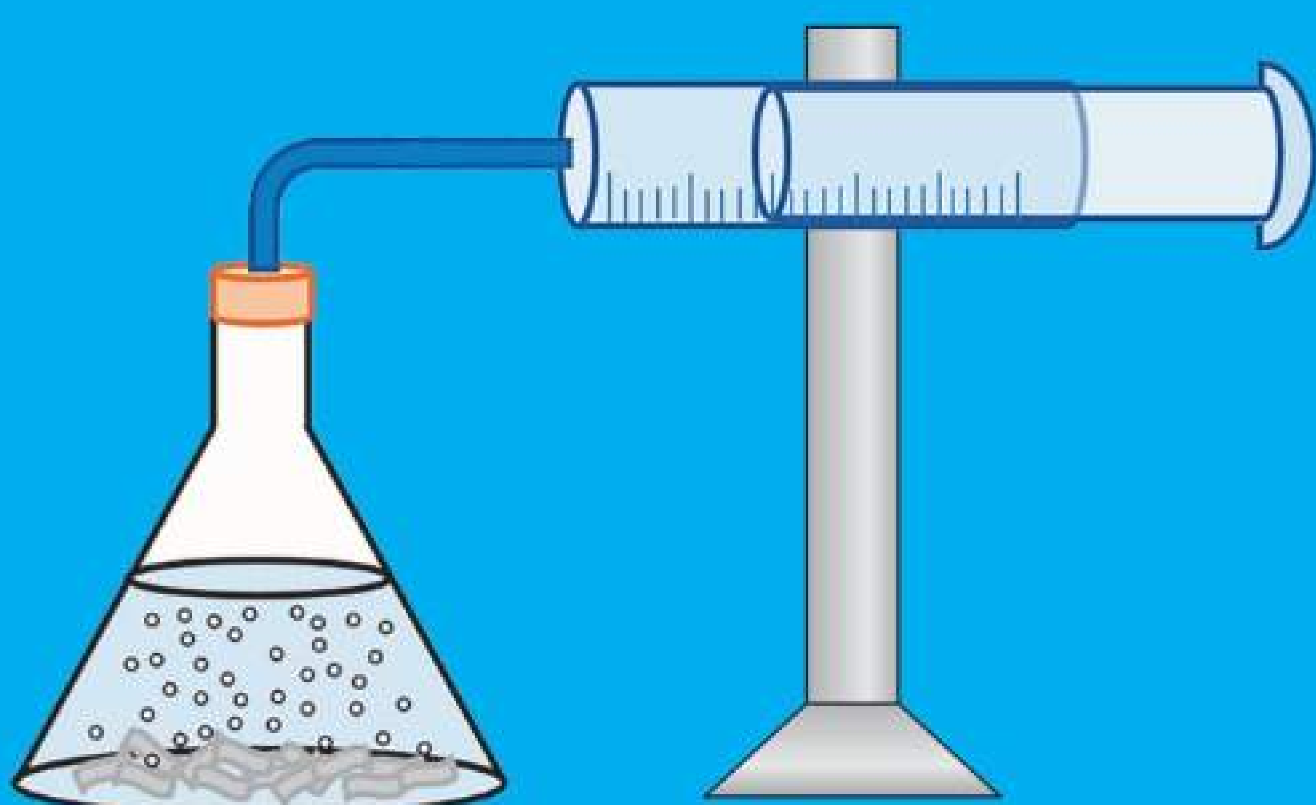
Chapter 17

Reaction Kinetics

Student Learning Outcomes

After studying this chapter, students will be able to:

- Describe collision theory in terms of number of particles per unit volume, frequency of collisions of particles, kinetic energy of particles and activation energy
- State that catalyst increases the rate of reaction provides alternate pathway with lower activation energy, and remains unchanged at the end of a reaction
- Describe the physical parameters that may be affected by the rate of, reaction including change in mass, temperature, and formation of gas
- Interpret data, including graphs, for investigating rate of reaction
- Explain the effect on rate of reaction of changing concentration of a reactant, pressure of gases, surface area of solids, temperature, presence of catalyst (including enzymes) using collision theory
- Justify the importance of chemical kinetics in the food industry to determine ideal harvesting and transportation times for produce.



Reaction Kinetics

Rate of reaction is the speed at which the reaction takes place. Chemical reactions are useful only when they occur at a reasonable rate. In this chapter we shall study the rates at which chemical reactions proceed. We shall also try to understand the factors that govern the rate of reaction. The studies eventually lead us to come to know how reactions occur at the molecular level.

17.1 Collision Theory of Reaction Rate

A reaction takes place only when the participating particles (atoms, molecules or ions) collide with one another. It has been observed that a very small fraction of collisions lead to the formation of products. In the majority of collisions the reactant particles simply bounce back without any change. Collisions which lead to reaction are called effective collisions.

The rate of a reaction depends upon the number of effective collisions which, in turn, depends upon the following factors.

1. The number of particles per unit volume

The larger the number of particles per unit volume, larger is the possibility of effective collisions. In other words, higher the concentration of the reactants, more the number of molecules and hence more will be the number of collisions between them.

2. The frequency of Collisions

A greater number of collisions per second will also result in the increase in the number of effective collisions. At higher temperature the velocities of the molecules increase resulting in the increase in the frequency of collisions. This increase in the frequency of collisions will also increase the number of successful collisions.

3. The kinetic energy of the particles

The kinetic theory of particles says that all matter is composed of tiny constant moving particles. Their motion is due to kinetic energy they possess. As the temperature increases, the kinetic energy of the particles also increases. As a result the particles start moving fast leading to more vigorous motion. The fast moving particles will have more chances to collide with each other.

4. Activation energy

According to collision theory, the colliding particles will lead to effective collisions only when they possess sufficient energy to break the bonds present in the reactant molecules. This minimum energy required to start a chemical reaction is called its activation energy.

Generally, at a particular temperature, most of the molecules of the reactant possess average energy. A fraction of total molecules will, however have more than the average energy. Particles will react only when average energy of this small fraction of molecules exceeds the energy needed to activate molecules so that they can undergo a chemical reaction.

When the reactant particles come close to each other at the time of collision, they slow down and the kinetic energy they possess, is converted to increase their potential energy. This process can be understood with the help of a graph drawn between the path of reaction and the potential energy of the system as shown in Figure 17.1. When the reactant particles possessing activation energy collide they form high energy state with the corresponding increase in the potential energy of the system. After this stage the reactants are converted into the stable products and the potential energy of the system falls down.

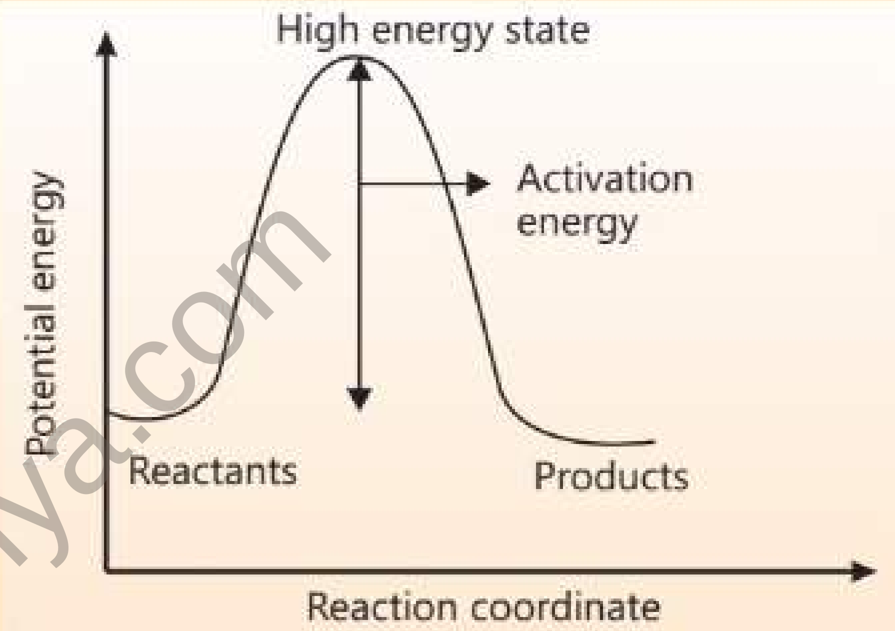


Figure 17.1: Path of the reaction

The information provided by the energy of activation is very important in understanding the mechanism of the reaction.

17.1 Quick Check!
1. How will you increase the frequency of collisions?
2. What happens to the reactant particles after collision?

17.2 Change in Mass during a Chemical Reaction

The total mass during a chemical reaction always remains the same. This is the requirement of the law of conservation of mass which is always obeyed. However, some reactions may appear to proceed with a change in mass which can usually be explained because a reactant or a product is a gas in such reactions.

If a reaction is carried out in an open container where gases can escape or enter, the apparent mass change can occur if a gas is either absorbed or evolved. For example, if a gas is evolved, we shall observe a decrease in mass and if a gas is absorbed, the apparent mass will increase.

If a ribbon of magnesium is burnt in an open crucible, the mass of the product (MgO) formed will be greater than the reactant (Mg). This increase in mass has occurred due to the reaction of magnesium with oxygen present in air. However, if the two reactants (Mg and O_2) are allowed to react in a closed container, the total mass will remain the same before and after the reaction.

Formation of a gas during a chemical reaction

If a reaction is performed between marble chips and dilute hydrochloric acid in an open container, the mass of products will apparently be less than that of reactants. This apparent decrease in mass is due to evolution of CO_2 gas during the reaction which escapes into the atmosphere.

$$CaCO_{3\,(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2\,(aq)} + H_2O_{(l)} + CO_{2\,(g)}$$

When a reaction moves ahead the concentrations of the reactants decrease until all the reactants are used up. At the same time, the concentrations of the products increase and reach the maximum value at the end of the reaction. This is shown in a graph in Figure 17.2.

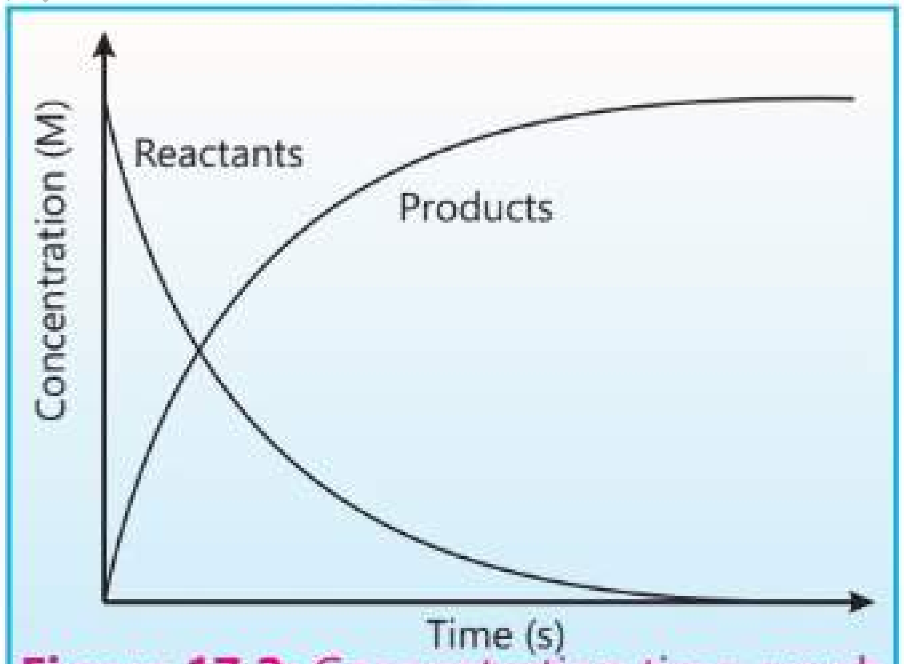


Figure 17.2: Concentration time graph

17.3 Change in Temperature during a Chemical Reaction

Chemical reactions are quite often accompanied by the changes in the temperature indicating whether they are exothermic or endothermic. In exothermic reactions heat energy is released which is absorbed by the surrounding causing their temperature to increase.

For example, when quick lime (CaO) reacts with water slaked lime $Ca(OH)_2$ is formed and a lot of heat energy is released.

$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2\,(s)}$$

In endothermic reactions heat energy is absorbed causing the surrounding to cool down.

For example, when ammonium chloride or ammonium nitrate is dissolved in water, heat energy is absorbed causing the container to cool down.

Increasing the temperature of the reaction increases its rate. For many reactions, the rate doubles with every 10 °C rise in temperature. Cooking food uses high temperature to speed up chemical reactions that break down the components of food making it edible.

17.4 Factors Affecting the Rates of Reactions

According to the collision theory all those factors which change the number of successful collisions per second affect the rates of chemical reactions. Some of the important factors are explained in the following paragraphs.

1. Effect of Concentrations of the Reactants

In order for the reaction to occur, the reactants must come in contact with each other. For this reason, the reactions are most often carried out in one phase, for example, in liquid solutions or in gas phase. When the reactants are present in the same phase, their particles are able to meet on the molecular level and thus are able to collide with each other easily. The higher the number of particles of the reactants per unit volume, higher will be chances of effective collisions and hence higher will be the rate of reaction. Hence an increase or decrease in concentrations of the reactants will result in increase or decrease in the rate of reaction respectively. For example, combustion of coal in air (21% oxygen) proceeds relatively slowly as compared to the reaction in pure oxygen. Similarly, lime stone reacts with different concentrations of hydrochloric acid at different rates.

Activity 17.1

An experiment can be performed to show the increase in the rate of reaction with the increase in the concentration of hydrochloric acid. Take a flat-bottomed conical flask fitted with a delivery tube which is connected to a syringe as shown in the Figure 17.3. The flask contains granules of lime stone taken in excess and a fixed volume of one molar hydrochloric acid. After the start of reaction carbon dioxide gas is generated which is collected in the syringe. The scale present on the syringe directly measures the volume of carbon dioxide gas evolved. It is essential to keep all the variables constant in this experiment, for example, the volume of one molar hydrochloric acid, the temperature at which the experiment is being carried out, the mass and size of lime stone granules, and the rate of stirring. The reaction is followed by measuring the volume of carbon dioxide gas evolved. The same experiment is then repeated taking the same volume of two molar hydrochloric acid.

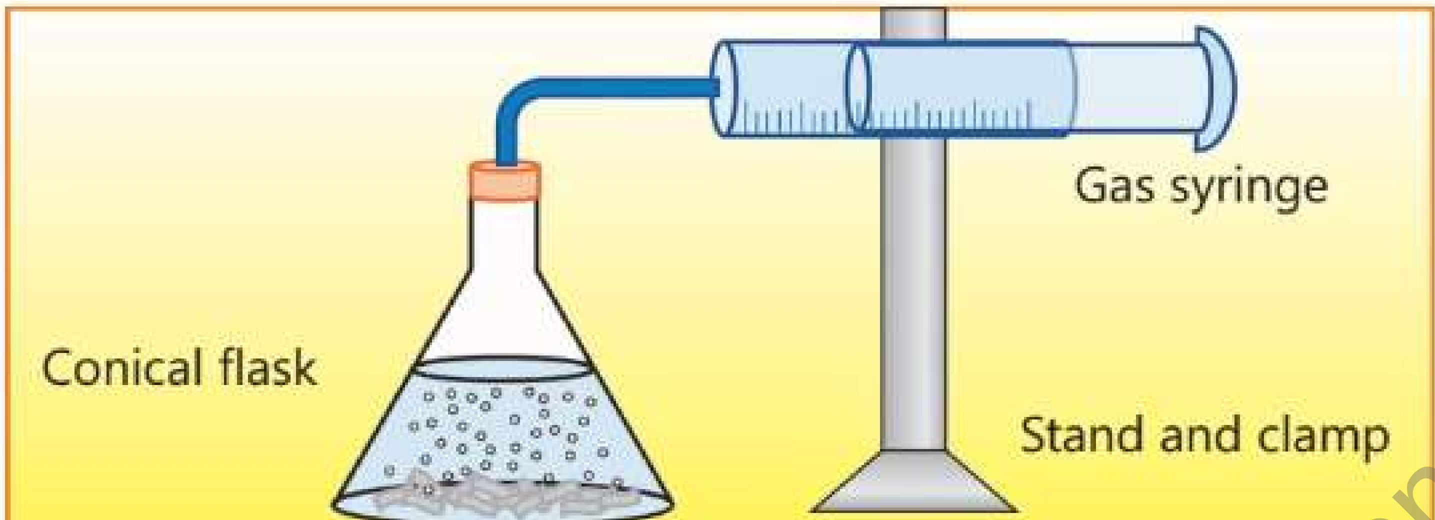


Figure 17.3: Reaction of hydrochloric acid with limestone

THINGS TO KNOW

Understanding kinetics helps us to control the reaction conditions in order to speed up or slow down reactions as needed.

The change in the rate of reaction is then seen when a graph is drawn between the time in seconds or minutes against the volume of gas evolved as shown in Figure 17.4.

The graph obtained is in the form of a curve. We can measure the rate of reaction during a time interval by drawing a tangent on this curve. The results show that the reaction starts with a very fast rate which then progressively slows down as the concentration of hydrochloric acid decreases. After a while the reaction stops because the whole of hydrochloric acid has been utilized.

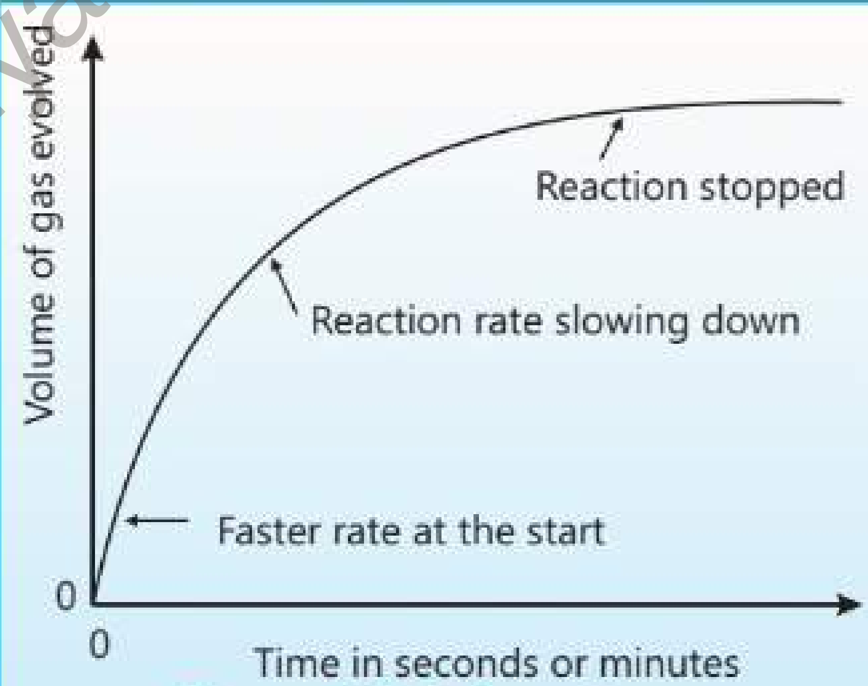


Figure 17.4: Reaction rate

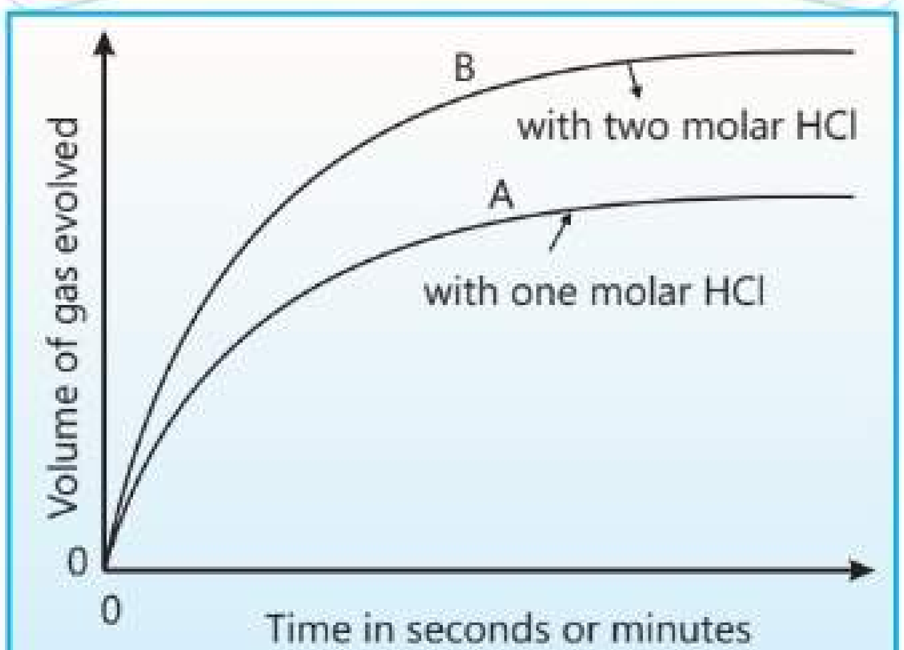


Figure 17.5: Reaction rates at two different concentrations

The two curves A and B shown in Figure 17.5 represent two separate experiments done with one and two molar concentrations of HCl respectively.

The greater the concentration, the steeper is the curve at the start of the experiment which means faster rate of reaction. The more concentrated is the acid, the more are the chances of effective collisions.

2. Reactants present in gas phase

If reactants in a reaction are present in gas phase, their concentrations can be changed by changing their pressure. For example, the rate of reaction between hydrogen and chlorine can be doubled if the pressure of chlorine gas is doubled provided the other component hydrogen is present in excess.

3. Effect of Surface Area of Solids

Reactions involving solids take place on their surfaces and the rates of their reactions depend to a great extent on the area of the surface contact between them. The larger the surface area of the solids, the more is possibility of their particles to come in contact with each other and the higher is the rate of reaction. Finely divided solids, because of the greater surface area available, react more rapidly than do large pieces of the same substances. For example, aluminum foil reacts slowly with warm sodium hydroxide but in finely divided state it reacts rapidly with even cold aqueous solution of sodium hydroxide evolving hydrogen gas.

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \longrightarrow 2NaAl(OH)_{4\,(aq)} + 3H_{2\,(g)}$$

Similarly, a large piece of wood will burn slowly while small pieces burn rapidly.

4. Effect of Temperature

It is an everyday observation that the rates of chemical reactions increase with increase in temperature. Food cooks faster at higher temperatures than at lower ones. Similarly, the oxidation of iron is very slow at room temperature but proceeds very fast at high temperature. In many cases the rate of reaction is nearly doubled when the temperature is increased by 10 °C. The graph shown in the Figure 17.6 explains this rapid increase in the rate of reaction with the rise in temperature.

According to the collision theory, the rate of reaction depends upon the frequency of successful collisions between reactant molecules. As the temperature of a reaction is increased, the kinetic energy of the participating reacting particles also increases. This, in turn increases the velocities of their movements. As a result the collisions which lead to the occurrence of reactions also increase, enhancing the rate of reaction.

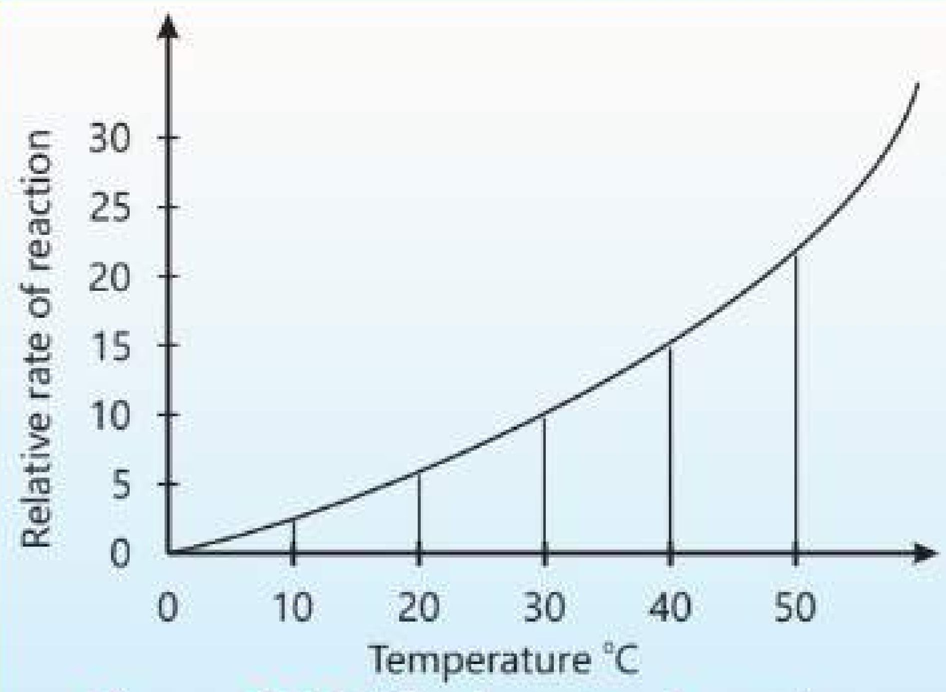


Figure 17.6: Rise in rate of reaction with temperature

Interesting Information

Kinetics helps us to increase the yield of a reaction and minimize the waste.

5. Effect of Catalyst

A catalyst is a substance which alters the rate of the reaction but it is not consumed during the course of reaction. It's role is to alter the way the reaction takes place by substantially lowering its activation energy. When the activation energy is lowered, more and more particles of the reactants will start forming the high energy state and the rate of reaction will increase. For example, platinum metal serves as a catalyst during the addition of hydrogen in ethene. Both hydrogen and ethene are known to adsorb on the surface of platinum metal and the bonds, present in them, get weakened. Thus, the surface of metal helps the reactant molecule to react together. This is shown in the Figure 17.7.

In the presence of a catalyst, the activation energy is sufficiently lowered allowing more and more molecules to react together.

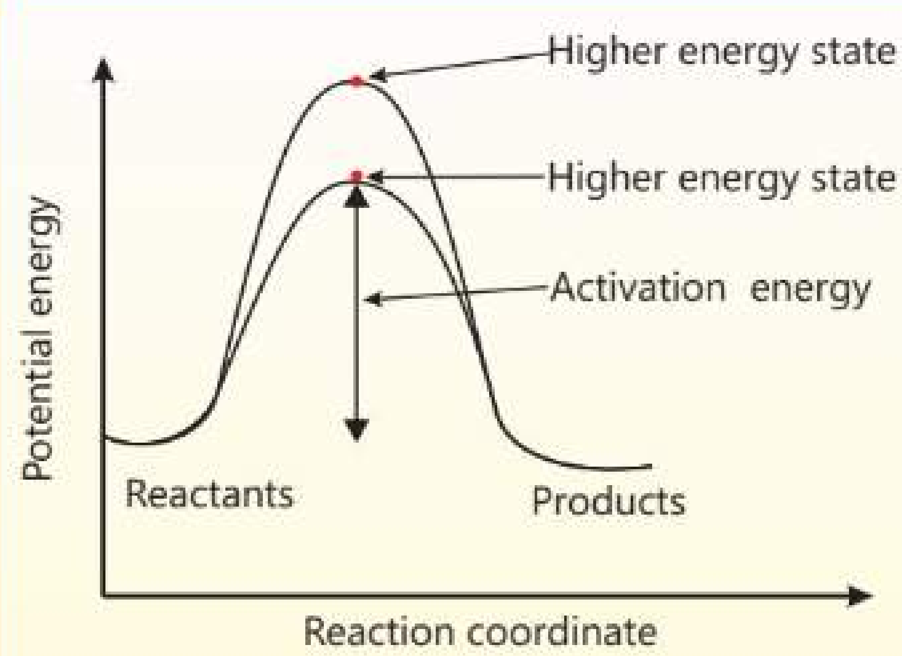


Figure 17.7: Path of reaction with or without the presence of a catalyst

6. Enzymes as Catalysts

Enzymes are biological catalysts. These are basically proteins which help to speed up specific chemical reactions taking place in our body. They react with the reactant molecules using the active sites present in them. Once bound with the reactant molecule the particular bonds in the reactant molecule are sufficiently weakened for the reaction to take place. The product formed then dissociates itself from enzyme which is then free to bind another reactant molecule. The active sites present in enzymes are very specific such that a particular enzyme can catalyze a specific reaction only.

17.2 Quick Check!

1. Why a catalyst is mostly used in finely divided form?
2. How do you increase the number of successful collisions?
3. How does the concentrations of the products change during reaction? Explain with the help of a graph.

17.5 Importance of Chemical Kinetics in Food Industry

The study of reaction rates and the factors which affect these rates play an important role in food industry.

The rates of chemical reactions which are involved during food ripening and food spoilage are studied for different types of fruits and vegetables. The information thus obtained is used to minimize the losses due to spoilage. Food scientists can determine the optimum conditions for harvesting, storage and transportation of food products by studying the rates of enzymatic reactions, oxidation or microbial growth.

Interesting Information

Enzyme based biosensors are used to detect glucose in blood.

Fruits and vegetables ripen owing to the reactions which involve enzymes. These reactions convert starches into sugars, soften tissues and develop characteristics flavour and colours. With the help of rates of these enzymatic reactions, farmers can predict when the product will reach at its peak quality and ready for harvesting. For example, the rate of production of ethene during ripening can be monitored to determine the best time to harvest the fruits.

Some enzymes which are naturally present in foods can spoil the foods which then undergo changes in texture, flavour and nutritional value. Again understanding the rates of these enzymatic reactions will allow us to plan how to stop this spoilage.

For example, if a fruit is known to degrade rapidly during transportation or storage owing to high temperature, refrigeration can be employed to prevent rapid spoilage.

Interesting Information

Understanding the kinetics of oxidation reactions of fats helps to prevent spoilage of butter.

17.3 Quick Check!

1. How would you determine the best time of fruit harvesting?
2. Why some fruits and vegetables get destroyed early during summer than during winter.

EXERCISE

A Multiple Choice Questions

Choose and tick the correct answer from the given choices.

1. The number of collisions per unit volume of the reaction mixture is called:

   (a) Collision energy (b) Activation energy

   (c) Collision frequency (d) Collision force

2. If the reactants possess an energy higher than the activation energy, then the reaction will be:

   (a) Slow (b) Fast

   (c) Not affected (d) Instantaneous

3. Which of the following explains the increase in rate of reaction in the presence of a catalyst?

   (a) Catalyst provides extra energy to the reactant molecules

   (b) Catalyst provides an alternative pathway which lowers the activation energy.

   (c) Catalyst increases the collision frequency

   (d) Catalyst decreases the collision frequency

4. Which of the following statements is correct?
   (a) Collisions with energy equal to or greater than the activation energy lead to reaction.
   (b) Collision frequency is not related to the reaction rate
   (c) All collisions lead to a reaction.
   (d) Collisions with energy less than the activation energy lead to the reaction.
5. When a reaction proceeds ahead, how the concentrations of reactants and products change?
   (a) Concentration of reactants increases and that of the products decreases.
   (b) Concentration of reactants decreases and that of the products increases.
   (c) Concentration of both reactants and products decreases.
   (d) Concentration of both reactants and products increases.

B Short Answer Questions

17.1 What is a successful collision?

17.2 How does increase in the temperature increase the rate of a reaction?

17.3 Define activation energy.

17.4 Why does the burning of sulphur proceed slower in air than in pure oxygen?

17.5 Why a catalyst used in a reaction is preferably taken in the powdered form?

17.6 Why is the rate of a reaction often very fast at the beginning of the reaction?

17.7 Magnesium does not react with air at room temperature but it reacts very fast at high temperature giving intense white light. Explain.

17.8 What happens to the reactants after they climb the energy hill during a reaction?

17.9 How does a catalyst lower the activation energy of a reaction?

17.10 Give any two features of the catalytic action of an enzyme.

C Constructed Response Questions

17.1 In what different ways you can increase the successful collisions between the particles of the reactants?

17.2 Give an example of a reaction which proceeds with the gain in mass.

17.3 From where do molecules get energy to attain higher energy state?

17.4 How does the presence of V_2O_5 catalyst lower the activation energy of the following reaction?

$$2\,SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$$

17.6 Explain the catalytic action of an enzyme.

17.7 If you desire to stop a reaction going on at 60 °C, what action you will take?

D Descriptive Questions.

17.1 Explain the effect of surface area on the rate of a reaction.

17.2 Describe the main points of the collision theory of reaction rate.

17.3 Discuss the following factors affecting the rate of a reaction:

(a) Effect of concentrations of the reactants.

(b) Effect of temperature at which a reaction is carried out.

17.4 How does chemical kinetics play an important role in the food industry?

17.5 Write briefly about the role enzymes play in our body as biological catalysts.