

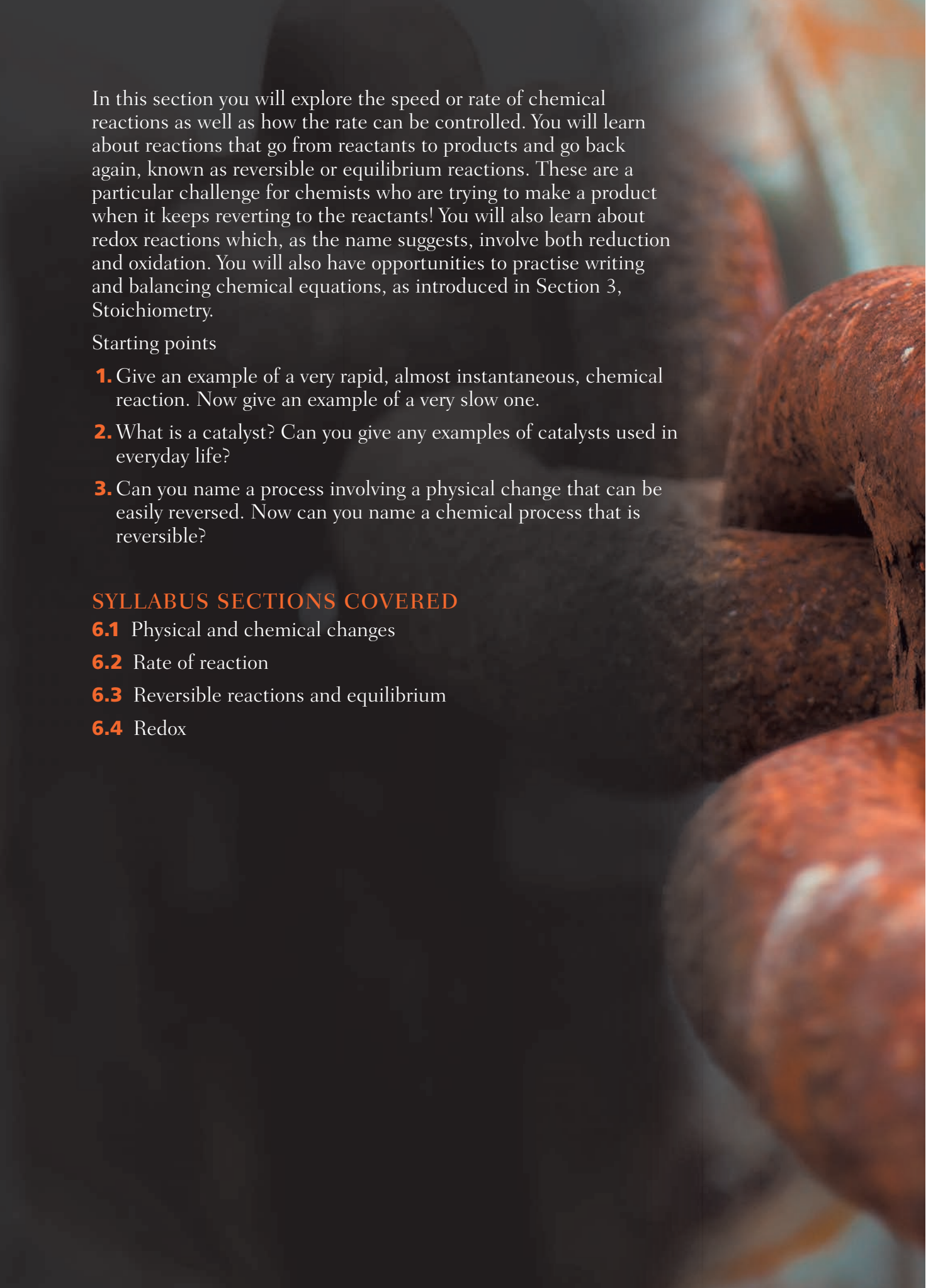
Collins

Cambridge IGCSE™

Chemistry

STUDENT'S BOOK

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In this section you will explore the speed or rate of chemical reactions as well as how the rate can be controlled. You will learn about reactions that go from reactants to products and go back again, known as reversible or equilibrium reactions. These are a particular challenge for chemists who are trying to make a product when it keeps reverting to the reactants! You will also learn about redox reactions which, as the name suggests, involve both reduction and oxidation. You will also have opportunities to practise writing and balancing chemical equations, as introduced in Section 3, Stoichiometry.

Starting points

- 1.** Give an example of a very rapid, almost instantaneous, chemical reaction. Now give an example of a very slow one.
- 2.** What is a catalyst? Can you give any examples of catalysts used in everyday life?
- 3.** Can you name a process involving a physical change that can be easily reversed. Now can you name a chemical process that is reversible?

SYLLABUS SECTIONS COVERED

- 6.1** Physical and chemical changes
- 6.2** Rate of reaction
- 6.3** Reversible reactions and equilibrium
- 6.4** Redox

6

Chemical reactions

Δ Rusting is a very slow reaction.



Δ Fig. 6.1 Petrol igniting.

Rate of reaction

INTRODUCTION

Some chemical reactions take place extremely quickly. For example, when petrol is ignited it combines with oxygen almost instantaneously. Reactions like these have a *high rate*. Other reactions are much slower, for example when an iron bar rusts in the air; reactions like these have a *low rate*.

Chemical reactions can be controlled and made to be quicker or slower. This can be very important in situations like food production, either by slowing down or increasing the rate at which food ripens, or

in the chemical industry, where the rate of a reaction can be adjusted to an optimum level.

KNOWLEDGE CHECK

- ✓ The particles in the three states of matter (solid, liquid and gas) have different arrangements, movement and energy.
- ✓ The course of a reaction can be shown in a reaction pathway diagram.
- ✓ Balanced chemical equations are used to describe reactions.

LEARNING OBJECTIVES

- ✓ Identify physical and chemical changes, and describe the differences between them.
- ✓ Describe the effect on the rate of reaction of changing: the concentration of solutions, the pressure of gases, the surface area of solids, the temperature, and adding or removing a catalyst including enzymes.
- ✓ State that a catalyst increases the rate of a reaction and is unchanged at the end of a reaction.
- ✓ Describe practical methods for investigating the rate of a reaction including change in mass of a reactant or a product and the formation of a gas.
- ✓ Interpret data, including graphs, from rate of reaction experiments.
- ✓ **SUPPLEMENT** Describe collision theory in terms of: number of particles per unit volume; frequency of collisions between particles; kinetic energy of particles; activation energy, E_a .
- ✓ **SUPPLEMENT** Describe and explain the effect on the rate of reaction of changing: the concentration of solutions, the pressure of gases, the surface area of solids, the temperature, and adding or removing a catalyst including enzymes, using collision theory.
- ✓ **SUPPLEMENT** State that a catalyst decreases the activation energy, E_a , of a reaction.
- ✓ **SUPPLEMENT** Evaluate practical methods for investigating the rate of a reaction including change in mass of a reactant or a product and the formation of a gas.

PHYSICAL AND CHEMICAL CHANGES

A chemical change, or chemical reaction, is quite different from physical changes that occur, for example, when sugar dissolves in water.

In a chemical change, one or more new substances are produced. In many cases an observable change is apparent, for example, the colour changes or a gas is produced.

An apparent change in mass can occur. This change is often quite small and difficult to detect unless accurate balances are used. Mass is conserved in *all* chemical reactions – the apparent change in mass usually occurs because one of the reactants or products is a gas (whose mass may not have been measured).

An energy change is almost always involved. In most cases energy is released and the surroundings become warmer. In some cases energy is absorbed from the surroundings, and so the surroundings become colder. Note: Some physical changes, such as evaporation, also have energy changes.

RATE OF REACTION

A quick reaction takes place in a short time. It has a high **rate of reaction**. As the time taken for a reaction to be completed increases, the rate of the reaction decreases. In other words:

Speed	Rate	Completion time
Quick or fast	High	Short
Slow	Low	Long

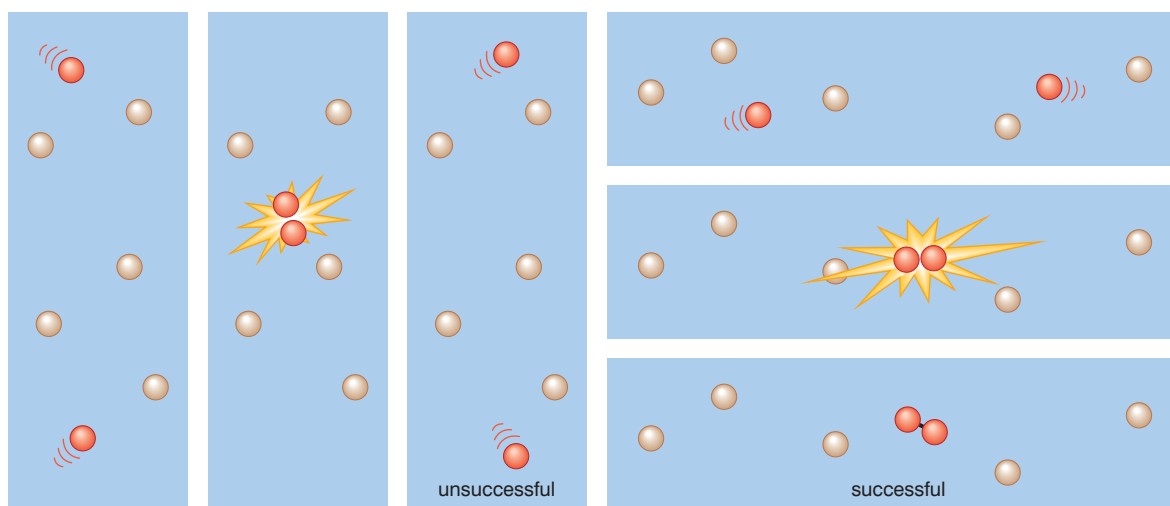
Δ Table 6.1 Speed, rate and time.

SUPPLEMENT

Collision theory

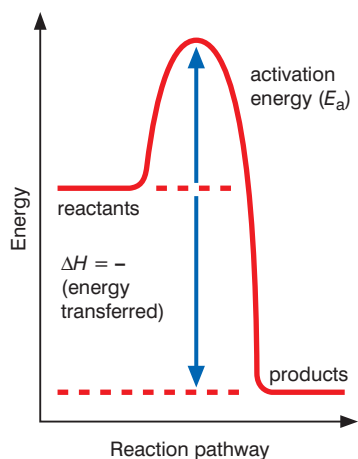
For a chemical reaction to occur, the reacting particles (atoms, molecules or ions) must collide. The energy involved in the collision must be enough to break the chemical bonds in the reacting particles – or the particles will just bounce off one another. The more particles there are in a particular volume, the greater the frequency of collisions. Similarly the greater the kinetic energy of the particles, the greater the frequency of collisions.

A collision that has enough energy to result in a chemical reaction is an **effective collision**.



Δ Fig. 6.2 Particles must collide with sufficient energy to make an effective collision.

Some chemical reactions occur extremely quickly (for example, the explosive reaction between petrol and oxygen in a car engine) and some more slowly (for example, iron rusts over days or weeks). This is because they have different **activation energies**. Activation energy acts as a barrier to a reaction. It is the minimum amount of energy required in a collision for a reaction to occur. As a general rule, the bigger the activation energy, the slower the reaction will be at a particular temperature.



Δ Fig. 6.3 Reaction pathway diagram.

REMEMBER

The 'barrier' preventing a reaction from occurring is called the activation energy. If the activation energy of a reaction is low, more of the collisions will be effective and the reaction will proceed quickly. If the activation energy is high, a smaller proportion of collisions will be effective and the reaction will be slower.

QUESTIONS

1. State the main difference between a physical change and a chemical change.
2. In a chemical change there is often an apparent change in mass even though mass cannot be created or destroyed in a chemical reaction. Suggest a possible cause of this apparent change in mass.
3. **SUPPLEMENT** In the collision theory, state what two things must happen for two particles to react.
4. **SUPPLEMENT** Define an *effective* collision.
5. **SUPPLEMENT** Describe, using a diagram, what is meant by the term *activation energy*.

Monitoring the rate of a reaction

The rate of a reaction changes as the reaction proceeds. There are some easy ways of monitoring this change.

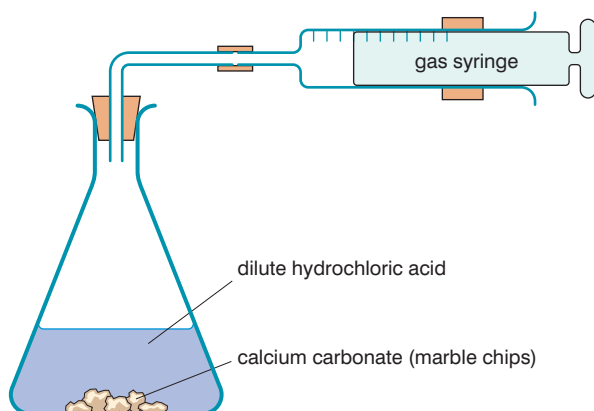
When marble (calcium carbonate) reacts with hydrochloric acid, the following reaction starts straight away:

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



The reaction can be monitored as it proceeds either by measuring the volume of gas being formed or by measuring the change in mass of the reaction flask.

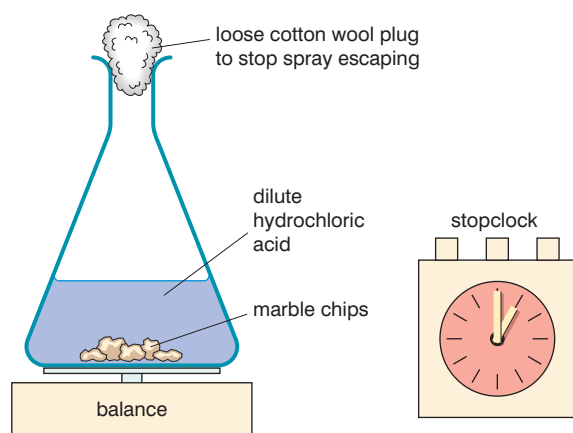
The volume of gas produced in this reaction can be measured using the apparatus shown in Fig. 6.4. The hydrochloric acid is put into the conical flask, the marble chips are added, the stopper is quickly fixed into the neck of the flask and the stopclock is started.



Δ Fig. 6.4 Monitoring the rate of a reaction.

The reaction will start immediately, effervescence (bubbling) will occur in the flask as the carbon dioxide gas is produced and the plunger on the syringe will start to move. Measuring the volume of gas in the syringe every 10 seconds will indicate how the total amount of gas produced changes as the reaction proceeds. The change in the rate of the reaction with time can be shown on a graph of the results (see Fig. 6.6).

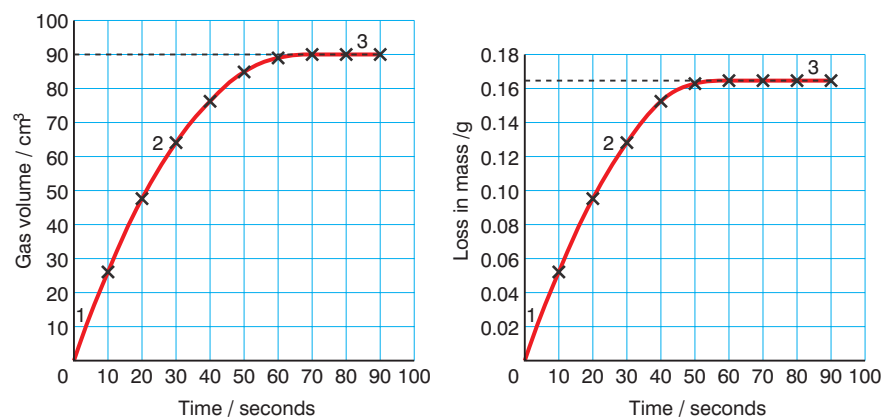
To measure the change in mass in the same reaction, the apparatus shown in Fig. 6.5 can be used. The hydrochloric acid is put into the conical flask, the marble chips are added, the cotton wool plug is put in the neck of the flask and the stopclock is started. The mass of the flask and contents is measured as soon as the plug is inserted and then every 10 seconds as the reaction occurs. The mass will decrease as carbon dioxide gas escapes from the flask.



Δ Fig. 6.5 Measuring the change in mass.

Drawing a graph of the results shows the change in the rate of the reaction over time.

Graphs of the results from both experiments have almost identical shapes. The rate of the reaction decreases as the reaction proceeds.



Δ Fig. 6.6 Volume of carbon dioxide produced or loss in mass.

Loss in mass during the reaction

The rate of the reaction at any point can be calculated from the gradient of the curve. The shapes of the graphs can be divided into three regions.

1. At this point, the curve is the steepest (has the highest gradient) and the reaction has its highest rate. The maximum number of reacting particles are present and the number of effective collisions per second is at its greatest.
2. The curve is not as steep (has a lower gradient) at this point and the rate of the reaction is lower. Fewer reacting particles are present and so the number of effective collisions per second is less.
3. The curve is horizontal (gradient is zero) and the reaction is complete. At least one of the reactants has been completely used up and so no further collisions can occur between the two reactants.

REMEMBER

In experiments like these it is helpful to have a good understanding of the types of **variables** involved. The factor you are investigating is called the **independent variable** – when investigating how the reaction between marble and hydrochloric acid changes over time, time is the independent variable. A **dependent variable** is changed by the independent variable – in the marble and hydrochloric acid reaction, the volume of carbon dioxide produced is the dependent variable. Other variables involved are **control variables** and are not allowed to change to ensure a ‘fair test’. So temperature could be a control variable in the reaction between marble and hydrochloric acid.

In chemical reactions it is very rare that exact (as predicted by the equation) quantities of reactants are used. In the marble and hydrochloric acid reaction all the marble may be used up (it is called the *limiting reactant*) but not all the hydrochloric acid; some is left when the reaction has stopped (it is *in excess*).

QUESTIONS

1. State what piece of apparatus can accurately measure the volume of gas produced in a reaction.
2. On a volume versus time graph, explain what a horizontal line shows.
3. When comparing two reactions, will the slower or quicker reaction have a steeper volume/time gradient at the beginning?

What can change the rate of a reaction?

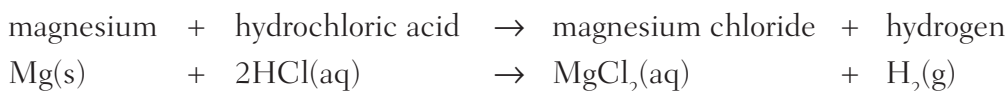
There are five key factors that can change the rate of a reaction:

- concentration (of a solution)
- pressure (of a gas)

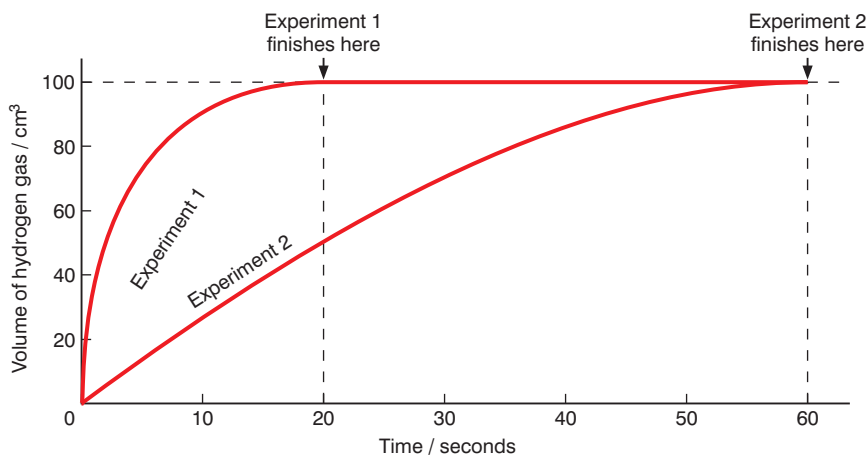
- temperature
- surface area/particle size (of a solid)
- a catalyst (including enzymes)

Concentration

Increasing the concentration of a reactant will increase the rate of reaction. When a piece of magnesium ribbon is added to a solution of hydrochloric acid, the following reaction occurs:



As the magnesium and acid come into contact, there is effervescence ('bubbling') and hydrogen gas is given off. Two experiments were performed using the same length of magnesium ribbon, but different concentrations of acid. In experiment 1 the hydrochloric acid used was 2.0 mol/dm^3 , in experiment 2 the acid was 0.5 mol/dm^3 . The graph in Fig. 6.7 shows the results of the two experiments.

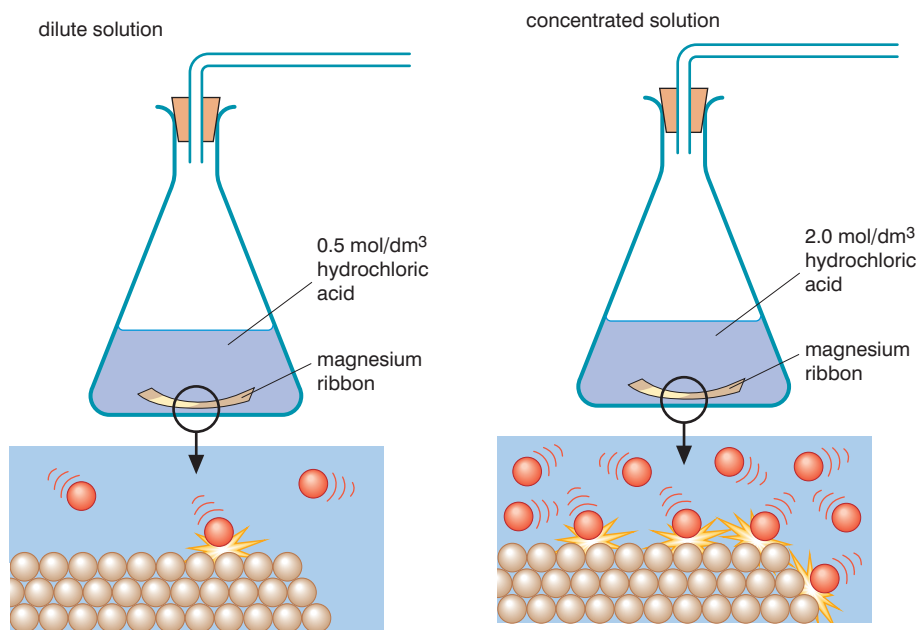


Δ Fig. 6.7 Volume of hydrogen produced in the reaction between magnesium and hydrochloric acid.

In experiment 1 the curve is steeper (has a higher gradient) than in experiment 2. In experiment 1 the reaction is complete after 20 seconds, whereas in experiment 2 it takes 60 seconds. The initial rate of the reaction is higher with 2.0 mol/dm^3 hydrochloric acid than with 0.5 mol/dm^3 hydrochloric acid.

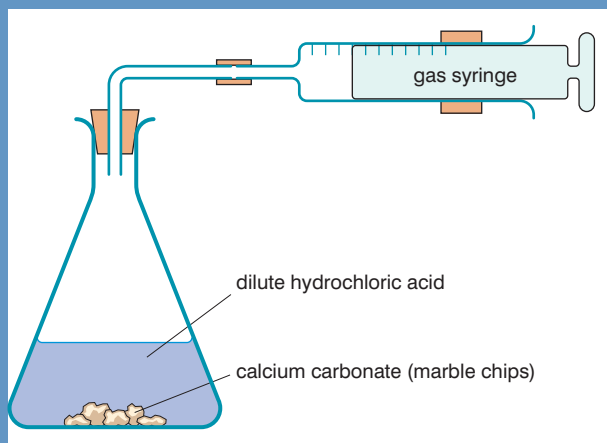
SUPPLEMENT

In the 2.0 mol/dm^3 hydrochloric acid solution there are more hydrogen ions in a given volume, a higher concentration of hydrogen ions, and so there will be a lot more effective collisions per second with the surface of the magnesium ribbon than in the 0.5 mol/dm^3 hydrochloric acid.



Δ Fig. 6.8 Using dilute and concentrated solutions in a reaction.

Developing practical skills



Δ Fig. 6.9 Experiment with hydrochloric acid and calcium carbonate. Safety note: Eye protection should be worn and great care taken in supporting and using the gas syringe, especially if the plunger may be pushed out completely.

Two students were investigating how the concentration of hydrochloric acid affects the rate of its reaction with calcium carbonate (marble chips). The reaction produces carbon dioxide gas and the time it takes to produce a certain volume of gas can be used as a measure of the rate of the reaction. They set up the apparatus shown in the diagram.

They placed 40 cm^3 of 0.2 mol/dm^3 hydrochloric acid in the conical flask and added 10 cm^3 of distilled water. One student then carefully weighed 5 g of calcium carbonate (an excess) into a small beaker and then added the calcium carbonate to the flask. As soon as the marble

chips were added the other student attached the delivery tube to the gas syringe and started the stop-watch. They then measured the time it took for 40 cm³ of gas to be produced. They repeated the process using the quantities of hydrochloric acid and water shown in the table. The results are shown in the table.

Volume of hydrochloric acid (cm ³)	40	35	30	25	20
Volume of water (cm ³)	10	15	20	25	30
Time taken for 40 cm ³ of gas to be produced (s)	14	18	23	36	67

Using and organising techniques apparatus, and materials

1. Explain why the total volume in the flask was always 50 cm³.
2. Suggest the name of the apparatus you would use to measure the volumes of hydrochloric acid and water.

Interpreting observations and data

3. Draw a graph of volume of hydrochloric acid against time taken to produce 40 cm³ of gas. Draw a smooth curve through the points.
4. Explain what the shape of the curve tells you about the effect of changing the concentration of hydrochloric acid on the rate of the reaction.
5. Use the results to predict what the time would have been if 22 cm³ of hydrochloric acid and 28 cm³ water had been used.

Evaluating methods

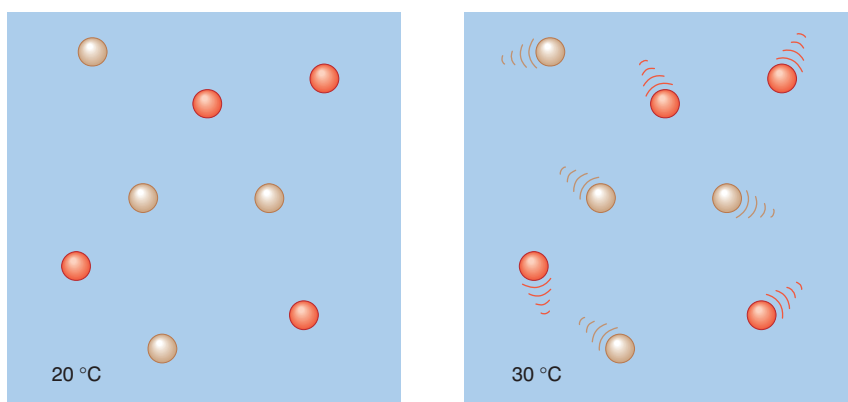
6. Evaluate the main sources of error in the design of this experiment.

Temperature

Increasing the temperature of the reactants will increase the rate of a reaction.

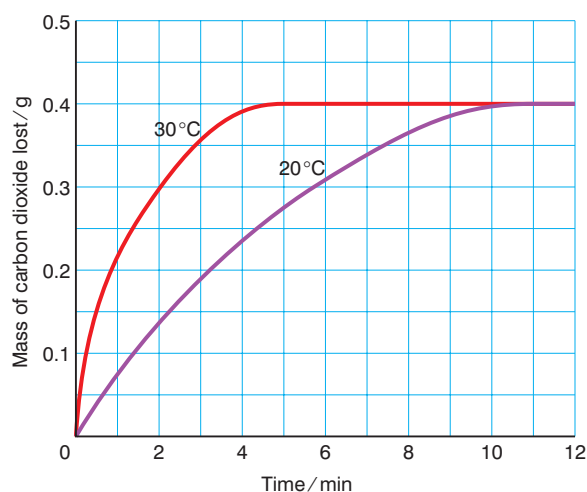
SUPPLEMENT

Warming a substance transfers kinetic energy to its particles. More kinetic energy means that the particles move faster. Because they are moving faster there will be more collisions each second. The increased energy of the collisions also means that the proportion of collisions that are effective will increase. A reaction was carried out at two different temperatures – first at 20 °C and then at 30 °C.



Δ Fig. 6.10 Effect of increasing temperature on particles.

Increasing the temperature of the reaction between some marble chips and hydrochloric acid will not increase the final amount of carbon dioxide produced. The same amount of gas will be produced in a shorter time. The rates of the two reactions are different but the final loss in mass is the same.



Δ Fig. 6.11 The effect of temperature on the reaction between hydrochloric acid and marble chips.

QUESTIONS

1. State the units used to measure the concentration of solutions.
2. **SUPPLEMENT** In terms of particles colliding, explain why increasing the concentration of a solution increases the rate of reaction.
3. Plan and design an experiment to compare the effect of temperature on the rate of reaction between magnesium and hydrochloric acid. You should:
 - a) demonstrate how to safely use techniques, apparatus and materials;
 - b) plan the procedure you will use;
 - c) show how you will record your measurements or observations.

4. **SUPPLEMENT** Explain two reasons why increasing temperature increases the rate of reaction.

SCIENCE
IN
CONTEXT

THE EXPLOSIVE TRUTH ABOUT FLOUR MILLS

The surface area of particles really does affect the rate of some reactions!

Baking bread is a common and important activity, but making the flour that goes into the bread can be a dangerous business. Ever since a serious explosion at a flour mill near Minneapolis in the USA in 1878 killed 18 people, the milling industry has tried to reduce the risk of flour particles igniting into 'flour bombs'. In fact flour dust is thought to be more explosive than coal dust! Similar explosions have occurred in other factories when dust has exploded.

The key components to a flour or dust explosion are very small particles suspended in a plentiful supply of air, in a confined space and with a source of ignition. In factories the source of ignition doesn't have to be something obvious such as a discarded cigarette or match; it could be a spark from an electric motor or other electrical device, or even a light switch. In the case of the 1878 flour mill explosion, the cause of the explosion was thought to be a spark from an ageing electric motor.

In the laboratory or at home, if you put a match to some flour you might be able to get it to burn, but it certainly won't explode – the flour needs to be suspended in the air as very small particles that are close enough together so that if one flour particle ignites it starts a rapid chain reaction with other particles and then an explosion. So don't underestimate the importance of particle size on the rate of some reactions.

Challenge Question: In all sorts of underground mines there will be dust. In a coal mine there is an additional hazard that can cause an explosion. Suggest another source of an explosion and explain why you might find it in a coal mine.



Δ Fig. 6.12 Dropping milk powder on a flame.

Surface area

Increasing the **surface area** (or decreasing the particle size) of a solid reactant will increase the rate of a reaction.

SUPPLEMENT

A reaction can only take place if the reacting particles collide. This means that the reaction takes place at the surface of a solid. The particles within the solid cannot react until those on the surface have reacted and moved away.

Powdered calcium carbonate has a smaller particle size (or much larger surface area) than the same mass of marble chips. A lump of coal will burn slowly in the air, whereas coal dust can react explosively. This is a hazard in coal mines where coal dust can react explosively with air. In addition, as well as the danger of explosive mixtures of coal dust and air, the build-up of methane gas can also form an explosive mixture with the air.



Δ Fig. 6.13 Powdered carbon has a much larger surface area than the same mass in larger lumps.

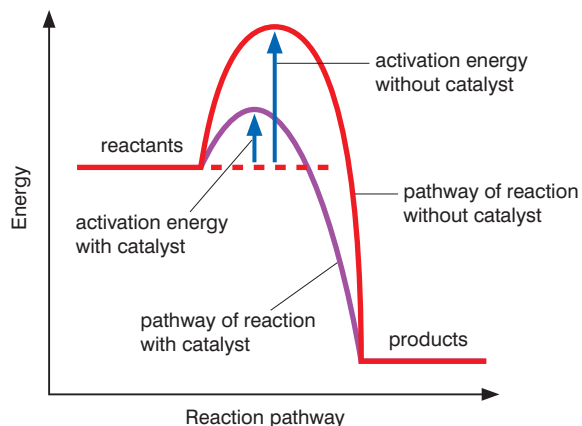
Catalysts

A **catalyst** is a substance that alters the rate of a chemical reaction and is chemically unchanged at the end of the reaction. An **enzyme** is a biological catalyst, for example amylase, which is found in saliva.

Note: Enzymes are involved in the fermentation of glucose. Enzymes are present in yeast and these increase the rate at which glucose is converted into ethanol and carbon dioxide. The reaction rate increases as the yeast multiplies – but as the concentration of ethanol increases, the rate decreases because the ethanol begins to kill or denature the enzymes.

SUPPLEMENT

Most catalysts work by providing an alternative 'pathway' for the reaction – one that has a lower activation energy. The lower activation energy means that more of the collisions between particles will be effective.



Δ Fig. 6.14 The catalyst provides a lower energy route from reactants to products.

One example of the effect of a catalyst on a reaction is the use of manganese(IV) oxide in the decomposition of hydrogen peroxide. Hydrogen peroxide decomposes at room temperature into water and oxygen. The rate of this reaction is considerably increased by adding manganese(IV) oxide. As a gas is produced, the rate of the reaction can be monitored by collecting the gas in a gas syringe.



Catalysts are often used in industry to manufacture important chemicals. Table 6.2 shows some important industrial catalysts.

Industrial process	Catalyst used
Manufacture of ethanol	Phosphoric acid
Cracking long-chain alkanes	Silica or alumina
Manufacture of ammonia	Iron
Manufacture of sulfuric acid	Vanadium(V) oxide

Δ Table 6.2 Uses of catalysts.



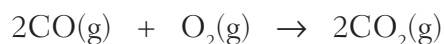
Δ Fig. 6.15 The effect of manganese(IV) oxide catalyst on the decomposition of hydrogen peroxide.

REMEMBER

Enzymes are often very specific to a particular reaction. They have an 'active site' which is just the right shape for the reacting particles to fit into. It is not necessary to learn this as it is not on the syllabus, but it provides useful context. Molecules with other structures and shapes cannot do this. Metals, such as iron used in the manufacture of ammonia, work in the same sort of way that enzymes do. The surface of the iron allows molecules of nitrogen and hydrogen to get 'trapped'. They then collide more frequently in the confined space and effective collisions become more likely.

Pressure

Increasing the pressure on the reaction involving a gas can increase the rate of reaction. For example, in the reaction between carbon monoxide and oxygen, carbon dioxide is formed as shown in the equation:



The reacting gases will react at a greater rate if the pressure is increased.

SUPPLEMENT

The reason for this increase in reaction rate can be explained in terms of collision theory. As the pressure is increased the volume of the gases will reduce and so there will be a greater number of particles per unit volume. As a result there will be a greater frequency of collisions between the particles. This will lead to more effective collisions taking place in a given time, so that there will be more collisions with sufficient energy to exceed the activation energy needed for the reaction to take place.

QUESTIONS

1. Define a *catalyst*.
2. State the name of a biological catalyst.
3. State in what type of reactions pressure is likely to have a significant effect on the rate of the reaction.
4. **SUPPLEMENT** Use collision theory to explain why changing the surface area of a solid in a reaction with an acid will affect the rate of that reaction.

End of topic checklist

Key terms

catalyst, control variable, dependent variable, enzyme, independent variable, particle size, rate of reaction, surface area, variable

SUPPLEMENT activation energy, collision theory, effective collision

During your study of this topic you should have learned:

- How to identify physical and chemical changes and understand the differences between them.
- How to describe the effect of concentration, pressure of gases, surface area, catalysts (including enzymes) and temperature on the rate of reactions.
- That a catalyst increases the rate of a reaction and is unchanged at the end of the reaction.
- How to describe a practical method for investigating the rate of a reaction involving the change in mass of reactants or products and evolution of a gas.
- How to interpret data, including graphs, from rate of reaction experiments.
- SUPPLEMENT** How to describe collision theory when referring to the number of particles per unit volume, the frequency of collisions between particles, the kinetic energy of the particles and the activation energy.
- SUPPLEMENT** How to describe and explain the effects of concentration, surface area, temperature, catalysts and pressure of gases on reaction rate.
- SUPPLEMENT** That a catalyst decreases the activation energy of a reaction.
- SUPPLEMENT** How to evaluate practical methods for investigating rate of reaction by measuring changes in mass or volume of gas produced.

End of topic questions

Note: The marks in brackets give an indication of the level of detail you should include in your answers.

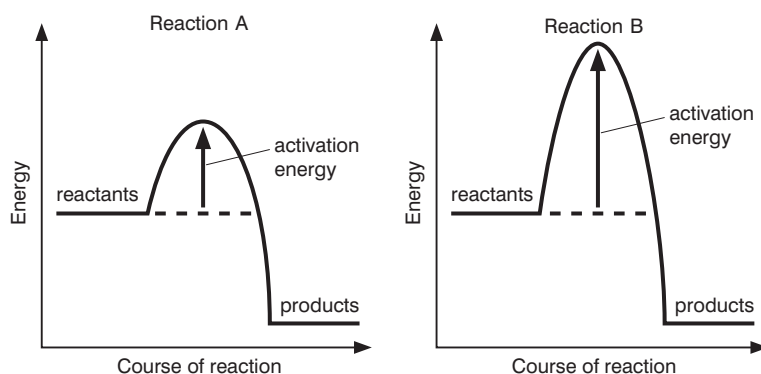
- Select which of the following changes will NOT significantly affect the rate of the reaction between sodium thiosulfate solution and dilute hydrochloric acid:
 - raising the temperature of the hydrochloric acid.
 - increasing the concentration of the sodium thiosulfate solution.
 - decreasing the concentration of the hydrochloric acid.
 - increasing the pressure of the air in the room where the reaction takes place. (1 mark)
- This question is about the reaction between magnesium and hydrochloric acid.
 - Draw and label a diagram of the apparatus that could be used to monitor the rate of the reaction by measuring the volume of hydrogen produced. (2 marks)
 - Predict how the following changes affect the rate of the reaction:
 - Using powdered magnesium rather than magnesium ribbon (1 mark)
 - Using a less concentrated solution of hydrochloric acid (1 mark)
 - Lowering the temperature of the hydrochloric acid. (1 mark)
- Explain why there is a risk of an explosion in a flour mill. (2 marks)
- Look at the table of results obtained when dilute hydrochloric acid is added to marble chips.

Time (seconds)	0	10	20	30	40	50	60	70	80	90
Volume of gas (cm ³)	0	20	36	49	58	65	69	70	70	70

- State the name of the gas produced in this reaction. (1 mark)
- Write a balanced equation, including state symbols, for the reaction. (2 marks)
- Draw a graph of volume of gas (y -axis) against time (x -axis).
Label it 'Graph 1'. (3 marks)
- Use the results to calculate the volume of gas produced:
 - in the first 10 seconds (1 mark)
 - between 10 and 20 seconds (1 mark)

End of topic questions continued

- iii) between 20 and 30 seconds (1 mark)
- iv) between 80 and 90 seconds. (1 mark)
- e) **SUPPLEMENT** Explain why the rate of the reaction changes as the reaction takes place. (2 marks)
- f) **SUPPLEMENT** Use the collision theory to explain the change in the rate of reaction. (2 marks)
- g) The reaction was repeated using the same volume and concentration of hydrochloric acid and with the same mass of marble, but as a powder instead of chips. Draw another curve on your graph paper, using the same axes as before (label it as Graph 2), to show how the original results will change. (3 marks)
- h) The reaction was repeated, but this time using the original mass of new marble chips and the same volume of hydrochloric acid, but with the acid only half as concentrated as originally. Draw another curve on your graph paper, using the same axes as before (label it as Graph 3), to show how the original results will change. (3 marks)
5. **SUPPLEMENT** For a chemical reaction to occur, the reacting particles must collide. Explain why not all collisions between the particles of the reactants lead to a chemical reaction. (2 marks)
6. **SUPPLEMENT** The diagrams below show the activation energies of two different reactions A and B.
- a) Explain the *activation energy* of a reaction. (1 mark)
- b) Select which reaction is likely to have the higher rate of reaction at a particular temperature. Explain your answer. (2 marks)



- c) Explain how the presence of a catalyst in a reaction increases the rate of a reaction. (2 marks)

Reversible reactions and equilibrium

INTRODUCTION

Many of the reactions used in the manufacture of important chemicals 'go both ways'. In other words, the reactants form the products, but the products, often at the same time, revert to the reactants. These reversible reactions came as something of a shock to the early chemists but today's chemists have found ways to maximise the direction of the reaction and so produce as much product as is possible.

If all the products and reactants are kept in a closed system (that is, nothing is allowed to escape or enter) all reversible reactions reach a 'balance point' or equilibrium. This balance point may be at a point where the concentrations of reactants and products are the same, but this is rarely the case – the balance point often favours the reactants or the products. For industrial chemists, altering the balance point or equilibrium is a key part of their work.

KNOWLEDGE CHECK

- ✓ The rate of a reaction is dependent on a number of factors.
- ✓ **SUPPLEMENT** Enthalpy changes are associated with exothermic and endothermic reactions.
- ✓ Reactions can be represented by chemical equations with associated state symbols.

LEARNING OBJECTIVES

- ✓ State that some chemical reactions are reversible, as shown by the symbol \rightleftharpoons
- ✓ Describe how changing the conditions can change the direction of a reversible reaction for: the effect of heat on hydrated compounds and the addition of water to anhydrous compounds, limited to copper(II) sulfate and cobalt(II) chloride.
- ✓ **SUPPLEMENT** State that a reversible reaction in a closed system is at equilibrium when: the rate of the forward reaction is equal to the rate of the reverse reaction; the concentrations of reactants and products are no longer changing.
- ✓ **SUPPLEMENT** Predict and explain, for any reversible reaction, how the position of equilibrium is affected by: changing temperature, changing pressure, changing concentration and using a catalyst, using information provided.



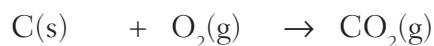
Δ Fig. 6.16 When hydrated copper(II) sulfate crystals are heated they turn from blue to white. The reaction can then be reversed by adding water.

- ✓ **SUPPLEMENT** State the symbol equation for the production of ammonia in the Haber process, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$.
- ✓ **SUPPLEMENT** State the sources of the hydrogen (methane) and nitrogen (air) in the Haber process.
- ✓ **SUPPLEMENT** State the typical conditions in the Haber process as 450 °C, 20 000 kPa / 200 atm and an iron catalyst.
- ✓ **SUPPLEMENT** State the symbol equation for the conversion of sulfur dioxide to sulfur trioxide in the Contact process, $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$.
- ✓ **SUPPLEMENT** State the sources of the sulfur dioxide (burning sulfur or roasting sulfide ores) and oxygen (air) in the Contact process.
- ✓ **SUPPLEMENT** State the typical conditions for the conversion of sulfur dioxide to sulfur trioxide in the Contact process as 450 °C, 200 kPa / 2 atm and a vanadium(V) oxide catalyst.
- ✓ **SUPPLEMENT** Explain, in terms of rate of reaction and position of equilibrium, why the typical conditions stated are used in the Haber process and in the Contact process, including safety considerations and economics.

Types of reversible reaction

Carbon burns in oxygen to form carbon dioxide:

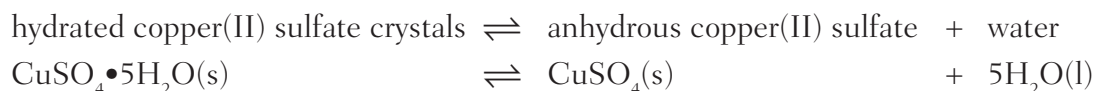
carbon + oxygen → carbon dioxide



Carbon dioxide cannot be changed back into carbon and oxygen.

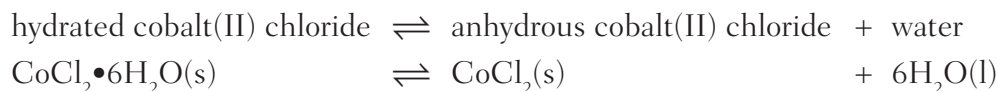
The reaction cannot be reversed.

When hydrated blue copper(II) sulfate crystals are heated, a white powder is formed (anhydrous copper(II) sulfate) and water is lost as steam. If water is added to this white powder, hydrated blue copper(II) sulfate is formed again. The reaction is **reversible**:



A reversible reaction can go from left to right or from right to left – notice the double-headed \rightleftharpoons arrow used when writing these equations.

A similar reaction occurs when hydrated cobalt(II) chloride crystals are heated.

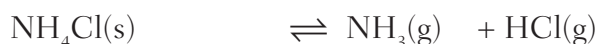


The pink hydrated cobalt(II) chloride crystals turn to blue anhydrous cobalt(II) chloride on strong heating. If water is added to the blue anhydrous cobalt(II) chloride, the pink hydrated cobalt(II) chloride is reformed.

SUPPLEMENT

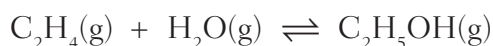
Another example of a reversible reaction is the decomposition of ammonium chloride. If ammonium chloride is heated in a long tube, the solid produces 'white fumes' of a mixture of gases. The volume of the solid decreases. In the cooler parts of the tube the fumes reform the white solid. The equation is:

ammonium chloride \rightleftharpoons ammonia + hydrogen chloride



The reaction between ethene and water to make ethanol is also a reversible reaction. This is one of the reactions used industrially to make ethanol:

ethene + water \rightleftharpoons ethanol



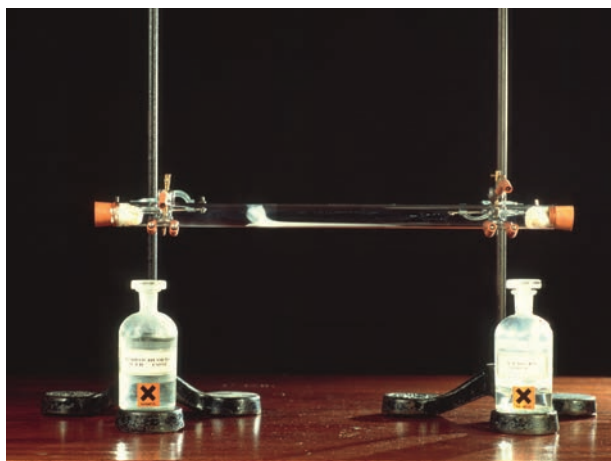
When ethene and water are heated in the presence of a catalyst in a sealed container, ethanol is produced.

As the ethene and water are used up, the rate of the forward reaction decreases. As the amount of ethanol increases, the rate of the backward reaction (the decomposition of ethanol) increases. Eventually the rate of formation of ethanol will exactly equal the rate of decomposition of ethanol. The concentrations of ethene, water and ethanol will be constant. The reaction is said to be in **equilibrium**.

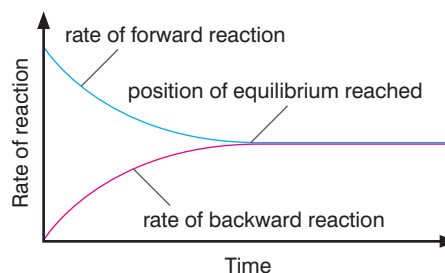
Equilibrium reactions

A chemical equilibrium is an example of a **dynamic equilibrium** (a moving equilibrium). Reactants are constantly forming products, and products are constantly reforming the reactants. Equilibrium is reached when the rates of the forward and backward reactions are the same.

To get an idea of a dynamic equilibrium, imagine you are walking up an escalator as the escalator is moving down. You are still moving forward and the escalator is moving towards you. If your rate of movement is the same as the escalator's rate of movement, but in the opposite direction, you will appear not to be moving. This 'moving balance point' is called a dynamic equilibrium. If you imagine a situation where you walk up the escalator when it is moving only slowly in the opposite direction, but gradually speeds up to the speed you are walking, you might get almost to the top of the escalator before your rates of movement are balanced. Alternatively, if the escalator starts slowly but then very quickly reaches your rate of movement, the balance point may be near the bottom of the escalator. In the same sort of way, different chemical reactions can have very different balance points (nearer to the reactants or nearer to the products).



Δ Fig. 6.17 In this experiment the gases ammonia and hydrogen chloride react in the tube and form ammonium chloride. This reaction is reversible as the two gases are reformed if the ammonium chloride is heated.



Δ Fig. 6.18 At equilibrium, the rate of the forward reaction equals the rate of the backward reaction.

REMEMBER

In a dynamic equilibrium, the rates of the forward and backward reactions are the same. Therefore once a reaction has reached equilibrium, the concentrations of the reactants and products don't change.

QUESTIONS

1. Use the example of copper(II) sulfate to explain what a reversible reaction is.
2. **SUPPLEMENT** Explain what it means if a reaction is in equilibrium.
3. **SUPPLEMENT** An equilibrium in a chemical reaction is dynamic. Explain what this means.

SUPPLEMENT

Changing the position of equilibrium

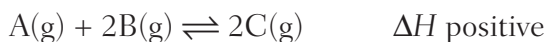
Reversible reactions can be a nuisance to an industrial chemist. You want to make a particular product, but as soon as it forms it starts to change back into the reactants! Fortunately scientists have found ways of increasing the amount of product that can be obtained (the yield) in a reversible reaction by moving the position of balance to favour the products rather than the reactants.

The position of equilibrium can be affected in the following ways:

- changing concentrations
- changing pressure
- changing temperature.

To be able to predict how the position of an equilibrium will change, it is useful to remember that whatever change is applied to the reaction, the reaction will oppose the change and try to nullify it. Reactions are awkward!

In the following example:



Change made	Effect on the equilibrium position	Method of predicting the effect
Increasing the concentration of A or B	Moves to the right-hand side	The equilibrium moves in the direction that reduces the concentration of A or B. It does this by converting A and B into C
Decreasing the concentration of C	Moves to the right-hand side	The equilibrium moves in a direction that increases the concentration of C. It does this by converting A and B into C

Change made	Effect on the equilibrium position	Method of predicting the effect
Increasing the pressure acting on the reaction	Moves to the right-hand side	The equilibrium moves in the direction that produces fewer molecules of gas. There are fewer molecules of gas on the right-hand side. It does this by converting A and B into C
Increasing the temperature of the reaction	Moves to the right-hand side	The equilibrium moves in the direction that absorbs thermal energy, that is, the endothermic reaction. The forward reaction is endothermic (ΔH is positive) so A and B are converted into C

Δ Table 6.3 Effects of changes on the equilibrium position.

Note: If the forward reaction is endothermic (ΔH positive), then the backward reaction will be exothermic (ΔH negative).

A catalyst increases the rate at which an equilibrium is achieved.

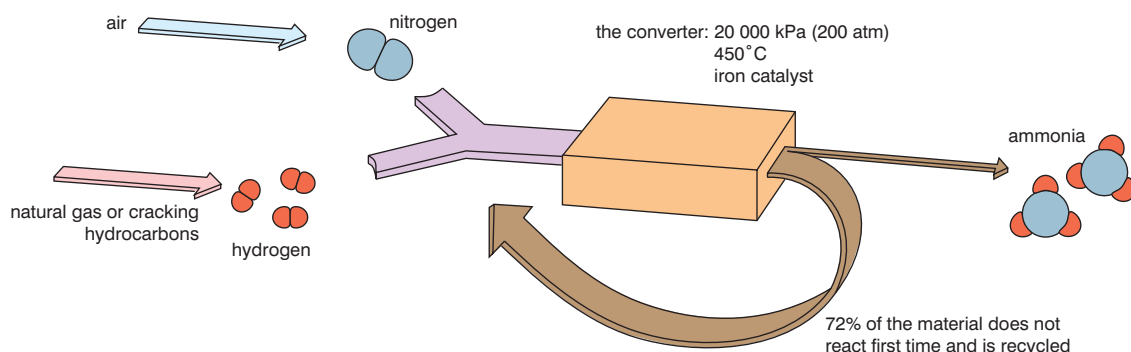
Because it changes the rates of both the forward and reverse reactions it does not change the position of the equilibrium. It does not change the yield either.

Getting the best balance between rate and equilibrium position is important in industrial processes, such as in the **Haber process** for making ammonia and the **Contact process** for making sulfur trioxide (in the manufacture of sulfuric acid).

The Haber process

Ammonia is used to make nitrogen-containing fertilisers. It is manufactured in the Haber process from nitrogen and hydrogen. This process requires an iron catalyst, a temperature of 450°C and a pressure of 20 000 kPa (200 atm).

The hydrogen is made mainly from methane and other hydrocarbons. The nitrogen is extracted from the air.



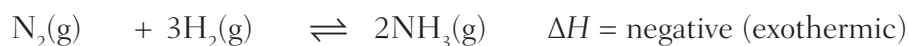
Δ Fig. 6.20 The Haber process for making ammonia. The reactants must be recycled to increase the efficiency of the process.



Δ Fig. 6.19 A tractor spreading fertiliser containing nitrogen.

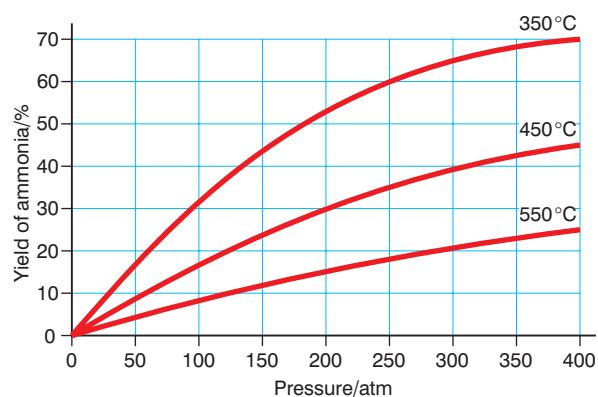
The conditions in the Haber process are chosen carefully to give the highest possible yield of ammonia with a suitable rate of reaction.

nitrogen + hydrogen \rightleftharpoons ammonia



The greatest yield of ammonia would be made using a low temperature (the reaction is exothermic), but it would be slow. The temperature of 450 °C is a compromise: less is made, but it is produced faster. The iron catalyst is also used to increase the rate; it does not increase the yield. High pressure increases the yield.

Fig. 6.21 shows the effect of temperature and pressure on the yield of ammonia.



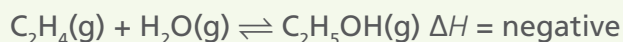
Δ Fig. 6.21 Effect of temperature and pressure on yield of ammonia.

The ammonia is liquefied and removed from the reaction vessel and the unused nitrogen and hydrogen are recycled.

Ammonia is commonly used in domestic cleaning agents, in the manufacture of nitric acid and to make NPK fertilisers. 'NPK' means the fertiliser contains nitrogen (N), phosphorus (P) and potassium (K).

QUESTIONS

1. **SUPPLEMENT** This question is about the reaction of ethene and steam:



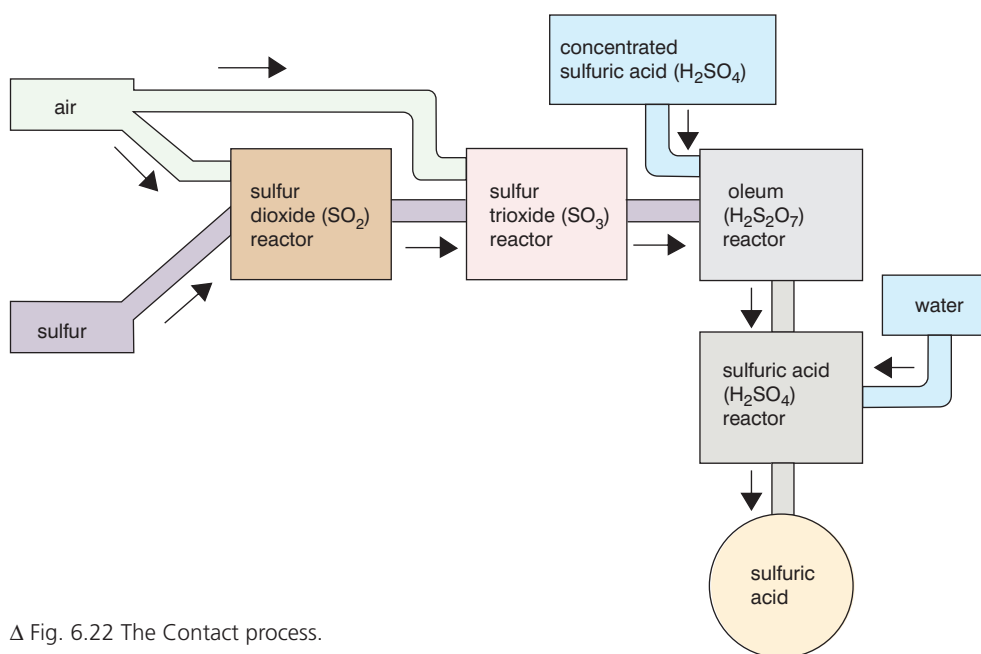
Suggest which conditions would maximise the amount of ethanol in the equilibrium mixture:

- high or low temperature.
 - high or low pressure.
 - catalyst or no catalyst.
2. **SUPPLEMENT** In the manufacture of ammonia:
- Explain why a catalyst used.
 - Suggest what would be the disadvantage of using a temperature below 350 °C.

THE CONTACT PROCESS

Sulfuric acid is a very important starting material in the chemical industry. It is used in the manufacture of many other chemicals including fertilisers, detergents and paints.

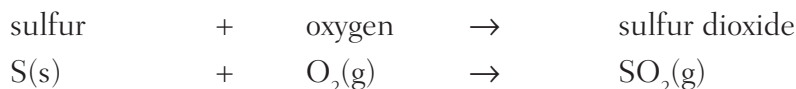
Sulfuric acid is manufactured in the **Contact process**, in which sulfur dioxide is oxidised to sulfur trioxide.



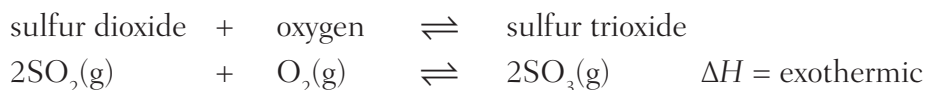
Δ Fig. 6.22 The Contact process.

The equations for the steps in making sulfuric acid are shown below:

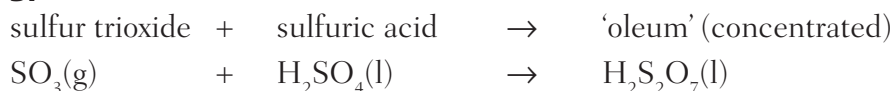
1.



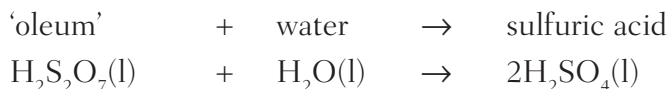
2.



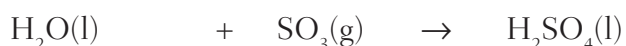
3.



4.



Does it seem simpler to you to make sulfuric acid by adding sulfur trioxide straight to water and skipping steps 3 and 4?



This is dangerous because the reaction is very exothermic and an 'acid mist' is made.

Step 2 is the main reaction of the Contact process. The highest yield of sulfur trioxide would be made at a low temperature (the reaction is exothermic), but this would be slow. Using a compromise temperature of 450°C makes less sulfur trioxide, but in a shorter time.

High pressure is not used because the yield is 98%. Unconverted reactants are recycled. Vanadium(V) oxide is used as a catalyst to increase the rate, but it does not increase the yield.

REMEMBER

A low temperature often gives a good conversion of reactant into product but a very slow rate of reaction.

The temperature chosen for an industrial process is often a compromise between one that favours the forward reaction (rather than the backward reaction) and one that gives a suitable rate of reaction.

End of topic checklist

Key terms

hydrated, reversible reaction, temperature

SUPPLEMENT catalyst, concentration, Contact process, dynamic equilibrium, equilibrium, Haber process, pressure, yield

During your study of this topic you should have learned:

- That some chemical reactions are reversible.
- How conditions affect the reversible reactions involving hydrated compounds such as copper(II) sulfate and cobalt(II) chloride.
- SUPPLEMENT** That in an equilibrium reaction the rates of the forward and reverse reactions are the same and the concentrations of reactants and products no longer change.
- SUPPLEMENT** How to predict and explain how the position of equilibrium is affected by changing the concentration, changing the temperature, changing the pressure, and using a catalyst.
- SUPPLEMENT** How to use a symbol equation to represent the Haber process.
- SUPPLEMENT** That in the Haber process the hydrogen is obtained from methane and the nitrogen from the air.
- SUPPLEMENT** That the conditions in the Haber process are 450 °C, 20 000 kPa (200 atm) and an iron catalyst.
- SUPPLEMENT** How to use a symbol equation to represent the Contact process.
- SUPPLEMENT** That in the Contact process the sulfur dioxide is obtained by burning sulfur and the oxygen from the air.
- SUPPLEMENT** That the conditions in the Contact process are 450 °C, 200 kPa and a vanadium(V) oxide catalyst.
- SUPPLEMENT** How to explain why the typical conditions are used in the Haber process and the Contact process.

End of topic questions

Note: The marks in brackets give an indication of the level of detail you should include in your answers.

1. Define a *reversible reaction*. (1 mark)
2. Describe what you would observe in the following reactions:
 - a) Hydrated copper(II) sulfate is heated strongly until there is no further change. (3 marks)
 - b) After cooling, water is added to the product formed in reaction a). (2 marks)
3. Write a balanced equation, including state symbols, for the reaction in question 2a. (3 marks)
4. Some hydrated cobalt(II) chloride is heated strongly in a boiling tube. Describe what you would expect to observe. (3 marks)
5. **SUPPLEMENT** State which of the following changes will NOT affect the position of the equilibrium in the reaction to produce ammonia in the Haber process.
 - A increasing the temperature
 - B using a catalyst
 - C decreasing the temperature
 - D changing the pressure (1 mark)
6. **SUPPLEMENT** Describe what it means when a chemical reaction is in *dynamic equilibrium*. (2 marks)
7. **SUPPLEMENT** This question is about the manufacture of ammonia.
 - a) State the two reactants used in the reaction. (2 marks)
 - b) State the source of each reactant. (2 marks)
 - c) Describe the essential reaction conditions. (3 marks)
 - d) Write a balanced equation for the reaction. (2 marks)

- 8. SUPPLEMENT** The reaction between sulfur dioxide and oxygen is reversible, as shown by the equation:



Predict what effect the following changes will have on the yield of sulfur trioxide (SO_3).

- a)** Increasing the volume of oxygen. Explain your answer. (2 marks)
- b)** Increasing the pressure on the reaction. Explain your answer. (2 marks)
- c)** Increasing the temperature of the reaction. Explain your answer. (2 marks)
- 9. SUPPLEMENT** The equation for the reaction between nitrogen and oxygen to form nitrogen oxide is shown below:



Predict what effect the following changes will have on the amount of nitrogen oxide in the equilibrium mixture.

- a)** Increasing the concentration of oxygen. Explain your answer. (2 marks)
- b)** Increasing the pressure on the reaction. Explain your answer. (2 marks)
- c)** Increasing the temperature of the reaction. Explain your answer. (2 marks)



Δ Fig. 6.23 Oxidation and reduction are both taking place in this bonfire.

Redox reactions

INTRODUCTION

Oxidation reactions are very familiar in everyday life – like the rusting of iron and bleaching, which is effective because bleach is a powerful oxidising agent. Whenever anything burns, an oxidation reaction takes place between the fuel and oxygen in the air. Reduction reactions may seem less familiar, but oxidation and reduction go hand in hand – if an element or compound in a chemical reaction is oxidised, then another element or compound in the same reaction must be

reduced. So even when a bonfire is burning furiously and using oxygen from the air, reduction is taking place at the same time!

KNOWLEDGE CHECK

- ✓ Ions are charged atoms and have particular charges.
- ✓ Chemical equations and associated state symbols provide details about particular reactions.
- ✓ **SUPPLEMENT** Half-equations are used to explain the changes taking place in a reaction.

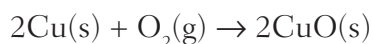
LEARNING OBJECTIVES

- ✓ Use a Roman numeral to indicate the oxidation number of an element in a compound.
- ✓ Define redox reactions as involving simultaneous oxidation and reduction.
- ✓ Define oxidation as gain of oxygen and reduction as loss of oxygen.
- ✓ Identify redox reactions as reactions involving gain and loss of oxygen.
- ✓ Identify oxidation and reduction in redox reactions.
- ✓ **SUPPLEMENT** Define oxidation in terms of: loss of electrons; an increase in oxidation number.
- ✓ **SUPPLEMENT** Define reduction in terms of: gain of electrons; a decrease in oxidation number.
- ✓ **SUPPLEMENT** Identify redox reactions as reactions involving gain and loss of electrons.
- ✓ **SUPPLEMENT** Identify redox reactions by changes in oxidation number using: the oxidation number of elements in their uncombined state is zero; the oxidation number of a monatomic ion is the same as the charge on the ion; the sum of the oxidation numbers in a compound is zero; the sum of the oxidation numbers in an ion is equal to the charge on the ion.
- ✓ **SUPPLEMENT** Identify redox reactions by the colour changes involved when using acidified aqueous potassium manganate(VII) or aqueous potassium iodide.

- ✓ **SUPPLEMENT** Define an oxidising agent as a substance that oxidises another substance and is itself reduced.
- ✓ **SUPPLEMENT** Define a reducing agent as a substance that reduces another substance and is itself oxidised.
- ✓ **SUPPLEMENT** Identify oxidising agents and reducing agents in redox reactions.

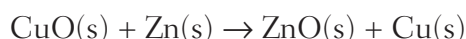
OXIDATION, REDUCTION AND REDOX

When oxygen is added to an element or a compound, the process is called **oxidation**:



The copper has been oxidised.

Removing oxygen from a compound is called **reduction**:



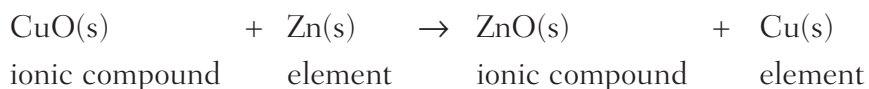
The copper(II) oxide has been reduced.

If we look more carefully at this last reaction, we see the zinc has changed to zinc oxide: that is, it has been oxidised at the same time as the copper(II) oxide has been reduced.

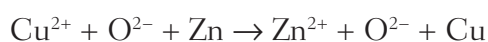
This is one example of reduction and oxidation taking place at the same time, in the same reaction. Reactions like these that involve the simultaneous gain and loss of oxygen are called **redox** reactions.

SUPPLEMENT

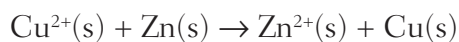
There is another way to look at redox reactions if we consider the reaction in a different way:



Rewrite it:



Remove the oxygen ions because they are on both sides of the equation (the O^{2-} ion is unchanged):



Split the equation into two half-equations and add electrons to balance them:



that is: CuO to Cu = reduction



that is: Zn to ZnO = oxidation

In this reaction the copper(II) oxide has been reduced by the zinc. The zinc is a **reducing agent**.

The zinc itself has been oxidised by the copper(II) oxide. The copper(II) oxide is an **oxidising agent** and is itself reduced.

You now have a new definition, using electrons instead of oxygen:

- Oxidation is loss of electrons.
- Reduction is gain of electrons.

Remember this as OIL-RIG: Oxidation *Is* Loss – Reduction *Is* Gain.

Oxidation numbers

When you learned to write chemical formulae, you were introduced to the use of Roman numerals for metals that had more than one ion – for example, iron as Fe²⁺ or Fe³⁺:

- iron(II) oxide = FeO
- iron(III) oxide = Fe₂O₃

The II and III are called **oxidation numbers**.

- Fe²⁺ has an oxidation number of +2
- Fe³⁺ has an oxidation number of +3
- O²⁻ has an oxidation number of –2

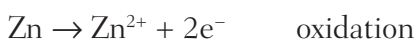
You take the ion charge and reverse it, so an ion of 3– has oxidation number –3.

The oxidation number of elements is always 0 (zero).

An oxidation number describes how many electrons an atom loses or gains when it forms a chemical bond.

SUPPLEMENT

If you look at the equation for the reaction between Cu²⁺ and Zn again, you will see that we can use oxidation numbers:



This gives another definition for oxidation/reduction:

- Oxidation involves an increase in oxidation number.
- Reduction involves a decrease in oxidation number.

Changes in oxidation number

Solid potassium manganate(VII) comes in the form of dark purple crystals.

Manganese has the oxidation number +7 (the 'VII' in the name) and is the cause of the purple colour.

Potassium manganate(VII) crystals dissolve in water to produce a dark purple solution, which is a powerful oxidising agent. When potassium

manganate(VII) is used, the manganate(VII) ion is reduced to the manganese(II) ion, which is almost colourless:



+7

+2

purple

colourless

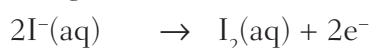
When the manganate(VII) ions are reduced, the colour changes from purple to colourless. The potassium ions do not change.



Δ Fig. 6.24 When manganate(VII) ions are reduced, colourless Mn^{2+} ions are formed.

Another example of colour changes linked to changes in oxidation states is given by potassium iodide, KI, which is a white solid dissolving in water to form a colourless solution.

In some reactions the iodide ion, I^- , as in potassium iodide, is oxidised to iodine (there is an increase in oxidation number). Iodine has a dark orange colour in solution:



2(-1)

2(0)

colourless

orange

Fumes of iodine are produced when potassium iodide is oxidised by concentrated sulfuric acid. Again the potassium ions do not change.

PHOTOCHROMIC GLASS

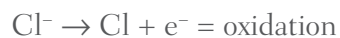
Some people who wear glasses prefer those with photochromic lenses, which darken when exposed to bright light. These glasses eliminate the need for sunglasses – they can reduce up to 80% of the light transmitted through the lenses to the eyes. The basis of this change in colour in response to light can be explained in terms of redox reactions.



Δ Fig. 6.25 A photochromic reaction was produced when the right lens of these glasses was exposed to bright light.

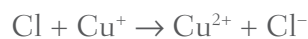
Glass is ordinarily transparent to visible light. In photochromic lenses, silver chloride (AgCl) and copper(I) chloride (CuCl) crystals are added during the manufacturing of the glass. These crystals become uniformly embedded in the glass.

One characteristic of silver chloride is that it is affected by light. The following reactions occur:

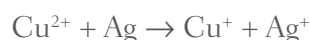


The chloride ions are oxidised to produce chlorine atoms and the silver ions are reduced to silver atoms. The silver atoms cluster together and block the transmission of light, causing the lenses to darken. This process occurs almost instantaneously.

The photochromic process would not be useful unless it were reversible. The presence of copper(I) chloride reverses the darkening process in the following way. When the lenses are removed from bright light, the following reaction occurs:



The chlorine atoms formed by the exposure to light are reduced by the copper(I) ions forming chloride ions (Cl⁻). The copper(I) ions are oxidised to copper(II) ions. The copper(II) ions then oxidise the silver atoms:



The result of these reactions is that the lenses become transparent again as the silver atoms are converted back to silver ions.

Challenge Question: Using the reactions above, state the oxidation numbers of the substances below.

- a) Cl
- b) Cl⁻
- c) Ag
- d) Ag⁺

QUESTIONS

1. Define the term *reduction*.
2. State the oxidation number of the metal ion in each of the following compounds:
 - a) copper(II) oxide
 - b) iron(III) chloride
 - a) potassium manganate(VII).
3. **SUPPLEMENT** In the following half-equation, has the Cu²⁺ ion been oxidised or reduced? Explain your answer.
$$\text{Cu}^{2+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Cu}^{+}(\text{aq})$$
4. **SUPPLEMENT** In the following half-equation, has the chromium (Cr) atom been oxidised or reduced? Explain your answer.
$$\text{Cr}(\text{s}) \rightarrow \text{Cr}^{3+}(\text{aq}) + 3\text{e}^{-}$$

End of topic checklist

Key terms

oxidation, oxidation number, redox, reduction

SUPPLEMENT oxidising agent, reducing agent

During your study of this topic you should have learned:

- The definitions of oxidation and reduction in terms of oxygen loss or gain.
- That oxidation numbers are used to name ions, for example, iron(II), iron(III), copper(II), manganate(VII).
- That redox reactions involve simultaneous reduction and oxidation.
- How to identify oxidation and reduction in redox reactions.
- SUPPLEMENT** The definition of redox in terms of the gain or loss of electrons.
- SUPPLEMENT** That uncombined elements have an oxidation number of zero, the oxidation number of an ion is the same as the charge on the ion and the sum of oxidation numbers in a compound is zero.
- SUPPLEMENT** How to identify redox reactions by changes in oxidation number and by the colour changes involved when using acidified potassium manganate(VII) and potassium iodide.
- SUPPLEMENT** That an oxidising agent is a substance that oxidises another substance and is itself reduced during a redox reaction.
- SUPPLEMENT** That a reducing agent is a substance that reduces another substance and is itself oxidised during a redox reaction.
- SUPPLEMENT** How to identify oxidising agents and reducing agents in redox reactions.

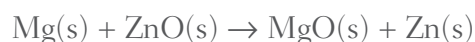
End of topic questions

Note: The marks in brackets give an indication of the level of detail you should include in your answers.

1. Select which of the following reactions shows a reduction reaction:



2. The following equation shows a redox reaction:



a) State what has been oxidised in the reaction. (1 mark)

b) State what has been reduced in the reaction. (1 mark)

c) Explain why this reaction is a redox reaction. (1 mark)

d) SUPPLEMENT State the oxidation number of Mg. (1 mark)

e) SUPPLEMENT Determine what is the oxidising agent. (1 mark)

f) SUPPLEMENT Determine what is the reducing agent. (1 mark)

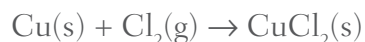
3. **SUPPLEMENT** The relationship between lead atoms and lead ions is shown in the following half-equation:



In this reaction, state whether the lead atom has been oxidised or reduced.

Explain your answer. (2 marks)

4. **SUPPLEMENT** The reaction between copper and chlorine produces copper(II) chloride.



a) State the oxidation number of copper as an element. (1 mark)

b) State the oxidation number of the copper in copper(II) chloride. (1 mark)

c) Is this reaction a redox reaction? Explain your answer. (2 marks)