CHAPTER 8

INTRODUCTION TO CHEMICAL KINETICS

INTRODUCTION

The word Kinetic is derived from a Greek word "kinetic" which means "moving". Hence chemical kinetics is that branch of chemistry which deals with the study of:

(i) Rates of chemical reactions
(ii) Factors affecting rate
(iii) The mechanism through which the reaction proceeds
(iv) Optimum conditions for the maximum yield of a product

8.1 RATE AND VELOCITY OF REACTION

During the course of a chemical reaction, the molar concentration of reactants gradually decreases, whereas that of products increases. Consider a general chemical reaction: $A \longrightarrow B$

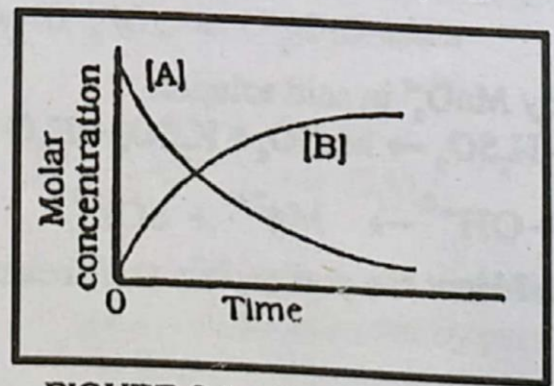


FIGURE:8.1 Reaction profile

Rate of reaction:– It is defined as the quantity of a reactant consumed or the quantity of a product formed per unit time i.e.

$$\text{Rate} = \frac{\text{Increase in concentration of products or decrease in concentration reactants}}{\text{Time taken for change}}$$

The graph clearly shows that the rate of reaction is not uniform and it changes with time. Initially the rate of disappearance of reactant [A] is fast and it tappers out gradually. Similarly the initial rate of formation of product [B] is fast but falls of latter on. Hence the overall rate of reaction as defined above is actually the Average Rate of Reaction.

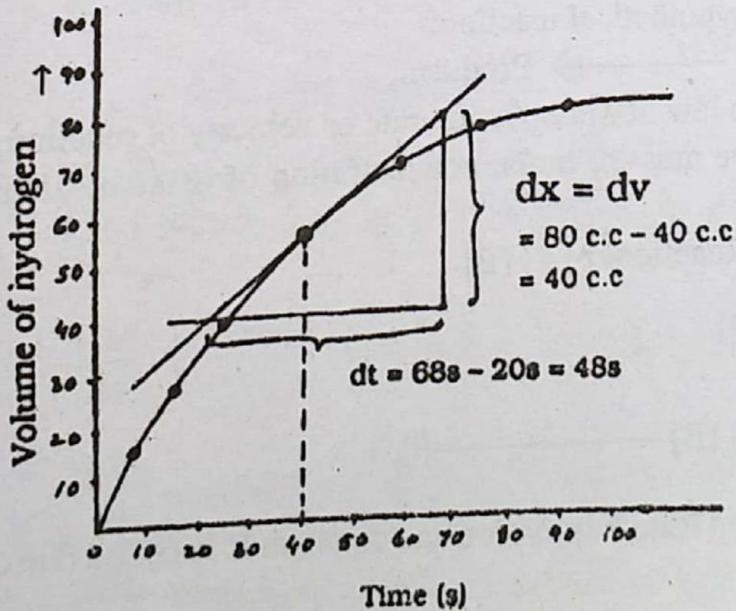
Velocity of reaction:– It is defined as the rate of a reaction at a particular given moment i.e. at a specific time. If we consider a very small interval of time "dt" in which the change in concentration (dx) is taken to be nearly constant then velocity of reaction is given by the expression:

$$\text{Velocity of reaction} = \frac{dx}{dt}$$

Velocity of reaction may also be termed as Instantaneous Rate of Reaction.

Instantaneous rate is the slope of the tangent to the curve at that time. Consider the reaction between Mg and HCl:

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$



Graph of rate of reaction

FIGURE.8.2

Reaction is followed by measuring the volume of H_2 gas evolved at regular interval of time. The results are plotted and a rate curve is obtained (Fig: 8.2).

To calculate velocity of reaction, say at 40s, the tangent to the curve at 40s is shown in the graph.

Now velocity of reaction at 40s=slope of tangent

$$= \frac{dx}{dt} = \frac{dv}{dt} = \frac{40c.c}{48s} = 0.83c.c/s$$

Thus rate of production of H_2 at 40s is $0.83\,cm^3/s$

For the purpose of simplicity in future discussion, we will not differentiate between rate and velocity of reaction and will be frequently using the symbol $\frac{dx}{dt}$ for rate as well.

Unit of rate of reaction:– The concentration is usually expressed in moles/dm^3 and time in seconds, hence

$$\text{Rate of reaction} = \frac{\text{Change in concentration}}{\text{Time taken for change}}$$

$$= \frac{mole/dm^3}{s} = \frac{mole}{dm^3} \times \frac{1}{s} = mole\left(dm^3\right)^{-1} s^{-1}$$

8.2 RATE CONSTANT AND RATE EXPRESSION

Consider a hypothetical reaction:

$$A+B \longrightarrow \text{Products}$$

According to law of Mass Action rate or velocity of reaction is directly proportional to active mass or molar concentration of reactants, hence for the above reaction or

Velocity of Reaction α [A] [B]

$$\frac{dx}{dt} \alpha [A][B]$$

$$\frac{dx}{dt} = K[A][B] \text{———————} (i)$$

Expression (i) is called Rate Expression and constant K is called rate or velocity constant.

When the concentration of each reactant is unity i.e. 1 mole/dm^3 then K is called specific rate constant i.e. substituting the values in expression (i).

$$\frac{dx}{dt}=K[1]\,[1]$$

$$\therefore \quad \frac{dx}{dt}=K$$

Hence specific rate constant at a given temperature, may be defined as the rate of reaction when the molar concentration of each reactant is unity.

Example 1:– Writing rate expression

Problem: Write rate expression for the following reactions:

(a) $PCl_5 \longrightarrow PCl_3 + Cl_2$

(b) $2NO + O_2 \longrightarrow 2NO_2$

(c) $H_2SeO_3 + 6I^- + 4H^+ \longrightarrow Se + 3I_2 + 3H_2O$

Solution:

(a) Rate of reaction $\alpha \left[PCl_5\right]$

$$\frac{dx}{dt} = K\left[PCl_5\right]$$

(b) Rate of reaction $\alpha \left[NO\right]^2\left[O_2\right]$

$$\frac{dx}{dt} = K[NO]^2[O_2]$$

(c) Rate of reaction $\alpha \left[H_2SeO_3\right]\left[I^{\ominus}\right]^6\left[H^{\oplus}\right]^4$

$$\frac{dx}{dt} = K\left[H_2SeO_3\right]\left[I^{\ominus}\right]^6\left[H^{\oplus}\right]^4$$

Example 2:– Significance of plus and minus sign.

Problem: For a chemical reaction $A \longrightarrow B$, the rate of reaction is denoted by:

$\frac{-dA}{dt}$ or $\frac{+dB}{dt}$. State the significance of plus and minus signs.

Solution: $\frac{-dA}{dt}$ represents the rate of reaction in terms of decrease in concentration of reactant A.

$\frac{+dB}{dt}$ represents the rate of reaction in terms of increase in concentration of product B.

Example3:– Calculating rate of disappearance

Problem: For a chemical reaction $C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$, the rate of appearance of C_2H_6 is 0.25 mole/dm^3.s. What is the rate of disappearance of C_2H_2 and H_2?

Solution:

Rate of disappearance of $C_2H_2 = 0.25 \text{mole/dm}^3.\text{s}$

Rate of disappearance of $H_2 = 0.25 \times 2 = 0.5 \text{ mole / dm}^3.\text{s}$

Example 4:– Calculating rate constant

Problem: For a chemical reaction $A + B \longrightarrow AB$. Calculate:

(a) Rate constant wher initial concentration of both the reactants is 0.1 moles/dm^3 each and rate of reaction is 3.02×10^{-4}moles/dm^3

(b) Rate constant if initial concentration of A or B is doubled.

Solution:

(a) For this reaction

Rate of reaction α [A] [B]

$$\frac{dx}{dt} = K [A] [B]$$

$$3.02 \times 10^{-4} \text{moles/dm}^3.\text{s} = K(0.1 \text{ mole/dm}^3)(0.1 \text{ mole/dm}^3)$$

$$\therefore K = \frac{3.02 \times 10^{-4} \text{ mole / dm}^3.\text{s}}{(0.1 \text{ mole / dm}^3)(0.1 \text{ mole / dm}^3)}$$

$$K = \frac{3.02 \times 10^{-4} \text{dm}^3}{0.01 \text{ mole.s}}$$

$$K = 3.02 \times 10^{-2} \text{dm}^3 / \text{mole.s}$$

(b) Let concentration of B is doubled

As [A] =0.1 mole/dm^3

$\therefore$ [B]=0.1×2=0.2 mole/dm^3

Since concentration of [B] is doubled, the rate of reaction will also become double i.e.

$$\text{Rate} = 3.02 \times 10^{-4} \times 2 = 6.04 \times 10^{-4} \text{ mole/dm}^3.\text{s}$$

Now

$$\text{Rate} = K\,[A]\,[B]$$

$$6.04\times10^{-4}\,\text{mole}/\text{dm}^3.\text{s} = K(0.1\,\text{mole}/\text{dm}^3)(0.2\,\text{mole}/\text{dm}^3)$$

$$\therefore \quad K = \frac{6.04\times10^{-4}\,\text{mole}/\text{dm}^3\text{s}}{(0.1\,\text{mole}/\text{dm}^3)(0.2\,\text{mole}/\text{dm}^3)}$$

$$K = 3.02\times10^{-2}\,\text{dm}^3/\text{mole.s}$$

Characteristics of K:

(i) It has a fixed value at a particular temperature.

(ii) Its value varies with temperature.

(iii) Its value at a temperature remains unchanged when the concentration of either or of all reactants is changed.

8.3 TYPES OF REACTIONS BASED ON REACTION VELOCITY

If we happen to observe many chemical reactions that are part of our daily life, we note that different reactions take different amount of time for completion. For example combustion of gasoline is very fast, cooking of food takes moderate time, but rusting of iron is a very very slow process. Hence we may classify the reactions with respect to their rates as follows:

(i) Reactions proceeding at a very slow speed:– These are the reactions which proceed at extremely slow speed and take very long time for completion. It is difficult to determine experimentally velocity of such reactions. Examples are: rusting of iron, radioactive decay of elements and formation of diamond from carbon in earth crust.

(ii) Reactions proceeding at a very fast speed:– These reactions are instantaneous reactions i.e. they are so fast that they are completed in very small time of the order of 10^{-6}s. All ionic reactions are of this type. It is impossible to determine rates of such reactions.

Examples:

$$\text{(a)}\quad \underset{\text{(Acid)}}{\overset{+}{H}\overset{-}{Cl}} + \underset{\text{(Base)}}{\overset{+}{Na}\overset{-}{OH}} \longrightarrow \overset{+}{Na}\overset{-}{Cl} + H_2O$$

$$\text{(b)}\quad \overset{+}{Ag}\overset{-}{NO}_{3(aq)} + \overset{+}{Na}\overset{-}{Cl}_{(aq)} \longrightarrow AgCl + \overset{+}{Na}\overset{-}{NO}_{3(aq)}$$

(iii) Reactions proceeding at moderate speed:– These are the reactions which proceed at experimentally measurable rate i.e. they have limited speed and are completed at the most in few hours. Generally reactions of organic and covalent compounds are of such type.

Examples are:

(a) $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Sucrose Glucose Fructose

(b) $CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$

Acetic acid Ethyl alcohol Ester

Why some reactions are fast and others slow ?

Concept of activation energy:– A reaction takes place when molecules of reacting substances collide together. But all the collisions are not effective i.e. do not lead to the formation of product. It has been found that only those collisions are effective in which the colliding molecules possess a minimum amount of energy called Threshold energy.

Before collision the molecules of reactants in their normal state do possess their respective internal energy, but their average internal energy is less than threshold energy. Now the molecules must acquire the difference of energy, in order that their collisions be effective. The excess energy that the reactant molecules, having average energy less than the threshold energy, must acquire in order to react and change into products is called Activation Energy.

Thus:

Activation Energy=Threshold Energy–Average Internal Energy of molecules

A relation between these energies is shown in the graph (Fig:8.3)

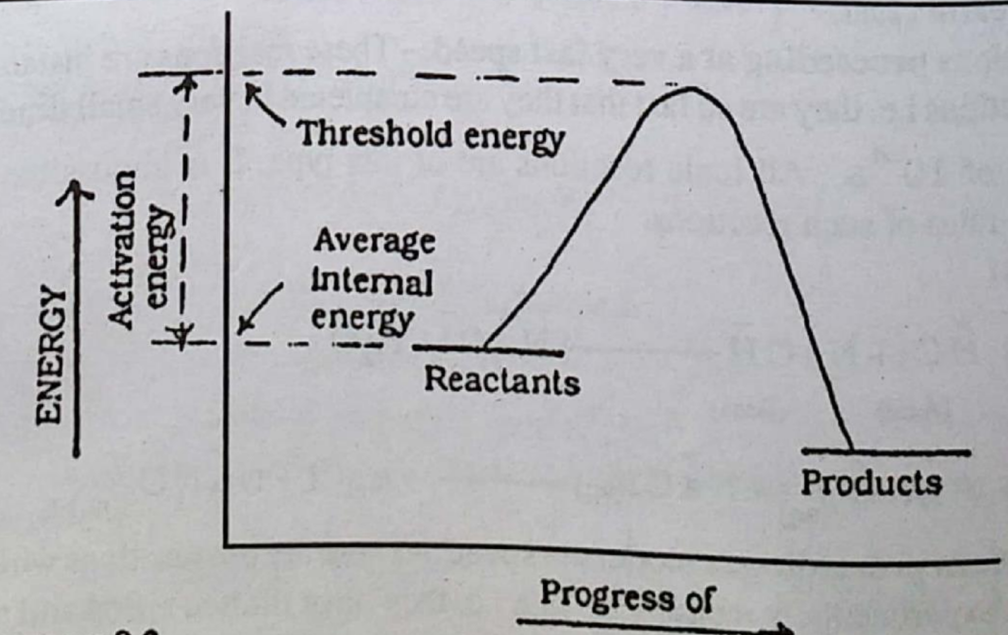


FIGURE.8.3

The speed of a reaction depends upon the activation energy of molecules. The reactions which have low values of activation energy are fast reactions and those which proceed slowly or moderately have comparatively high value of energy of activation.

Fast reactions can be slowed down and the slow reactions can be spedup by controlling the activation energy.

Example 5:– Calculating activation energy

Problem: For a chemical reaction $A \longrightarrow B$, the threshold energy of reaction is 31 K.J/mole. The average internal energy of A is 12 K.J/mole. Calculate activation energy of A.

Solution: Activation Energy=Threshold energy–Average internal energy

= 31 K.J/mole–12 K.J/mole

Activation Energy of A=19 K.J/mole.

8.4 DETERMINATION OF RATE OF REACTION

Two methods are employed for the determination of rate of a chemical reaction.

These are: (a) Physical methods (b) Chemical methods

(a) Physical methods:– In these methods the reaction is followed by measuring change in some physical property of reactants or products. Following are the methods generally employed:

	Name of physical methods	Observed physical property
(i)	Refractometric method	Change in refractive index.
(ii)	Spectroscopic method	Absorption of ultraviolet or infrared radiations.
(iii)	Calorimetric method	Change in colour intensity
(iv)	Conductivity method	Change in electrical conductivity
(v)	pH Method	Change in pH is observed
(vi)	Polarimetric method	Change in optical rotation of plane polarized light

(b) Chemical methods:– When physical methods are not available or suitable then a proper chemical method is used.

In a chemical method generally samples are drawn from the reacting vessel at regular intervals of time. Reaction is stopped at that particular moment by suddenly chilling the sample adding it to a suitable chemical. The amount of a reactant or product present at that time is generally found by titrating the sample against a proper reagent.

An example is the hydrolysis of methyl acetate (CH_3COOCH_3)in acidic medium.

$$CH_3COOCH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3COOH + CH_3OH$$

Reaction is followed by measuring the amount of acetic acid (CH_3COOH) formed at regular interval by titrating the chilled samples against standard alkali (NaOH). With the passage of time more and more acetic acid is formed till reaction goes to completion.

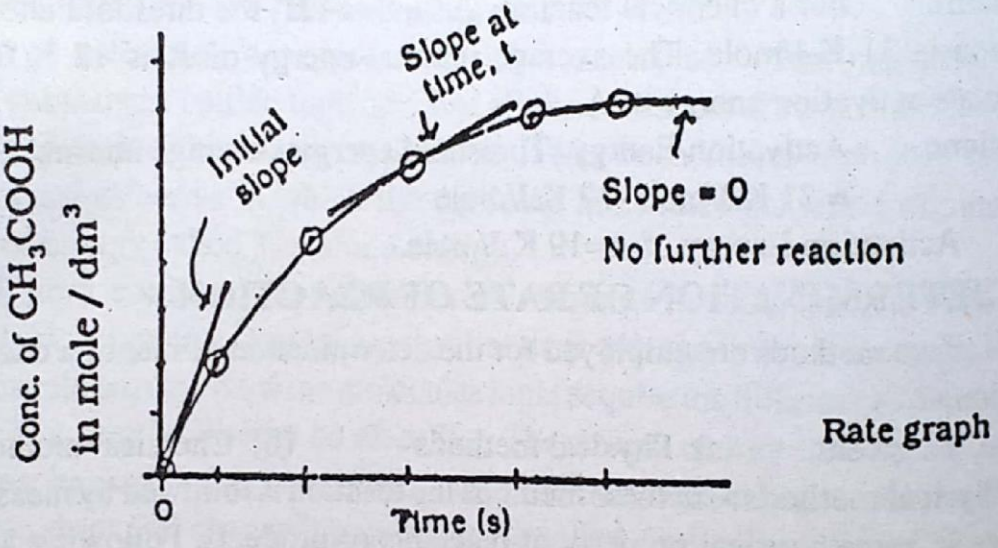


FIGURE.8.4

The results are plotted as a graph and rate curve is obtained.

The slope of rate curve at different times gives the rate of reaction $\left(\frac{dx}{dt}\right)$ at that moment; as discussed in section 8.1.

8.5 FACTORS AFFECTING RATE OF REACTION

The rate of a reaction involving collisions of molecules is influenced by many factors, enlisted below:

(i) Concentration of reactants
(ii) Nature of reactants
(iii) Temperature
(iv) Presence of catalyst
(v) Surface area of reactants (heterogeneous reactions)
(vi) Radiation

(i) Concentration of reactants:– Concentration is defined as number of moles or molecules of a substance per unit volume.

Rate of reaction varies with the concentration of reactants. According to law of mass action, the rate of a reaction is directly proportional to the concentration of reactants. The greater the concentration the greater the rate of reaction. This is because with the increase in concentration, the number of molecules of reactants also increases. There is now more crowding of molecules so frequency of collisions between them increases, resulting in the increase in rate of formation of products.

Consider a general reaction

$$xA + yB \longrightarrow C$$

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

$$\frac{dx}{dt} = K[A]^x [B]^y$$

In this rate expression the sum of exponents of concentration i.e. (x+y) is called Order of Reaction.

Order of chemical reaction: The relation between the rate and the concentration of the reactants taking part in the reaction can be described by the following reaction:

$$A + B \rightarrow \text{Product}$$

rate of reaction i.e. $\frac{dx}{dt} \alpha \ [A][B]$

or $\frac{dx}{dt} = K[A][B] ----(1)$

Similarly for the reaction

$$A + 2B \rightarrow \text{Product}$$

$$\frac{dx}{dt} = K[A][B]^2 ---- (2)$$

The equation of this type which describes the relationship between the concentrations of the reacting substances involved in the reaction and the rate, is called "rate expression". It is the rate expression which leads to the concept of order of reaction.

The order of reaction is defined as sum of all the exponents of the concentration in terms of the reactants involved in the rate equation.

Thus in rate equation (2)

Order of reaction (n)=1+2=3 (Third order reaction).

Consider the following examples:

(i) $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_{2(g)}$

$\frac{dx}{dt} = K[N_2O_5]$ The reaction is of the first order.

(ii) $2CH_3CHO \rightarrow 2CH_4 + 2CO$

$\frac{dx}{dt} = K[CH_3CHO]^2$ The reaction is of second order.

(iii) $2NO + O_2 \rightarrow 2NO_2$

$\frac{dx}{dt} = K\ [NO]^2\ [O_2]$ The reaction is of third order.

The order of reaction is assigned to a reaction only on the basis of experimental measurement and not by seeing the total nmber of molecules present in the reaction because there are reactions which contain more reacting molecules but the concentrations of only one or two molecules may alter during the reactions. For a reaction, minimum order of reaction may be of zero order and maximum upto third order.

Example 6:– Predicting effect of concentration on rate

Problem: The rate of a chemical reaction for the reaction:

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

was found experimentally to be represented by the expression

$$\text{Rate} = K[NO]^2[O_2]$$

What will be the effect on rate if

(a) Concentration of NO is doubled

(b) Concentration of NO is halved

(c) Concentration of O_2 is doubled

Solution: (a) As Rate $\alpha[NO]^2$, hence if concentration of NO is doubled, the rate will increase by $[2]^2 = 4$ times.

(b) If concentration of NO is halved the rate will be decreased by $\left[\frac{1}{2}\right]^2 = \frac{1}{4}$ times.

(c) As Rate $\alpha[O_2]$ hence if concentration of O_2 is doubled the rate will also be doubled.

Example 7:– Predicting effect of concentration on rate constant

Problem: For a chemical reaction at 450°C

$$2NH_3 \longrightarrow N_2 + 3H_2$$

$$Rate = K[NH_3]^2$$

What will be the effect on rate constant if concentration of NH_3 is increased four times ?

Solution: Now $K = \frac{Rate}{[NH_3]^2}$

The value of K will remain constant for either increasing or decreasing rate with reference to the ammonia concentration. K remains constant because as concentration of NH_3 is increased four times, the rate also increases by that factor.

(ii) Nature of reactants:– The nature of the reactants also affects the rate because activation energy for effective collision is different for different reacting substances.

Consider the following two reactions in which the collision probabilities are same, even then their rates are not equal.

$$2NO + O_2 \longrightarrow 2NO_2 \text{ Fast}$$

$$2CO + O_2 \longrightarrow 2CO_2 \text{ Slow}$$

Reaction between NO and O_2 is fast while that for CO and O_2 is slow. This is because activation energy for CO is higher than that of NO; as shown in Fig.8.5.

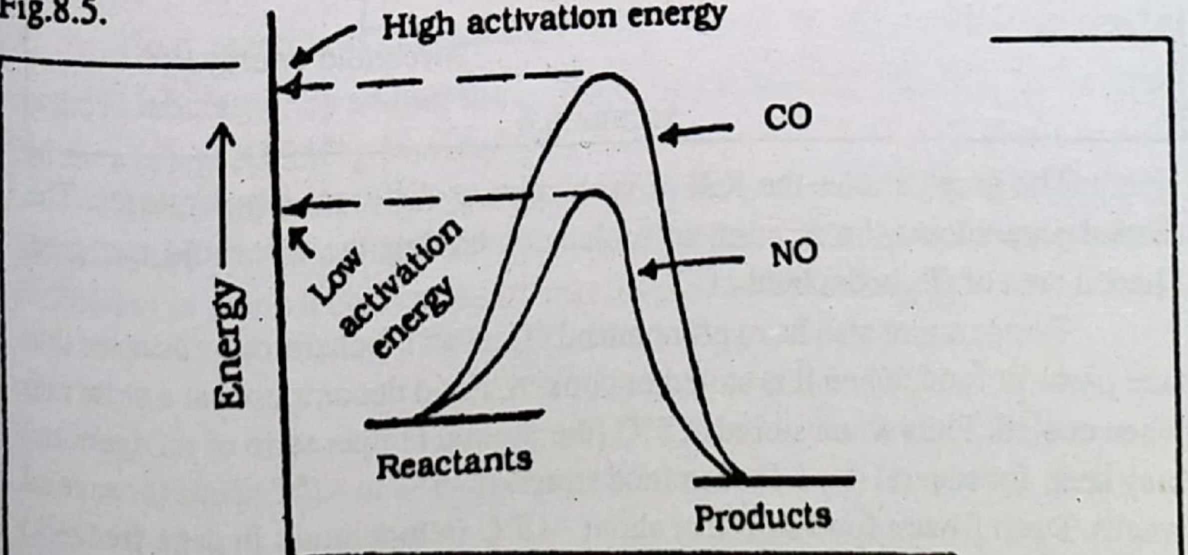


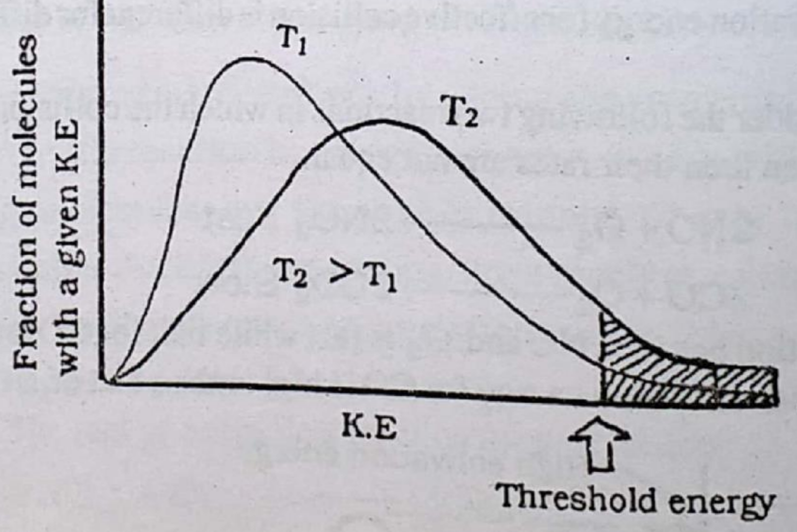
FIGURE.8.5

(iii) Temperature:– The rates of reaction are greatly influenced by the temperature at which the reaction is carried out. For example H_2 and O_2 do not combine at ordinary temperature, but combine very rapidly at high temperature.

As a general rate of thumb, the rate of reaction doubles for every 10°K rise in temperature. The reasons are:

(i) As temperature increases the velocity of molecules also increases, this results in the increase of frequency of collisions.

(ii) The rise in temperature raises the kinetic energy of each molecule. It has been found by raising the temperature by 10°C, the fraction of molecules possessing Threshold or activation energy becomes double, as a result number of effective collisions is also doubled, hence rate is doubled.



Effect of temperature on kinetic energy

FIGURE.8.6

The graph shows the K.E of molecules at different temperatures. The shaded area shows the fraction of molecules having the threshold energies. Shaded area of T_2 is doubled of T_1.

Temperature also has a pronounced effect on biochemical processes that take place in food, when it is stored or cooked. Food decomposes at a slow rate when cooled. Thus when stored at 5°C (the normal temperature of refrigerator) may keep for several days. Frozen food stored at –5°C to –2°C keeps for several weeks. Deep frozen food stored at about –18°C (temperature in deep freezers) keeps for several months.

(iv) Presence of catalyst:– A catalyst is a substance which alters the rate of a chemical reaction without itself being consumed in the process. Basically they may be classified as:

(i) **Positive catalysts:–** They increase the rate of a chemical reaction.

For example: MnO_2 is a positive catalyst for decomposition of H_2O_2

$$2H_2O_{2(aq)} \xrightarrow{Mn\,O_2} 2H_2O_{(l)} + O_{2(g)}$$

Positive catalysts function by providing an alternate path to the reaction. The activation energy of this alternative route is lower as a result more reactants molecules possess the energy required for a successful collision. The total number of effective collisions per unit time increases and thus the rate of reaction increases.

(ii) Negative catalysts:– They decrease the rate of a chemical reaction. They are also called Inhibitors. For example glycerine is an inhibitor for the above decomposition of H_2O_2.

Negative catalysts on the other hand do not lower the activation energy rather they combine with reactant molecules, thus decreasing the number of colliding reactant molecules. This decreases the effective collisions, hence rate.

Some times one of the products of reaction acts as catalyst, such a process is called Auto catalysts. Initial rate of such reactions is slow but later on increases as the product concerned is formed. Example is Redox titration between $KMnO_4$ and oxalic acid.

$$2KMnO_{4(aq)} + 5H_2C_2O_{4(aq)} + 3H_2SO_{4(aq)} \longrightarrow 2MnSO_{4(aq)} + 10CO_{2(g)} + 8H_2O_{(l)} + K_2SO_4$$

Here reaction is catalysed by Mn^{+2} ion of $MnSO_4$. This fact can be tested in laboratory by adding some Mn^{+2} ions in form of $MnSO_4$ in the flask before adding $KMnO_4$ from burette.

There are certain catalysts known as Biocatalysts. These are enzymes. Enzymes are proteins which catalyse the chemical reactions in living systems. Following is given a chart of some reactions and their catalysts:

CHART

Reaction	Catalyst	Nature of catalysts
1. Synthesis of Ammonia by Haber's process $N_2 + 3H_2 \rightleftharpoons 2NH_3$	Reduced iron powder and small amount of Al_2O_3 or K_2O as .promoter	Positive
2. Conversion of SO_2 to SO_3 $2SO_2 + O_2 \rightleftharpoons 2SO_3$	V_2O_5 or Pt in finely divided form	Positive
3. Decomposition of laughing gas N_2O $2N_2O \overset{1000^\circ K}{\rightleftharpoons} 2N_2 + O_2$	Traces of Cl_2	Positive
4. Decomposition of H_2O_2 $2H_2O_2 \longrightarrow 2H_2 + O_2$	(i) Glycerine (ii) MnO_2	Negative Positive
5. Oxidation of chloroform $(CHCl_3)$ to form poisonous gas Phosgene $(COCl_2)$ $CHCl_3 + \frac{1}{2}O_2 \longrightarrow COCl_2 + HCl$	2% Ethyl alcohol	Negative

(v) Surface area of reactants:– In case of heterogeneous reactions in which the reacting species are in different physical states, the surface area of solid reactant plays an important role with respect to rate of reaction. Greater the surface area, the higher is the rate of reaction. For example reaction between a piece of marble $(CaCO_3)$ and an acid is slow.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

But finally divided marble reacts vigorously because the powdered marble offers greater surface area for HCl to act upon. Similarly for the same reason amorphous boron is much more reactive than crystalline boron.

In case of liquid, the greater surface area, increases their rate of evaporation. For this reason spilled milk or a liquid evaporates faster than . present in a glass or cup.

(vi) Radiation:– Some chemical reactions proceed only under the influence of light. These are called Photochemical Reaction: The concentration of reactants does not influence rate of such reactions, so they are Zero Order Reaction. Examples are:

(i) Reaction between H_2 and Cl_2

$$H_2 + Cl_2 \xrightarrow[\text{Bright sunlight}]{} 2HCl$$

(ii) Reaction between CH_4 and Cl_2

$$CH_4 + Cl_2 \xrightarrow[\text{Sunlight}]{} CH_3Cl + HCl$$

Radiation or light consists of photons. When photons strike the reactant molecule, they provide the necessary activation energy to the reactant molecules to react.

Example 8:– Determining order of reaction

Problem: A certain reaction $A + 2B \longrightarrow C + D$ gave the following data:

No:	Initial Concentration mole / dm^3 A	B	Initial rate of Reaction mole / dm^3.s
1.	0.1	0.1	3×10^{-3}
2.	0.2	0.1	6×10^{-3}
3.	0.1	0.2	9×10^{-6}

What is rate law and order of reaction?

Solution: Rate expression based on experimental data is called Rate law. According to data:

(a) When concentration of A is doubled, the rate is also doubled; hence

$$\text{Rate } \alpha [A] \text{———} (1)$$

(b) When concentration of B is doubled, rate increases by square i.e. from 3×10^{-3} to 9×10^{-6} i.e. $(3)^2\times10^{-6}$; hence

$$\text{Rate } \alpha [B]^2 \text{———} (2)$$

(c) Now combining (1) and (2), we have

$$\text{Rate } \alpha [A]\,[B]^2$$

or $\text{Rate} = K[A][B]^2$

This is Rate Law for the given reaction.

Now Order of Reaction=Sum of exponents of concentration in rate law.

Order of Reaction=1+2=3

Example 9:– Estimating value of K with change in temperature

Problem: As a rule of thumb rate, hence rate constant of a reaction increases by a factor of 2 for each 10°C rise in temperature, although the actual amount of increase differs from one reaction to another. Consider a reaction $A \longrightarrow B$, for which at 400°C, rate constant K, has a value of $3 \times 10^{-12}\ s^{-1}$. What can be the possible value of K at 450°C.

Solution: Temperature increases from 400°C to 450°C. Thus rise in temperature = 50°C. For each 10°C, K is more or less doubled. Hence value of K will increase 5 times i.e.

$$K = (3 \times 10^{-12}\ .s^{-1}) \times 5$$

$$K = 15 \times 10^{-12}\ .s^{-1}$$

PROGRESS TEST 8

1. Only some collisions between molecules are effective in producing chemical reaction. Explain why?
2. Explain the concept of activation energy and the variation of reaction rate with temperature.
3. Distinguish between:
   (a) Rate and velocity of a reaction (b) Rate and rate constant (c) Positive catalyst and Inhibitor.
4. Give one example each for the following:
   (a) Rate of reaction (b) Velocity of reaction (c) Rate equation (d) Specific rate constant.
5. For the reaction $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$, the rate equation is $\frac{dx}{dt} = K[NO]^2[O_2]$. What is the effect on the rate of the reaction when (a) the concentration of NO is redaced by one half (b) the concentraation of O_2 Is doubled (c) a catalyst is added to the reaction mixture.
6. The decomposition of formic acid is catalyzed by strong acids.

$$HCOOH_{(l)} \xrightarrow{H^+} CO_{(g)} + H_2O_{(l)}$$

(a) Write its rate expression (b) What is the effect on its rate if the acid concentration is doubled.

7. Write note on: Slow and fast reactions.

8. Among the factors that influence reaction rates, which are involved in each of the following:

   (i) Milk sours more rapidly in summar than in winter.

   (ii) Powdered zinc reacts more rapidly with water than the chunks of metallic zinc.

   (iii) Combustion of gasoline occurs more rapidly in an internal combustion engine than in an open container.

   (iv) Unless ignited, hydrogen does not react with oxygen of the air but a stream of hydrogen passed over platinum gauze bursts into flame.

9. Make a list of factors which affect the rates of chemical reactions. Describe the way in which each factor affects the rate of reaction. For each factor, mention whether it is specific to a certain type of reaction, or whether it is general.

10. Describe the rate of a chemical reaction as a change of concentration with time.

11. The reaction rate, R, for reaction $2A + B \longrightarrow A_2B$ was found experimentally to be given by the expression.

$$R = K[A]^2[B]$$

   (a) Will K increase, decrease or remain unchanged if the concentration of A is doubled? If the concentration of B is doubled?

   (b) Will R increase, decrease or remain unchanged, if the concentration of A is doubled? If the concentration of B is doubled?

12. For the decomposition of ethyl chlorocarbonate $(ClCO_2C_2H_5)$

$$ClCOOCH_2CH_3 \longrightarrow CO_2 + ClCH_2CH_3$$

$K = 1.3 \times 10^{-3} s^1$ at 200°C. What is the initial rate when the initial concentration of $ClCOOCH_2CH_3$ is 0.25 M?

Ans:-$(3.25 \times 10^4 Ms^1)$

Hint: Rate $K[ClCOOCH_2CH_3]$

$$= (1.3 \times 10^{-3}\ s^1)(0.25M) = 3.25 \times 10^{-4} Ms^1$$

13. The rate constant for decomposition of nitrogen dioxide

$$2NO_{2(g)} \longrightarrow 2NO_{(g)} + O_{2(g)}$$

is $1.8\times10^3 dm^3 mole^{-1} s^{-1}$. What is the initial rate when the initial concentration of NO_2 is 0.50 M?

(Hint: Rate = $K[NO_2]^2$, Ans:- 4.5×10^9 mole $dm^3 s^1$)

or $(4.5\times10^9 Ms^{-1})$

14. Following is given a data for the reaction $A + B \longrightarrow C$. Find order of reaction?

No.	Concentration (mole / dm^3) A	B	Rate of Reaction
1.	0.1	0.1	8×10^{-4}
2.	0.2	0.1	16×10^{-4}
3.	0.1	0.2	16×10^{-4}

(Ans:- Order of reaction=2)

15. For the reaction $2H_2 + O_2 \xrightarrow{Pt} 2H_2O$.

$$Rate = \frac{dx}{dt} = [H_2]^2[O_2]$$

Fill in the following blanks:

No.	Conc. of $[H_2]$	Conc. of $[O_2]$	Rate at 25°
1.	1 mole / dm^3	1 mole / dm^3	5×10^6 mole / dm^3.s
2.	2 mole / dm^3	1 mole / dm^3	______
3.	1 mole / dm^3	3 mole / dm^3	______

Answer: (2) 25×10^{12} mole / dm^3.s

(3) 15×10^6 mole / dm^3.s

16. Write rate expression for the following reactions:

(i) $CH_2 = CH_2 + CH_2 \longrightarrow CH_3 - CH_3$

(ii) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

(iii) $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$

17. Draw energy diagrams for:
(a) an endothermic reaction
(b) an exothermic reaction in the presence and absence of a catalyst.

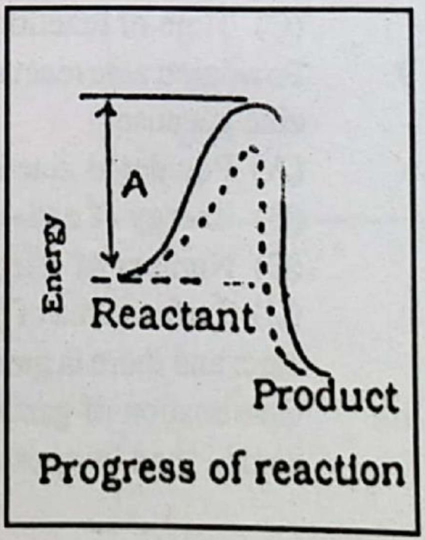
Multiple choice questions

1. Which of the following are best to explain the action of catalyst in speeding up a chemical reaction:
(A) It increases the equilibrium constant for the reaction.
(B) It increases the kinetic energy of reacting molecules.
(C) It prevents reverse reaction from occurring.
(D) It decreases energy of activation for the reaction.
(E) It decreases the enthalpy change for the reaction.

2. Which of the following are best to explain the rapid increase in the rate of a chemical reaction as the temperature rises:
(A) The collisions frequency of molecules increases.
(B) The collisions become more violent.
(C) A considerably higher proportion of molecules has the necessary minimum energy to react.
(D) The bonds in reacting molecules are more easily broken.

3. The energy of activation for the reaction $2H_2O_2 \xrightarrow{P_t} 2H_2O + O_2$ in absence of catalyst is 75 K.Jmole^{-1}.
The most likely value for the energy of activation in presence of catalyst is: (A) 53 K.Jmole^{-1} (B) 75 K.Jmole^{-1} (C) 98 K.Jmole^{-1}

4. The energy profile diagrams for the reaction in presence and absence of a catalyst are shown below. In these profile A represents:
(A) Threshold Energy
(B) Energy of activation in absence of catalyst
(C) Average internal energy of reactants
(D) Energy of activation in presence of catalyst



5. The acid–catalysed reaction of an organic compound propanone (CH_3COCH_3) with iodine may be represented by the equation.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_2ICOCH_3 + H^+ + I^-$$

other conditions remaining same, what will be the effect on initial rate of reaction if the concentrations of propanone, iodine and acid, all are doubled ?

(A) 2x (B) 4x (C) 6x (D) 8x

6. The decomposition of dinitrogen pentoxide in a suitable solvent may be represented by the equation:

$$2N_2O_5 \longrightarrow 4NO_2 + O_{2(g)}$$

The measurements of which are of the following physical quantities could not be used to determine the rate of this reaction:

(A) Volume of oxygen evolved.
(B) Electrical conductivity of solution.
(C) Absorbance of solution using calorimeter.
(D) Mass of reacting mixture.
(E) Pressure of oxygen evolved.

7. Which of the following statements for the reaction between H_2 and Cl_2 in presence of sunlight is correct ?

(A) Rate $= K[H_2]\,[Cl_2]$
(B) The light lowers the energy of activation .
(C) Rate is independent of concentration of hydrogen and chlorine.

8. Rate constant of a reaction depends upon:

(A) Temperature (B) Initial concentration of reactants
(C) Time of reaction (D) Extent of reaction

9. Powdered zinc reacts more rapidly with water than the chunks of metallic zinc because:

(A) Powdered zinc is more reactive
(B) Energy of activation is lowered.
(C) Number of effective collisions has increased.
(D) Surface area of powdered zinc is much more than that of chunks of zinc: and there is greater contact between individual reacting molecules.

10. Combustion of gasoline occurs more rapidly in an internal combustion engine than in open air because:

(A) Number of molecules per unit volume increases

(B) Number of molecules per unit volume increases hence there is more collisions between the molecules

(C) There are more effective collisions

(D) In internal combustion engine, the temperature is higher than in open air. There is more collision among molecules, moreover the fraction of molecules possessing activation energy, increases.

Key:

1.	D	6.	B
2.	C	7.	C
3.	B	8.	A
4.	B	9.	D
5.	B	10.	D

UNITS OF MEASUREMENT AND SOME IMPORTANT CONSTANTS

Table 1
S.I BASE UNITS.

Physical Quantity	Name of unit	Symbol
Length	metre	m
Mass	kilogram	Kg
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A

Table 2
DERIVED S.I. UNITS

Physical quantity	S.I. name or special name	S.I symbol
Area	square metre	m^2
Volume	cubic metre, cubic decimetre	$m^3;dm^3$
Density	kilogram per cubic metre	$kg\ m^{-3}$
Velocity	metre per second	$m\,s^{-1}$
Force	newton	$N\ (kg\ m\ s^{-2} = Jm^{-1})$
Pressure	newton per square metre *(Force per unit area)*	$Nm^{-2}(kgm^1s^{-2} = Pa)$
Energy: Work	Joule	$J(kg\ m^2s^{-2} = Nm)$
Electric charge	Coulomb (C)	C(A.h.)
Quantity of heat	Joule	J
Heat capacity	Joule per Kelvin	$J\ K^{-1}$
Electric potential difference	Volt	$V(JA^{-1}s^{-1} = JC^{-1})$
Electromotive force	Volt	V
Frequency	Hertz	Hz

Table 3
NON-S.I.UNITS

Physical quantity	Name and symbol	S.I. equivalent
Length	Angstrom (A°),	10^{-10} m; 10^{-8} cm;
	Inch (In)	0.0254m; 2.54cm.
Volume	Litre (L)	10^{-3} m^3 : 1dm^3
Mass	Pound (lb)	0.4536 kg
Pressure	Atmosphere (atm),	101,325 Nm^{-2},
	torr (m.m.Hg)	133.322 Nm^{-2}
Force	Dyne (dyn)	10^{-5} N
Energy	erg,	10^{-7} J,
	calorie (cal),	4.184 J,
	electron volt (ev).	1.6021×10^{-19} J.
Viscosity	Poise	10^{-1} kg m^{-1}s^{-1}
Surface Tension	dyne cm^{-1}	10^{-3} Nm^{-1}
Dipole moment	Debye	3.338×10^{-30} mC

Table 4
S.I. PREFIXES

Multiple	Prefix	Symbol
10^{15}	peta	P
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	K
10^{2}	hecto	h
10	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f

Table 5
CONVERSION FACTORS

1 a.m.u = 1.6605×10^{-27} kg
1 °A = 10^{-10} m = 10^{-8} cm
1 Litre (L) = 1 dm^3 = $10^{-3} m^3$
1 atm =101 325 Nm^{-2} = 1.01325×10^5 Pa = 760 torr
1 erg = 10^{-7} J = 1kg.m^2.s^{-2}
1 cal = 4.1840 J
1 e.v = 1.6022×10^{-19} J = 23k cals / mol.

Table 6
PHYSICAL CONSTANTS

Avogadro's number	$N_A = 6.022\times10^{23}\ /\ \text{mol}$
Electron rest mass	$m_e = 9.11\times10^{-31}\,\text{kg}$
Faraday constant	$F = 96485\text{C}\ /\ \text{mol}$
Molar gas constant	$R = 0.0821\ \text{L}\left(\text{dm}^3\right).\text{atm}, \text{mol}^{-1}\text{k}^{-1}$
	$= 8.3145\ \text{J.mol}^{-1}\text{k}^{-1}$
	$= 1.9872\ \text{cal.mol}^{-1}\text{k}^{-1}$
	$= 22.414\ \text{L}\left(\text{dm}^3\right)/\ \text{mol}$
Ideal gas molar volume at S.T.P	$V_m = 0.0224\text{m}^3\ /\ \text{mol}$
Planck's Constant	$h = 6.6261\times10^{-34}\,\text{Js}$
	$= 2.179874\times10^{-18}\,\text{J}$
Rydberg Constant for H–atom	$R_H = 1.09678\times10^{5}\,\text{cm}^{-1}$
Absolute Zero	$0\ \text{K} = -273.16°\text{C}$
Boltzman's Constant	$K = 1.381\times10^{-23}\,\text{Jk}^{-1}$
Proton rest mass	$m_p = 1.673\times10^{-27}\,\text{kg}$