqueous solution catalysed by  $\text{I}^-$  ions.



At room temperature the rate of reaction is slower in the absence of catalyst with its activation energy being 76 kJ mol<sup>-1</sup>. In the presence of iodide ion/ the catalyst  $\text{I}^-$  the reaction is faster since the activation energy decreases to 57 kJ mol<sup>-1</sup>.



**Fig. 6.11 : Comparison of fraction of molecules for catalyzed and uncatalyzed reactions**

Fig 6.11 shows a plot of fraction of molecules as a function of energy. A catalyst lowers the the threshold energy. Consequently more molecules acquire the minimum amount of energy and tend to cross the energy barrier. A fraction of activated molecules is greater for the catalyzed reaction. The rate of catalyzed reaction thus is larger than the reaction with no catalyst.

## Exercises

### 1. Choose the most correct option.

- i. The rate law for the reaction  $aA + bB \longrightarrow P$  is  $\text{rate} = k[A][B]$ . The rate of reaction doubles if
  - a. concentrations of A and B are both doubled.
  - b. [A] is doubled and [B] is kept constant
  - c. [B] is doubled and [A] is halved
  - d. [A] is kept constant and [B] is halved.
- ii. The order of the reaction for which the units of rate constant are  $\text{mol dm}^{-3} \text{s}^{-1}$  is
  - a. 1
  - b. 3
  - c. 0
  - d. 2
- iii. The rate constant for the reaction  $2 \text{N}_2\text{O}_5(\text{g}) \longrightarrow 2 \text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$  is  $4.98 \times 10^{-4} \text{s}^{-1}$ . The order of reaction is
  - a. 2
  - b. 1
  - c. 0
  - d. 3
- iv. Time required for 90 % completion of a certain first order reaction is  $t$ . The time required for 99.9 % completion will be
  - a.  $t$
  - b.  $2t$
  - c.  $t/2$
  - d.  $3t$
- v. Slope of the graph  $\ln[A]_t$  versus  $t$  for first order reaction is
  - a.  $-k$
  - b.  $k$
  - c.  $k/2.303$
  - d.  $-k/2.303$
- vi. What is the half life of a first order reaction if time required to decrease concentration of reactant from 0.8 M to 0.2 M is 12 h?
  - a. 12 h
  - b. 3 h
  - c. 1.5 h
  - d. 6 h
- vii. The reaction,  $3 \text{ClO}^\ominus \longrightarrow \text{ClO}_3^\ominus + 2 \text{Cl}^\ominus$  occurs in two steps,
  - (i)  $2 \text{ClO}^\ominus \longrightarrow \text{ClO}_2^\ominus$
  - (ii)  $\text{ClO}_2^\ominus + \text{ClO}^\ominus \longrightarrow \text{ClO}_3^\ominus + \text{Cl}^\ominus$
 The reaction intermediate is
  - a.  $\text{Cl}^\ominus$
  - b.  $\text{ClO}_2^\ominus$
  - c.  $\text{ClO}_3^\ominus$
  - d.  $\text{ClO}^\ominus$
- viii. The elementary reaction  $\text{O}_3(\text{g}) + \text{O}(\text{g}) \longrightarrow 2 \text{O}_2(\text{g})$  is
  - a. unimolecular and second order
  - b. bimolecular and first order
  - c. bimolecular and second order
  - d. unimolecular and first order
- ix. Rate law for the reaction,  $2 \text{NO} + \text{Cl}_2 \longrightarrow 2 \text{NOCl}$  is  $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$ . Thus  $k$  would increase with

- a. increase of temperature
  - b. increase of concentration of NO
  - c. increase of concentration of  $\text{Cl}_2$
  - d. increase of concentrations of both  $\text{Cl}_2$  and NO
- x. For an endothermic reaction,  $\text{X} \rightleftharpoons \text{Y}$ . If  $E_f$  is activation energy of the forward reaction and  $E_r$  that for reverse reaction, which of the following is correct?
- a.  $E_f = E_r$                       b.  $E_f < E_r$
  - c.  $E_f > E_r$
  - d.  $\Delta H = E_f - E_r$  is negative

## 2. Answer the following in one or two sentences.

- i. For the reaction,  

$$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \longrightarrow 2 \text{NH}_3(\text{g}),$$
 what is the relationship among  $\frac{d[\text{N}_2]}{dt}$ ,  $\frac{d[\text{H}_2]}{dt}$  and  $\frac{d[\text{NH}_3]}{dt}$  ?
- ii. For the reaction,  

$$\text{CH}_3\text{Br}(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{CH}_3\text{OH}^-(\text{aq}) + \text{Br}^-(\text{aq}),$$
 rate law is  $\text{rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$ 
  - a. How does reaction rate changes if  $[\text{OH}^-]$  is decreased by a factor of 5 ?
  - b. What is change in rate if concentrations of both reactants are doubled?
- iii. What is the relationship between coefficients of reactants in a balanced equation for an overall reaction and exponents in rate law. In what case the coefficients are the exponents?
- iv. Why all collisions between reactant molecules do not lead to a chemical reaction?
- v. What is the activation energy of a reaction?
- vi. What are the units for rate constants for zero order and second order reactions

if time is expressed in seconds and concentration of reactants in mol/L?

- vii. Write Arrhenius equation and explain the terms involved in it.
- viii. What is the rate determining step?
- ix. Write the relationships between rate constant and half life of first order and zeroth order reactions.
- x. How do half lives of the first order and zero order reactions change with initial concentration of reactants?

## 3. Answer the following in brief.

- i. How instantaneous rate of reaction is determined?
- ii. Distinguish between order and molecularity of a reaction.
- iii. A reaction takes place in two steps,  

$$1. \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{NOCl}_2(\text{g})$$

$$2. \text{NOCl}_2(\text{g}) + \text{NO}(\text{g}) \longrightarrow 2 \text{NOCl}(\text{g})$$
  - a. Write the overall reaction. b. Identify reaction intermediate. c. What is the molecularity of each step?
- iv. Obtain the relationship between the rate constant and half life of a first order reaction.
- v. How will you represent zeroth order reaction graphically?
- vi. What are pseudo-first order reactions? Give one example and explain why it is pseudo-first order.
- vii. What are requirements for the colliding reactant molecules to lead to products?
- viii. How catalyst increases the rate of reaction? Explain with the help of potential energy diagram for catalyzed and uncatalyzed reactions.
- ix. Explain with the help of Arrhenius equation, how does the rate of reaction changes with (a) temperature and (b) activation energy.

- x. Derive the integrated rate law for first order reaction.
- xi. How will you represent first order reactions graphically.
- xii. Derive the integrated rate law for the first order reaction,  $A(g) \longrightarrow B(g) + C(g)$  in terms of pressure.
- xiii. What is zeroth order reaction? Derive its integrated rate law. What are the units of rate constant?
- xiv. How will you determine activation energy: (a) graphically using Arrhenius equation (b) from rate constants at two different temperatures?
- xv. Explain graphically the effect of temperature on the rate of reaction.
- xvi. Explain graphically the effect of catalyst on the rate of reaction.
- xvii. For the reaction  $2A + B \longrightarrow$  products, find the rate law from the following data.

[A]/M	[B]/M	rate/M s <sup>-1</sup>
0.3	0.05	0.15
0.6	0.05	0.30
0.6	0.2	1.20

#### 4. Solve

- i. In a first order reaction, the concentration of reactant decreases from 20 mmol dm<sup>-3</sup> to 8 mmol dm<sup>-3</sup> in 38 minutes. What is the half life of reaction? (28.7 min)
- ii. The half life of a first order reaction is 1.7 hours. How long will it take for 20% of the reactant to react? (32.9 min)
- iii. The energy of activation for a first order reaction is 104 kJ/mol. The rate constant at 25 °C is  $3.7 \times 10^{-5} \text{ s}^{-1}$ . What is the rate constant at 30°C? ( $R = 8.314 \text{ J/K mol}$ ) ( $7.4 \times 10^{-5}$ )
- iv. What is the energy of activation of a reaction whose rate constant doubles when the temperature changes from 303 K to 313 K? (54.66 kJ/mol)
- v. The rate constant of a reaction at 500°C is  $1.6 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ . What is the frequency factor of the reaction if its activation energy is 56 kJ/mol. ( $9.72 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ )
- vi. Show that time required for 99.9% completion of a first order reaction is three times the time required for 90% completion.
- vii. A first order reaction takes 40 minutes for 30% decomposition. Calculate its half life. (77.66 min)
- viii. The rate constant for the first order reaction is given by  $\log_{10} k = 14.34 - 1.25 \times 10^4/T$ . Calculate activation energy of the reaction. (239.3 kJ/mol)
- ix. What fraction of molecules in a gas at 300 K collide with an energy equal to activation energy of 50 kJ/mol? ( $2 \times 10^{-9}$ )

#### Activity :



1. You wish to determine the reaction order and rate constant for the reaction,  $2AB_2 \longrightarrow A_2 + 2B_2$ . a) What data would you collect? b) How would you use these data to determine whether the reaction is zeroth or first order?

2. The activation energy for two reactions are  $E_a$  and  $E'_a$  with  $E_a > E'_a$ . If the temperature of reacting system increase from  $T_1$  to  $T_2$ , predict which of the following is correct?

- a.  $\frac{k'_1}{k_1} = \frac{k'_2}{k_2}$
- b.  $\frac{k'_1}{k_1} > \frac{k'_2}{k_2}$
- c.  $\frac{k'_1}{k_1} < \frac{k'_2}{k_2}$
- d.  $\frac{k'_1}{k_1} < 2 \frac{k'_2}{k_2}$

$k_s$  are rate constants at lower temperature and  $k'_s$  at higher temperature.