

## MODULE - 5

### Chemical Dynamics



Notes



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# CHEMICAL KINETICS

You know that a knowledge of Gibbs energy change in a given process can tell you whether the process is feasible or not. However, the Gibbs energy decrease does not indicate anything about the speed of a reaction. For example, the reaction between hydrogen and oxygen to give water is accompanied by a large decrease in Gibbs energy. However, you would not be able to observe the formation of water, even if hydrogen and oxygen are kept in contact with each other for ever. On the other hand, there are reactions which take place instantaneously. For example, when HCl is added to  $\text{AgNO}_3$ , white precipitate of  $\text{AgCl}$  is formed instantaneously. In this lesson we shall study the speed or rate of reactions which are neither very slow nor very fast. We shall also study the factors that control the rate of a reaction.



## OBJECTIVES

After reading this lesson you will be able to :

- explain the rate of a chemical reaction;
- differentiate between average rate and instantaneous rate;
- correlate the average and instantaneous rates with changes in concentrations of various reactants and products;
- explain the factors that affect the rate of a reaction;
- define rate law and rate constant;
- define order and molecularity of a reaction;
- distinguish between order and molecularity;
- derive rate law for first order reaction and define half life period for first order reaction;

- derive a relationship between half life and rate constant for first order reaction;
- solve numericals on the relationships;
- explain collision theory of reaction rates.
- explain the effect of temperature on reaction rate, and
- explain Arrhenius equation and activation energy.



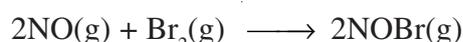
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### 14.1 RATE OF A CHEMICAL REACTION

When the reactants are mixed to perform a reaction, there are no products present initially. As time passes, the concentration of the products increases and that of the reactants decreases. The rate of any chemical reaction can be expressed as the rate of the change in concentration of a reactant (or a product).

$$\begin{aligned} \text{Rate of a chemical reaction} &= \frac{\text{Change in concentration}}{\text{Time taken}} \text{ of a reactant or a product} \\ &= \frac{\text{mol litre}^{-1}}{\text{second}} \end{aligned}$$

Let us consider the following chemical reaction :



The rate for this reaction can be determined by measuring the increase in the molar concentration of NOBr at different time intervals.

Let us see how we can express the rate of this reaction. You know that molar concentration of a substance is expressed by enclosing the formula of the substance in square bracket.

For example, [NOBr] represents the molar concentration of NOBr.

Let us suppose that [NOBr]<sub>1</sub> is the molar concentration at time  $t_1$  and [NOBr]<sub>2</sub> is the molar concentration at time  $t_2$ .

Then, change in molar concentration = [NOBr]<sub>2</sub> – [NOBr]<sub>1</sub> =  $\Delta$ [NOBr]

Time required for the change =  $t_2 - t_1 = \Delta t$

Here,  $\Delta$  means change in the respective quantity.

Therefore, the rate of formation of NOBr =  $\frac{\Delta[\text{NOBr}]}{\Delta t}$

This expression gives the rate of reaction in terms of NOBr.

If the decrease in the molar concentration of NO or Br<sub>2</sub> is measured we can write the rate of the reaction with respect to NO as

$$= \frac{-\Delta[\text{NO}]}{\Delta t}$$

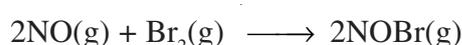


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$$\text{and w.r.t. Br}_2 \text{ as } = \frac{-\Delta[\text{Br}_2]}{\Delta t}$$

Thus, the rate of a reaction can be expressed either in terms of reactants or products. We find in the reaction mentioned above that two moles of NO react with one mole of Br<sub>2</sub>. Therefore, the change in concentration of NO in a given time  $\Delta t$  will be double than that for Br<sub>2</sub>. Thus, in order to make the rates with respect to different reactants or products equal, the rate expression is divided by the stoichiometric coefficient in the balanced chemical equation.

For example, in the equation,



The rate of reaction with respect to reactants and products is expressed as

$$\text{rate of reaction} = + \frac{1}{2} \frac{\Delta[\text{NOBr}]}{\Delta t} = - \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = - \frac{\Delta[\text{Br}_2]}{\Delta t}$$

### 14.2 AVERAGE RATE AND INSTANTANEOUS RATE

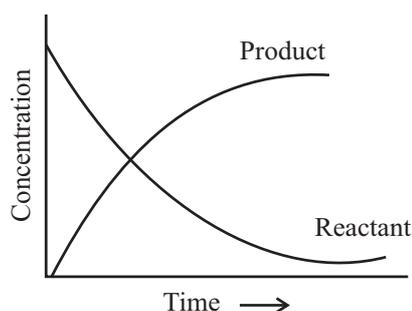
The rate of a reaction depends on the concentration of reactants. As the reaction proceeds the reactants get consumed and their concentration decreases with time. Therefore, the rate of reaction does not remain constant during the entire reaction.

The rate of a reaction given as  $\frac{\Delta[\text{concentration}]}{\Delta t}$  gives an average rate.

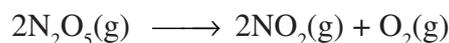
For example,  $\frac{\Delta[\text{NOBr}]}{\Delta t}$  gives the average rate of reaction. Instantaneous rate of a reaction is the rate of reaction at any particular instant of time, we express instantaneous rate by making  $\Delta t$  very small  $\phi$

$$\lim_{\Delta t \rightarrow 0} \frac{[\text{NOBr}]}{\Delta t} = \frac{d[\text{NOBr}]}{dt}$$

When concentration of any of the reactants or products is plotted against time, the graph obtained is as given below :



For the reaction,



Average rate of reaction

$$= -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

and instantaneous rate =  $-\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$



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### 14.3 FACTORS AFFECTING RATE OF A REACTION

The rate of a chemical reaction is affected by the following factors :

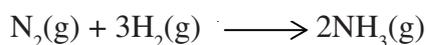
- 1. The concentration of reactants** : Generally the rate of a reaction increases as the concentration of the reactants is increased.
- 2. Temperature** – A reaction is faster when the reaction temperature is increased.
- 3. Presence of a catalyst** – A catalyst alters the reaction rate without being consumed by the reaction.

For example :

- (i) Reaction between hydrogen and oxygen to form water is extremely slow. It occurs very fast in the presence of platinum as catalyst.

You would study these effects in more detail in the following sections of this lesson.

**Example 14.1** : Express the average and instantaneous rate of the following reaction



- in terms of
- rate of formation of  $\text{NH}_3$ ,
  - rate of disappearance  $\text{N}_2$ , and
  - rate of disappearance of  $\text{H}_2$ .

Write the different expressions for the rate of reactions.

**Solution** : The expression for the three rates are :

$$\text{Average rate of formation of } \text{NH}_3 = \frac{\Delta[\text{NH}_3]}{\Delta t}$$

$$\text{Average rate of disappearance of } \text{N}_2 = -\frac{\Delta[\text{N}_2]}{\Delta t}$$



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$$\text{Average rate of disappearance of H}_2 = \frac{\Delta[\text{H}_2]}{\Delta t}$$

$$\text{Instantaneous rate of formation of NH}_3 = \frac{d[\text{NH}_3]}{dt}$$

$$\text{Instantaneous rate of disappearance of N}_2 = -\frac{d[\text{N}_2]}{dt}$$

$$\text{Instantaneous rate of disappearance of H}_2 = \frac{d[\text{H}_2]}{dt}$$

To equate the three rates, divide each rate by the coefficient of the corresponding substances in the balanced equation.

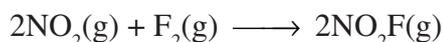
$$\text{Average rate} = +\frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t}$$

$$\text{Instantaneous rate} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$$



## INTEXT QUESTIONS 14.1

- Which of the following units could be used to express the rate of reaction between magnesium and hydrochloric acid?
  - $\text{cm}^{-3} \text{ s}$
  - $\text{cm}^3 \text{ min}^{-1}$
  - $\text{cm}^3 \text{ s}^{-1}$
  - $\text{mol dm}^{-3} \text{ min}^{-1}$
- For the following reaction,



Write the expression for the average, rate of reaction in terms of :

- rate of formation of  $\text{NO}_2\text{F}$
  - rate of disappearance of  $\text{NO}_2$
  - rate of disappearance of  $\text{F}_2$
  - equivalent rate of formation of product and disappearance of reactants.
- Express the instantaneous rates of formation of product and disappearance of reactants for the above reaction.
  - Explain why the reaction  $\text{CO}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$  occurs more slowly when the volume of the system is increased.

## 14.4 DEPENDENCE OF REACTION RATE UPON CONCENTRATION

**Rate law :** If we follow a chemical reaction over a period of time, we find that its rate slowly decreases as the reactants are consumed. We can say that the rate is related to the concentration of the reactants. Rate is directly proportional to the concentration of the reactants raised to some power.

For example, consider the reaction



where  $a$  and  $b$  are coefficients of  $A$  and  $B$  respectively in the balanced equation.

We can express the rate as

$$\text{Rate} \propto [A]^x [B]^y$$

$$\text{or Rate} = k [A]^x [B]^y$$

where  $k$  is the constant of proportionality.

The above equation is known as the rate law for the reaction.

**Rate law is defined as the mathematical relationship between rate of a reaction and the concentration of the reactants.**

It is important to note that  $x$  and  $y$  are not necessarily equal to the stoichiometric coefficient of  $A$  and  $B$  in the reaction. The constant  $k$  in the rate law is called the **rate constant**. It is numerically equal to the rate of the reaction if all the concentrations were set equal to unity.

$$\text{rate} = k [1]^x [1]^y$$

$$\therefore \text{rate} = k$$

It means that large values of  $k$  indicate fast reaction and small values of  $k$  indicate slow reactions. Each reaction is characterised by its own rate constant, whose value is dependent on the temperature, but independent of concentration of the reactants.

## 14.5 ORDER AND MOLECULARITY OF A REACTION

Order and molecularity are two properties of a chemical reaction. In this section we shall learn about these.

### 14.5.1 Order of a Reaction

The powers to which the concentration terms are raised in the rate expression describes the order of the reaction with respect to that particular reactant

In the rate law,

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



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the values of  $x$  and  $y$  are order of the reaction with respect to the reactants A and B respectively. The sum of the powers  $x + y$  represents the overall order of the reaction.

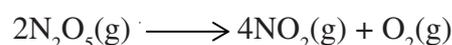


The rate law as found by experiment is

$$\text{rate} = k [\text{NO}]^2 [\text{O}_2]^1$$

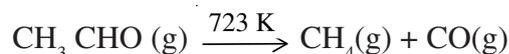
Here the order of reaction with respect to NO is 2 and with respect to  $\text{O}_2$  is 1. The sum of the powers is termed as overall order of reaction. In the above example it is  $2 + 1 = 3$ .

It must be remembered that order of a reaction *must be determined experimentally* and cannot be deduced from the coefficients in the balanced equation



The overall order is 1 and it is termed as first order reaction.

The order of reaction can be 0, 1, 2, 3 called as zero order, first order, second order and third order respectively. The order of a reaction can be a fraction as well; for example the decomposition of ethanal to methane and carbon monoxide,



is experimentally found to the following rate law :

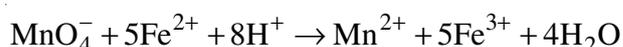
$$\text{rate} = k [\text{CH}_3\text{CHO}]^{3/2}$$

### 14.5.2 Difference between Rate of Reaction and Rate Constant

Rate of reaction	Rate constant
1. It is the speed at which the reactants are converted into products. It is measured as the rate of decrease of concentration of reactant or rate of increase in the concentration of the products.	It is the proportionality constant in the rate law and is defined as the rate of the reaction when the concentration of each of the reactant is unity.
2. It depends upon the initial concentration of the reactant.	It is independent of the initial concentration of reactant.

### 14.5.3 Molecularity of a Reaction

A reaction occurs when its reactants are mixed. At molecular level, this ‘mixing’ occurs through molecular collisions. The balanced chemical equation does not always give the correct picture of how a reaction is occurring at molecular level. For the following reaction to occur



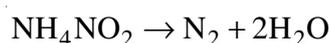
apparently 14 ionic species must collide. However, the probability of a collision involving more than 3 particles is practically zero. Therefore, this reaction must be occurring in many steps, each step involving collision of not more than 3 species. Such reactions are called complex reactions and each step is called an **elementary reaction step**. Some reactions occur in a single step and such reactions are called **simple reactions**.

**Molecularity is the number of molecules, atoms or ions taking part in an elementary reaction step, which must collide simultaneously in order to bring about the chemical reaction.**

Molecularity of a reactions is its characteristic property and reactions are classified according the their molecularity.

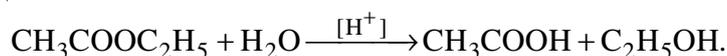
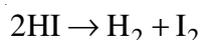
#### (i) Unimolecular reactions

These are reactions whose molecularity is one. For example



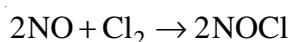
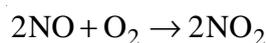
#### (ii) Bimolecular reactions

These are the reactions with molecularity equal to two, for example:



#### (iii) Termolecular or trimolecular reactions

These reactions have molecularity equal to three, for example



Termolecular reactions are rare because the probability of three molecules colliding simultaneously is very small. Most of the reactions are unimolecular or bimolecular.

Molecularity of a reaction can only be a whole number, 1, 2 or 3. It is never zero, fractional or more than 3.

## 14.6 UNITS OF RATE CONSTANT

For zero order

$$\text{Rate} = k [\text{A}]^0$$

$$\text{Rate} = k$$



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## Notes

The unit for rate of a reaction is  $\text{mol L}^{-1} \text{s}^{-1}$ . The unit of  $k$  for zero order is same as that for rate.

For a first order reaction

$$\text{Rate} = k [\text{A}]^1$$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k \text{ mol L}^{-1}$$

$$k = \text{s}^{-1}$$

For a first order reaction, the unit for rate constant is  $\text{time}^{-1}$ .

For second order reaction

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

$$\frac{\text{mol L}^{-1}}{\text{s}} = k (\text{mol L}^{-1})^2$$

Therefore

$$k = \text{mol}^{-1} \text{L s}^{-1}$$

In general for any order  $n$  the unit for rate constant  $k$  is given as

$$k = (\text{mol L}^{-1})^{1-n} \text{s}^{-1}$$

### 14.6.1 Zero Order Reactions

Zero order reactions are those whose rate is proportional to zeroth power of concentration, that is, the rate is independent of concentration of the reactant.

**Table: Comparison of Order and molecularity**

Order	Molecularity
1. It is the sum of powers of concentration terms in the experimentally determined rate equation	It is the number of molecules, atoms or ions which must collide simultaneously in order to bring about the chemical reaction.
2. Order of a reaction can be 1, 2, 3, zero or fractional.	Molecularity can be 1, 2 or 3 only. It cannot be zero or fractional.
3. It is an experimental quantity.	It is a theoretical quantity and depends on the mechanism of the reaction.
4. It is applicable to elementary as well as complex reaction.	It is applicable to only elementary reaction.
5. For complex reactions, order is determined by the slowest step and the order and molecularity of the slowest step are the same.	For complex reactions, molecularity has no meaning.

**Examples of Zero Order Reactions**

Some reactions show zero order *under certain conditions*.

- (1) Decomposition of HI on the surface of gold catalyst when the *pressure of HI is high*.
- (2) Photochemical combination of H<sub>2</sub> and Cl<sub>2</sub> to form HCl *when carried out over water*.
- (3) Enzyme reactions *when the substrate concentration is high* in comparison to the enzyme concentration.

Consider the reaction:



Since the order of the reaction is zero, its differential rate equation is

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^0$$

Since anything raised to the power zero is equal to 1,

$$\text{Rate} = -\frac{d[A]}{dt} = k \quad (1)$$

Separating the variables, we get

$$d[A] = -kdt$$

Integrating both sides

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

$$[A] = -kt + I \quad (2)$$

Where [A] is the concentration of A at time  $t$  and  $I$  is the constant of integration. It can be evaluated from the initial conditions. When  $t = 0$ ,  $[A] = [A]_0$ , where  $[A]_0$  is the initial concentration of the reactant. Substituting in equation (2)

$$[A]_0 = -k \times 0 + I = 0 + I$$

$$\therefore [A]_0 = I \quad (3)$$

Substituting for  $I$  in equation (2)

$$[A] = -kt + [A]_0 \quad (4)$$

This equation is the **integrated rate equation for a zero order reaction**. This equation is an equation of a straight line and is of the form

$$y = mx + c$$



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## Notes

If  $[A]$  is plotted as a function of  $t$ , the plot is a straight line graph with intercept equal to  $[A]_0$  and slope equal to  $-k$ .

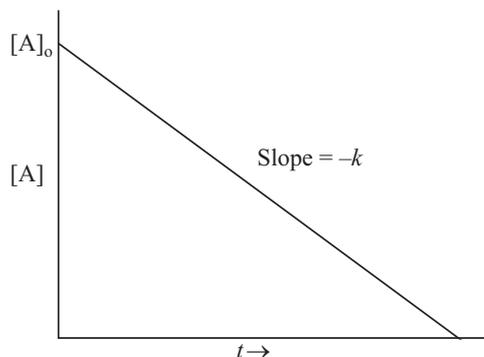


Fig. Concentration versus time plot for a zero order reaction.

Units of  $k$ 

Equation (4) can be rearranged as

$$kt = [A]_0 - [A]$$

$$\text{or } k = \frac{[A]_0 - [A]}{t} = \frac{\text{concentration}}{\text{time}} \quad (5)$$

$$= \text{Concentration time}^{-1} = \text{mol L}^{-1}\text{s}^{-1}$$

Half-Life Period,  $t_{1/2}$ 

It is the time during which one-half of the initial amount of the reactant reacts. It is denoted by  $t_{1/2}$  or  $t_{0.5}$ . It is also called **half-change period**. It can be obtained from equation (4). Rearranging it, we get

$$t = \frac{[A]_0 - [A]}{k} \quad (6)$$

$$\text{when } t = t_{1/2}, [A] = \frac{1}{2}[A]_0$$

that is after half-life period, one-half of the reactant is consumed. Also, one-

$$\text{half reactant is left unreacted or } [A] = \frac{1}{2}[A]_0.$$

Putting in equation (6)

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

$$t_{1/2} = \frac{[A]_0}{2k} \quad (7)$$

Thus, the half-life period of a zero order reaction depends upon the initial concentration of the reactant  $[A]_0$  and from the above equation

$$t_{1/2} \propto [A]_0$$

the half-life period is directly proportional to the initial concentration of the reactant.

**Example:** The rate constant of a zero order reaction is  $2.4 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$ . What would be the half-life of the reaction if the initial concentration of the reactant is  $1.2 \times 10^{-2} \text{ mol L}^{-1}$ ?

### Solution

For a zero order reaction

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

Given: initial concentration of the reactant,  $[A]_0 = 1.2 \times 10^{-2} \text{ mol L}^{-1}$  and  $k = 2.4 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$ .

$$\begin{aligned} \therefore t_{1/2} &= \frac{1.2 \times 10^{-2} \text{ mol L}^{-1}}{2 \times 2.4 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}} \\ &= 2.5 \text{ s.} \end{aligned}$$

### 14.6.2 First Order Reaction

We will now discuss how to determine the rate constant for a first order reaction. For the first order reaction, this equation would tell us how does the concentration vary with time. The predicted variations can then be compared with the experimental data to obtain the order of the reaction.

Let us consider for the reaction  $A \longrightarrow \text{Product}$ .

For first order reaction.

$$\text{rate} = \frac{-d[A]}{dt} = k_1[A]$$

where  $k_1$  is the rate constant,



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Rearranging the rate expression, we have :

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

Integrating the two sides we get :

$$-1 \ln [A] = k_1 t + \text{constant} \quad \dots(i)$$

where the constant can be determined from the initial conditions.

Let  $[A]_0$  be concentration of  $[A]$  when  $t = 0$  i.e., at the beginning of the reaction, then  $-1 \ln [A] = -1 \ln [A]_0$ , when  $t = 0$

$$\text{or} \quad \text{constant} = -1 \ln [A]_0$$

Putting the value of the constant in equation

$$-1 \ln [A] = k_1 t - 1 \ln [A]_0$$

$$\text{or} \quad -1 \ln [A] + 1 \ln [A]_0 = k_1 t$$

$$\text{or} \quad \frac{\ln [A]_0}{[A]} = k_1 t$$

$$\text{Rate constant, } k_1 = \frac{1}{t} \cdot \ln \frac{[A]_0}{[A]}$$

We can convert it in to log to the base 10

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

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

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

$$\log [A] = -\left(\frac{k_1}{2.303}\right) t + \log [A]_0$$

The unit of  $k_1 = \text{time}^{-1}$

This equation has the same form as the equation of a straight line.

$$y = mx + c$$

where  $m$  is the slope and  $c$  is the intercept. If we plot  $\log_{10} [A]$  vs  $t$ , it would give

a straight line with a slope equal to  $-\frac{k_1}{2.303}$ . The rate constant,  $k_1$  can then be

calculated from the slope as shown in Fig. 14.1.

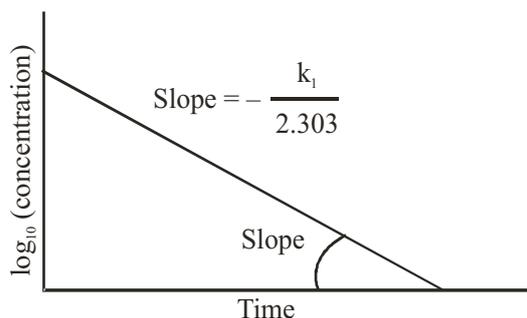


Fig. 14.1 : A graph of  $\log_{10}$  (concentration) against time for a first-order reaction.



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### 14.6.3 Half-Life Period

The time taken for a reaction to reach the half-way stage i.e. when half of the starting material has reacted is called half-life period of the reaction. It is denoted by  $t_{1/2}$  or  $t_{0.5}$ . Let us now see how the half-life period of a first order reaction is calculated.

You know that

$$\ln[A] = \ln[A]_0 - k_1 t$$

when  $[A] = \frac{1}{2} [A]_0$  (reactant reduces to half of the initial concentration)

then

$$t = t_{1/2} \text{ (half life period)}$$

Therefore, we have

$$\ln \left\{ \frac{[A]_0}{2} \right\} = \ln[A]_0 - k_1 t_{1/2}$$

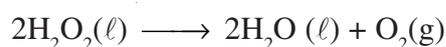
or 
$$\ln \left\{ \frac{[A]_0}{2} \right\} - \ln [A]_0 = -k_1 t_{1/2}$$

or 
$$\ln \frac{1}{2} = -k_1 t_{1/2}$$

or 
$$t_{1/2} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1}$$

You would notice that half-life period is independent of the initial concentration.

**Example 14.2 :** The decomposition of hydrogen peroxide to water and oxygen.



is a first order reaction with a rate constant of  $0.0410 \text{ min}^{-1}$ . If we start with  $0.20 \text{ M}$  solution of  $\text{H}_2\text{O}_2$ , what will be concentration after 10 minutes?



## Notes

**Solution :** We have equation for first order reaction as

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]}$$

converting it into  $\log_{10}$  base

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

If  $[A] = x$ , after 10 minutes then substituting the values of  $k$  and  $t$ , we have

$$0.0410 \text{ (min}^{-1}\text{)} = \frac{2.303}{10 \text{ (min)}} \log \frac{0.20}{x}$$

or

$$\log \frac{0.20}{x} = \frac{10 \text{ (min)} (0.0410 \text{ min}^{-1})}{2.303} = 0.178$$

Taking antilog

$$\frac{0.20}{x} = \text{antilog } 0.178 = 1.51$$

Solving

$$x = \frac{0.20}{1.51} = 0.132 \text{ mol litre}^{-1}.$$

**Example 14.3 :** In example 14.2 if we start with initial concentration of 0.50 how long will it take for this concentration to drop to 0.10 M.

**Solution :** We have to find the time taken by the reaction starting from concentration of  $\text{H}_2\text{O}_2$  of 0.5M to concentration of 0.1 M.

We have the equation,

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

Substituting the values of  $k$ ,  $[A]_0$  and  $[A]$  we have

$$0.0410 \text{ min}^{-1} = \frac{2.303}{t} \log \frac{0.50}{0.10}$$

$$t = \log 5 \times \frac{2.303}{0.0410 \text{ min}^{-1}} = \frac{0.699 \times 2.303}{0.041} \text{ min}$$

or

$$t = 39 \text{ minutes}$$

**Example 14.4 :** In example 14.2, how long will it take for the sample to decompose to 50%.

**Solution :** When half the sample has decomposed, we have

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

Putting the value of  $k = 0.0414 \text{ min}^{-1}$  we have

$$t = \frac{0.693}{0.0414} \text{ min} = 16.9 \text{ minutes}$$



### INTEXT QUESTIONS 14.2

- The rate of a certain reaction,  $A \longrightarrow \text{Product}$  is  $1.0 \times 10^{-3} \text{ mol/litre}$ .  
When conc.  $A = 0.020\text{M}$ , what is rate constant  $k$ , if the reaction is :  
(a) zero order  
(b) first order
- For the following reaction  

$$\text{C}_2\text{H}_4(\text{g}) + \text{I}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_4\text{I}_2(\text{g})$$
 the rate equation is  

$$\text{rate} = k [\text{C}_2\text{H}_4(\text{g})] [\text{I}_2(\text{g})]^{3/2}$$
 (a) What is the order of reaction with respect to each reactant?  
 (b) What is the overall order of reaction?  
 (c) What is the unit of  $k$ , if concentrations are measured in  $\text{mol dm}^{-3}$ ?
- The first order rate constant for the decomposition of  $\text{C}_2\text{H}_5\text{Cl}$  at  $700\text{K}$  is  $2.5 \times 10^{-3} \text{ min}^{-1}$ . If the initial concentration is  $0.01 \text{ mol L}^{-1}$ , calculate the time required for the concentration of  $\text{C}_2\text{H}_5\text{Cl}$  to drop to half of its original value.

### 14.7 COLLISION THEORY OF REACTION RATES

Collision theory was proposed to explain the rates of reactions occurring in gas phase. It is largely based on kinetic molecular theory of gases. According to this theory:

- A reaction would occur only when the reactant molecules collide with one another. Thus, the rate of a reaction would depend upon the *collision frequency*,  $Z_{AB}$  which is the number of collisions involving one molecule each of two reactants A and B occurring in unit volume of the gaseous reaction mixture and in unit time.
- Not all molecular collisions result in chemical reaction. Only effective collisions can bring about chemical reaction. An effective collision is the one



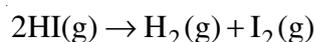
Notes



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in which the combined kinetic energy of colliding molecules is equal to or more than the activation energy of the reaction  $E_a$ . The fraction of molecules possessing a minimum of activation energy  $E_a$  at a particular temperature  $T$  is given by  $e^{-\frac{E_a}{RT}}$ .

3. For a reaction to occur not only the collision should be energetically effective, the orientation of the colliding molecules should be such which would permit the formation of new bonds. Consider, for example, the decomposition reaction of HI



The product would be formed only if during the collision the two H atoms are near each other and so are the two I atoms. (Fig 14.3(a)). This would permit the formation of bond between two H atoms and another bond between two I atoms. If orientation is not proper (Fig 14.3(b), it is not possible as two I atoms are too far apart for the bond formation. After the collision, the two HI molecules rebound back without any reaction. Only a certain fraction of energetically effective collisions would have proper orientation and would result in a chemical reaction. This fraction is represented in terms of probability  $P$ , that molecules during a given collision would have proper orientation.  $P$  is called **probability factor** or **steric factor**.

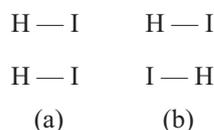


Fig. 14.3 (a) Proper orientation of two HI molecules (b) Improper orientation.

Taking these three factors into account, the rate of the reaction is given by the relation

$$\text{Rate} = Z_{AB} \cdot e^{-\frac{E_a}{RT}} \cdot P$$

## 14.7 DEPENDENCE OF REACTION RATE ON TEMPERATURE

You have learnt earlier that an increase in temperature causes an increase in the rate of reaction. The rate is about doubled, for many reactions, by a 10 degree rise in temperature. How can we explain this behaviour?

In order for a chemical reaction to occur, the reacting molecules must collide with each other. Only fast moving molecules i.e. the molecules having high energy are able to react. There must be some minimum energy possessed by the reacting molecules during the collision. This is called the **threshold energy**. All molecules

having energy higher than the threshold energy are therefore, capable of reacting. What would happen if we increase the number of molecules having higher energy? More molecules will react. In other words rate of reaction would increase. Thus, if we increase the temperature, we increase the rate of reaction. Let us see if we can express it quantitatively.

The change in energy that takes place during the course of a reaction is shown in Fig. 14.2. The horizontal axis denotes the progress of the reaction and it indicates the extent to which the reaction has progressed towards completion. The graph indicates that the reactant molecules A and B must possess enough energy. This is known as Activation energy, to climb the potential energy hill to form the activated complex. All the reacting molecules do not possess energy equal to threshold energy in their normal energy state. Therefore a certain extra energy needs to be supplied so that their energy equals the threshold energy. The potential energy of activated complex is maximum. The reaction thereafter proceeds to completion (i.e. formation AB).  $E_a$  indicates the activation energy of forward reaction and  $E_a'$  is the activation energy of the backward reaction.

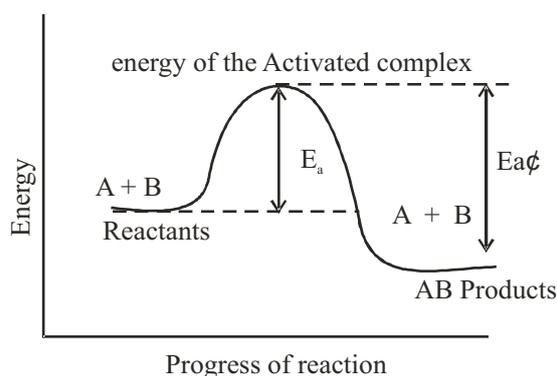


Fig. 14.2 Energy diagram for a reaction

You know that rate of reaction =  $k$  [concentration]. If we have value of concentration as unity, then rate of reaction is equal to the rate constant,  $k$ . The rate constant  $k$  depends on the magnitude of the activation energy,  $E_a$ , and also on the absolute temperature ( $T$ ),  $k$  is small when  $E_a$  is very large or the temperature is low.

We can express this relationship by a mathematical equation known as *Arrhenius equation* after its discoverer, S. Arrhenius as follows :

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

Where  $A$  is a proportionality constant and is also known as frequency factor,  $R$  is the gas constant. How can we utilise this relationship between  $k$ ,  $E_a$  and  $T$ ? We



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can calculate activation energy, if we measure the rate constant at two different temperatures.

Taking natural logarithm of equation, we get

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

We can compare this equation with that of a straight line  $y = mx + c$  as follow :

$$\ln k = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln A$$

The plot of  $\ln k$  vs  $1/T$  gives a straight line whose slope is equal to  $-E_a/R$  and whose intercept is  $\ln A$  (in Fig. 14.3).

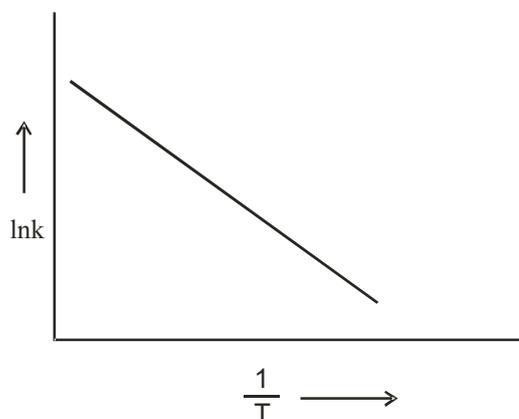


Fig. 14.3 Graphical determination of  $E_a$ .

We can also obtain  $E_a$  from  $k$  at two temperatures by direct computation.

At  $T_1$ , the equation becomes

$$k_1 = Ae^{-E_a/RT_1}$$

At  $T_2$ , we can write

$$k_2 = Ae^{-E_a/RT_2}$$

Dividing  $k_1$  by  $k_2$  we get

$$\frac{k_1}{k_2} = \frac{Ae^{-E_a/RT_1}}{Ae^{-E_a/RT_2}}$$

taking natural logarithm

$$\ln \frac{k_1}{k_2} = \frac{-E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Converting into logarithm (base 10)

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

Multiply by  $-1$  on both sides and inverting the fraction

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

This equation can also be used to calculate the rate constant at some specific temperature if  $E_a$  and  $k$  at some other temperature are known.

**Example 14.5 :** What must be the value of  $E_a$  if the rate constant for a reaction is doubled when the temperature increases from 300K to 310K?

**Solution :** Given  $\frac{k_2}{k_1} = 2$ ,  $R = 8.31 \text{ JK}^{-1}$

$$T_2 = 310 \text{ K}$$

$$T_1 = 300 \text{ K}$$

$$E_a = ?$$

We have equation :

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

substituting the values we have

$$\log 2 = \frac{E_a}{2.303 \times 8.31 \text{ JK}^{-1}} \frac{(310 - 300)\text{K}}{(310\text{K} \times 300\text{K})}$$

solving, we have

$$E_a = 53.5 \text{ kJ}$$



### INTEXT QUESTIONS 14.3

1. As a rough rule of thumb, the rates of many reactions double for every  $10^\circ\text{C}$  rise in temperature? Explain.
2. The rate constant of a reaction at 288 K is  $1.3 \times 10^{-5}$  litre/mol. While at 323K its rate constant is  $8.0 \times 10^{-3}$  lit./mol. What is the  $E_a$  for the reaction.
3. The rate of the reaction triples when temperature changes from 293 K to 323 K. Calculate the energy of activation for such a reaction.
4.  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  combine to form  $\text{H}_2\text{O}(\ell)$  by an exothermic reaction. Why do they not combine when kept together for any period of time.
5. What is an effective collision?



### WHAT YOU HAVE LEARNT

- The rate of a chemical reaction can be expressed as the rate of change in concentration of a reactant or product.



Notes



## Notes

- The factors that affect the rate of a chemical reaction are : the concentration of the reactants, temperature and catalyst.
- Rate law is defined as the mathematical relationship between rate of a reaction with the concentration of the reactant.
- The constant  $k$  in the rate law is called the rate constant. It is numerically equal to the rate of the reaction if all the concentrations were set equal to unity.
- The sum of the powers to which the concentration terms are raised in the rate expression describe the order of the reaction.
- The rate constant of a first order reaction,  $k_1$ , is given by

$$k_1 = \frac{1}{t} \ln \frac{[A]_0}{[A]}$$

- The time taken for a reaction to reach the half way stage, i.e., when half of the starting material has reacted is called half-life period of a reaction.
- According to the collision theory, a reaction occurs only when the reactant molecules collide provided they have sufficient energy and proper orientation.
- The dependence of the rate constant on the magnitude of the activation energy,  $E_a$ , and the absolute temperature,  $T$ , is given by the Arrhenius equation,  $k = Ae^{-E_a/RT}$ .
- The activation energy for the decomposition of a compound corresponds to the difference between the energy of the reactants and the maximum on the energy curve.



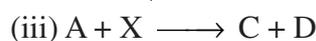
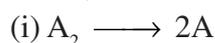
## TERMINAL EXERCISE

1. Sketch an energy vs progress of reaction diagram for a reaction. Indicate the activation energy for both forward ( $E_a$ ) and reverse reaction ( $E'_a$ ).
2. For the reaction  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ , it is found that  $\text{N}_2\text{O}_5$  is decomposing at the rate of 0.02 mol/litre sec. Calculate to rate of reaction defined as  $\frac{\Delta[\text{NO}_2]}{\Delta t}$  with  $\Delta t$  in seconds.
3. The rate constant for a certain first order decomposition reaction is  $0.23 \text{ s}^{-1}$  at 673K. Calculate the half-change period for this reaction.

- The rate constant for a certain first order reaction is  $1.00 \times 10^{-3} \text{ s}^{-1}$  at 298K. The rate constant for the reaction is  $1.4 \times 10^{-2} \text{ s}^{-1}$  at 323K. Calculate the activation energy for this reaction.
- The rate of a reaction was found to be  $3.0 \times 10^{-4} \text{ mol/litre second}$ . What will be the rate if it were expressed in the units  $\text{mol/litre minute}$ .
- List the three factors that affect the rate of a chemical reaction.
- For a certain first order reaction the concentration of the reactant decreases from  $2.00 \text{ mol/litre}$  to  $1.50 \text{ mol/litre}$  in 64 minutes. Calculate the rate constant for this reaction.
- The rate constant for a certain first order reaction is  $1.0 \times 10^{-3} \text{ min}^{-1}$  at 298K. If the activation energy is  $10.0 \text{ k cal}$ , calculate the rate constant at 323K.
- The reaction



Occurs in the following steps



The order of this reaction is one. What is its molecularity. What one of the three steps is the slowest or rate determining step?



## ANSWERS TO INTEXT QUESTIONS

### 14.1

- d

$$2. \text{ (i) } \frac{\Delta[\text{NO}_2\text{F}]}{\Delta t}$$

$$\text{(ii) } \frac{-\Delta[\text{NO}_2]}{\Delta t}$$

$$\text{(iii) } \frac{-\Delta[\text{F}_2]}{\Delta t}$$

$$\text{(iv) } \frac{1}{2} \frac{\Delta[\text{NO}_2\text{F}]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{-\Delta[\text{F}_2]}{\Delta t}$$

$$3. \frac{1}{2} \frac{d[\text{NO}_2\text{F}]}{dt} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{F}_2]}{dt}$$

- Increase in volume would decrease the pressure which would decrease the rate of reaction.



Notes



## Notes

## 14.2

- $1.0 \times 10^{-3} \text{ mol litre}^{-1} \text{ s}^{-1}$
  - $5.0 \times 10^{-2} \text{ s}^{-1}$
- First order with respect to  $\text{C}_2\text{H}_4$  and 1.5 with respect to  $\text{I}_2$ .
  - The over all order of reaction is 2.5

$$\begin{aligned} \text{(c) } k &= \frac{\text{sec}^{-1}}{(\text{mol dm}^{-3})^{3/2}} \\ &= \text{mol}^{-3/2} \text{ dm}^{9/2} \text{ s}^{-1}. \end{aligned}$$

$$3. \text{ (a) } 2.5 \times 10^{-3} \text{ (min}^{-1}\text{)} = \frac{2.303}{10 \text{ min}} \log_{10} \frac{0.01 \text{ mol L}^{-1}}{x}$$

- When half of the sample is decomposed

$$t_{1/2} = \frac{0.693}{2.5 \times 10^{-3}} \text{ min} = 0.277 \times 10^3 \text{ min} = 2.77 \times 10^2 \text{ min}$$

## 14.3

- 10
- $34.0 \text{ K cal mol}^{-1}$
- $28.82 \text{ kJ}$
- Molecules do not have enough energy to be equal to threshold energy.