Unit -09

Chemical Kinetics

After studying this unit, the students will be able to:

- Define chemical kinetics. (Remembering)
- Explain and use the terms rate of reaction, rate equation, order of reaction, rate constant and rate determining step. (Understanding)
- Explain qualitatively factors affecting rate of reaction. (Applying)
- Give the order with respect to each reactant; write the rate law for the reaction. (Applying)
- Explain what is meant by the terms activation energy and activated complex. (Understanding)
- Relate the ideas of activation energy and the activated complex to the rate of a reaction. (Applying)
- Use the collision theory to explain how the rate of a chemical reaction is influenced by the temperature, concentration and size of molecules. (Applying)
- Give a potential energy diagram for a reaction, discuss the reaction mechanism for the reaction. (Applying)
- Explain effects of concentration, temperature, and surface area on reaction rates. (Applying)

Teaching
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Assessment
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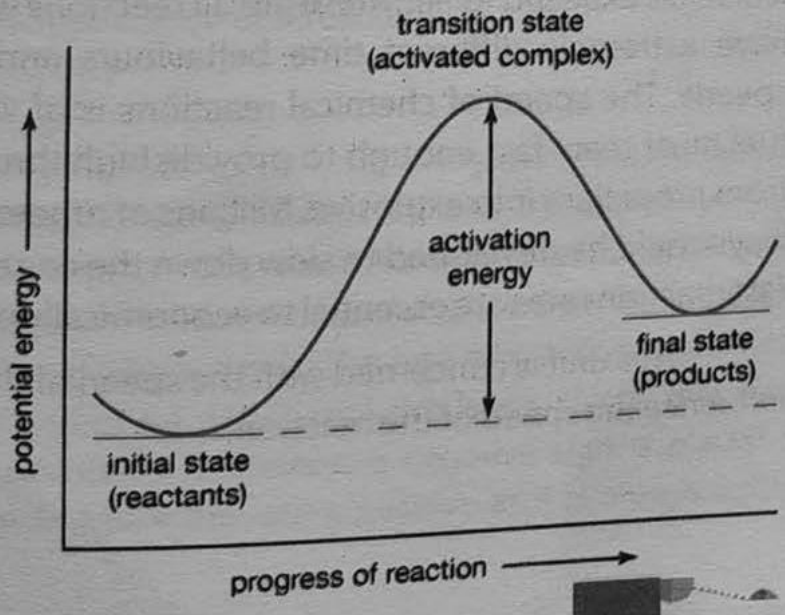

- Explain the significance of the rate determining step on the overall rate multi-step reaction.(Analysing)
- Describe the role of the rate constant in the theoretical determinatio reaction rate. (Applying)
- Describe that increase in collision energy by increasing the temperature improve the collision frequency. (Applying)
- Define terms catalyst, catalysis, homogeneous catalysis and heterogene catalysis. (Understanding)
- Explain that a catalyst provides a reaction pathway that has low activa energy. (Applying)
- Describe enzymes as biological catalysts. (Understanding)
- Explain why powdered zinc reacts faster. (Analysing)

Introduction

A candle remains in contact with air indefinitely without observa reaction but it reacts (burns) when given a start with a lighted match. A mixture natural gas and air in a closed room remains indefinitely without reacting bu may explode violently if a spark is brought into the room. A piece of iron rea quite slowly with air (rusting) but a piece of white phosphorous burst into fla when it is exposed to air. These are all reactions with oxygen from the air but th have extremely different time behaviours and proceed at different rates speeds. The speed of chemical reactions is of vital interest to chemists. Roc fuel must react fast enough to provide high thrust but not so fast that they b from propellant into explosive. Millions of rupees could be saved each year if n ways could be developed to slow down the corrosion of metals. Also, sufficien fast reaction rates are essential to economically produce industrial chemicals.

This unit is concerned with the speed of the reaction and the factors wh influence the speed of the reaction.

9.1 Chemical Kinetics

The branch of chemistry which deals with the speed or rate, at which a chemical reaction occurs, factors affecting the rate and the mechanism of the reaction is called Chemical Kinetics. The knowledge of chemical kinetics is important for the industry, engineering, biological reactions, and other fields. For example, industrial chemists are interested in speeding up of reaction and obtaining products in shorter period of time.

In this connection it is important to know some basic terminologies used in the study of chemical kinetics, for example, rate of the reaction, rate equation and order of reaction etc.

9.2 Rate of Reaction

Rate of reaction is the change in the concentration of reactant or product per unit time. Consider, for example, the reaction between carbon monoxide and nitrogen dioxide. The products are carbon dioxide, CO_2, and nitric oxide, NO. The chemical equation for the reaction is;

$$CO_{(g)} + NO_{2(g)} \longrightarrow CO_{2(g)} + NO_{(g)} \qquad (9.1)$$

The rate of this reaction can be taken to be the change in concentration of reactants or products per unit time, i.e.

$$\text{Rate} = \frac{\text{change in concentration of } CO_2}{\text{Time interval}} = \frac{\Delta[CO_2]}{\Delta t}$$

$$\text{Rate} = \frac{\text{Quantity of } CO_2 \text{ produced}}{\text{Time interval}} \qquad (9.2)$$

i.e. quantity of CO_2 produced per unit time. Alternatively, the rate could be expressed in term of the disappearance of a reactant, i.e.

$$\text{Rate} = \frac{-\Delta[CO]}{\Delta t} \qquad (9.3)$$

Notice that, according to equation 9.1, for every mole of CO_2 formed one mole of CO is consumed. Thus rate expressions 9.2 and 9.3 are equivalent. If, in one second, the concentration of CO_2 were to increase by 0.02 mol dm^{-3} ($\Delta[CO_2]=+0.02 mol.dm^{-3}$), then the concentration of CO would have to decrease by the same amount ($\Delta[CO]=-0.02 mol.dm^{-3}$). The rate of reaction calculated from either equation 9.2 or 9.3 would be +0.02 $mol.dm^{-3}sec^{-1}$. (Note that since the concentration of reactant decreases, therefore, a negative sign is placed before the rate expression in order to make the rate a positive as it is always considered to be a positive quantity).

It can be demonstrated that the rate of the reaction is not a cons quantity but changes with the concentration of reactant molecules pre Initially, when the concentration of reactant is high, the rate is correspond high. With the passage of time the concentration of the reactants decre therefore, the rate also gradually decreases and eventually becomes zero whe of the reactants have been consumed completely. Fig. 9.1 shows the profi reactant concentration with time. As can be seen from it, initially concentration decreases rapidly and at later stage the decrease is slow. The s of the curve gives the rate of the reaction

i.e. $$\frac{\Delta y}{\Delta x} = \frac{-\Delta[\text{Reactant}]}{\Delta \text{time}}$$

Fig. 9.1 shows that the rate of reaction decreases as the concentrati the reactants decreases. At initial stage it takes 15 minutes to decrease concentration from 1.2 to 1.1 mol. dm^{-3}, while at later stage of the reacti takes 150 minutes to decrease the concentration by the same amount i.e. f 0.2 to 0.1mol.dm^{-3}.

A graph, similar to that shown in Fig. 9.1 can be plotted for concentration of product against time which would demonstrate that the ra formation of product is higher initially and low at the later stage.

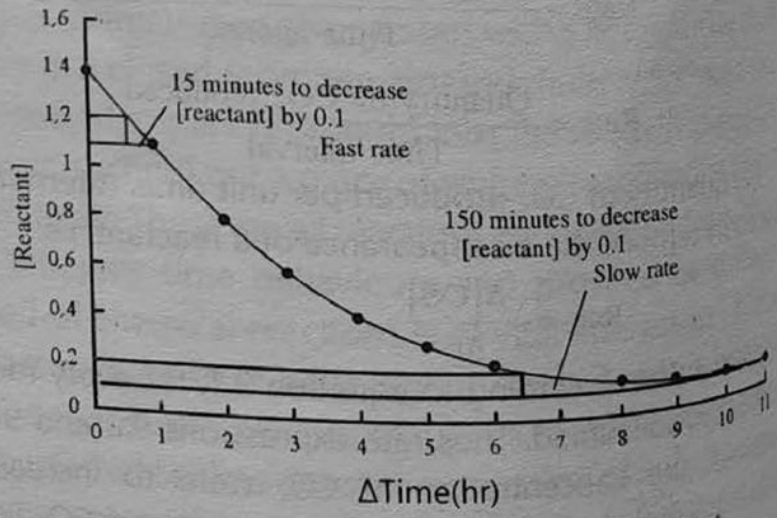

Figure 9.1 Plot of concentration of reactant against

Rate of reaction or formation of product is given by $\frac{\Delta[\text{Product}]}{\Delta t}$, or if we u for the product concentration, it can be expressed as $\frac{\Delta x}{\Delta t}$. This rate is calle

average rate which is measured between larger interval of time, Δt, however, if we use very small interval of time then we express the rate as $\frac{dx}{dt}$ and this rate is called the *instantaneous rate* i.e. rate at a particular instant.

Elementary Reaction and Rate Determining Step

A chemical reaction is usually written in a single stoichiometric equation showing reactants, products, and other conditions of the reaction.

Most of the chemical reactions take place in a series of steps, called as elementary steps. A complete sequence of these elementary reactions is called a reaction mechanism. The overall reaction is the sum of these elementary steps. In each step some chemical species, called as reaction intermediates are produced, these reaction intermediates are consumed in subsequent steps. The overall reaction equation is obtained by adding these elementary reactions; while adding these reactions, the intermediate species are cancelled out and in the final equation only reactants and products are left. Each of these elementary reactions will have their own rate. The overall rate of the complete reaction will be determined by the step which has the slowest rate, the slowest step will be the rate determining step.

Let us consider a reaction $A \longrightarrow B$, which is occurring in the following elementary steps.

i) $A \longrightarrow X$ fast

ii) $X \longrightarrow Y$ slow (Rate determining step)

iii) $Y \longrightarrow B$ fast

Overall reaction

$$A + X + Y \longrightarrow X + Y + B$$

The reaction intermediates X and Y are present on both sides, therefore, they will be cancelled out and net reaction will be $A \longrightarrow B$.

The above sequence of reactions of elementary steps is referred to as mechanism of reaction. The slowest step is called the rate determining step. The rate of overall reaction depends on this step. It is also the step with the highest activation energy.

9.2.1 Rate Expression or Rate Law (Rate Equation)

In the example discussed in Section 9.2 it can be noted that the rate of reaction decreases with time. This is because the concentration of reactants, CO or NO_2 decreases. This observation is generally valid for a number of chemical reactions. We generally find that reactions proceed more slowly as the

concentrations of reactants decrease. Increasing the concentration of reactants increases the reaction rate.

Justification

In order to study the effect of concentration on reaction rate we may conduct a series of experiments in which we measure the initial rate of CO-NO_2 reaction at different concentration of CO, holding the concentration of NO_2 constant. Data for three such series are presented in Table 9.1

$$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g) \text{ at } 400\,^{\circ}C$$

Table 9.1 Initial Rates of Reaction (mole $dm^{-3} sec^{-1}$) ($k = 0.50$ litre $mole^{-1} sec^{-1}$)

SERIES 1			SERIES 2			SERIES 3		
[CO]	[NO_2]	Rate	[CO]	[NO_2]	Rate	[CO]	[NO_2]	Rate
0.10	0.10	0.005	0.10	0.20	0.010	0.10	0.30	0.015
0.20	0.10	0.010	0.20	0.20	0.020	0.20	0.30	0.030
0.30	0.10	0.015	0.30	0.20	0.030	0.30	0.30	0.045
0.40	0.10	0.020	0.40	0.20	0.040	0.40	0.30	0.060

Looking at the vertical columns in Table 9.1 we observe that the rate is directly proportional to the concentration of CO. If, for example, the concentration of CO is doubled (e.g. from 0.1 to 0.2 mol.dm^{-3}), the rate also doubles (from 0.005 to 0.01 mol.dm^{-3} sec^{-1} in series 1, from 0.01 to 0.02 mol. dm^{-3} sec^{-1} in series 2, and so forth). Thus we conclude that the rate of the reaction is directly proportional to the concentration of CO.

Thus we can write as,

$$\text{Rate} \propto [CO] \qquad (9.4)$$

In a similar way we can deduce the effect of NO_2 concentration on rate by examining the horizontal rows of data in Table 9.1. Notice, for example, that when the concentration of CO is held constant at 0.1 mol dm^{-3} (first horizontal row) the rate increases in direct proportion to the concentration of NO_2, thus,

$$\text{Rate} \propto [NO_2] \qquad (9.5)$$

Thus, we conclude that the rate of this reaction is directly proportional to the concentration of both CO and NO_2. Combining Eq. 9.4 and 9.5 we can write that

$$\text{Rate} \propto [CO][NO_2]$$

$$\text{Rate} = k[CO][NO_2] \qquad (9.6)$$

Such expression as given in Eq. 9.6 is called the rate expression, rate equation, or rate law. The rate equation gives the dependence of the rate of

reaction on the concentrations of the reactants. It states that the rate of chemical reaction is proportional to the product of molar concentrations of the reacting substances raised to appropriate powers. Here, the proportionality constant 'k' is called specific rate constant or simply rate constant.

9.2.2 Specific Rate Constant

Consider a general reaction, A + B ⟶ Products.

Rate of this reaction can be expressed as

$$\text{Rate} = \frac{-\Delta[A]}{dt} = \frac{-\Delta[B]}{dt} = k\,[A]^m[B]^n$$

The proportionality constant "k" is called rate constant or velocity constant. m and n may be either whole numbers, zero, or fraction. If the concentrations of A and B are taken as unity, the rate constant k is equal to the rate of the reaction. "k" has a fixed value for a reaction under given conditions of temperature.

$$\frac{dx}{dt} = k[1]^m\,[1]^n$$

$$\frac{dx}{dt} = k$$

In this case the rate is independent of the concentrations of reactants

9.2.3 Order of Reaction and its Determination

Consider a general reaction, A ⟶ Products

Rate of the reaction,

$$\frac{dx}{dt} \propto [A] \qquad \text{or} \qquad \frac{dx}{dt} = k[A]$$

This expression is called as *rate expression which shows a relationship between the rate of reaction and the concentration of the reacting species. It is also called as rate equation or rate law*. The power of reactant terms in the rate equation is called the order of reaction. The order of reaction indicates the way the rate depends on the concentration of the reactants or it shows the proportional relation between rate and concentration of reactants. Thus, *the order of reaction is defined as the sum of the exponents (powers) of the concentration terms of the reactants in the rate expression of the reaction*. For example, in the above rate equation power of reactant term is one, it is first order reaction. Here the rate of the reaction is proportional to the first power of the concentration of single reactant. The reactions may be zero order, 1st order, 2nd order, 3rd order and also may have a fractional order. For a hypothetical reaction

$$A + B \longrightarrow \text{Product.}$$

At constant temperature, the rate of reaction depends on the concentrations of the reactants A and B. This dependence can be written in the form of the rate equation

$$\text{Rate} = \frac{dx}{dt} = k\,[A]^m[B]^n$$

Where 'k' is the rate constant of the reaction, the power, m is the order with respect to reactant A and n is the order with respect to reactant B and the overall order of the reaction is (m+n). Remember that the order is strictly an experimental parameter, it cannot be predicted from coefficients of the reactants in the balanced chemical equation or calculated theoretically. Some examples of the reactions of different orders are given in the subsequent sections.

Tidbit

1. Molecularity is the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
2. It cannot be zero, and must be a positive integer, 1, 2, or 3.
3. It can be calculated by simply adding the number of molecules of the reactants in the slowest step.
4. Generally, molecularity of the slowest step is same as the order of the overall reaction.

9.2.3.1 First Order Reactions

The reactions in which the rate of reaction is proportional to the first power of the concentration of a single reactant. e.g.

(i) $Br_2 \longrightarrow 2Br$

$$\frac{dx}{dt} = k[Br_2]$$

(ii) $${}_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_{2}He^{4}$$

$$\frac{dx}{dt} = k\,[Ra]$$

(iii) The thermal decomposition of nitrogen pentaoxide in gaseous state.

$$N_2O_{5(g)} \longrightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)}$$

$$\frac{dx}{dt} = k[N_2O_5]$$

9.2.3.2 Second Order Reactions

The reactions for which the rate of the reaction is proportional to the second power of concentrations of reactants are second order reactions.

$$2A \rightarrow \text{Products}$$

$$\frac{dx}{dt} = k[A]^2$$

It is a second order reaction because the rate of reaction is proportional to the second power of concentration of the reactant.

Example: 9.1

(i) Thermal decomposition of nitrogen dioxide,

$$2NO_2 \rightarrow N_2 + 2O_2$$

$$\frac{dx}{dt} = k[NO_2]^2$$

(ii) Thermal decomposition of hydrogen iodide

$$2HI \rightarrow H_2 + I_2$$

$$\frac{dx}{dt} = k[HI]^2$$

The second order reaction can also be represented in general form as

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

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

It is a second order reaction because the rate of reaction is proportional to the concentrations of two reactants A and B each raised to the first power.

Example: 9.2

(i) Formation of hydrogen iodide from hydrogen and iodine.

$$H_2 + I_2 \longrightarrow 2HI$$

$$\frac{dx}{dt} = k[H_2][I_2]$$

9.2.3.3 Third Order Reactions

(i) Those reactions for which the rate of reaction is proportional to the third power of concentrations of reactants. It can be represented as

$$A + B + C \longrightarrow \text{products}$$

And rate of the reaction is given as follows

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

It is third order reaction, provided that it is first order with respect to concentration of each of the reactants A, B and C,

(ii) Similarly for reaction of the type

$$A + 2B \longrightarrow \text{products}$$

The respective rate equation is as follows

$$\frac{dx}{dt} = k[A][B]^2$$

It is first order with respect to A and second order with respect to B.

(iii) For the reaction

$$3A \longrightarrow \text{products}$$

The rate equation is,

$$\frac{dx}{dt} = k[A]^3$$

It is also a third order reaction.

Example: 9.3

Gas phase oxidation of nitric oxide

$$2NO + O_2 \longrightarrow 2NO_2$$

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

Tidbit

Units of Rate Constant

For a general reaction $A + B \longrightarrow$ Product

The rate equation is

$$\frac{dx}{dt} = k[A]^{\alpha}[B]^{\beta}$$

The overall order 'n' of this reaction is $n = (\alpha + \beta)$

The expression for the units of rate constant can be given as;

$k = (\text{concentration})^{1-n}\ \text{time}^{-1}$, concentration is given in mol dm^{-3} and time may be in any unit of sec., min., hr. etc. Thus, the unit of zero order is mol dm^{-3} s^{-1}, for first order is s^{-1}, for second order dm^3 mol^{-1} s^{-1} and for third order reaction the unit is $(dm^3)^2$ mol^{-2} s^{-1}.

Role of Rate Constant in Theoretical determination of Reaction Rate

The rate equations, discussed in the preceding sections, *give relationship between rate of reaction, the concentration of reactants, and the rate constant 'k' which is the rate of the reaction when the concentration of reactants is unity.* Rate constant is temperature dependent and is constant for a given reaction at a particular temperature. It is important to realize that the rate equation can only be obtained by experiment, since the values of order therein are experimental quantities, and cannot be deduced either theoretically, or from the stoichiometric equations. Once the rate equation has been established with the knowledge of the order; the rate equation can be used to calculate rate of reaction theoretically for any desired concentrations of the reactants, provided that the value of rate constant is known. The following example illustrates this further.

Self-Assessment

- Define order of reaction.
- Differentiate between first order and second order reactions.

Example 9.4

For a first order reaction A $\rightarrow$ B, the rate constant is 0.0458 s^{-1}, calculate rate of the reaction if the concentration of reactant is 0.35 mol dm^{-3}.

Solution:

Rate constant k= 0.0458s^{-1}

Concentration of reactant [A] = 0.35mol dm^{-3}

Equation: Rate = k x [A]

Rate= 0.0458 s^{-1}x 0.35mol dm^{-3} = 0.016 mol dm^{-3} s^{-1}

Example 9.5

For the decomposition of nitrogen pentaoxide N_2O_5, dissolved in carbon tetrachloride $2N_2O_5 \xrightarrow{CCl_4} 4NO_2+O_2$

The following data was obtained at 30°C

Rate of decomposition of N_2O_5 (mole dm^{-3} $hour^{-1}$]

Mole dm^{-3}	Rate of reaction
0.170	0.050
0.340	0.10
0.680	0.20

(a) Write the rate equation for the reaction. What is the order of the reaction?

(b) Calculate the rate constant for the reaction at 30C°.

Solution

(a) The data show that doubling the concentration of N_2O_5 from 0.170 to 0.340 mol dm^{-3}, or from 0.340 to 0.680 mol dm^{-3}, doubles the rate from 0.05 to 0.10 mol dm^{-3} $hour^{-1}$, or from 0.10 to 0.20 mol dm^{-3} $hour^{-1}$. Therefore, the rate of this reaction is directly proportional to the first power of N_2O_5 concentration, or.

$$\text{Rate} = k\,[N_2O_5]$$

Since the rate is proportional to the first power of one reactant, the reaction is first order.

(b) To calculate the rate constant, we first solve the rate equation for k:

$$k = \text{rate}/\,[N_2O_5]$$

Then substitute any of the three sets of data

$$k = \frac{0.05 \text{ mol dm}^{-3} \text{ hour}^{-1}}{0.170 \text{ mol dm}^{-3}} = 0.29/\text{hour}$$

or $$k = \frac{0.10 \text{ mol dm}^{-3} \text{ hour}^{-1}}{0.340 \text{ mol dm}^{-3}} = 0.29/\text{hour}$$

or $$k = \frac{0.20 \text{ mol dm}^{-3} \text{ hour}^{-1}}{0.680 \text{ mol dm}^{-3}} = 0.29/\text{hour}$$

Notice that, in a first order reaction the rate constant has only the unit of $time^{-1}$.

9.2.4 Factors affecting Rate of Reaction

Experimentally, we find that the rate of a chemical reaction depends upon a number of factors. These are:

i. The nature of the reactants.
ii. The concentration of the reactants.
iii. The particle size of a solid reacting with gases.
iv. The temperature of the reaction mixture.
v. The presence or absence of a catalyst.
vi. Light (in photosensitive reactions).

i. The nature of the reactants

During a chemical reaction chemical bonds are broken and new bonds are formed. The nature (or type) and number of these bonds and their strength play a critical role in the rate of reaction. Ionic compounds react faster than covalent compounds as in the aqueous medium ions are only exchanged which were already separated (dissociated) in aqueous solution, e.g.

$$AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow AgCl_{(s)} \downarrow + NaNO_{3(aq)}$$

On the other hand, reactions between covalent compounds take place slowly because they require energy for breaking of existing bonds and for the formation of new bonds, the molecules must come in contact at particular orientations, e.g. esterification of acetic acid occurs slowly due to the given reasons.

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

The reaction of magnesium with oxygen in the presence of a flame proceeds very rapidly to form magnesium oxide. However, under identical conditions, copper reacts slowly to form copper oxide. The rate of oxidation is different for the two metals.

ii. Effect of Concentration on Rate of the Reaction

Reactions occurring in gaseous mixtures or in solutions are said to be homogeneous if they occur only in one phase. If the gaseous mixture or solution is concentrated it contains more active particles per unit volume and reaction is faster than in a dilute mixture, since in the former case more particles come in contact with each other per unit time.

The effect of concentration on reaction rate is observed from the fact that a piece of wood burns much more rapidly in pure oxygen (high concentration, 100% oxygen) than it does in ordinary air, in which the oxygen makes up only about 21% of the mixture (low concentration).

iii) The Particle Size of a Solid Reacting in Heterogenous Reactions

In the case of heterogeneous system, in which the reactants are in different states, the area of contact between the reacting substances will influence the reaction rate considerably.

Thus magnesium powder will react much rapidly than magnesium ribbon with dilute sulfuric acid. Similarly, zinc powder reacts more rapidly with acid to liberate hydrogen gas than lumps of zinc metal. In general, smaller the size of the reacting particles, the greater is the total surface area exposed for reaction and, consequently, the faster the reaction.

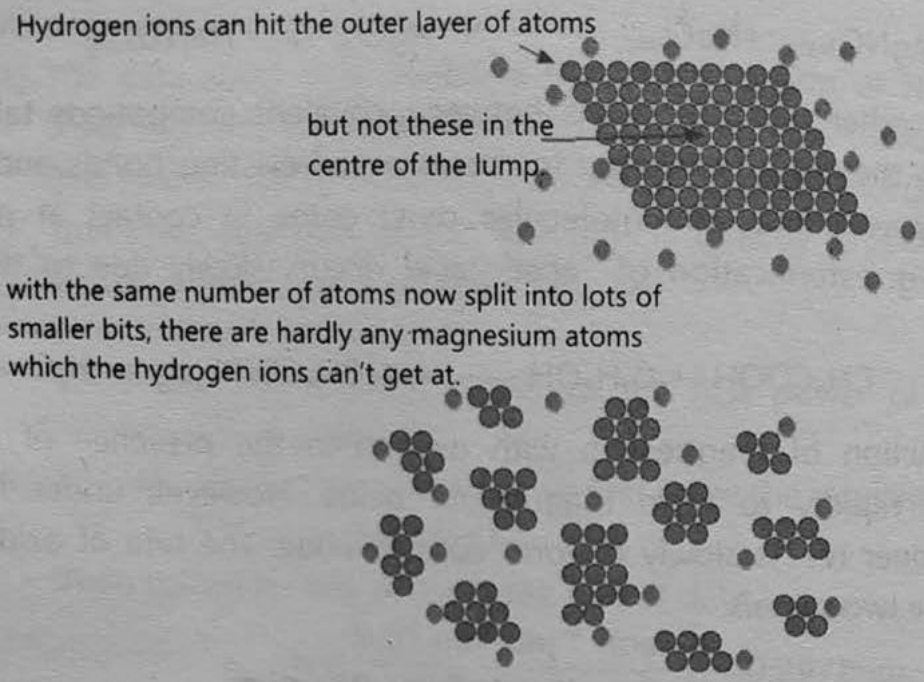

Fig. 9.2

iv. Effect of Temperature on Rate of Reaction

In general, an increase in temperature increases the rate of the reaction. Temperature affects the rate of reaction in two ways:

1. Raising the temperature increases the kinetic energy of the molecules and hence speeds up the molecular motion. This results in more collisions between molecules in a given time and chances of the reaction increase.
2. Secondly, the molecules (or atoms) to react, they must have a minimum energy available to them; known as activation energy. The higher the temperature, the greater is the chance of the reactants having energy greater than the activation energy of the reaction and higher will be the rate of the reaction.

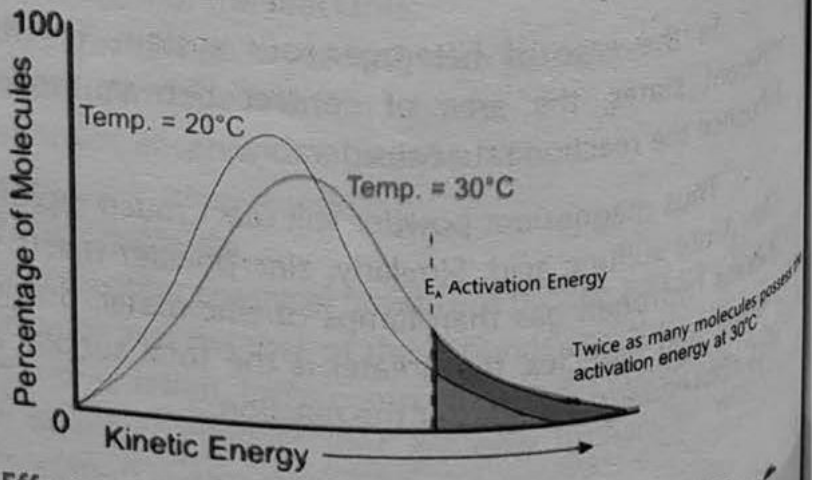

Fig: 9.3 Effect of Temperature on Rate of Reaction

Only those particles represented by the area to the right (shaded with colours) will have enough energy to react when they collide. With the increase in temperature, the number of particles with energy equal to or greater than activation energy increases (total shaded area under the curve), thus the rate of reaction increases.

v. The Presence or absence of Catalyst

A reaction rate generally increases by the presence of a substance called a catalyst. A catalyst is a substance that increases the rate of a chemical reaction but is left chemically unchanged at the end of the reaction. This substance is certainly involved in the reaction but is not permanently changed by it. Often only a very small quantity is needed to influence the reaction. In the laboratory preparation of oxygen, a sample of potassium chlorate is heated as shown:

$$2\,KC\ell O_3 \xrightarrow{\Delta} 2\,KC\ell + 3O_2$$

However, this thermal decomposition is very slow in the absence of a catalyst. By adding a small amount of manganese dioxide (MnO_2) the reaction rate can be increased. The detailed discussion on catalyst will appear in Section 9.4.

vi) Light

Reactions which are influenced by light are called photochemical reactions. Photosynthesis and photography both involve light sensitive reactions. The leaves of the plant contain a green pigment called chlorophyll. This can absorb sunlight and use this energy to transform carbon dioxide and water into oxygen and sugar such as glucose. Thus, photosynthesis is very useful both for the plants and other living organisms. Without light, such an important reaction could not take place and it would have made life impossible. Other examples of photochemical reactions include; decomposition of hydrogen peroxide, and reaction between methane and chlorine etc. In such reactions molecules of reactants get activated by absorption of light and react rapidly.

Reading Check

- Name the factors affecting the rate of reaction.
- Explain the effect of temperature on rate of reaction with graph.

9.3 Collision Theory, Transition State and Activation Energy

Kinetic studies give us information about the effects of concentration, temperature, and catalyst on reaction rates. One of the goals of the chemical kinetics is to explain these effects on a theoretical basis so that we can better

understand the mechanism of the reaction. In this section, we shall discuss a important theory, but first let us familiarize ourselves with the concept activation energy.

9.3.1 Activation Energy and Transition State

For a reaction to occur between molecules, a certain amount of energ must be absorbed to weaken the bonds holding the atoms of the reactan molecules together. The quantity 'E_a' represents the minimum energy required t bring the reactants to a state where they can rearrange to form products.

For two molecules to react, they must collide with each other but energy c collision may not be enough for the reaction to take place. Any molecule in motio possesses kinetic energy; the faster it moves, the greater is the kinetic energy. A fas moving molecule, when collides with another molecule a part of their kinetic energ is converted to potential energy (e.g.; as vibrational energy). If the initial kineti energies are large, then the colliding molecules will vibrate so strongly as to brea some of the chemical bonds. If the initial kinetic energies are small, the molecule will just touch each other with certain force without bringing any change. Thus, there is some minimum collision energy below which no reaction occurs. This energy i called 'activation energy', Ea. *It is the minimum amount of energy required to initiate a chemical reaction.*

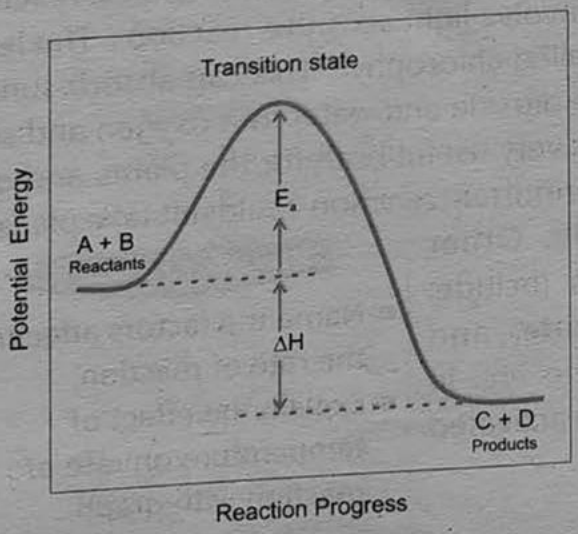

Fig. 9.4.A. A potential energy diagram for an exothermic reaction

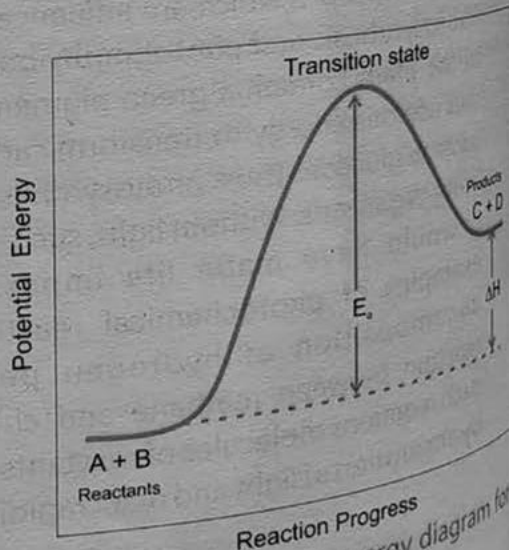

Fig. 9.4.B. A potential energy diagram fo an endothermic reaction

Note: Where E_a is activation energy and ΔH is heat of reaction.

We can represent the potential energy of the reacting system during a chemical reaction using a potential energy diagram in which potential energy of a reaction is plotted against the progress of the reaction through time (Fig. 9.4 A and B). The 'hill' or energy barrier in diagram shows the activation energy of the reaction. If the activation energy is high, the reaction may be slow because a few molecules would be able to cross this high energy barrier, and on the other hand, if the activation energy is less, the reaction will be fast as more number of molecules can cross this barrier.

A potential energy diagram for an exothermic reaction is shown in Fig 9.4 A. The reactants at the beginning of the reaction are at a higher energy level than the products. The overall difference in the potential energy between the energy of the reactants and the products is the enthalpy change 'ΔH' of the reaction. A potential energy diagram of an endothermic reaction is shown in Fig 9.5B. The reactants at the beginning of the reaction are at a lower energy level than the product. The overall difference in potential energy is the enthalpy change of the reaction.

The top of the activation energy barrier of a potential energy diagram represents the transition state of the reaction. The chemical species that exists at the transition state is referred to as the activated complex. The activated complex is the transition species that is neither product nor reactant. It has partial bonds and is highly unstable. It can either break down to form products or it can decompose to reform the reactants. It cannot be isolated as a chemical species and it has short life span. Its formation can be shown in Fig. 9.4.

There is a difference between the transition state and the activated complex. The transition state refers to the top of the energy barrier on the potential energy diagram, while the chemical species that exists at this transition point is called the activated complex.

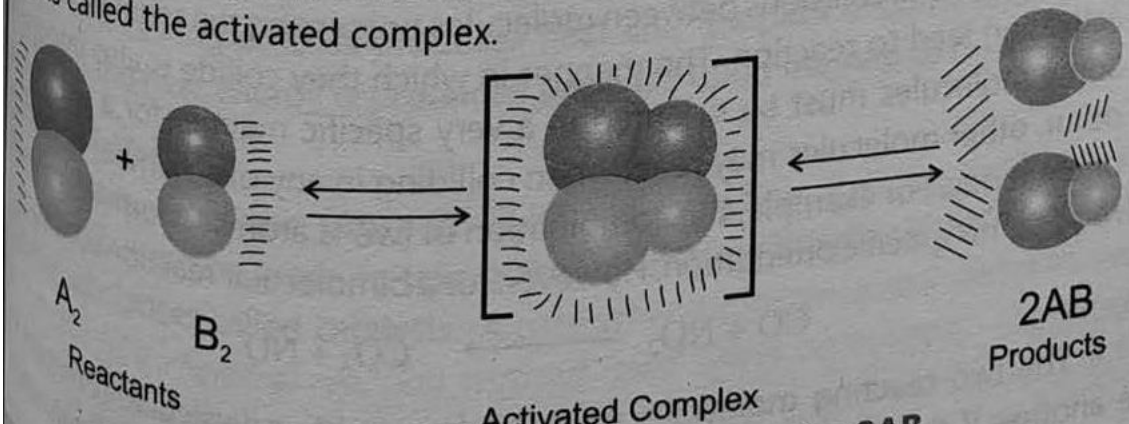

Fig. 9.5 Collision of A_2 and B_2 to give 2AB

9.3.2 Collision Theory of Reaction Rate

It is obvious that for a chemical reaction between two molecules to occur they must come into contact with each other i.e.; the chemical reactions occur as a result of collision between reacting molecules. This fact is the basis of the collision theory of reaction rate. This theory is based upon the following assumptions:

1) For a chemical reaction to occur, particles (atoms, molecules etc.) of the reactants must collide with each other. In the resulting collisions, atoms are re-arranged, bonds are broken and formed, leading to the production of new substances as products.
2) Reaction between the colliding particles can only take place if upon collision they possess a certain minimum amount of energy, the activation energy.
3) Not every collision between the molecules having the required energy of activation leads to reaction. Only those collisions are effective which take place with proper orientation or arrangement of the colliding molecules.

Explanation

1. The first postulate tells us that if we increase the number of molecules present in a given volume, the number of collisions increases, and consequently, the rate of reaction increases.
2. The second assumption of the theory that molecules react only if upon collision they possess a certain minimum amount of energy, the energy of activation, necessary to break the bonds of reactant molecules. The activation energy depends upon the nature of the reactants (associated with bond energies) and is therefore, a characteristic value for each reactant. If energy of colliding molecule is equal to or greater than the energy of activation the reaction would occur, if it is less than that, no reaction would occur.
3. However, not all collisions between molecules possessing the required energy of activation lead to reaction. The manner in which they collide is also important. Some molecules must be oriented in a very specific manner for a reaction to occur, other molecules may react when colliding in any of a number of random orientations. For example, the combination of two H atoms to form H_2 molecule requires no specific orientation. However, for a bimolecular reaction such as,

$$CO + NO_2 \longrightarrow CO_2 + NO$$

The two reacting molecules must be favourably oriented with respect to one another if they are to react upon collision. On CO and NO_2 collision, which

carbon and nitrogen atoms come in contact with one another it is unlikely that the necessary transfer of an oxygen atom will take place from NO_2 to CO molecule. The probability of such transfer increases when carbon atom of CO happens to collide with one of the oxygen atoms of NO_2. (Fig.9.6)

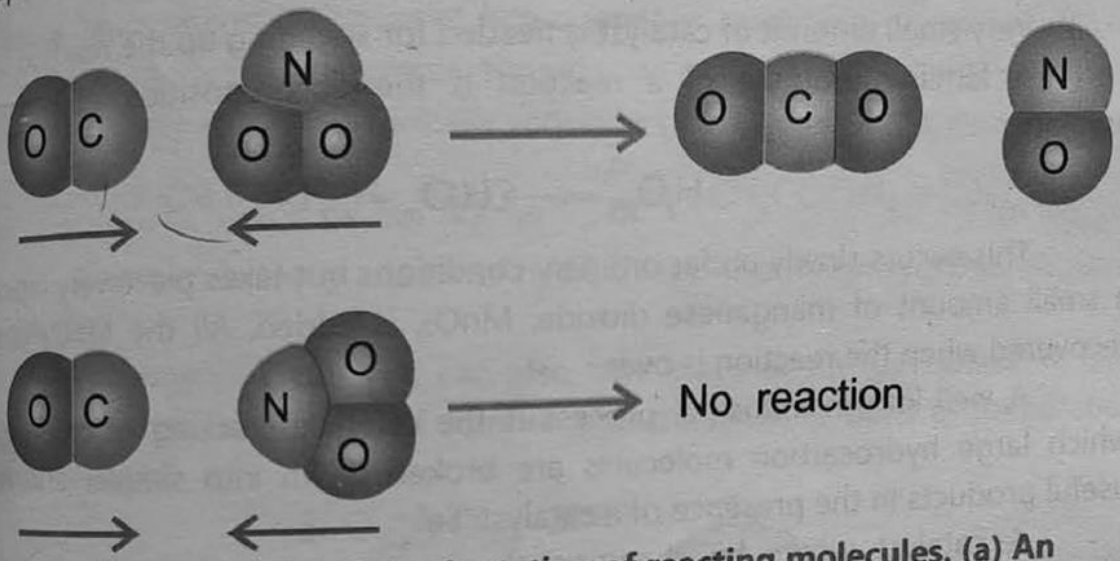

Figure 9.6. Relative orientation of reacting molecules. (a) An effective collision and (b) An ineffective collision

Science, Technology and Society

Walkers and climbers use warm packs in hilly area covered with snow to keep their body warm. These packs, when in use become hot and maintain the temperature at about 40°C for several hours.

A warm pack contains chemicals like, finely powdered iron, water, sodium chloride absorbed on an inert powdered carbon catalyst, evenly mixed together in a porous bag. The whole pack is contained in a polythene bag. When the polythene bag is opened, air enters the pack. The iron in the pack rusts, forming iron oxide, Fe_2O_3.

The rusting process produces heat and the pack becomes warm. The rate at which the heat energy is produced depends upon the rate of rusting.

9.4 Catalysis

Many reactions proceed quite slowly when the reactants are mixed together but can be made to take place much more rapidly by the introduction of other substances called catalysts. *A catalyst is a substance that generally increase the rate of a chemical reaction without itself being consumed. The process of increasing the rate of a reaction through the use of a catalyst is referred to as catalysis.*

9.4.1 Characteristics of Catalysts

Catalysts have the following characteristics:

1) Catalyst generally increases the rate of reaction
2) They are not consumed in the reaction and are recovered chemically unchanged at the end of the reaction.
3) Very small amount of catalyst is needed for speeding up the reaction.

A familiar example of a reaction is the decomposition of hydrogen peroxide;

$$H_2O_{2(l)} \longrightarrow H_2O_{(l)} + \frac{1}{2} O_{2(g)}$$

This occurs slowly under ordinary conditions but takes place very rapidly if a small amount of manganese dioxide, MnO_2, is added. All the MnO_2 can be recovered when the reaction is over.

A well-known industrial process is the catalytic cracking of crude oil, in which large hydrocarbon molecules are broken down into simpler and more useful products in the presence of a catalyst 'Fe'.

A catalyst works by changing the reaction path via a lower energy activated complex requiring lower activation energy than the un-catalyzed reaction

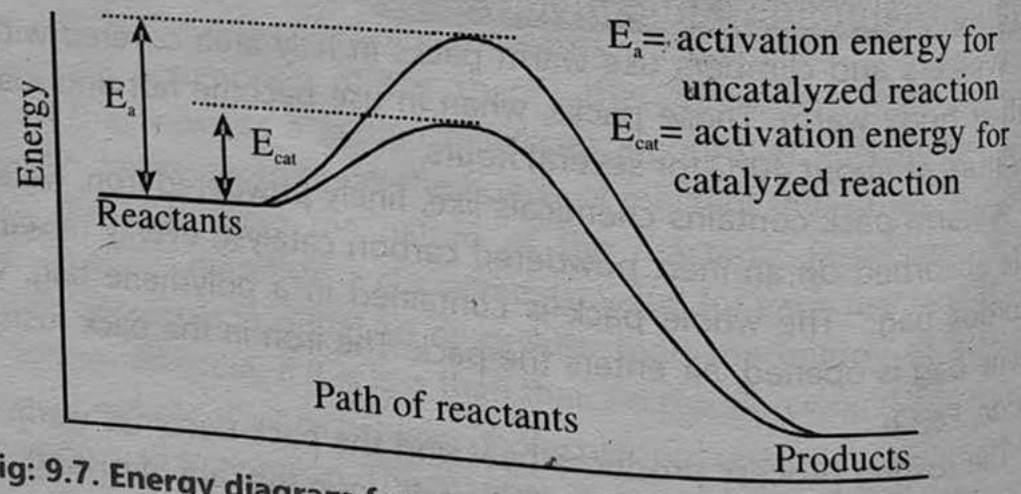

Fig: 9.7. Energy diagram for catalyzed and uncatalyzed reaction.

Fig. 9.7 compares the reaction paths for catalyzed and un-catalyzed reactions. E_a is the activation energy in the presence of a catalyst. Many molecules that do not have kinetic energy to overcome the E_a (potential energy barrier), are able to cross the lower energy E_{cat} (energy barrier) thus making the reaction faster.

Catalysts exist in several different forms, accordingly, there are corresponding catalysis processes. We shall discuss three main types of catalysis

i.e. homogeneous catalysis, heterogeneous catalysis and enzyme catalysis.

9.4.2 Homogenous Catalysis

In homogeneous catalysis, the reactants and catalyst are in a single phase. Most important types of homogeneous catalysis in liquid solution is the acid-base catalysis. For example, the reaction of ethyl acetate with water to form acetic acid and ethanol is normally very slow in the absence of catalyst.

$$CH_3COOC_2H_{5(\ell)} + H_2O_{(\ell)} \xrightarrow{H_3O^+_{(aq)}} CH_3COOH_{(\ell)} + C_2H_5OH_{(\ell)}$$

However, in the presence of hydrochloric acid as catalyst the reaction rate increases.

Homogenous catalysis can also take place in the gas phase. A familiar example is the production of sulphur trioxide which is used in preparation of sulphuric acid.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{\text{catalyst}} 2SO_{3(g)}$$

In this reaction, sulphur dioxide is not converted directly to sulphur trioxide; this reaction is more efficiently carried out in the presence of $NO_{2(g)}$ as a catalyst.

9.4.3 Heterogeneous Catalysis

The catalysis in which reactants and the catalyst are not in the same phase is called heterogeneous catalysis. Mostly catalyst is solid and reactants are gases or liquid in such catalysis. On catalyst's surface a reactant molecule can be held (adsorbed) in a position favourable for reaction until a molecule of another reactant reaches the same point on the solid. Metals such as iron, nickel, platinum and palladium seem to act in this way in reactions involving gases or liquids. There is evidence that in some cases of surface adsorption, bonds of reactant molecules are weakened or broken, thus addition of other reactants takes place easily.

Heterogeneous catalysis is the most important type of catalysis in industrial processes for the production of many important and useful chemicals such as ghee and ammonia. A good example is the reaction between ethene and hydrogen.

$$C_2H_{4(g)} + H_{2(g)} \xrightarrow{Ni_{(s)}} C_2H_{6(g)}$$

This reaction is catalysed by nickel. Hydrogenation of vegetable oil to form ghee is increased if nickel (Ni) is present in powdered form as it has a much larger surface area than a large lump.

9.4.4 Enzyme Catalysis

A large number of catalysts called enzymes are found in living tissue. Enzymes are proteins with high molecular weight and act as catalyst in biochemical reactions occurring in all living matter. For example ptyalin, an enzyme found in saliva, accelerates the conversion of starch into sugar. Although starch will react with water to form sugar, several weeks will require for the conversion to occur in the absence of the enzyme. A trace of ptyalin makes the reaction proceed in minutes at body temperature. Likewise, pepsin in gastric juice breaks down protein into simpler molecules which can be utilized by body cells. Nearly every step of breakdown of a complex molecule to a series of smaller ones, in biological systems, is catalysed by specific enzymes.

Self-Assessment

1. Define activation energy and transition state.
2. Differentiate between homogenous and heterogenous catalysis.

KEY POINTS

- A study of rates and mechanisms of chemical reactions is chemical kinetics.
- The change in concentration of a given substance per unit time is called rate of reaction.
- An equation which relates the rate of a reaction to the molar concentration of the reactants raised to appropriate,experimentally determined powers, is known as rate equation.
- A proportionality constant relating the reaction rate to the molar concentrations of reactants that appear in the rate equation is called rate constant 'k'

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

- The sum of powers of the concentration terms appearing in the rate equation is known as order of a reaction; for example,

$$\text{if rate} = k[A]^2[B]^1, \text{ the reaction is } (2+1=3) \text{ of third order.}$$

- Order is experimentally determined parameter.
- Rate of reaction depends on the nature of reactants, concentration, particle size (in case of solid reactants), temperature, and catalyst.
- A catalyst is a substance which changes the rate of reaction without apparently being consumed.
- The minimum energy needed for a reaction to take place is called activation energy.
- According to collision theory a reaction occurs when molecules collide with sufficient energy called activation energy, to break the bonds and initiate the reaction.
- Catalysis may be homogeneous or heterogeneous while enzymes are also catalysts which play their role in living organisms.

EXERCISE

Choose the suitable option.

i. Activated complex is a substance which is
   a. stable
   b. unstable
   b. can be isolated
   d. can exist as product

ii. A reaction is first order with respect to A and second order with respect to B, the rate equation is
   a. rate = k $[A][B]^2$
   b. rate = k $[A]^2[B]$
   c. rate = k [A][B]
   d. rate = k [A].

iii. For a reaction A → Product, doubling the concentration of A, quadruples the rate. The reaction is;
   a. first order
   b. second order
   c. zero order
   d. third order

iv. With the increase in temperature the rate of reaction increases due to
   a. decrease in collisions
   b. decrease in activation energy
   c. increase in kinetic energy of the molecules
   d. more number of molecules attains activation energy.

v. You can speed up a reaction by:
   a. using less concentrated solution.
   b. by lowering the temperature.
   c. using more concentrated solution.
   d. stopping stirring.

vi. When the catalyst and reactants are in different physical phases, we call the catalysis:
   a. Heterogeneous
   b. Homogeneous
   c. Concentrated
   d. positive catalysis

vii Increasing the temperature increases the rate of reaction by
   a. lowering the activation energy.
   b. increasing the activation energy.
   c. lowering the frequency of effective collisions between reacting molecules.
   d. increasing the frequency of effective collisions between reacting molecules.

viii. The energy needed to start the reaction is called
a. potential energy b. activation energy
c. kinetic energy d. ionization energy

ix. As the number of effective collisions between the reacting particles increases, the rate of reaction
a. Decreases b. Increases
c. remains the same d. both b and c

x. Which condition will increase the rate of reaction?
a. Decrease in temperature and concentration of reactants.
b. Decrease in temperature and increase in concentration of reactants.
c. Increase in temperature and decrease in concentration of reactants.
d. Increase in temperature and increase in concentration of reactants.

xi. A catalyst
a. decrease the activation energy and decrease the rate of reaction.
b. decrease the activation energy and increase the rate of reaction.
c. increase the activation energy and decrease the rate of reaction.
d. increase the activation energy and increase the rate of reaction.

xii. Which aluminum sample would react most rapidly with 1 M $CuSO_4$ solution under the same conditions?
a. 1 g Al rod b. 1 g Al pellets
c. 1 g Al ribbon d. 1 g Al powder

xiii. One mole of a reactant reacts with a rate of 0.6 mol dm^{-3} s^{-1}. What is the rate constant of this reaction?
a. 1 s^{-1} b. 0.3 s^{-1}
c. 0.6 s^{-1} d. 0.9 s^{-1}

Short Questions

i. Determine the overall orders from the following rate equations
a. $\text{rate} = k[NO]^2[O_2]$
b. $\text{rate} = k[NO]^2$

ii. Explain why a molecular collision should be sufficiently energetic to cause a reaction.

iii. Name the four factors that increase the rate of reaction.

iv. In the light of collision theory of reaction rate, give reasons of increase in the rate by the increase of temperature.

v. Consider two gases, A and B, in a container at room temperature. What effe would the following changes have on the rate of the reaction between the gases?

a. The pressure is doubled.
b. The number of molecules of gas A is doubled.
c. The temperature is decreased by 10 °C

vi. The rate constant for the reaction

$$CO + NO_2 \longrightarrow CO_2 + NO$$

at 400 °C is 0.50 $dm^3\ mol^{-1}\ sec^{-1}$, and the reaction is first order with respect t both CO and NO_2.

a. What is the overall order of the reaction?
b. What is the rate of the reaction at 400 °C when the concentration o CO is 0.025 mol dm^{-3} and that of NO_2 is 0.040 mol dm^{-3}?

(Ans: $5x10^{-4}$ mol $dm^{-3}sec^{-1}$

vii. Explain briefly why all collisions between reactant molecules do not lead t reaction?

Descriptive Questions

Q1: Define the following terms.

a. Rate of the reaction
b. Rate constant.
c. Order of the reaction.
d. Rate law or rate equation.
e. Catalyst

Q2: (a) Define the activation energy. What role does it play in chemical reaction

(b) Household gas (methane) burns in the presence of oxygen and gives ener for our daily use. If a mixture of methane and oxygen is kept in a contain for indefinite period, no reaction takes place, explain?

Q3. Explain how does a catalyst increase the rate of a reaction? Compare catalyzed and un-catalyzed reaction on a potential energy diagram.

Q4. Explain the relationship between reactant concentration and rate of reaction.

Q5. Discuss why, (according to collision theory of chemical reactions) so molecular collisions result in a chemical reaction while others do not. D and explain a reaction energy diagram (reaction profile) for

a. an exothermic reaction.
b. an endothermic reaction.

Also show in the diagram

a. position of the energy of reactants
b. position of the energy of products
c. activation energy.
d. ΔH of the reaction.

Numerical

1. The conversion of X to Y follows second order kinetics. If concentration X is increased 3 times to what factor the rate of formation of Y will be increased. (Ans. 9 times)
2. A first order reaction (A→ Product) has a rate of 0.008 Ms^{-1} with [A]=0.002 M, what is the rate constant for this reaction? (Ans. 4 s^{-1})
3. (a) The decomposition of N_2O_5 proceeds according to the following equation.

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

(b) If the rate of decomposition of N_2O_5 at a particular instant is 4.2×10^{-7} Ms^{-1}, what is the rate of appearance of (a) NO_2 (b) O_2?

(Ans.(a)$8.4 \times 10^{-7} Ms^{-1}$ (b)$2.1 \times 10^{-7} Ms^{-1}$)

Project

Hydrogen peroxide decomposes to produce oxygen and water according to reaction shown below.

$$2H_2O_{2(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$

The reaction is quite slow unless catalysed by substances such as iodide ions, manganese dioxide, ferric ions etc. Take a test tube and add about 10 to 15cm^3 of hydrogen peroxide in it. Add a few crystals of potassium iodide to it and watch the bubbles of oxygen coming out from the test tube. Bring a glowing match stick at the mouth of the test tube and observe. What do you expect to happen with the stick? Explain.