Chapter 11 - Rates of reaction

Factors that affect the rate of a reaction

Surface area
Concentration
Temperature
Light
Catalysts

Enzymes

Checklist

Additional questions

Figure 11.1 shows some slow and fast reactions. The two photographs on the left show examples of slow reactions. The ripening of apples takes place over a number of weeks, and the making and maturing of cheese may take months. The burning of solid fuels, such as coal, can be said to involve chemical reactions taking place at a medium speed or rate. The other example shows a fast reaction. The chemicals inside explosives, such as TNT, react very rapidly in reactions which are over in seconds or fractions of seconds.

As new techniques have been developed, the processes used within the chemical industry have become more complex. Therefore, chemists and chemical engineers have increasingly looked for ways to control the rates at which chemical reactions take place. In doing so, they have discovered that there are five main ways in which you can alter the rate of a chemical reaction. These ideas are not only incredibly useful to industry but can also be applied to reactions which occur in the school laboratory.

Figure 11.1 Some slow (ripening fruit and cheese making), medium (coal fire) and fast (explosion) reactions.

Factors that affect the rate of a reaction

- Surface area of the reactants.
- Concentration of the reactants.
- Temperature at which the reaction is carried out.
- Light.
- Use of a catalyst.

Surface area

In Chapter 8, we discussed the use of limestone (calcium carbonate) as a substance which can be used to neutralise soil acidity. Powdered limestone is used as it neutralises the acidity faster than if lumps of lime-stone are used. Why do you think this is the case?

In the laboratory, the reaction between acid and limestone in the form of lumps or powder can be observed in a simple test-tube experiment. Figure 11.2 shows the reaction between dilute hydrochloric acid and limestone in lump and powdered form.

hydrochloric acid + calcium carbonate → calcium chloride + carbon dioxide + water

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

The rates at which the two reactions occur can be found by measuring either:

- the volume of the carbon dioxide gas which is produced, or

- the loss in mass of the reaction mixture with time.

These two methods are generally used for measuring the rate of reaction for processes involving the formation of a gas as one of the products.

Figure 11.2 The powdered limestone (left) reacts faster with the acid than the limestone in the form of lumps.

The apparatus shown in Figure 11.3 is used to measure the loss in mass of the reaction mixture. The mass of the conical flask plus the reaction mixture is measured at regular intervals. The total loss in mass is calculated for each reading of the balance, and this is plotted against time. Some sample results from experiments of this kind have been plotted in Figure 11.4.

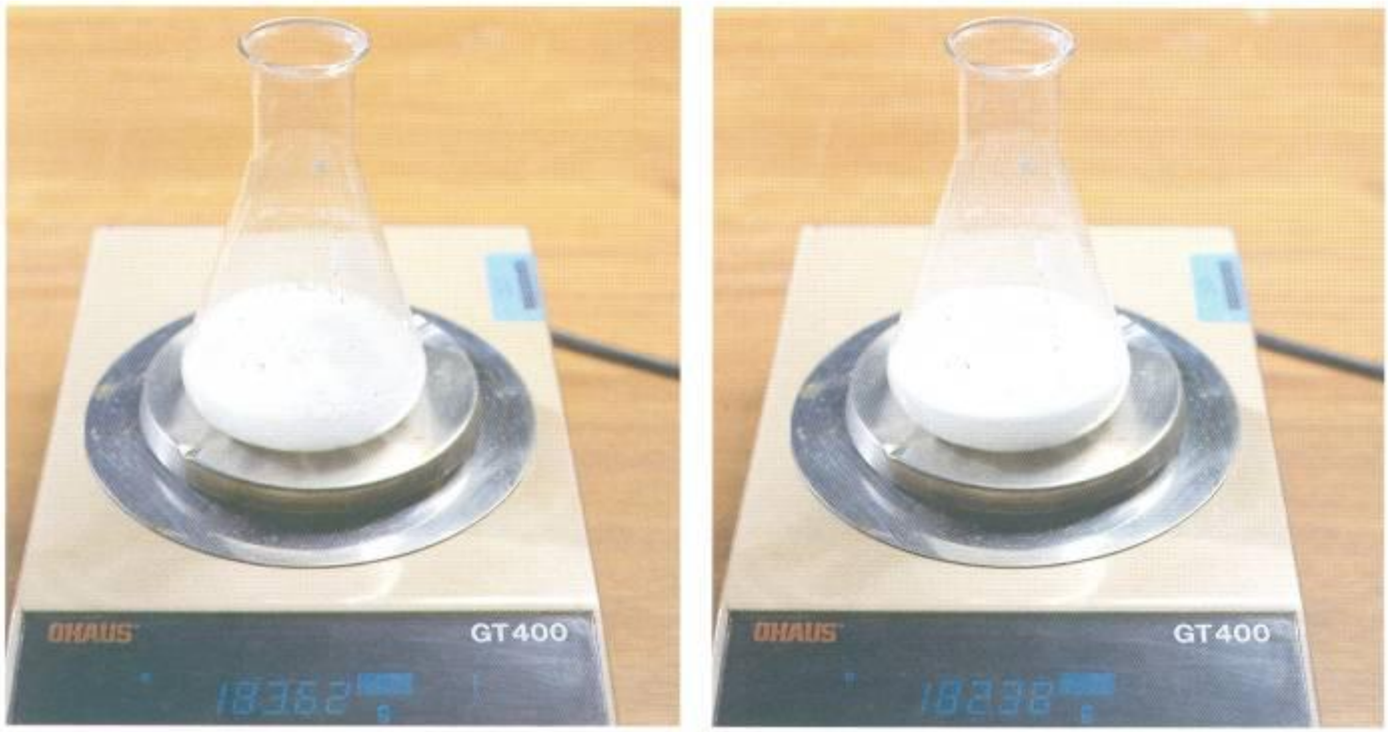


Figure 11.3 After 60 seconds the mass has fallen by 1.24 g.

The reaction is generally at its fastest in the first minute. This is indicated by the slopes of the curves during this time. The steeper the slope, the faster the rate of reaction. You can see from the two traces in Figure 11.4 that the rate of reaction is greater with the powdered limestone than the lump form.

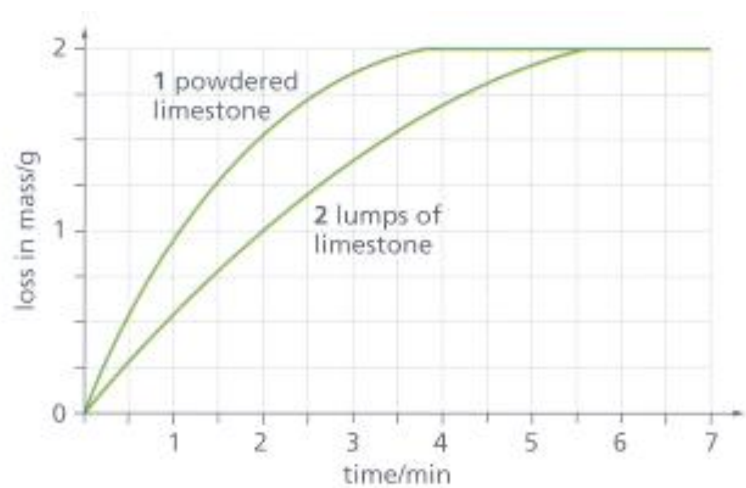


Figure 11.4 Sample results for the limestone/acid experiment.

The surface area has been increased by powdering the limestone (Figure

11.5). The acid particles now have an increased amount of surface of limestone with which to collide. The products of a reaction are formed when collisions occur between reactant particles. Therefore, the increase in surface area of the limestone increases the rate of reaction.

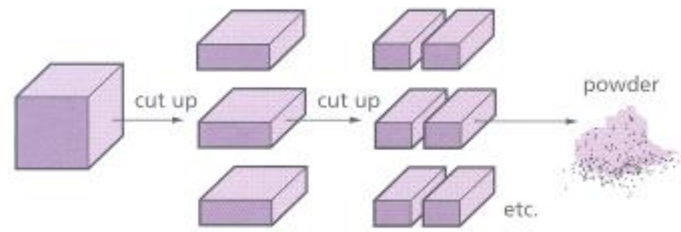


Figure 11.5 A powder has a larger surface area.

Questions

1. What apparatus would you use to measure the rate of reaction of the limestone with dilute hydrochloric acid by measuring the volume of carbon dioxide produced?

2. The following results were obtained from an experiment of the type you were asked to design in question 1.

Time/min	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Total volume of CO_2 gas/cm^3	0	15	24	28	31	33	35	35	35	35	35

a. Plot a graph of the total volume of CO_2 against time.

b. At which point is the rate of reaction fastest?

c. What volume of CO_2 was produced after 1 minute 15 seconds?

d. How long did it take to produce 30 cm^3 of CO_2?

Concentration

A yellow precipitate is produced in the reaction between sodium thiosulphate and hydrochloric acid.

sodium thiosulphate + hydrochloric acid → sodium chloride + sulphur + sulphur dioxide + water

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$$

The rate of this reaction can be followed by recording the time taken for a given amount of sulphur to be precipitated. This can be done by placing a conical flask containing the reaction mixture on to a cross on a piece of paper (Figure 11.6). As the precipitate of sulphur forms, the cross is obscured and finally disappears from view. The time taken for this to occur is a measure of the rate of this reaction. To obtain sufficient information about the effect of changing the concentration of the reactants, several experiments of this type must be carried out, using different concentrations of sodium thiosulphate or hydrochloric acid.

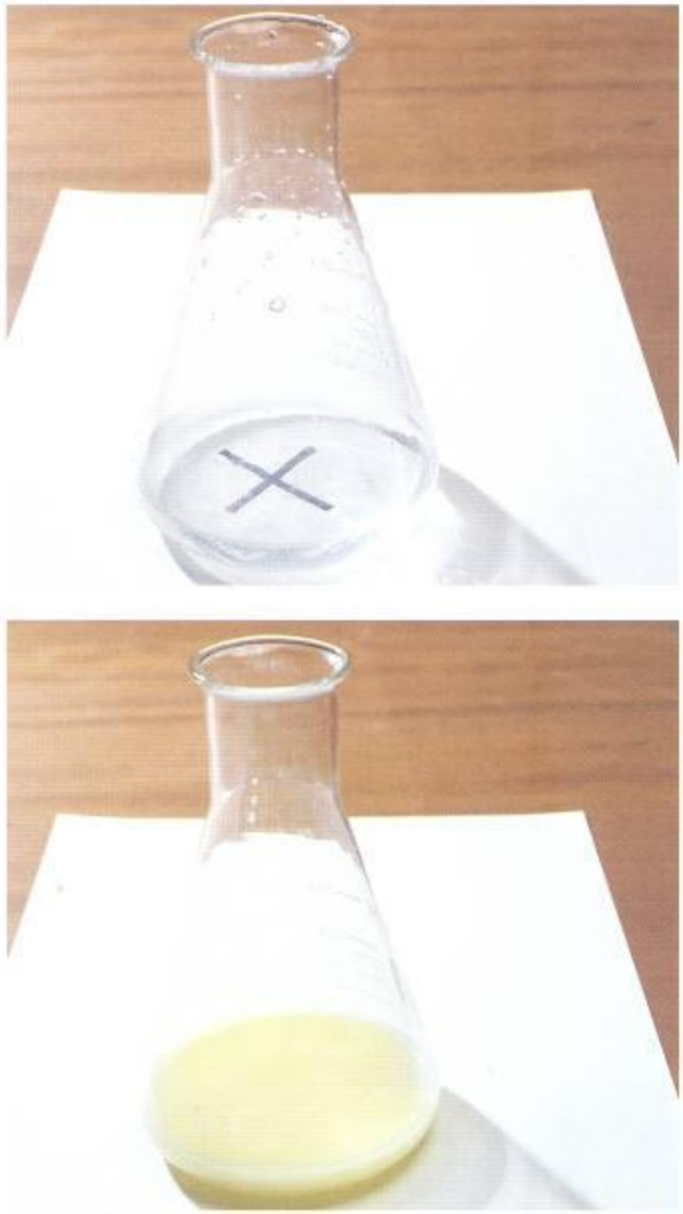


Figure 11.6 The precipitate of sulphur obscures the cross.

Some sample results of experiments of this kind have been plotted in Figure 11.7. You will note from the graph that when the most concentrated sodium thiosulphate solution was used, the reaction was at its fastest. This is shown by the shortest time taken for the cross to be obscured.

As discussed earlier, the products of the reaction are formed as a result of the collisions between reactant particles. There are more particles in a more concentrated solution and collisions occur more often. The more often they collide, the greater the chance they have of reacting. This means that the rate of a chemical reaction will increase if the concentration of reactants is increased.

In reactions involving only gases, for example the Haber process (Chapter 15), an increase in the overall pressure at which the reaction is carried out increases the rate of the reaction. The increase in pressure results in the gas particles being pushed closer together. This means that they collide more often and so react faster.

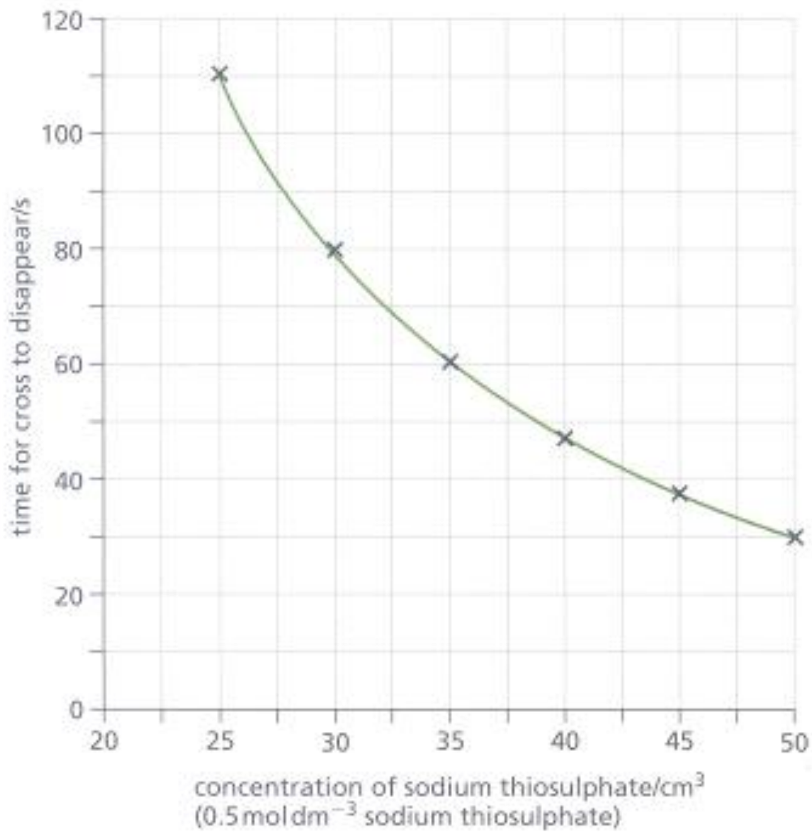


Figure 11.7 Sample data for the sodium thiosulphate/acid experiment at different concentrations of sodium thiosulphate.

Question

1. Devise an experiment to show the effect of changing the concentration of dilute acid on the rate of reaction between magnesium and hydrochloric acid.

Temperature

Why do you think food is stored in a refrigerator? The reason is that the rate of decay is slower at lower temperatures. This is a general feature of the majority of chemical processes.

The reaction between sodium thiosulphate and hydrochloric acid can also be used to study the effect of temperature on the rate of a reaction. Figure 11.8 shows some sample results of experiments with sodium thiosulphate and hydrochloric acid carried out at different temperatures.

You can see from the graph that the rate of the reaction is fastest at high temperatures. When the temperature at which the reaction is carried out is increased, the energy that the particles have also increases – the particles move faster. This increases the number of collisions of sodium thiosulphate and hydrochloric acid particles, and the collisions which occur are more energetic and so more likely to form products. Therefore, if the temperature at which a reaction takes place is increased then the rate of reaction will increase.

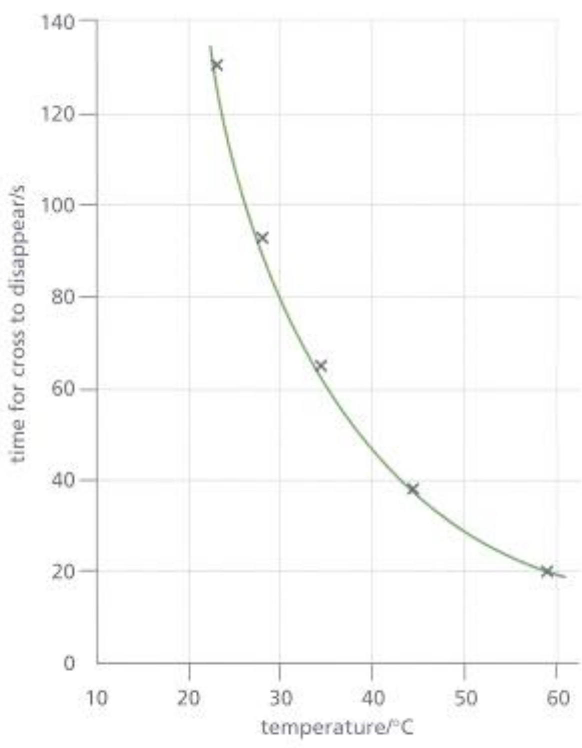


Figure 11.8 Sample data for the sodium thiosulphate/acid experiment at different temperatures.

Questions

1. Explain why potatoes cooked in oil cook faster than those cooked in water.

2. Devise an experiment to study the effect of temperature on the reaction between magnesium and hydrochloric acid.

3. Explain why food cooks faster in a pressure cooker.

Light

Some chemical reactions are affected by light. Photosynthesis is a very important reaction (Chapter 8) which occurs only when sunlight falls on leaves containing the green pigment chlorophyll. Another chemical reaction which takes place only when exposed to light is that which occurs when you take a photograph. Photographic film is a transparent plastic strip coated with emulsion: a layer of gelatin throughout which are spread many millions of tiny crystals of silver halides, in particular silver bromide (AgBr). The emulsion used is similar for both black-and-white and colour film. In the case of colour film there are three layers of emulsion with each layer of emulsion containing a different dye.

When light hits a silver bromide crystal, silver cations (Ag^+) accept an electron from the bromide ions (Br^-) and silver atoms are produced.

$$\text{silver ion} + \text{electron} \rightarrow \text{silver atom}$$

$$Ag^+ + e^- \rightarrow Ag$$

The bromine atom produced in the process is trapped in the gelatin. The more light that falls on the photo-graphic film the greater the amount of silver deposited.

Question

1. Devise an experiment to show how sunlight affects the rate of formation

of silver from the silver salts, silver chloride and silver bromide.

Catalysts

Over 90% of industrial processes use **catalysts**. A catalyst is a substance which can alter the rate of a reaction without being chemically changed itself In the laboratory, the effect of a catalyst can be observed using the decomposition of hydrogen peroxide as an example.

$$\text{hydrogen peroxide} \rightarrow \text{water} + \text{oxygen}$$

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The rate of decomposition at room temperature is very slow. There are substances, however, which will speed up this reaction, one being manganese (IV) oxide. When black manganese (IV) oxide powder is added to hydrogen peroxide solution, oxygen is produced rapidly. The rate at which this occurs can be followed by measuring the volume of oxygen gas produced with time.

Some sample results from experiments of this type have been plotted in Figure 11.9. At the end of the reaction, the manganese (IV) oxide can be filtered off and used again. The reaction can proceed even faster by increasing the amount and surface area of the catalyst. This is because the activity of a catalyst involves its surface. Note that, in gaseous reactions, if dirt or impurities are present on the surface of the catalyst, it will not act as efficiently; it is said to have been 'poisoned'. Therefore, the gaseous reactants must be pure.

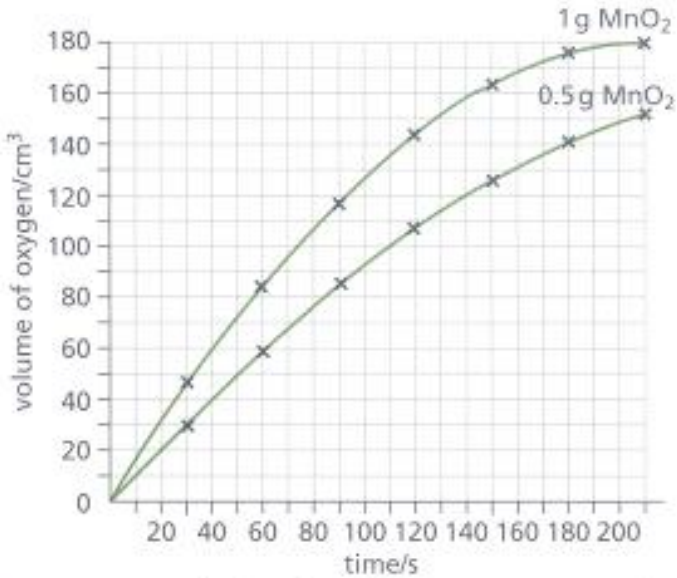


Figure 11.9 Sample data for differing amounts of MnO_2 catalyst.

Chemists have found that:

- a small amount of catalyst will produce a large amount of chemical change
- catalysts remain unchanged chemically after a reaction has taken place, but they can change physically. For example, a finer manganese(IV) oxide powder is left behind after the decomposition of hydrogen peroxide
- catalysts are very specific to a particular chemical reaction.

Some examples of chemical processes and the catalysts used are shown in Table 11.1.

Table 11.1 Examples of catalysts.

Process	**Catalyst**
Haber process – for the manufacture of ammonia	Iron
Contact process – for the manufacture of sulphuric acid	Vanadium (v) oxide

Oxidation of ammonia to give nitric acid	Platinum
Fermentation of sugars to produce alcohol	Enzymes (in yeast)
Hydrogenation of unsaturated oils to form fats in the manufacture of margarines	Nickel

A catalyst increases the rate by providing an alternative reaction path with a lower **activation energy**. The activation energy is the energy barrier which reactants must overcome, when their particles collide, to react successfully and form products (Figure 11.10).

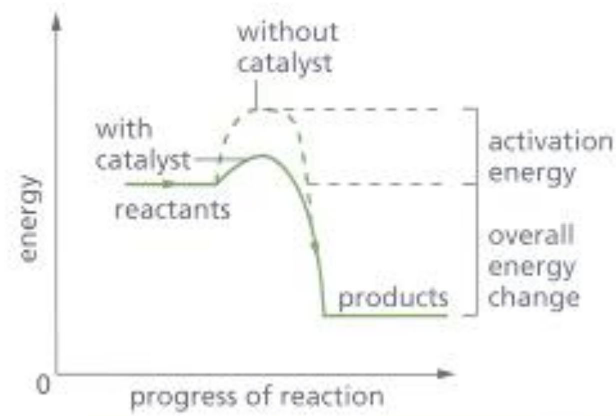


Figure 11.10 Energy level diagram showing activation energy.

Catalytic converters

In the previous chapter you saw that European regulations state that all new cars have to be fitted with catalytic converters as part of their exhaust system (Figure 11.11). Car exhaust fumes contain pollutant gases such as carbon monoxide (CO) and nitrogen (II) oxide (NO). The following reactions proceed of their own accord but very slowly under the conditions inside an exhaust.

carbon monoxide + oxygen → carbon dioxide

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

nitrogen (II) oxide + carbon monoxide → nitrogen + carbon dioxide

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$$

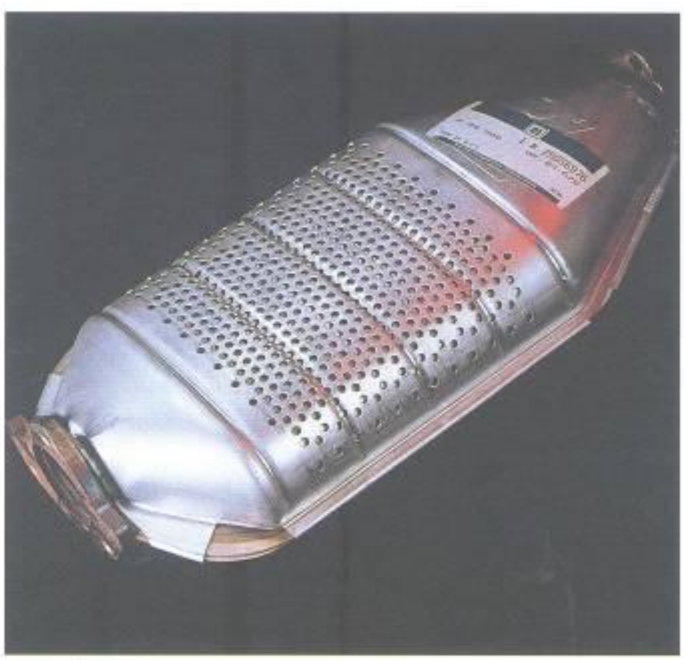
The catalyst in the converter speeds up these reactions considerably. In these reactions, the pollutants are converted to carbon dioxide and nitrogen, which are naturally present in the air. It should be noted, however, that the catalytic converter can only be used with unleaded petrol and that, due to impurities being deposited on the surface of the catalyst, it becomes poisoned and has to be replaced every five or six years.

Questions

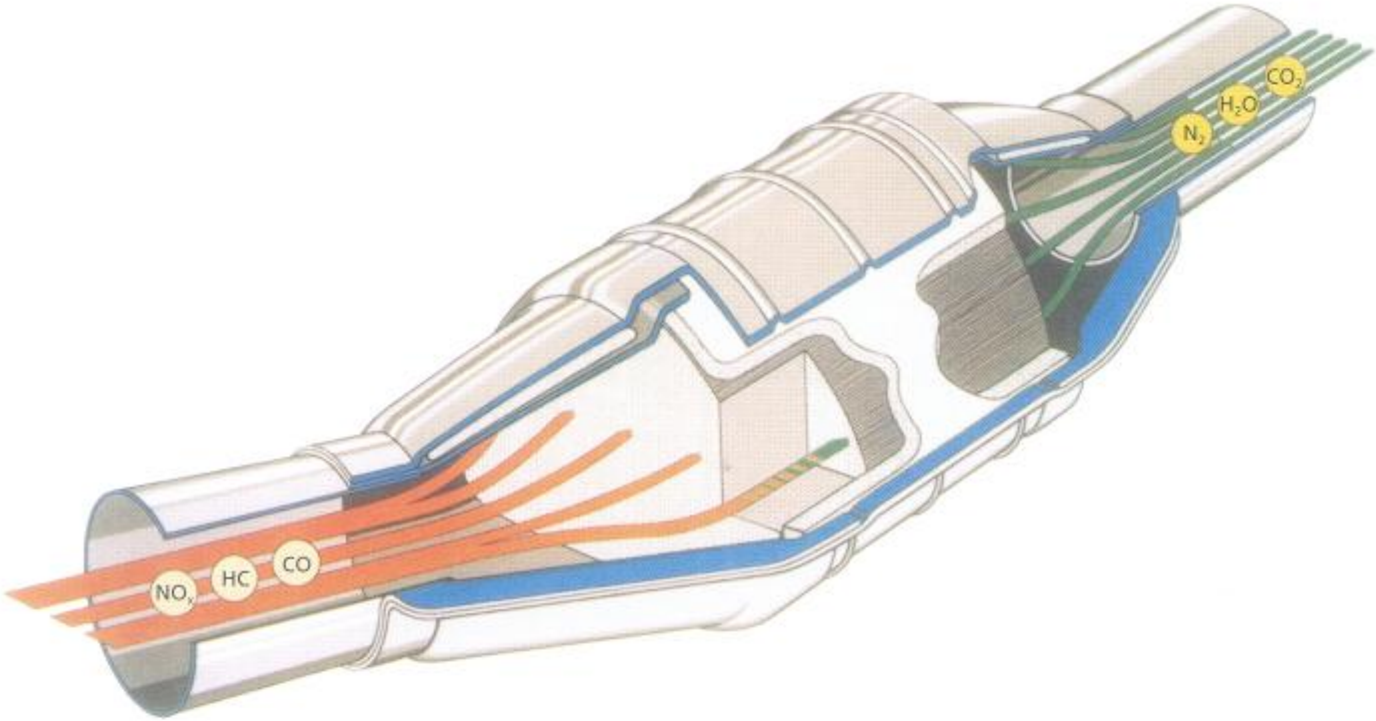
1. Using a catalysed reaction of your choice, devise an experiment to follow the progress of the reaction and determine how effective the catalyst is.

2. Why do some people consider catalytic converters not to be as environmentally friendly as suggested in their advertising material?

3. Unreacted hydrocarbons such as octane, C_8H_{18} (from petrol), also form part of the exhaust gases. These gases are oxidised in the converter to carbon dioxide and water vapour. Write an equation for the oxidation of octane.



a Catalytic converter.



b A section through a catalytic converter.

Figure 11.11

Enzymes

Enzymes are protein molecules produced in living cells. These substances are used by living organisms as catalysts to speed up hundreds of different chemical reactions going on inside them. These biological catalysts are very specific in that each chemical reaction taking place has a different enzyme catalyst. You can imagine, therefore, that there are literally hundreds of different kinds of enzyme. For example, hydrogen peroxide is a substance naturally produced within our bodies (a natural metabolic product). However, it is extremely damaging and must be decomposed very rapidly. Catalase is the enzyme which converts hydrogen peroxide into harmless water and oxygen within our livers:

$$\text{hydrogen peroxide} \xrightarrow{\text{catalase}} \text{water + oxygen}$$

$$2H_2O_2(aq) \xrightarrow{\text{catalase}} 2H_2O(l) + O_2(g)$$

Although many chemical catalysts can work under various conditions of temperature and pressure as well as alkalinity or acidity, biological catalysts operate only under very particular conditions. For example, they operate over a very narrow temperature range and if the temperature becomes too high, they become inoperative. At temperatures above about 45 °C, they denature. This means that the specific shape of the active site of the enzyme molecule changes due to the breaking of bonds. This means that the reactant molecules are no longer able to fit into the active site (Figure 11.12).

Figure 11.12 A computer simulation of an enzyme active site. The enzyme molecules (red, pink, green and blue) have an active site that locks on exactly to a particular reactant (yellow). Once locked on, they can work to break up the pieces of the molecules.

A huge multimillion-pound industry has grown up around the use of enzymes to produce new materials. Biological washing powders (Figure 11.13) contain enzymes to break down stains such as sweat, blood and egg, and they do this at the relatively low temperature of 40°C. This reduces energy costs, because the washing water does not need to be heated as much.

Figure 11.13 These biological washing powders contain enzymes.

There were problems associated with the early biological washing powders. Some customers suffered from skin rashes, because they were allergic to the enzymes (Figure 11.14). This problem has been overcome to a certain extent by advising that extra rinsing is required. Also, many manufacturers have placed warnings on their packets, indicating that the powder contains enzymes which may cause skin rashes.

Figure 11.14 An allergic reaction to a biological detergent.

Other industrial processes make use of enzymes.

- In the manufacture of baby foods, enzymes called proteases are used to 'pre-digest' the protein part of the baby food.

- The enzyme isomerase is used to convert glucose syrup to fructose syrup. Fructose syrup is much sweeter than glucose syrup and can be used as a sweetener in slimming foods as less is needed.

- In the production of yoghurt, milk is initially heated to 90 °C for 15-30 minutes to kill any bacteria in the milk. After cooling to 40 °C, a starter culture of Lactobacillus bacteria is added and the mixture incubated at 40 °C for eight hours (Figure 11.15). The bacteria ferment the lactose in the milk to lactic acid, which causes the milk protein to become solid.

Figure 11.15 Yoghurt is incubated in these tanks, and allowed to mature.

- In cheese making, milk is initially heated to kill bacteria and then cooled. A starter culture of Streptococcus bacteria is then added, which coagulates the milk into curds and whey (Figure 11.16). The curds are put into steel or wooden drums and pressed and allowed to dry.

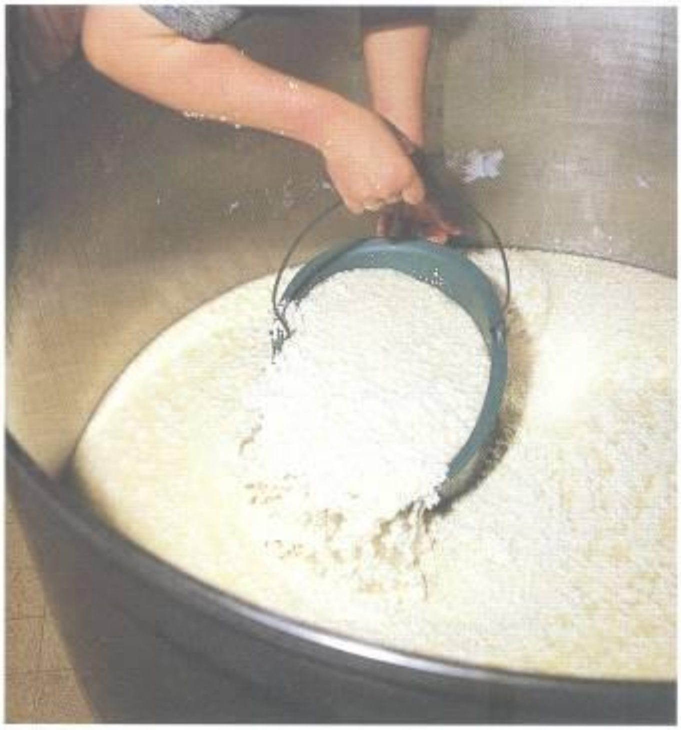


Figure 11.16 Cheese is separated into curds and whey by the addition of bacteria. The liquid, whey, is separated from the curds which are then pressed.

In industry, enzymes are used to bring about reactions at normal temperatures and pressures that would other-wise require expensive conditions and equipment. Successful processes using enzymes need to ensure that:

- the enzyme is able to function for long periods of time by optimising the environment
- the enzyme is not lost by trapping it on the surface of an inert solid
- continuous processes occur rather than batch processes.

Questions

1. When using biological washing powders what factors have to be taken into consideration?

2. Enzymes in yeast are used in the fermentation of glucose. Why, when the temperature is raised to 45°C, is very little ethanol actually produced compared with the amount formed at room temperature?

Checklist

After studying Chapter 11 you should know and understand the following terms.

Activation energy The excess energy that a reaction must acquire to permit the reaction to occur.

Catalyst A substance which alters the rate of a chemical reaction without itself being chemically changed.

Catalytic converter A device for converting dangerous exhaust gases from cars into less harmful emissions. For example, carbon monoxide gas is converted to carbon dioxide gas.

Enzymes Protein molecules produced in living cells. They act as biological catalysts and are specific to certain reactions. They operate only within narrow temperature and pH ranges.

Reaction rate A measure of the change which happens during a reaction in a single unit of time. It may be affected by the following factors:

- surface area of the reactants
- concentration of the reactants
- the temperature at which the reaction is carried out
- light
- use of a catalyst.

Rates of reaction

Additional questions

1. Explain the following statements.

a. A car exhaust pipe will rust much faster if the car is in constant use.

b. Carrots cook faster when they are chopped up.

c. Industrial processes become more economically viable if a catalyst can be found for the reactions involved.

d. In fireworks it is usual for the ingredients to be powdered.

e. Tomatoes ripen faster in a greenhouse.

f. The reaction between zinc and dilute hydrochloric acid is slower than the reaction between zinc and concentrated hydrochloric acid.

2. A student performed two experiments to establish how effective manganese (IV) oxide was as a catalyst for the decomposition of hydrogen peroxide. The results below were obtained by carrying out these experiments with two different quantities of manganese (IV) oxide. The volume of the gas produced was recorded against time.

Time/s	0	30	60	90	120	150	180	210
Volume for 0.3 g/cm^3	0	29	55	79	98	118	133	146
Volume for 0.5 g/cm^3	0	45	84	118	145	162	174	182

a. Draw a diagram of the apparatus you could use to carry out these experiments.

b. Plot a graph of the results.

c. Is the manganese (IV) oxide acting as a catalyst in this reaction? Explain your answer.

d. (i) At which stage does the reaction proceed most quickly?

(ii) How can you tell this from your graph?

(iii) In terms of particles, explain why the reaction is quickest at the point you have chosen in (i).

e. Why does the slope of the graph become less steep as the reaction proceeds?

f. What volume of gas has been produced when using 0.3 g of manganese (IV) oxide after 50 s?

g. How long did it take for 60 cm^3 of gas to be produced when the experiment was carried out using 0.5 g of the manganese (IV) oxide?

h. Write a balanced chemical equation for the decomposition of hydrogen peroxide.

3. a Which of the following reaction mixtures will produce hydrogen more quickly at room temperature:

(i) zinc granules + dilute nitric acid?
(ii) zinc powder + dilute nitric acid?

b. Give an explanation of your answer to a.

c. Suggest two other methods by which the speed of this reaction can be altered.

4. A flask containing dilute hydrochloric acid was placed on a digital balance. An excess of limestone chippings was added to this acid, a plug of cotton wool was placed in the neck of the flask and the initial mass was recorded. The mass of the apparatus was recorded every two minutes. At the end of the experiment the loss in mass of the apparatus was calculated and the following results were obtained.

Time/min	0	2	4	6	8	10	12	14	16
Loss in mass/g	0	2.1	3.0	3.1	3.6	3.8	4.0	4.0	4.0

a. Plot the results of the experiment.

b. Which of the results would appear to be incorrect? Explain your answer.

c. Write a balanced chemical equation to represent the reaction taking place.

d. Why did the mass of the flask and its contents decrease?

e. Why was the plug of cotton wool used?

f. How does the rate of reaction change during this reaction? Explain this using particle theory.

g. How long did the reaction last?

h. How long did it take for half of the reaction to occur?

5. a. What is a catalyst?

b. List the properties of catalysts.

c. Name the catalyst used in the following processes:

(i) the Contact process
(ii) the Haber process
(iii) the hydrogenation of unsaturated fats.

d. Which series of metallic elements, in the periodic table, do the catalysts you have named in c belong to?

e. What are the conditions used in the industrial processes named in c? The following references will help you: Chapters 12, 14 and 15.

6. This question concerns the reaction of copper(ii) carbonate with dilute hydrochloric acid. The equation for the reaction is:

$$CuCO_3(s) + 2HCl(aq) \rightarrow CuCl_2(aq) + CO_2(aq) + H_2O(l)$$

a. Sketch a graph to show the rate of production of carbon dioxide when an excess of dilute hydrochloric acid is added. The reaction lasts 40 s and produces 60 cm^3 of gas.

b. Find on your graph the part which shows:

(i) where the reaction is at its fastest
(ii) when the reaction has stopped.

c. Calculate the mass of copper (II) carbonate used to produce 60 cm^3 of carbon dioxide. (A_r: C = 12; O = 16; Cu = 63.5. One mole of a gas occupies 24 dm^3 at room temperature and pressure (rtp).)

d. Sketch a further graph using the same axes to show what happens to the rate at which the gas is produced if:

(i) the concentration of the acid is decreased
(ii) the temperature is increased.

7. European regulations state that all new cars have to be fitted with catalytic converters as part of their exhaust system.

a. Why are these regulations necessary?

b. Which gases are removed by catalytic converters?

c. Which metals are often used as catalysts in catalytic converters?

d. What does the term 'poisoned' mean with respect to catalysts?

e. The latest converters will also remove unburnt petrol An equation for this type of reaction is:

$$2C_7H_{14}(g) + 21O_2(g) \rightarrow 14CO_2(g) + 14H_2O(g)$$

(i) Calculate the mass of carbon dioxide produced by 1.96 g of unburnt fuel.

(ii) Convert this mass of carbon dioxide into a volume measured at rtp.

(iii) If the average car produces 7.84 g of unburnt fuel a day, calculate the volume of carbon dioxide produced by the catalytic converter measured at rtp. (A_r: H = 1; C = 12; O = 16. One mole of any gas occupies 24 dm^3 at rtp.)

8a. Give examples of chemical reactions which happen:

(i) very slowly
(ii) at a moderate rate
(iii) very quickly.

b. How could you speed up the reaction named in a (i)?

c. How could you slow down the reaction named in a (ii)?