

# 12

## CHEMICAL KINETICS : RATES OF CHEMICAL REACTION

### 12.1. INTRODUCTION

You know that a knowledge of free energy change in a given process can tell you whether the process will occur or not. However, the free energy decrease is no indication of the speed of reaction. Reaction between hydrogen and oxygen to give water is highly probable, but it is extremely slow. 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 AgNO<sub>3</sub>, white precipitate of 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.

### 12.2. OBJECTIVES

After reading this lesson you will be able to:

- explain the rate of a chemical reaction.
  - differentiate between average rate and instantaneous rate.
  - explain the factors that affect the rate of a reaction.
  - define rate law and rate constant.
  - explain the significance of rate constant.
  - explain order of a reaction.
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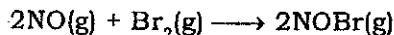
- cite examples of few zero and first order reactions.
- derive an expression for rate constant of a first order reaction.
- solve numerical problems on first order reaction.
- define half-life period for first order reaction.
- derive an expression for half-life period of first order reaction.
- solve numerical problems on half-life period of first order reactions.
- explain Arrhenius equation.
- compare the rate constants for the reaction of two different temperatures.
- explain energy of activation.
- define catalysis.
- describe characteristics of catalytic reactions.
- explain the effect of catalyst on the activation energy of a reaction.

### 12.3. RATE OF CHEMICAL REACTION

When a reaction is carried out no product is present initially and as time passes, the concentration of the product increases and the concentration of the reactant decreases. The rate (or speed) of any chemical reaction can be expressed as the rate of the change in concentration of a reactant (or product).

$$\begin{aligned} \text{rate of chemical reaction} &= \frac{\text{Change in concentration}}{\text{Time taken}} \\ &= \frac{\text{mol litre}^{-1}}{\text{Second}} \end{aligned}$$

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 in a given time interval.

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 brackets.

For example,  $[\text{NOBr}]$  represents the molar concentration of NOBr, i.e. formation of product.

Let us suppose that  $[\text{NOBr}]_i$  is the molar concentration at initial time  $t_1$  and  $[\text{NOBr}]_f$  is the molar concentration at final time  $t_2$ .

Then change in molar concentration =  $[\text{NOBr}]_f - [\text{NOBr}]_i = \Delta[\text{NOBr}]$

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

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

We can now write the rate of formation of NOBr =  $\frac{\Delta[\text{NOBr}]}{\Delta t}$

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

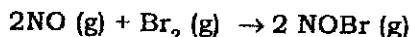
$$= \frac{-\Delta[\text{NO}]}{\Delta t}$$

and w.r.t. Br<sub>2</sub> as =  $\frac{-\Delta[\text{Br}_2]}{\Delta t}$

Negative sign means the molar concentration is decreasing with time.

Therefore, we can specify the rate of a reaction with respect to either the reactants or products. To make the rates with respect to different reactants or products equivalent, we divide the rate expression by the stoichiometric coefficient present in the balanced chemical equation.

For example, in the equation



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

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

We call the above rate expressions as average rate over the time interval  $\Delta t$ . If we make  $\Delta t$  very small (i.e. as  $\Delta t$  approaches zero) then we call the rate as instantaneous rate. For example, we express :

$$\text{average rate} = \frac{\Delta[\text{NOBr}]}{\Delta t}$$

and

$$\text{instantaneous rate} = \lim_{\Delta t \rightarrow 0} \left( \frac{\text{NOBr}}{\Delta t} \right) = \frac{d[\text{NOBr}]}{dt}$$

## 12.4. FACTORS AFFECTING RATE OF A REACTION

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

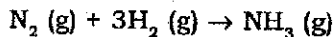
- 1. The concentration of reactants** (related to this is the pressure of gaseous reactants) : Generally, the rate of a reaction increases as the concentration of the reactants is increased.
- 2. Temperature:** Generally, a reaction is faster when the reaction temperature is increased.
- 3. Presence of catalyst:** A catalyst increases the reaction rate without being consumed by the reaction.

For examples :

- (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 12.1:** Express the average and instantaneous rate of the following reaction



- in terms of (i) rate of formation of  $\text{NH}_3$   
 (ii) rate of disappearance of  $\text{N}_2$   
 (iii) rate of disappearance of  $\text{H}_2$

Write the different expressions for the rate equivalent.

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

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

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

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

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

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

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

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 12.1

1. Which of the following units could be used to express the rate of the reaction between magnesium and hydrochloric acid ?

(a)  $\text{cm}^{-3} \text{ s}$

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(b)  $\text{cm}^3 \text{ min}^{-1}$

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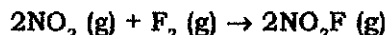
(c)  $\text{cm}^3 \text{ s}^{-1}$

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(d)  $\text{mol dm}^{-3} \text{ min}^{-1}$

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2. Nitrogen dioxide  $\text{NO}_2$ , reacts with fluorine ( $\text{F}_2$ ) to yield nitryl fluoride ( $\text{NO}_2\text{F}$ ) as



Write the rate of reaction in terms of :

- (a) rate of formation of  $\text{NO}_2\text{F}$
- 

- (b) rate of disappearance of  $\text{NO}_2$
- 

- (c) rate of disappearance of  $\text{F}_2$
- 

- (d) equivalent rate of formation of product and disappearance of reactants.
- 

3. Express the instantaneous rates of formation of product and disappearance of reactants in the above equation.
- 

4. Explain why the reaction  $\text{CO} (\text{g}) + \text{NO}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + \text{NO} (\text{g})$

- (a) occurs more rapidly at high temperature.
- 

- (b) occurs more slowly when the volume of the system is increased.
- 

## 12.5. DEPENDENCE OF REACTION RATE UPON CONCENTRATION

**Rate law :** If we follow a chemical reaction over a period of time, we find that its rate is slowly decreasing 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  $\text{A}$  and  $\text{B}$  respectively in the balanced equation.

We can express the rate as

$$\text{Rate} \propto [\text{A}]^x [\text{B}]^y \quad (\text{ii})$$

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

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

## 12.6. ORDER OF A REACTION

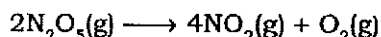
The sum of the powers to which the concentration terms are raised in the rate expression describes the order of the reaction. In equation (iii), if  $x = 1$ , we say that the reaction is first order with respect to A. If  $y = 2$ , the reaction is second order with respect to B. The overall order of the reaction is sum of  $x$  and  $y$ , i.e. In general  $n = \text{overall order of reaction} = x + y + z + \dots = 1 + 2 = 3$

A zero order reaction is where  $n = 0$

A first order reaction is one in which  $n = 1$

A second order reaction is where  $n = 2$  and so on.

*It must be remembered that order of a reaction must be determined experimentally and cannot, in general, be deduced from the co-efficient of the balanced equation.*



It is first order reaction.

### 12.6.1 Zero Order Reaction

Zero order reactions are those, in which  $n = 0$ . Here rate is independent of reactant concentration. Such reactions are uncommon. One such example is the decomposition of ammonia on a platinum or tungsten metal surface. Under high pressure of ammonia the rate at which ammonia decomposes is always the same regardless of its concentration.

### 12.6.2. First Order Reaction

We will now discuss how to determine the rate constant for a first order reaction. We would arrive at an expression for the rate constant, and then we can calculate the reaction rate at any desired concentration. For the first order reaction, this equation would tell us how 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 :



For first order reaction,

$$\text{rate (in differential form)} = \frac{-d[A]}{dt} = k_1[A]$$

where  $k_1$  is the rate constant.

Rearranging the rate expression, we have :

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

Integrating the two sides we get :

$$-\ln [A] = kt + \text{constant}$$

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  $-\ln[A] = -\ln [A]_0$ , when  $t = 0$

The value of the constant is given by the equation

$$-\ln [A]_0 = 0 + \text{constant}$$

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

Putting the value of the constant in equation

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

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

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

$$[A] = [A]_0 e^{-k_1 t}$$

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

We can convert to log base 10

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

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 Figure 12.1.

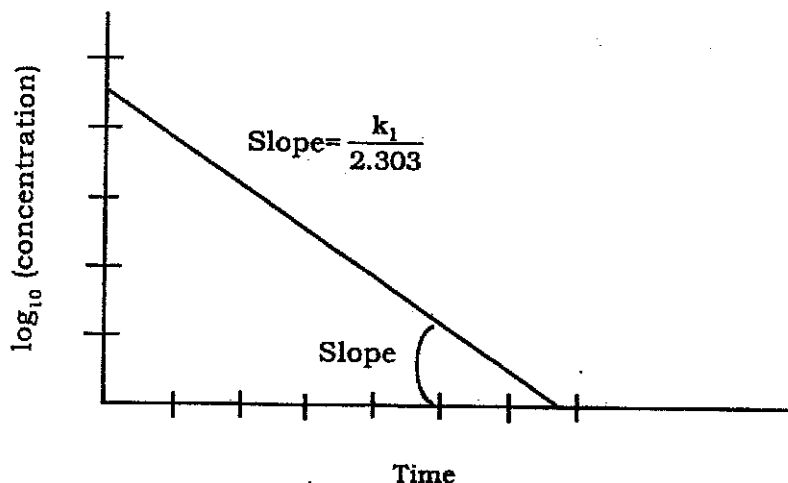


Fig. 12.1 A graph of  $\log_{10}$  (concentration) against time for a first-order reaction.

### 12.6.3 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 of a reaction. It is denoted by  $t_{1/2}$  or  $t_{0.5}$ . Let us now see how the half-life 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  $t = t_{1/2}$  (half life period)

Therefore, we have

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

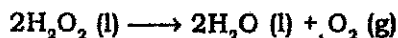
$$\text{or } \ln \left\{ \frac{[A]_0}{2} \right\} - \ln [A]_0 = -k_1 t_{1/2}$$

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

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

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

**Example 12.2 :** 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?

**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

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

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

Taking antilog

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

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

**Example 12.3 :** In example 12.2 if we start with initial concentration of 0.50M, how long will it take for this concentration to drop to 0.10M.

**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 0.1M.

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 12.4 :** In example 12.2, how long will it take for the sample to decompose to 50%.

**Solution:** When half the sample has decomposed, then 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 12.2

- The rate of 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 :
  - zero order  
.....
  - first order  
.....
- For the following reaction  

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

$$\text{rate} = k [\text{C}_2\text{H}_4(\text{g})] [\text{I}_2(\text{g})]^{3/2}$$
  - What is the order of reaction with respect to each reactant ?  
.....
  - What is the overall order of reaction ?  
.....
  - What is the unit of  $k$ , if concentrations are measured in  $\text{mol dm}^{-3}$   $\text{sec}^{-1}$  ?  
.....
- 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  
.....

## 12.7 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  $10^\circ$  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 two molecules for reaction during the collision. We call it 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. How can we do that? You know that increase in temperature increases the energy of the molecules. Thus if we increase the temperature, we increase the rate of reaction. Let us see if we can express it quantitatively.

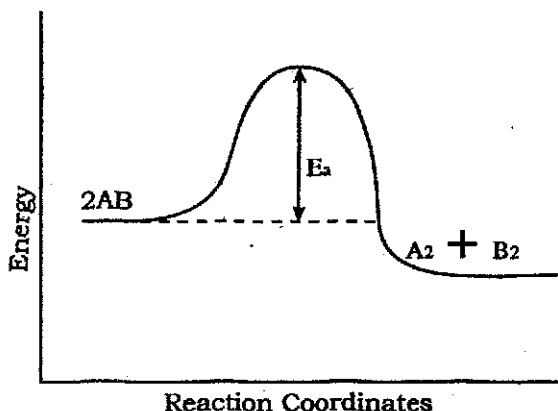


Fig 12.2 Energy diagram for a reaction

The change in energy that takes place during the course of a reaction is shown in figure 12.2. The horizontal axis is called the reaction coordinate (or path of a reaction) and position along this axis show the extent to which the reaction has progressed towards completion. On the left of this energy diagram we find two molecules of AB. As they approach each other, the energy increase to a maximum. As we continue toward the right along the reaction coordinate, the energy of the system decreases as the products A<sub>2</sub> and B<sub>2</sub>, move apart. When A<sub>2</sub> and B<sub>2</sub> molecules are finally separated from one another, the total energy drops to essentially a constant value. The *activation energy* for the decomposition of AB corresponds to the difference between the energy of the reactants and the maximum on the energy curve. Slow moving molecules of AB don't possess sufficient energy to overcome this energy barrier, while fast-moving ones do.

You know that rate of reaction =  $k$  [concentration]. If we have value of concentration as one, then rate of reaction is equal to the rate constant,  $k$ . The rate constant  $k$  depends on the magnitude of the activation energy, say  $E_a$ , and also on the absolute temperature.  $k$  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 follow

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

Where  $A$  is a proportionality constant and is also known as frequency factors,  $R$  is the gas constant. How can we utilise this relationship between  $k$ ,  $E_a$  and  $T$ ? We can calculate activation energy, if we measure rate constant at at least two different temperatures.

Taking the 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 :

$$\begin{aligned} \ln k &= \frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A \\ y &= m x + c \end{aligned}$$

Thus plot of  $\ln k$  vs  $1/T$  (in fig. 12.3) gives a straight line whose slope is equal to  $E_a/R$  and whose intercept is  $\ln A$ .

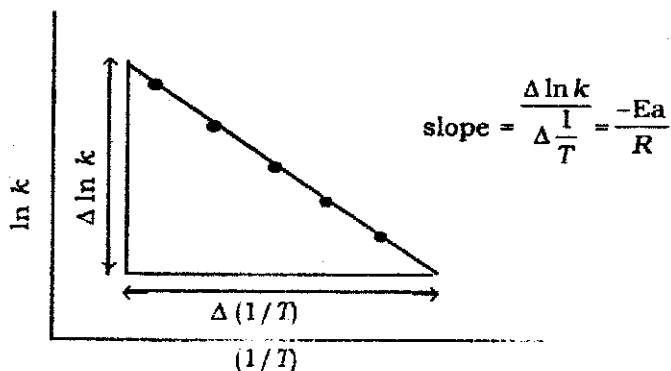


Fig. 12.3 Graphical determination.

We can also obtain  $E_a$  from  $k$  at the 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

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

$$\text{or } \frac{k_1}{k_2} = e^{-\frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

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 12.5 :** What must be the value of  $E_a$  if the rate constant for a reaction is the double when the temperature increases from 27°C to 37°C ?

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

$$T_2 = 273 + 37 = 310 \text{ K}$$

$$T_1 = 273 + 27 = 300 \text{ K}$$

$$E_a = ?$$

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

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

## 12.8 CATALYSIS

You know that when hydrogen gas and oxygen gas are in contact, no observable reaction occurs, but if we add a small amount of platinum gauge in the mixture of these gases, the reaction occurs spontaneously. Here platinum gauge speeds up the reaction and is called a catalyst. We define a catalyst as,

**A substance which changes the rate of a reaction without itself undergoing any permanent chemical change and also without being consumed.**

The phenomenon of the reaction rate being changed by catalyst is called catalysis. In certain cases, a catalyst slows down a reaction. For example, if a little alcohol is added to sodium sulphide solution, its oxidation to sodium sulphate is greatly reduced. We call this type of catalyst a negative catalyst.

### 12.8.1 Characteristics of Catalytic Reactions

We will now describe some common characteristics of catalytic reactions.

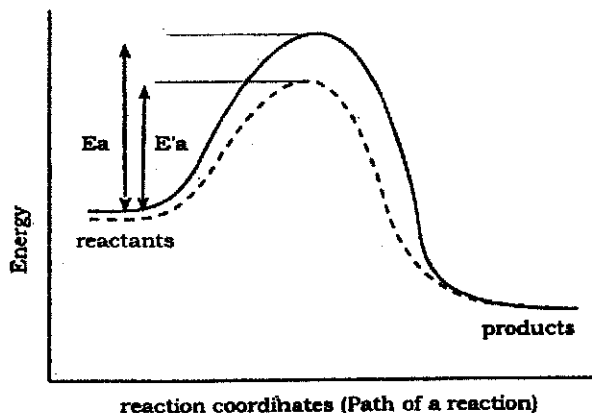
1. The catalyst is unchanged chemically at the end of reaction .
2. A small amount of catalyst is often sufficient to catalyse the reaction.
3. The catalyst does not affect the position of the equilibrium in reversible reaction.
4. A catalyst is not consumed during a chemical reaction.
5. A catalyst is specific in its action.
6. A catalyst cannot initiate a reaction, it only changes the speed of the reaction.

### 12.8.2 Catalysis and Activation Energy

We have seen that a catalyst increases the rate of a reaction. We explain it by considering the fig 12.4.

In this figure  $E_a$  is the activation energy of uncatalysed reaction and  $E'_a$  is the activation energy of the catalysed reaction. A catalyst lowers the activation energy as you can see in the figure ( $E'_a < E_a$ ). The reduction in activation energy is achieved by providing an alternative pathway of lower energy for the reaction.

You can also see in this figure that the relative energies of reactants and products are not changed. The enthalpy changes are the same for the catalysed and uncatalysed reactions.



Reaction coordinates (Path of a Reaction)

Fig. 12.4 Graphical representation of the effect of catalyst on a reaction.

$E_a$  is the activation energy of the catalysed reaction. A catalyst lowers the activation energy as you can see in the figure ( $E_a < E_a$ ). The reduction in activation energy is achieved by providing an alternative pathway of lower energy for the reaction.

You can also see in this figure that the relative energies of reactants and products are not changed. The enthalpy change are the same for the catalysed and uncatalysed reactions.

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### INTEXT QUESTIONS 12.3

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- As a rough rule of thumb, the rates of many reactions double for every ..... °C. rise in temperature.
  - The rate constant of a reaction at 15°C is  $1.3 \times 10^{-5}$  litre/mol. sec. While at 50°C its rate constant is  $8.0 \times 10^{-3}$  lit./mol. sec. What is the  $E$  for the reaction.  
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  - How does a catalyst alter the activation energy of a reaction ?  
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  - Name two characteristics of a catalytic reaction.  
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- 

### 12.9 WHAT YOU HAVE LEARNT

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

- 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.
- A catalyst is a substance which changes the rate of a reaction without itself undergoing any permanent chemical change and also without being consumed.
- The phenomenon of the reaction rate being changed by a catalyst is called catalysis.
- Some of the characteristics of a catalytic reaction are a catalyst is unchanged chemically at the end of the reaction, a small amount of the catalyst is often sufficient to catalyse the reaction, a catalyst is not consumed during a chemical reaction etc.

## 12.10 TERMINAL EXERCISE

1. Sketch an energy vs path of reaction diagram for a reaction. Indicate the activation energy for both forward ( $E_a$ ) and reverse reactants ( $E'_a$ ).  
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2. For the reaction  $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$  it is found that  $N_2O_5$  is decomposing at the rate of 0.02 mol/litre sec. Calculate to rate of reaction defined as  $\frac{\Delta [NO_2]}{\Delta t}$  with  $\Delta t$  in seconds.  
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3. The rate constant for a certain first order decomposition reaction is 0.23  $\text{sec}^{-1}$  at  $400^\circ\text{C}$ . Calculate the half-life for this reaction.  
-----
4. The rate constant for a certain first order reaction is  $1.00 \times 10^{-3} \text{sec}^{-1}$  at  $25^\circ\text{C}$ . The rate constant for the reaction is  $1.47 \times 10^{-2} \text{sec}^{-1}$  at  $50^\circ\text{C}$ . Calculate the activation energy for this reaction.  
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5. 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 mol./litre minute.  
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6. List the three factors that affect the rate of a chemical reaction.  
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7. For a certain first order reaction the concentration of the reactant decreases from 2.00 mol/litre to 1.50 mol./litre in 64 minutes. Calculate the rate constant for this reaction.

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8. The rate constant for a certain first order reaction is  $1.0 \times 10^{-3} \text{ min}^{-1}$  at 25° C. If the activation energy is 10.0 k cal, calculate the rate constant at 50° C.

-----

9. Explain why a catalyst cannot be used to make a non-spontaneous reaction occur.

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**CHECK YOUR ANSWERS****INTEXT QUESTIONS 12.1**

1. D

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

(iii)  $\frac{-\Delta[\text{F}_2]}{\Delta t}$  (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.  $\frac{1}{2} \frac{d[\text{NO}_2\text{F}]}{dt} = \frac{-1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{-1}{2} \frac{d[\text{F}_2]}{dt}$

4. (i) Increase in temperature increases the rate of reaction.

(ii) Increase in volume would decrease the pressure or would decrease the concentration which would decrease the rate of reaction.

**INTEXT QUESTIONS 12.2**1. (a)  $1.0 \times 10^{-3} \text{ mol litre}^{-1} \text{ sec}^{-1}$ (b)  $5.0 \times 10^{-2} \text{ sec}^{-1}$ 2. (a) First order with respect to  $\text{C}_2\text{H}_4$  and 1.5 with respect to  $\text{I}_2$ .

(b) The over all order of reaction is 2.5

(c)  $k = \frac{\text{sec}^{-1}}{(\text{mol dm}^{-3})^{3/2}}$

$$= \text{mol}^{-3/2} \text{ dm}^{9/2} \text{ sec}^{-1}$$

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

(b) When half of the sample is decomposed

$$t_{1/2} = \frac{0.693}{2.5 \times 10^{-3}} \text{ min} = 0.2772 \times 10^3 \text{ min} = 2.77 \times 10^2 \text{ min}$$

**INTEXT QUESTIONS 12.3**

1. 10

2.  $34.0 \text{ K cal mol}^{-1}$ 

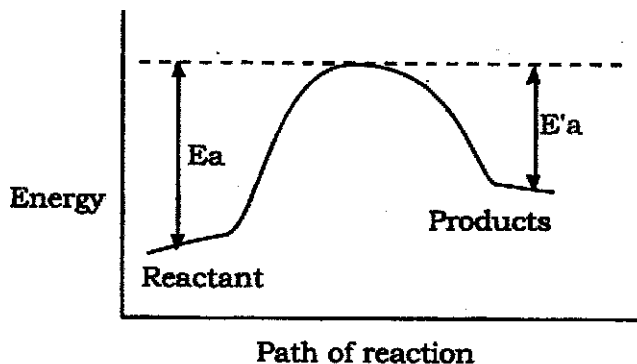
3. It provides a different low energy path.

4. (i) The catalyst is not consumed in the reaction

(ii) A small amount of catalyst is needed for the reaction.

### TERMINAL EXERCISE

1.



2.  $0.04 \text{ mol litre}^{-1} \text{ sec}^{-1}$

3.  $t_{\frac{1}{2}} = \frac{0.693}{0.23 \text{ sec}^{-1}} = 3 \text{ sec}$

4.  $\log \frac{1.4 \times 10^{-2}}{1 \times 10^{-3}} = \frac{E_a}{2.303 \times 1.99} \frac{(323 - 298)}{(323 \times 298)}$

$$\log 1.4 \times 10 = 5.7 \times 10^{-5} (E_a)$$

$$E_a = \frac{1.15}{5.7 \times 10^{-5}} = 2 \times 10^4 \text{ cal.}$$

5.  $1.8 \times 10^{-2} \text{ mol litre}^{-1} \text{ min}^{-1}$

6. (i) Concentration of the reactants

(ii) Temperature

(iii) Catalyst

7.  $\log \frac{2.0}{1.5} = \frac{k (64.0 \text{ min})}{2.303}$

$$k = 4.49 \times 10^{-3} \text{ min}^{-1}$$

8.  $k_1 = 3.7 \times 10^{-3} \text{ min}^{-1}$

9. A catalyst changes the value of  $\Delta G$ .