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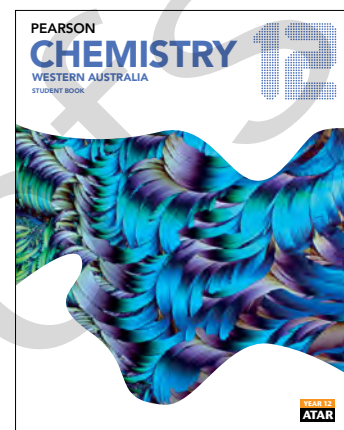
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How to use this book

Pearson Chemistry 12 Western Australia

Pearson Chemistry 12 Western Australia has been written to the WACE Chemistry ATAR Course, Year 12 Syllabus 2017. Each chapter is clearly divided into manageable sections of work. Best practice literacy and instructional design are combined with high quality, relevant photos and illustrations. Explore how to use this book below.

Chapter opening page

The chapter opening page links the syllabus to the chapter content. Science Understanding and Science as a Human Endeavour addressed in the chapter is clearly listed.

ChemFile

ChemFiles include a range of interesting information and real world examples.

Chemistry in Action

Chemistry in Action boxes place Chemistry in an applied situation or relevant context and encourages students to think about the development of chemistry and its use and influence of chemistry in society.

CHAPTER 11 Key products from the chemical industry

The chemical industry provides numerous chemicals, including laurates, such as perfumes, and essential, such as agricultural chemicals, fibres and fuels. Their production is an important part of Australia's industry. Chemical industries convert raw materials, such as plant material, minerals or atmospheric gases, into useful products. The production of two key chemicals—ammonia and sulfuric acid—will be studied in this chapter. You will learn that the concepts of rate and equilibrium that you studied in previous chapters are fundamental to the design of manufacturing processes so that production of useful chemicals is efficient and economically viable. As well, you will see that the synthesis of a final chemical often involves a sequence of individual reactions.

Science understanding

- the percentage yield of a chemical synthesis reaction can be calculated by comparing theoretical versus actual product quantities
- reagents and reaction conditions are chosen to optimise yield and rate for chemical synthesis processes, including in the production of ammonia (Haber process), sulfuric acid (Contact process) and biodiesel (base-catalysed and lipase-catalysed methods)
- quantities of products in a chemical synthesis reaction can be calculated by comparing stoichiometric quantities with actual quantities and by determining the limiting reagent
- chemical synthesis to form products with specific properties may require the construction of reaction sequences with more than one chemical reaction and involves the selection of particular reagents and reaction conditions in order to optimise the rate and yield of product

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DEPENDENCE ON TEMPERATURE

The effect of temperature on the rate of a reaction involves an Arrhenius plot. You can see from the steep sides of the curve that the rate of reaction drops off quickly either side of a narrow temperature range (30–40°C). The temperature at which the enzyme activity is greatest is known as the enzyme's **optimum temperature**. Enzymes that operate inside human cells have an optimum temperature of about 37°C.

At temperatures above and below the optimum temperature, enzyme function is impaired. This is one of the reasons why conditions such as hypothermia and fever (where you have an abnormally low or high temperature) are life-threatening.

Rate of reaction increases as temperature increases.

Rate of reaction decreases after this temperature as the enzyme is denatured (shape changed permanently).

ChemFile

Hypertrophinophilic

A hypertrophinophilic is a type of bacteria that thrives in extremely hot temperatures, at temperatures of 60°C and higher. Many hypertrophinophiles are anaerobes that are non-oxidising, such as high sulfur or sodium. Hypertrophinophiles were first discovered in 1960, in the hot springs of Yellowstone National Park (Figure 9.3.4). Since then, more than 27 different species of bacteria capable of withstanding these high temperatures have been discovered.

Figure 9.3.4 An aerial photograph of the hot springs of Yellowstone National Park. The water temperature can reach more than 70°C. The bright colour of the pool and lake is minerals that are deposited from the mineral-rich water. The colour differences within the pool are due to different species of hypertrophinophilic bacteria.

In order for hypertrophinophiles to survive under these extreme conditions, these hypertrophinophiles possess their three-dimensional shape at high temperatures rather than being denatured. Indeed, many of the proteins in these organisms have high levels of hydrogen bonding and ionic interactions stabilising their three-dimensional shape under proteins in normal bacterial cells.

These hypertrophinophiles proteins are of interest commercially, because they may be able to catalyse industrial processes at higher temperatures, increasing the rate of reaction.

Figure 9.3.5 Effect of temperature on rate of reaction for an enzyme-catalysed reaction. Enzymes are only effective in a relatively narrow range of temperature. Reaction rate is highest at the optimum temperature.

Figure 9.3.6 An increase above or decrease below the optimum temperature has a different effect on an enzyme.

An increase above the optimum temperature, the increased kinetic energy of the molecules disrupts the structure of the enzyme. The increased movement throughout the enzyme breaks some of the intermolecular forces responsible for the tertiary structure. This change in three-dimensional shape of the enzyme means the active site can no longer effectively catalyse the reaction so the reaction rate decreases rapidly.

An increase below the optimum temperature, the enzyme and substrate molecules have lower kinetic energies, resulting in less frequent and less energetic collisions between the molecules. Additionally, under the conditions it is found discussed in section 19.2, enzymes need a certain amount of flexibility so that the shape of the active site can change upon substrate binding. When the temperature is too low, the enzyme is not flexible enough for this change of shape to take place, and therefore it cannot function properly.

Denaturation

Check the temperature becomes too high, the increased kinetic energy of the polypeptide chains of the enzyme breaks some of the bonds between side chains of the amino acid units, and new bonds are formed. A change in the tertiary structure causes a change in the shape of the active site and the enzyme loses its catalytic activity. It is said to be denatured. This change to the protein structure is often reversible (Figure 9.3.7).

9.1 Galvanic cells

Electronic devices such as mobile phones, notebook computers, cameras and hearing aids all depend on small portable sources of electricity: cells and batteries. Figure 9.1.1. Portable energy in the form of cells and batteries enables you to operate electrical equipment without the restriction of a power cord.

The demand for electronic devices has stimulated the production of a variety of cells. From tiny button cells for watches and calculators, to large batteries used to operate lightbulbs. The energy provided by cells and batteries may be more expensive than energy from other sources, such as fossil fuels, but this cost is offset by their convenience.

In this section, you will find out how cells are constructed, and how they provide you with a source of electrical energy.

Chemistry in Action

A technological leap beginning with a frog's leg

The history of electrochemistry began in 1793 when Italian biologist Luigi Galvani and his assistant were experimenting with dissected frogs. They hung a frog's leg on a copper rod and were startled to see the leg twitch when it touched an iron nail. The muscles of the frog were stimulated by an electric shock. Galvani had just discovered how to generate a current. His 'error' was in thinking that the current was some sort of life force, a perfectly reasonable idea for the time.

Other scientists set out to investigate the possibility that metals were involved in this phenomenon. After several years' work, in 1800, Alessandro Volta developed a device that used a chemical reaction to produce an electric current. Figure 9.1.2 shows the device, now called a 'voltaic pile'. It consisted of a stack of alternating copper and zinc discs separated by cardboard soaked in salt water.

Figure 9.1.1 Your way of life depends on cells and batteries.

Figure 9.1.2 Construction of a galvanic cell from simple laboratory equipment.

INTRODUCING GALVANIC CELLS

An electrochemical cell is a device in which chemical energy is converted into electrical energy, or vice versa. A galvanic cell (also known as a **voltaic cell**) is a type of electrochemical cell in which chemical energy is converted into electrical energy. The cells in your mobile phone and laptop are galvanic cells.

If you connect several cells in series to obtain a higher potential difference or 'voltage', the combination of cells is called a **battery**. The term 'battery' strictly only applies to a combination of cells, but it is very loose to describe cells as well.

Figure 9.1.3 Shows how you can produce a galvanic cell from simple laboratory equipment.

Extension

Extension boxes include material that goes beyond the core content of the syllabus. They are intended for students who wish to expand their depth of understanding in a particular area.

9.4 Everyday sources of power

The battery was invented by Alessandro Volta in 1800. More than two centuries later, cells and batteries are a common power source for many household and industrial applications. Cells and batteries can be used as fixed energy storage systems, such as in solar energy systems, burglar alarms and smoke detectors. They are also used extensively in portable applications, including mobile phones, watches, digital cameras and laptop computers. The portability of these devices relies on these sources of electrical energy.

Cells and batteries use spontaneous redox reactions as the source of energy. In this section, you will look at the three main types of cells in use and how chemical reactions in these cells are used to produce electricity for everyday applications.

The three basic types of cells are:

- primary cells**, which are disposable and designed not to be recharged
- secondary cells**, which are rechargeable and designed to be recharged many times
- fuel cells**, which continuously produce electricity for as long as fuel is fed into the cells.

Primary cells, secondary cells and fuel cells are all types of galvanic cells.

PRIMARY CELLS

Common commercial **alkaline cells**, such as those you would usually use in a torch or a remote control, are **non-rechargeable cells** (Figure 9.4.1). They 'go flat' when most of the reactants are used up, the cell reaches equilibrium, and you have to buy a replacement.



Figure 9.4.1 Non-rechargeable alkaline cells are used to power many devices, including torches, smoke detectors and calculators. They are discarded once they go flat.

Primary cells—alkaline cells

Following World War II, an expanding range of electrical appliances became available that required small, high-capacity power sources. The earlier types of cells were unable to meet these demands, so the alkaline cell was developed in the late 1940s.

Figure 9.4.2 shows the construction of an alkaline cell. This cell is similar to the simple galvanic cells discussed earlier in this chapter, but has been designed so the two half-reactions occur in separate places within the cell container. A potassium hydroxide electrolyte performs the same function as a salt bridge in the simple cells.

An alkaline cell needs less electrolyte than a dry cell, which it has largely replaced for household use. The smaller quantity of electrolyte allows more reactant to be included. A typical D-size alkaline cell contains about 40g of manganese dioxide, compared with 25g in a dry cell of equivalent size.

The following reactions occur in an alkaline cell.

- At the cathode (c), manganese dioxide is reduced: $2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq})$
- At the anode (a), zinc powder around the central metal rod is oxidised and reacts with hydroxide ions, forming zinc hydroxide: $\text{Zn}(\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Zn}(\text{OH})_2(\text{s}) + 2\text{e}^-$

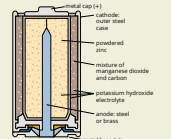


Figure 9.4.2 Construction of an alkaline cell.

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Highlight box

Focuses students' attention on important information such as key definitions, formulae and summary points.

FUEL CELLS

The main limitation of the cells that have been examined so far is that they contain relatively small amounts of reactants. Furthermore, when the reaction reaches equilibrium, the cell must be discarded or recharged.

Cells can be constructed in which the reactants are supplied continuously, allowing constant production of electrical energy. These devices are called fuel cells.

Many differences between a fuel cell and a primary or secondary cell is that the reactants are not stored in the fuel cell. They must be continuously supplied from an external source.

Fuel cells use the chemical energy of hydrogen or other fuels to cleanly and efficiently generate electricity. Even though fuel cell technology is still being developed, fuel cells can be used in numerous applications. These include a source of power for transport (see Figure 9.4.9), and for emergency back-up power applications.

A fuel cell is a type of galvanic cell, but, unlike the cells you studied previously in this chapter, fuel cells do not run down or need recharging. Electricity is produced for as long as fuel is supplied to them.

Efficiency of fuel cells

Fuel cells transform chemical energy directly into electrical energy, enabling efficient use of the energy released by spontaneous redox reactions. They are a useful source of continuous electricity and could be used to provide energy for vehicles, buildings and even cities. Energy losses such as those that occur in coal-fired power stations and combustion engines are avoided, with a consequential reduction in the volume of greenhouse gases produced.

Fuel cells are generally quoted as being 40–60% efficient, compared with efficiencies of 30–40% for thermal power stations and 25–30% for our engines, which involve a series of different energy transformations.

In addition, some modern fuel cells use the waste heat that they produce to make electricity. This stream can be used for heating or to operate a turbine, thus raising the efficiency of the cells to up to 85%.

Fuel cells have a much higher efficiency than thermal power stations because chemical energy is directly converted to electrical energy.

A fuel cell using hydrogen as a fuel produces electricity, water, heat and very small amounts of nitrogen dioxide and other oxides.

Although the basic principles behind the operation of a fuel cell were discovered in 1838, it was not until the 1950s that fuel cells were used for small-scale power production. Fuel cells, such as the one shown in Figure 9.4.10, were the main on-board power supply used and source of water during the Apollo space program that put humans on the Moon. An explosion in a fuel cell was responsible for the failure of the Apollo 13 mission.

Fuel cell design

Figure 9.4.11 shows a simplified diagram of the key parts of a hydrogen-oxygen fuel cell. The fuel cell is divided into two compartments: one for the hydrogen gas and the other for the oxygen gas. The gas compartments are separated from each other by two porous electrodes and an electrolyte solution. The electrode at the hydrogen compartment is the anode; the electrode at the oxygen compartment is the cathode.



Figure 9.4.9 A hydrogen fuel cell for an electric bicycle. The hydrogen bicycle operates like a standard electric bicycle, but the battery uses three times longer.



Figure 9.4.10 Fuel cells like this were used to power Apollo 13. Fuel cells were also used in the later lunar rovers.

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Worked examples

Worked examples are set out in steps that show both thinking and working. This enhances student understanding by clearly linking underlying logic to the relevant calculations.

Each Worked example is followed by a Try Yourself: Worked example. This mirror problem allows students to immediately test their understanding.

Fully worked solutions to all Try Yourself: Worked examples are available on *Pearson Chemistry 12 Western Australia Teacher Reader+*

Worked example 11.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION
30.0 g of solid calcium carbonate was mixed with excess hydrochloric acid solution. The calcium chloride recovered from the reaction mixture had a mass of 25.4 g. Calculate the percentage yield of this reaction.

Thinking	Working
Write a balanced equation for the reaction.	$\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$
Use the appropriate formula, in this case $n(\text{CaCl}_2) = \frac{m}{M}$, to determine the amount, in moles, of reactant.	$n(\text{CaCl}_2) = \frac{25.4}{110.98}$ $= 0.230 \text{ mol}$
Use the mole ratio for the reaction to determine the amount, in moles, of the product that would be made if all of the reactant reacted.	Mole ratio = $\frac{n(\text{CaCl}_2)}{n(\text{CaCO}_3)} = 1$ $n(\text{CaCl}_2) = n(\text{CaCO}_3)$ $= 0.230 \text{ mol}$
Use the formula $m = n \times M$ to determine the mass of the product if all of the reactant reacts. This is the theoretical yield of the product.	$m(\text{CaCl}_2) = n \times M$ $= 0.230 \times 110.98$ $= 25.5 \text{ g}$
Calculate the percentage yield for this reaction from the formula:	Percentage yield = $\frac{\text{actual yield}}{\text{theoretical yield}} \times 100$ $= \frac{25.4}{25.5} \times 100$ $= 76.9\%$

Worked example: Try yourself 11.1.1

CALCULATING THE PERCENTAGE YIELD OF A REACTION
A 50.0 mL volume of 0.250 mol L⁻¹ silver nitrate aqueous solution is mixed with excess sodium chloride solution. The precipitate is filtered and dried to give 1.37 g of silver chloride. Calculate the percentage yield of this reaction.

Percentage yields in multistep syntheses
When a reaction proceeds by a number of steps, the overall percentage yield is reduced at each step. The yield for each step has an effect on the overall yield. A low yield in one of the intermediate reactions can have a significant effect on the amount of final product obtained.
You can compare the overall percentage yields for different pathways to the same product to determine whether a particular synthetic pathway is the best way to produce a compound. Multistep synthesis is particularly common for making organic compounds (see Chapter 14). Finding the most efficient way for the production of a desired chemical is critical to industry because wasting valuable resources is not a good option, economically or environmentally.

Unit Review

Each unit finishes with a comprehensive set of exam-style questions, that assist students draw together their knowledge and understanding and apply it to this style of questions.

UNIT 3 = EQUILIBRIUM, ACIDS AND BASES, AND REDOX REACTIONS

REVIEW QUESTIONS

Section 1: Multiple choice

- Which of the following 105 species arranged with the nitrogen atoms in order of increasing oxidation number?
 - NH₃, N₂, NO, NO₂
 - NO₂, NO, N₂, NH₃
 - N₂, NH₃, NO, NO₂
 - NO₂, NO, N₂, NH₃
- Use the electrochemical series to determine which one of the following would not be expected to occur in an spontaneous reaction.
 - $2\text{H}^+(\text{aq}) + \text{Fe}(s) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
 - $2\text{Ag}^+(\text{aq}) + \text{Ni}(s) \rightarrow 2\text{Ag}(s) + \text{Ni}^{2+}(\text{aq})$
 - $\text{Br}_2(\text{l}) + 2\text{Fe}^{2+}(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$
 - $\text{Cl}_2(\text{g}) + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + \text{Pb}(s)$
- An electrochemical cell was made by dipping a copper rod into a solution of 1 mol L⁻¹ CuSO₄ in one beaker and dipping a nickel rod into a solution of 1 mol L⁻¹ NiSO₄ in another beaker. The metals were connected with wire and the two solutions were connected by a glass of paper towel that had been soaked in a potassium nitrate solution. The cell is shown in the following diagram.

Which of the following shows the activation energy and ΔH of the reverse reaction?

	Activation energy of reverse reaction (kJ mol ⁻¹)	ΔH of reverse reaction (kJ mol ⁻¹)
A	-390	-260
B	+130	-260
C	+130	+260
D	-390	+260
- A student conducted an acid-base volumetric analysis experiment. A 20.0 mL aliquot of a 0.10 mol L⁻¹ solution of hydrochloric acid was pipetted into a flask. A 0.10 mol L⁻¹ solution of potassium hydroxide was added from a burette. After the addition of 19.5 mL, the expected 20.0 mL value, which of the following procedures could be a reason for the low titre?
 - The student accidentally used a 25.0 mL pipette.
 - The 20.0 mL pipette was rinsed with water immediately prior to delivering the aliquot.
 - The conical flask was rinsed with water prior to the titration.
 - The burette was rinsed with water immediately prior to adding the potassium hydroxide solution.

Section summary

Each section includes a summary to assist students consolidate key points and concepts.

9.4 Review

SUMMARY

- Primary secondary and fuel cells are examples of galvanic cells, converting chemical energy directly into electrical energy.
- Primary cells cannot be recharged whereas secondary cells can be recharged by connecting them to an external source of electricity.
- For a cell to be recharged, the products of the discharge reaction have to remain in contact with the electrodes.
- During the recharging of a secondary cell, the equation for the reaction that occurs during the recharging of a secondary cell is the reverse of the equation for the cell (discharging).
- When a secondary cell discharges it acts as a galvanic cell, releasing electrical energy when it is recharged, it acts as an electrolytic cell, converting electrical energy to chemical energy.
- Fuel cells are devices in which the reactants are supplied continuously, allowing constant production of electrical energy.
- Electricity generation using fuel cells is more efficient than of the electricity were generated by the combustion of the same fuel.
- The emissions of greenhouse gases from a fuel cell are less than those from a fossil fuel burner in a power station or vehicle.
- Some scientists predict that fuel cells will play a key role in the transition from a dependence on fossil fuels for energy to a hydrogen economy.

KEY QUESTIONS

- Describe the key differences between a primary cell and a secondary cell.
- Most modern mobile phones contain lithium-ion cells. Select the correct statement about the process that occurs when a phone battery is recharged.
 - A non-spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
 - A non-spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.
 - A spontaneous reaction occurs and the lithium-ion cell acts as an electrolytic cell.
 - A spontaneous reaction occurs and the lithium-ion cell acts as a galvanic cell.
- Which one or more of the following features do secondary cells and fuel cells have in common as they produce electricity?
 - A catalyst is used to increase reaction rate.
 - Cations in the electrolyte move towards the cathode.
 - The anode is negative.
 - The cathode is distinguished from a porous material.
 - Oxidation occurs at the cathode.
 - The oxidising agent is a gas.
 - Chemical energy is converted into electrical energy.
- Which one of the following is a correct statement about what happens in a hydrogen-oxygen fuel cell?
 - Hydrogen gas is oxidised at the anode.
 - Electrons flow through the external circuit from cathode to anode.
 - Soluble, impermeable electrodes are required to prevent contact between reactants and the electrolyte.
 - Oxygen gas is oxidised at the anode.
- In a silver-zinc button cell, the cell reaction is: $2\text{AgCl}(s) + \text{Zn}(s) + 2\text{OH}^-(aq) \rightarrow 2\text{Ag}(s) + \text{ZnO}(s) + 2\text{H}_2\text{O}(l)$. The zinc acts as the anode and the cell contains a potassium hydroxide electrolyte. Write a half-equation for the reaction occurring at the:
 - anode
 - cathode.

Section review questions

Each section finishes with questions to test students' understanding and ability to recall the key concepts of the section

Chapter review

Each chapter finishes with a set of higher order questions to test students' ability to apply the knowledge gained from the chapter.

Chapter review

KEY TERMS

accumulator	electrolyte	nickel-metal hydride cell
alkaline cell	electrolytic cell	non-rechargeable cell
alloy	electromotive force	oxidant
anode	electroplating	oxidising agent
battery	external circuit	potential difference
biogas	fuel cell	primary cell
cathode	galvanic cell	standard electrode potential
cathodic protection	galvanic half-cell	standard hydrogen half-cell
conjugate redox pair	half-cell	standard reduction potential
direct corrosion	hydrogen economy	reducing agent
dry corrosion	inert electrode	reducing agent
electrochemical cell	internal circuit	sacrificial anode
electrochemical series	lead-acid battery	sacrificial protection
electrode	lithium-ion cell	salt bridge
		secondary cell

Galvanic cells

- Which one of the following statements best describes the role of the salt bridge in a galvanic cell?
 - It allows positive charges to accumulate in one half-cell and negative charges to accumulate in the other.
 - It provides a pathway for electrons to move between the half-cells.
 - It allows reactants from one half-cell to mix with reactants from the other half-cell.
 - It allows movement of ions to balance charges formed at the electrodes.
- Which one of the following materials would be least suitable for use as an electrode in a $\text{Cu}(\text{aq})/\text{Cu}(s)$ half-cell?
 - Iron
 - Platinum
 - Graphite
 - Diamond
- Explain the difference between:
 - oxidising agent and reducing agent
 - anode and cathode
 - conjugate redox pair and conjugate acid-base pair
 - external circuit and internal circuit.
- The overall reaction for a galvanic cell constructed from the $\text{Cl}_2(\text{g})/\text{Cl}^-(\text{aq})$ and $\text{Pb}^{2+}(\text{aq})/\text{Pb}(s)$ half-cells is: $\text{Cl}_2(\text{g}) + \text{Pb}(s) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{Pb}^{2+}(\text{aq})$. A platinum electrode is used in the $\text{Cl}_2(\text{g})/\text{Cl}^-(\text{aq})$ half-cell.
 - Draw a diagram of the galvanic cell and on your diagram show:
 - the direction of electron flow in the external circuit
 - a half-equation for the reaction at each electrode
 - which electrode is the anode
 - which electrode is positive
 - which way cations flow in the salt bridge.
 - Write the galvanic cell in shorthand cell notation.
- Two half-cells are set up. One contains a solution of magnesium ions and a strip of magnesium as the electrode. The other contains lead nitrate with a strip of lead as the electrode. The solutions in the two half-cells are connected by a piece of filter paper soaked in potassium nitrate solution. When the electrodes are connected by wires to a galvanometer, the magnesium electrode is shown to be negatively charged.
 - Sketch the galvanic cell described. Label the positive and negative electrodes. Mark the direction of the electron flow.
 - Write the half-equations for the reactions that occur in each half-cell and an equation for the overall reaction.
 - Label the anode and cathode.
 - Indicate the direction in which ions in the salt bridge migrate.

The electrochemical series

- Show that under standard conditions, according to the electrochemical series, the Daniell cell (Figure 9.1.A, page 213) should have a cell potential difference of 1.10 V.

Glossary

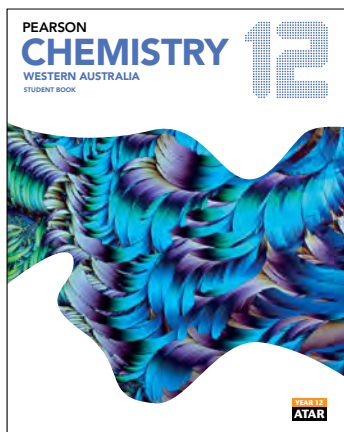
Key terms are shown in bold and listed at the end of each chapter. A comprehensive glossary at the end of the book includes and defines all the key terms.

Answers

Numerical answers and key short response answers are included at the back of the book. Comprehensive answers and fully worked solutions for all section review questions, Try Yourself: Worked examples, chapter review questions and Unit review questions are provided via *Pearson Chemistry 12 Western Australia Teacher Reader+*

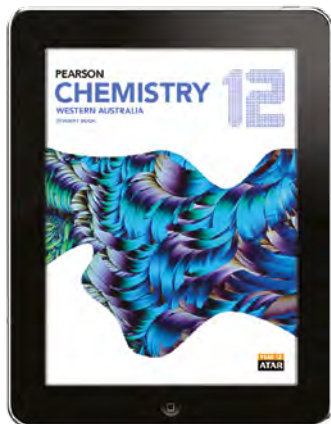
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Equilibrium, acids and bases, and redox reactions

The idea of reversibility of reactions is vital in a variety of chemical systems at different scales, ranging from the processes that release carbon dioxide into the atmosphere to the reactions of ions within individual cells in our bodies. Processes that are reversible will respond to a range of factors and can achieve a state of dynamic equilibrium. In this unit, students investigate acid–base equilibrium systems and their applications. They use contemporary models to explain the nature of acids and bases, and their properties and uses. This understanding enables further exploration of the varying strengths of acids and bases. Students investigate the principles of oxidation and reduction reactions and the production of electricity from electrochemical cells.

Learning outcomes

By the end of this unit, students:

- understand the characteristics of equilibrium systems, and explain and predict how they are affected by changes to temperature, concentration and pressure
- understand the difference between the strength and concentration of acids, and relate this to the principles of chemical equilibrium
- understand how redox reactions, galvanic and electrolytic cells are modelled in terms of electron transfer
- understand how models and theories have developed over time and the ways in which chemical knowledge interacts with social and economic considerations in a range of contexts
- use science inquiry skills to design, conduct, evaluate and communicate investigations into the properties of acids and bases, redox reactions and electrochemical cells, including volumetric analysis
- evaluate, with reference to empirical evidence, claims about equilibrium systems and justify evaluations
- communicate, predict and explain chemical phenomena using qualitative and quantitative representations in appropriate modes and genres.



A premise of kinetic theory is that all particles are in a constant state of motion. A result of this constant chaotic movement is that the particles that make up a substance can, and often do, collide with each other. Usually, these collisions result in no change to the particles, but under the right conditions, the force of the collision can cause chemical bonds to break, which allows for the formation of new chemical bonds.

As you saw in Year 11, how rapidly this breaking and formation of chemical bonds takes place is influenced by a range of experimental factors and can be explained through the application of collision theory.

Science understanding

- collision theory can be used to explain and predict the effects of concentration, temperature, pressure
- the presence of catalysts and surface area of reactants on the rates of chemical reactions
- observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level
- the reversibility of chemical reactions can be explained in terms of the activation energies of the forward and reverse reactions

1.1 Rate of chemical reactions

Some chemical reactions occur very rapidly while others can take an extended period of time. Acid–base reactions and reactions involving ions in solution, such as precipitation, tend to occur rapidly, whereas reactions involving the breaking and formation of covalent bonds, particularly in large molecules, tend to be slower. The nature of the reactants, including the type and strength of bonds involved, can greatly influence the rate of conversion of reactants into products.

Experimentally, the **rate of a reaction** can be determined by measuring, either directly or indirectly, the formation of products or the depletion of reactants over time. Factors that can be measured to determine the rate of a reaction include:

- mass lost by reagent
- mass gained by product
- volume of gas
- pressure of gas
- colour intensity
- solution concentration
- pH.

Different reactions may lend themselves to specific experimental methods of determining the reaction rate. For a reaction that generates a gaseous product, it may be convenient to capture the gas and measure its pressure or volume. For a redox reaction involving coloured compounds, a spectrophotometer could be used to measure the intensity of colour as a function of ion concentration.

In a chemical reaction, reagents are normally mixed together in some way and the particles that make up the substances—atoms, molecules or ions—collide with each other. The number of collisions that takes place is astonishingly large. However, the vast majority of these collisions are not successful and do not result in the formation of products. For a collision to be successful, two criteria must be met. Our understanding of these criteria and their impact on the rate of reaction is explained by **collision theory**.

COLLISION THEORY

A chemical reaction is the result of a successful collision between reactant particles. In order for a collision to be successful, the reactant particles must collide with:

- correct orientation
- sufficient energy.

If either of these criteria is not met, the collision will not be successful and no chemical change will occur.

Correct orientation

Molecules that collide with sufficient energy only do so successfully if they collide with an orientation that allows for the breaking of existing chemical bonds and formation of new chemical bonds.

Figure 1.1.1 shows the importance of collision orientation. In the decomposition of hydrogen iodide gas into hydrogen gas and iodine gas, two hydrogen iodide molecules must collide with hydrogen and iodine atoms orientated towards each other, for a reaction to possibly occur. If the collision orientation is incorrect, the particles simply bounce off each other, and no reaction occurs.

The orientation of colliding particles is the result of their random motion and it is not something that can be easily modified to increase the rate of reaction. Large or complex molecules where the reactive sites represent only a small part of the whole molecule only have a very small number of collisions with the appropriate orientation; this tends to result in a slow reaction rate. Similarly, molecules with extensive structures where the reactive sites are obscured from colliding with other reactant particles don't always react to any appreciable extent.

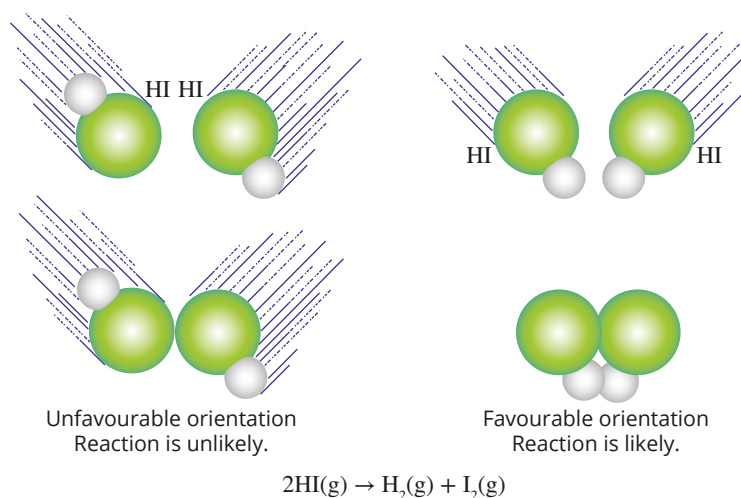


FIGURE 1.1.1 A reaction between colliding molecules is more likely to occur if the orientation of the collision is favourable.

However, the energy required for the particles to collide successfully is more easily modified.

Sufficient energy

When two reactant particles collide, even if they are in the correct orientation, they still need to have a certain amount of **kinetic energy** for the collision to be successful and generate products. This energy is a requirement of the bond breaking (and formation) process. However, at any given temperature, the energies possessed by the particles are not all the same. The particles have a range of kinetic energies as a result of the particles moving at different velocities. This range of kinetic energies can be illustrated by a probability distribution known as a **Maxwell–Boltzmann distribution**, or a **kinetic energy distribution diagram**.

Distribution curves such as the Maxwell–Boltzmann distribution are different from most other graphs that you use in Chemistry. Maxwell–Boltzmann distribution curves do not show the relationship between two simple variables. They represent how a specific variable (in this case, kinetic energy) is distributed amongst the population of particles.

Maxwell–Boltzmann distribution

A Maxwell–Boltzmann distribution (Figure 1.1.2) is a probability distribution function that shows the range of kinetic energies possessed by the particles in a substance at a specific temperature.

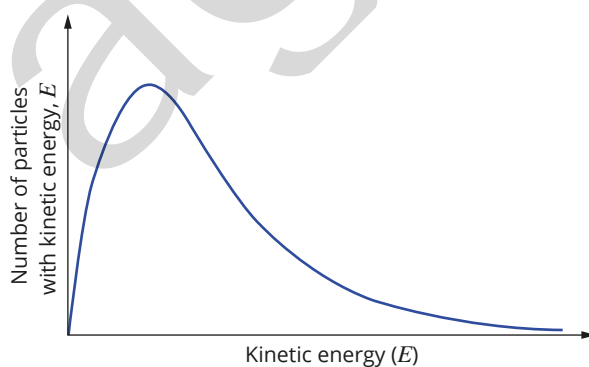


FIGURE 1.1.2 This Maxwell–Boltzmann curve shows the distribution of energies of particles in a sample at a particular temperature.

i Kinetic energy is the energy that a particle or body has due to its motion ($\text{KE} = \frac{1}{2}mv^2$)

There are a number of important details you can observe from the kinetic energy distribution. There are zero particles with zero kinetic energy, a large number of particles with a moderate amount of kinetic energy and fewer and fewer particles with higher levels of kinetic energy. Note that the curve approaches, but never touches, the x -axis, which shows that although the probability is very small, there will always be the chance of some particles possessing extremely high kinetic energies.

The maximum of this graph does not show the maximum energy, it represents the energy possessed by the greatest number of particles in the substance. The average kinetic energy of the particles (which represents the temperature of the substance) occurs slightly to the right of this maximum. The area beneath the curve represents the total number of particles in the sample.

Only the particles that have kinetic energy greater than a certain value will (assuming correct orientation) successfully collide to generate products. This minimum amount of energy required to break the existing chemical bonds, allowing the collisions to be successful, is known as the **activation energy**, E_a .

Activation energy

When the energy of a collision is equal to, or greater than, the activation energy, there is potential for a reaction to occur. If this activation energy is included on a Maxwell–Boltzmann distribution (Figure 1.1.3), it is easy to see how only a small fraction of the total particles in a substance actually has sufficient energy to collide successfully. Of this small fraction, even fewer will collide with the correct orientation.

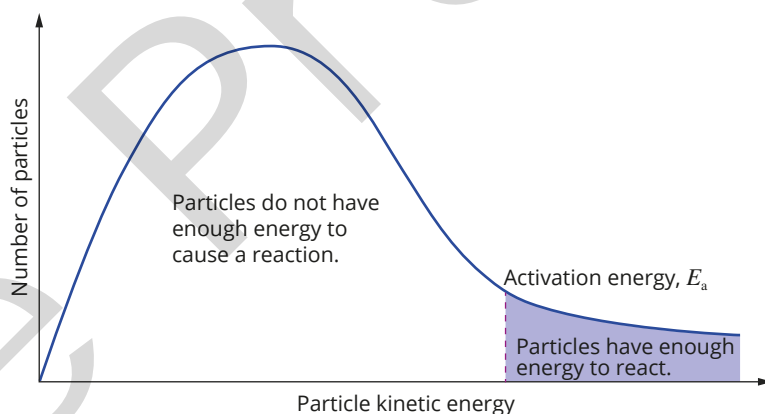


FIGURE 1.1.3 Only a small number of higher energy particles (represented by the shaded area) have sufficient energy to overcome the activation energy barrier.

The activation energy of a reaction can also be illustrated by an **energy profile diagram**. In Figure 1.1.4, the activation energy is represented by the difference in energy from the reactants to the transition state. The **transition state** is the highly energised and highly unstable arrangement of reactant particles where the bond breaking and formation takes place.

i An exothermic reaction releases energy to the surroundings; ΔH is negative.

While we are accustomed to reactions converting reactants into products, some reactions exist in a constant state of flux. This means that at the same time as some reactant particles are converted into products, some of the product particles revert back to the original reactant particles. Note that in the energy profile diagram Figure 1.1.4, the activation energy for the **reverse reaction** (products \rightarrow reactants) is the sum of the activation energy for the forward reaction and the change of enthalpy for the forward reaction. These reversible chemical systems and the state they establish, known as equilibrium, are covered in Chapter 2.

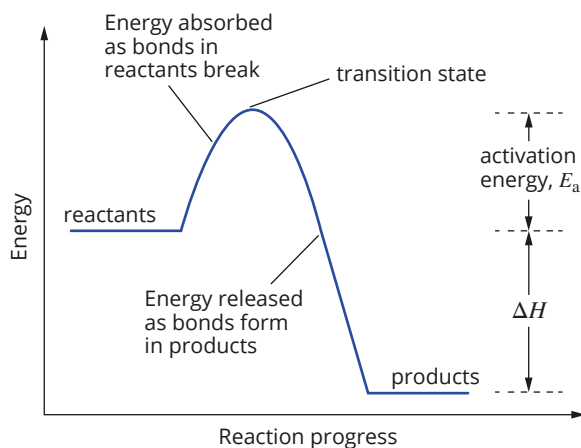


FIGURE 1.1.4 The energy profile diagram for an exothermic reaction such as the combustion of natural gas

It is important to note that although the energy profile diagram and the kinetic energy distribution diagram both include the activation energy, the two diagrams show the same event from very different perspectives. The energy profile diagram shows the reaction ‘journey’ of individual atoms, ions or molecules, whereas the kinetic energy distribution diagram shows the overall picture of all particles potentially involved in a reaction.

Activation energy and reaction rate

The magnitude of a reaction’s activation energy determines the ease with which a given reaction occurs. A reaction that has been determined to be viable may not happen due to its high activation energy. For such reactions, the activation energy is usually supplied from a spark or flame (Figure 1.1.5).

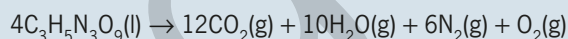


FIGURE 1.1.5 The reagents required for the combustion of the candle wax are present and their particles are colliding, but not with sufficient energy. The activation energy to start the reaction is provided by the flame.

CHEMFILE

A little too reactive!

In 1846, the Italian chemist Ascanio Sobrero reacted glycerol with a mixture of sulfuric and nitric acids to make the explosive liquid nitroglycerin. Nitroglycerin is so unstable that even a small bump can cause it to explode. It decomposes according to the equation:



Despite being many times more powerful than conventional gunpowder, nitroglycerin was far too dangerous to be practical. Some years later, the Swedish scientist Alfred Nobel learnt how to manage nitroglycerin more safely through his invention of dynamite.

The reason for nitroglycerin’s instability is the very small activation energy for its decomposition reaction (Figure 1.1.6).

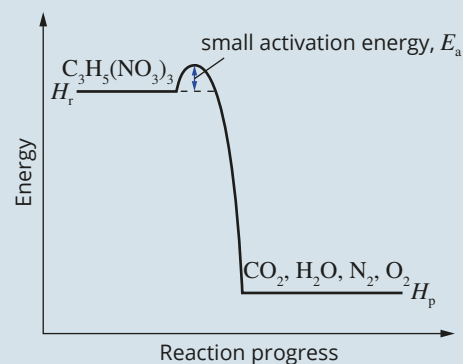


FIGURE 1.1.6 Nitroglycerin has a very low activation energy, making its rate of reaction very large.

1.1 Review

SUMMARY

- The rate of a reaction is the formation of products or the depletion of reactants over time.
- A range of experimental quantities can be used to calculate the rate of a reaction; they include:
 - mass lost by reagent
 - mass gained by product
 - volume of gas
 - pressure of gas
 - colour intensity
 - solution concentration
 - pH.
- The activation energy of a reaction is the minimum amount of energy required to break reactant bonds to allow a reaction to proceed. It is the minimum amount of energy that a collision between reactant particles must possess for a reaction to occur.
- Collision theory is a theoretical model that accounts for the rates of chemical reactions in terms of collisions between particles during a chemical reaction.
- According to collision theory, for a reaction to occur, the reactant particles must:
 - collide with sufficient energy to break the bonds within the reactants
 - collide with the correct orientation to break the bonds within the reactants and so allow the formation of new products.
- The range of kinetic energies possessed by particles in a substance at a given temperature is shown by a Maxwell–Boltzmann distribution.

KEY QUESTIONS

- 1 Which one of the following would not be a suitable method to measure the rate of the reaction between zinc metal and hydrochloric acid?
 - A Loss of mass from the reaction vessel
 - B Mass of hydrogen gas produced
 - C The concentration of zinc metal remaining
 - D The volume of hydrogen gas produced
- 2 What are the two criteria required for a collision to be successful?
- 3
 - a Draw a fully labelled Maxwell–Boltzmann distribution to represent the range of kinetic energies possessed by the particles in a substance at a certain temperature.
 - b On the same diagram, in a different colour, draw the distribution that would exist at a higher temperature.
- 4 What is activation energy?
- 5 Draw a fully labelled energy profile diagram for an endothermic reaction.
- 6 Figure 1.1.7 shows the apparatus used to measure the rate of reaction between marble chips and hydrochloric acid.
 - a Write a fully balanced chemical equation for this experiment.
 - b Once the reaction has finished, describe how you can determine which reagent is completely used up (the limiting reagent).
 - c A student stated that the data obtained from this experiment violated the law of conservation of mass because the mass of the chemicals in the flask reduced during the reaction. Explain why this statement is incorrect.

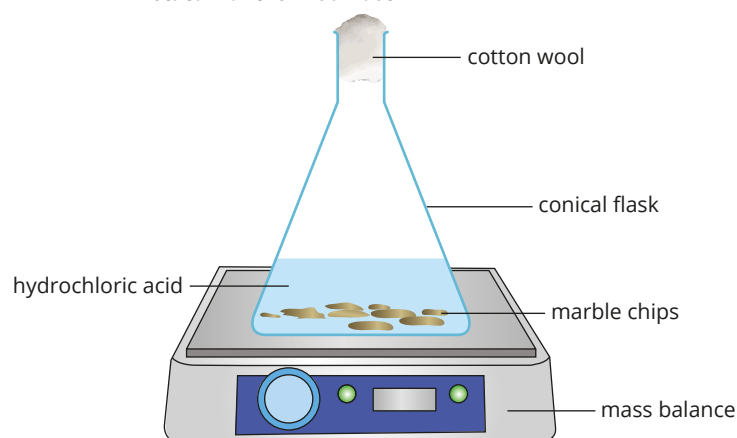


FIGURE 1.1.7 Measuring the rate of reaction between marble chips and hydrochloric acid

1.2 Factors that influence reaction rate

The rate of a reaction depends on the number of successful collisions between reactant particles per unit of time. Successful collisions require both the correct orientation and sufficient energy to meet or exceed the activation energy of the reaction.

Experimental investigations have shown that five main factors can change the rate of a chemical reaction:

- surface area of solid reactants
- concentration of reactants in a solution
- gas pressure
- temperature
- the presence of a catalyst.

The effect on the reaction rate demonstrated by these factors can be attributed to either: (i) generating a greater number of collisions (both successful and unsuccessful) per unit time or (ii) increasing the probability that any given collision will be successful.

INCREASING COLLISION FREQUENCY

In any given reaction mixture, only a certain percentage of the collisions that occur are successful. If you can increase the overall frequency of collisions, because a certain percentage of these collisions will be successful, then you can increase the total number of successful collisions per unit of time, and hence increase the reaction rate.

The experimental factors that rely on an increased frequency of collisions to achieve a higher reaction rate include:

- surface area
- concentration
- gas pressure.

Surface area

When a solid is involved in a reaction, only the particles at the surface of the solid are available to collide with other reactant particles. The number of particles at the surface depends on the surface area of the substance.

The **surface area** is a consequence of the particle size. As can be seen in Figure 1.2.1, when the size of the particles of a substance is reduced, the total surface area of the substance increases.

Grinding or breaking a solid into smaller pieces provides a greater total surface area, allowing more reactant particles to collide (Figure 1.2.2). This increased frequency of collisions results in a higher number of successful collisions per unit of time and hence an increased reaction rate.

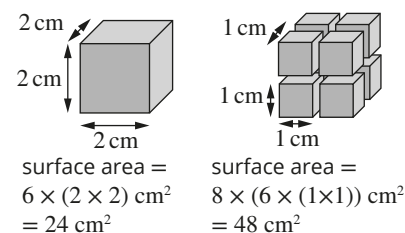


FIGURE 1.2.1 Given two samples of equal volume of a solid, it is clear that the sample with the smaller particle size has a greater total surface area.

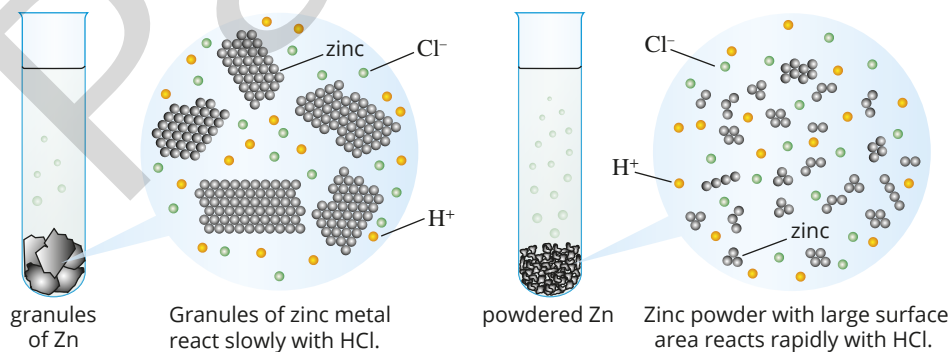


FIGURE 1.2.2 The reaction of hydrochloric acid and zinc. As the surface area of zinc increases, the rate of reaction with hydrochloric acid increases.

CHEMFILE

Oil fires and water don't mix

At some stage, every cook will encounter a fat, oil or grease fire in the kitchen. In the first moment of panic, many people would think to throw water on the fire, but that action can lead to disastrous and possibly fatal results (Figure 1.2.3).

Water is denser and has a lower boiling point than the fat or oil fueling a grease fire. When water is added to a pan with burning oil, the water sinks beneath the oil and instantly boils. The expansion of the water vapour ejects the oil from the pan as a fine spray of droplets. This fine spray of droplets collectively has a much larger surface area than the oil in the pan. This causes the combustion reaction to accelerate with explosive results.

The safest way to extinguish an oil fire is to eliminate one of the reactants of the combustion reaction: oxygen. Covering the pan or spreading a large amount of baking soda or salt over it will prevent additional oxygen molecules from colliding with the oil, stopping the combustion.



FIGURE 1.2.3 Using water on a fat, oil or grease fire can accelerate the rate of a combustion reaction with life-threatening results.

Concentration

The **concentration** of a substance is the number of particles per unit of volume; for example, the number of moles of a substance per litre of a solution. A high concentration of solutes dissolved in a solution increases the frequency of collisions.

In Figure 1.2.4, you can see that the concentration of one of the reactants has been increased ten-fold while the volume remains constant. This more concentrated solution will experience a greater total number of collisions between reactant particles. A certain percentage of collisions will be successful, resulting in a greater number of successful collisions per unit of time and hence, a faster reaction rate.

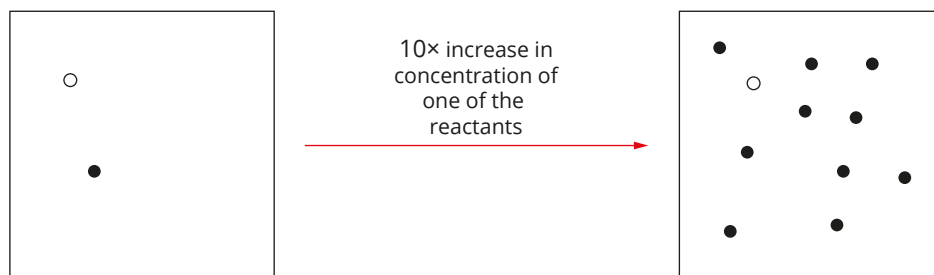


FIGURE 1.2.4 A greater number of reactant particles in the same volume will result in a greater number of collisions.

CHEMISTRY IN ACTION

Acid rain

Stone statues in locations prone to **acid rain** deteriorate relatively rapidly. This deterioration provides an example of the effect of concentration on the rate of a chemical reaction.

Most rainwater is slightly acidic as a result of the presence of carbonic acid, formed by carbon dioxide gas dissolved in the water. Oxides of nitrogen and sulfur released by cars and industry also dissolve in water, raising the concentration of acids in rainwater further. As a result, the rates of the reactions that disfigure stone statues (Figure 1.2.5) are also increased.



FIGURE 1.2.5 A reaction between acid rain and the limestone used to make this statue of a stone lion has caused the statue to deteriorate significantly.

Pressure

Pressure is the force per unit area that gas particles exert when they collide with the walls of their container. A high gas pressure is the consequence of having an increased number of gas particles in a given volume, at constant temperature.

When more gas particles are introduced into a given volume, raising the pressure, the frequency of collisions per unit time increases. Of this greater total number of collisions, a certain percentage will be successful, resulting in a greater number of successful collisions per unit of time and hence, a faster reaction rate.

Partial pressures

For a mixture of gases, such as air, the total pressure exerted by the mixture is the sum of the individual pressures of the composite gases. These individual gas pressures, when considered as part of a mixture, are known as **partial pressures**. The partial pressure of a gas in a mixture of gases can be considered as the equivalent of the concentration of a solute in a solution.

For example, air is generally considered to be composed of 78% nitrogen (N_2), 21% oxygen (O_2) and about 1% argon (Ar) and other gases. Atmospheric pressure at sea level is 101.3 kPa. So 78% of this value can be attributed to the partial pressure of nitrogen, 21% to the partial pressure of oxygen and the remaining 1% to the partial pressure of argon and other gases.

In this course, you will not need to undertake calculations involving partial pressures. However, if required, the partial pressure of nitrogen in air could be calculated according to the equation:

$$\text{partial pressure } (N_2) = \left(\frac{78}{100}\right) \times 101.3 = 79.0 \text{ kPa}$$

This also means that if two reacting gases are in a vessel of fixed volume, and the total pressure is increased by adding an inert gas such as helium, although the total pressure of the system increases, the partial pressure of the two reacting gases does not change, and hence the reaction rate remains unchanged.

INCREASING COLLISION PROBABILITY

Most collisions between reactant particles are unsuccessful. Even if particles have the correct orientation, the particles may not have the required activation energy. If you can increase the probability of a given collision being successful, you can increase the total number of successful collisions per unit of time and hence increase the reaction rate.

Experimental conditions that can affect the probability of a successful collision and so produce a higher reaction rate include:

- temperature
- the presence of catalysts.

Temperature

An increase in the **temperature** of a substance corresponds with an increase in the average kinetic energy of the particles that make up the substance. This is illustrated in Figure 1.2.6 in which the range of kinetic energies for a gas at three different temperatures is shown. As the temperature increases, the increasing average kinetic energy of the particles can be seen by the movement to the right of the peak in the Maxwell–Boltzmann curve.

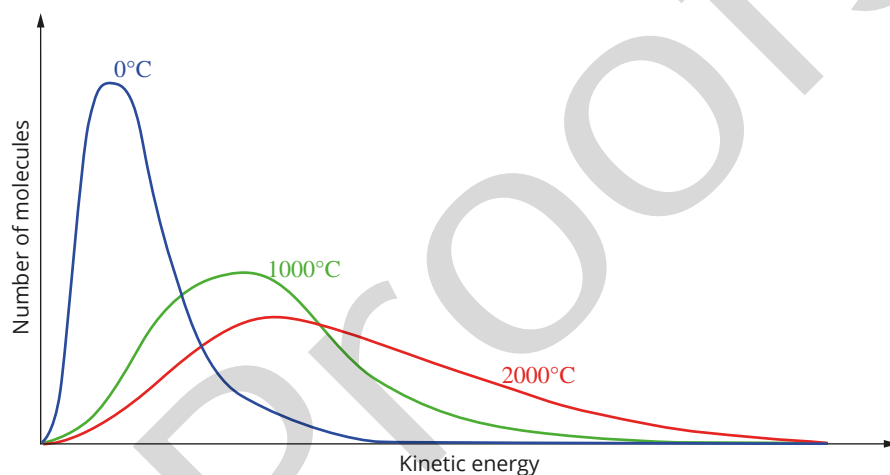


FIGURE 1.2.6 The Maxwell–Boltzmann distribution for a sample of gas at a range of temperatures. Note the reducing height of the maximum of each curve in the graph. This is to maintain the same area under the curve (which is equal to the total number of particles in the sample) as heating the gas does not generate additional particles.

This increase in average kinetic energy causes the particles to move, on average, with an increased speed, causing a greater frequency of collisions, both successful and unsuccessful. An increase in the temperature of the substance will also result in a greater percentage of these collisions satisfying the activation energy requirement for the reaction (Figure 1.2.7). This will cause a higher percentage of the existing collisions to be successful per unit of time and hence, a faster reaction rate.

So, a higher temperature increases the overall number of collisions and increases the proportion of successful collisions.

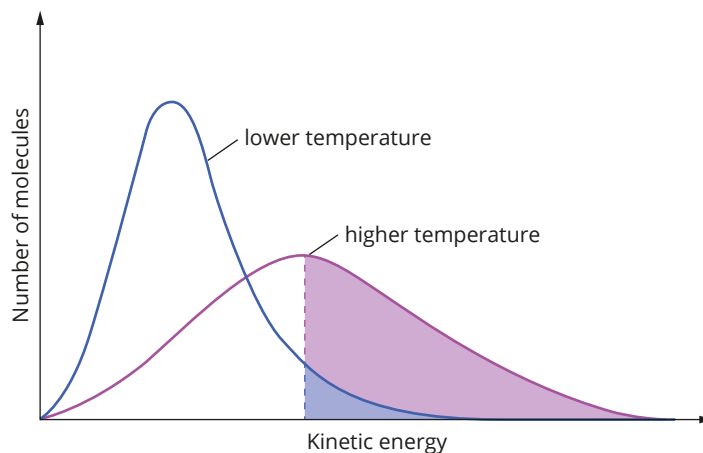


FIGURE 1.2.7 The proportion of particles that exceed the activation energy, E_a , is much greater for the sample at the higher temperature than the lower temperature.

A temperature increase of just 10°C doubles the rate of many reactions, but it can be shown that this is not due to the increased frequency of collisions. The frequency of collisions only increases by about 3% when the temperature increases by 10°C. The main reason why the reaction rate increases is that a greater proportion of the particles have sufficient energy to overcome the activation energy barrier of the reaction.

Catalysts

Most collisions are unsuccessful, even when they have correct orientation, because the particles don't have enough energy to overcome the activation energy. A **catalyst** works by providing an alternative **reaction pathway** with lower activation energy. In this way, a greater proportion of the reactant particles will have enough energy to overcome the, now reduced, activation energy (Figure 1.2.8). This increased probability of a successful collision results in a greater number of successful collisions per unit time and hence a faster reaction rate.

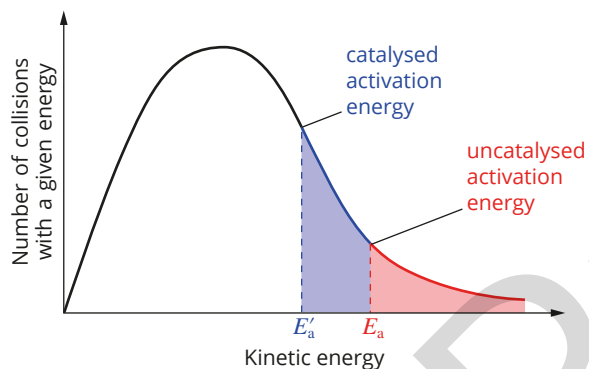


FIGURE 1.2.8 A catalyst provides an alternative reaction pathway with a low activation energy, increasing the proportion of collisions that exceed the activation energy and lead to a reaction.

Catalysts are specific to certain reactions; what catalyses one reaction may not catalyse another. Catalysts are not consumed in the reactions they catalyse and can be recovered and reused. However, they can be deactivated or poisoned at which point they cease to increase the reaction rate. The alternative reaction pathway with a lower activation energy can be illustrated on a reaction energy profile (Figure 1.2.9).

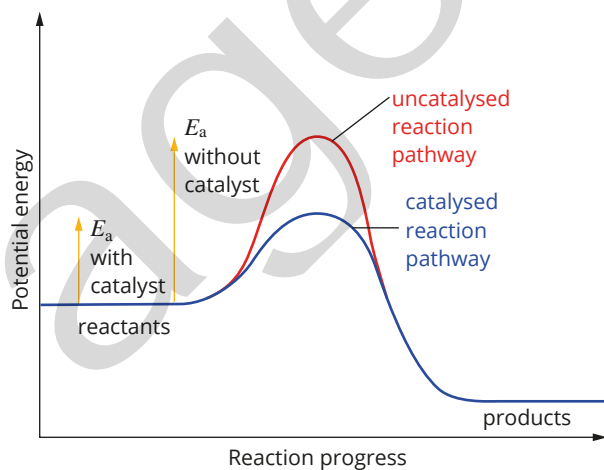


FIGURE 1.2.9 Energy profile diagrams with a catalysed and uncatalysed reaction. Note that the presence of a catalyst also reduces the activation energy for the reverse (products → reactants) reaction.

1.2 Review

SUMMARY

- The rate of a reaction can be increased by:
 - increasing the surface area of solid reactants
 - increasing the concentration of a reactant in solution
 - increasing the pressure of a gaseous reactant
 - increasing the temperature of the reaction system
 - adding a suitable catalyst.
- Increasing the surface area of solid reactants:
 - exposes a greater number of reactant particles to collisions
 - increases the frequency of collisions between reactants
 - increases the number of successful collisions in a given time.
- Increasing the concentration of a reactant in solution increases the:
 - number of solute particles per unit of volume
 - frequency of collisions between reactant particles
 - number of successful collisions in a given time.
- Increasing the pressure of a gaseous reactant increases the:
 - number of gas particles per unit of volume (assuming constant temperature)
 - frequency of collisions between reactant particles
 - number of successful collisions in a given time.
- Increasing the temperature of the reaction system increases the:
 - frequency of collisions between reactant particles
 - proportion of collisions which are successful
 - and therefore number of successful collisions in a given time.
- Adding a suitable catalyst:
 - provides an alternative reaction pathway with a lower activation energy
 - increases the proportion of successful collisions
 - increases the number of successful collisions in a given time.
- A Maxwell–Boltzmann distribution may be used to represent the range of kinetic energies possessed by particles in a substance at a given temperature.
- Energy profile diagrams, which can include catalysed and uncatalysed pathways, may be used to represent the enthalpy changes and activation energy associated with a chemical reaction.

KEY QUESTIONS

- 1 According to the collision theory, which one of the following is *not* essential for a reaction to occur?
 - A Molecules must collide to react.
 - B The reactant particles should collide with the correct orientation.
 - C The reactant particles should collide with enough energy to overcome the activation energy barrier.
 - D The reactant particles should collide with double the energy of the activation energy.
- 2 Which one of the following is the energy required to produce the transition state in a reaction?
 - A Activation energy
 - B Difference in energy between the products and reactants
 - C Difference in energy between the products and the activation energy
 - D Transition state energy
- 3 Which one of the following correctly explains why a sample of magnesium reacts more rapidly with 1 mol L^{-1} HCl than with 0.1 mol L^{-1} HCl?
 - A The energy of collisions between reactant particles is greater for the reaction containing 1 mol L^{-1} HCl.
 - B The rate of collisions between reactant particles is greater for the reaction containing 0.1 mol L^{-1} HCl.
 - C There are more collisions between the magnesium and 1 mol L^{-1} HCl.
 - D The frequency of collisions between reactant particles is greater for the reaction containing 1 mol L^{-1} HCl.

- 4 The effect of particle size on the reaction rate between marble chips and hydrochloric acid was examined. Carbon dioxide gas was collected by the downward displacement of water and its volume measured at regular intervals until the reaction had stopped. The results are given in Figure 1.2.10.

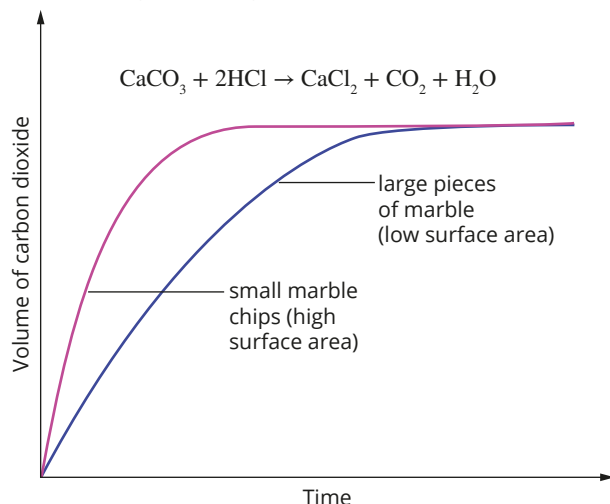
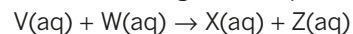


FIGURE 1.2.10 The volume of carbon dioxide produced by small and large marble chips over time

- What does the steeper gradient of the small marble chips signify?
 - What does the region of zero gradient on the curve represent?
 - Why do both curves plateau at the same point?
- 5 When 1.00 mol of methane gas burns completely in oxygen, the process of bond breaking uses 3380 kJ of energy and 4270 kJ of energy is released as new bonds form.
- Write a balanced chemical equation for the reaction.
 - Calculate the value of the heat of reaction, ΔH , for the reaction.
 - Draw and label a diagram to show the changes in energy during the course of the reaction.
- 6 The formation of hydrogen iodide from its elements is represented by the equation:
- $$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$$
- This reaction has an activation energy of 167 kJ mol^{-1} and the heat of reaction, ΔH , is $+28.0 \text{ kJ mol}^{-1}$. What is the activation energy for the reverse reaction, the decomposition of 2.00 mol of hydrogen iodide?

- 7 Consider the reaction between solutions V and W that produces X and Z according to the equation:



The energy profile diagram for this process is shown in Figure 1.2.11.

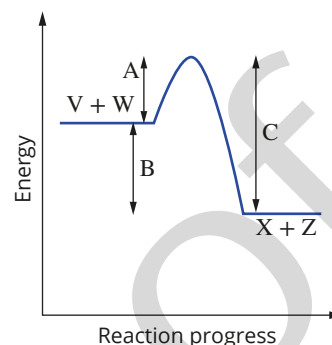


FIGURE 1.2.11 The energy profile diagram for the reaction between V(aq) and W(aq)

- Is the reaction endothermic or exothermic?
 - What does the value marked A represent for the forward reaction?
 - What does the value marked B represent for the forward reaction?
 - What does the value marked B represent for the reverse of this reaction?
 - What does the value marked C represent for the reverse of this reaction?
- 8 Draw the Maxwell-Boltzmann distribution for an uncatalysed and catalysed reaction on the same set of axes. In what way do they differ?

Chapter review

KEY TERMS

acid rain	kinetic energy distribution diagram	reaction pathway
activation energy	Maxwell–Boltzmann distribution curve	reverse reaction
catalyst	partial pressure	surface area
collision theory	pressure	temperature
concentration	rate of reaction	transition state
energy profile diagram		
kinetic energy		

Rate of chemical reactions

- 1 According to collision theory, what must happen for a reaction to occur?
- 2 Which of the following combinations of reactants will produce the greatest initial reaction rate?
 $2\text{HCl}(\text{aq}) + \text{CaCO}_3(\text{s}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
 - A CaCO_3 chips and 1.0 mol L^{-1} HCl
 - B CaCO_3 chips and 2.0 mol L^{-1} HCl
 - C CaCO_3 powder and 2.0 mol L^{-1} HCl
 - D CaCO_3 powder and 1.0 mol L^{-1} HCl
- 3 Which one of the following alternatives correctly explains why the rate of reaction between 1.0 mol L^{-1} CuSO_4 and powdered zinc is greater than with an equal amount of large zinc pieces?
 - A The energy of collisions between the $\text{Cu}^{2+}(\text{aq})$ ions and powdered zinc is greater than with the large zinc pieces.
 - B The frequency of collisions between the $\text{Cu}^{2+}(\text{aq})$ ions and powdered zinc is greater than with the large zinc pieces.
 - C The energy of collisions between the $\text{Cu}^{2+}(\text{aq})$ ions and large zinc pieces is greater than with the powdered zinc.
 - D The frequency of collisions between the $\text{Cu}^{2+}(\text{aq})$ ions and large zinc pieces is greater than with the powdered zinc.
- 4 Which one of the following statements correctly describes what must occur when reactant particles collide and react?
 - A Colliding particles must have an equal amount of kinetic energy.
 - B Colliding particles must have different amounts of kinetic energy.
 - C Colliding particles must have kinetic energy equal to or greater than the average kinetic energy.
 - D Colliding particles must have kinetic energy equal to or greater than the activation energy of the reaction.
- 5 Explain why time on its own is not a useful quantity to measure the rate of a reaction.
- 6 In situations where the reaction mixture is heterogeneous, stirring can increase reaction rate. Explain this using collision theory.
- 7 A characteristic of all materials is their auto ignition temperature. This is the lowest temperature at which a substance will spontaneously ignite under normal atmospheric conditions without an external ignition source such as a spark or flame. Explain, using collision theory, what is occurring to a substance at its auto ignition temperature.
- 8 Evaluate the statement 'Put food in the freezer so it doesn't go off', using your knowledge of collision theory and reaction rates.
- 9
 - a Figure 1.3.1 shows the distribution of energies of particles in a substance at two different temperatures, 40°C and 60°C . Indicate the temperatures represented by graphs A and B.

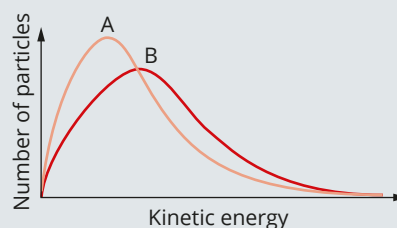


FIGURE 1.3.1 Energy profiles at 40°C and 60°C

- b Copy this diagram for temperature B and use the diagram to show the effect of a catalyst on a reaction.
- c Use the diagram you have drawn in part b to explain in terms of collision theory how a catalyst increases the rate of a reaction.

Factors that influence reaction rate

- 10 a** List the five factors that influence the rate of a reaction.
- b** Classify the five factors from part **a** according to whether they increase the proportion of successful collisions by increasing:
- collision frequency
 - the proportion of collisions that have energy equal to or greater than the activation energy.
- 11** Which one of the following factors would *not* increase the rate of decomposition of hydrogen peroxide?
- $$2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$$
- A** Increasing the pressure of oxygen gas
B Increasing the concentration of hydrogen peroxide
C Increasing the temperature of hydrogen peroxide
D Adding a potassium iodide catalyst
- 12** A student is attempting to use an excess of 1.0 mol L^{-1} hydrochloric acid to dissolve an iron nail. If the student doubles the initial starting volume of acid, using collision theory, predict and explain how this would change the time taken to completely dissolve the nail.
- 13** The first step in most toffee recipes is to dissolve about three cups of sugar in one cup of water. Although sugar is quite soluble in water, this step could be time-consuming. Use your knowledge of reaction rates to suggest at least three things you could do to increase the rate of dissolution without ruining the toffee.
- 14** Which statement is correct for the effects of catalyst and concentration on the rate of reaction?

	Adding a catalyst	Increasing the concentration
A	Collision frequency increases	Collision frequency increases
B	Activation energy decreases	Activation energy decreases
C	Activation energy decreases	Collision frequency increases
D	Collision frequency increases	Activation energy decreases

- 15** Many major car-makers have plans for hydrogen-powered cars. In the fuel cells of these cars, hydrogen reacts with oxygen from the air to produce water:
- $$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$$

Energy changes for the reaction are shown in the graph in Figure 1.3.2.

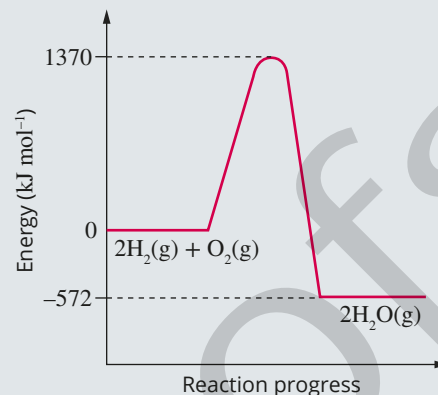


FIGURE 1.3.2 Energy changes for the reaction of hydrogen and oxygen

- What is the magnitude of the activation energy of this reaction?
- What is ΔH for this reaction?
- Several groups of scientists have claimed to have split water into hydrogen and oxygen using a molybdenum catalyst:

$$2\text{H}_2\text{O}(\text{g}) \xrightarrow{\text{Mo}} 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$$
 Sketch energy change graphs for this reaction with and without the presence of a catalyst.
- What is the value of ΔH for this water-splitting equation?

Connecting the main ideas

- 16** A 5.00 g piece of copper was dissolved in a beaker containing an excess of 2.00 mol L^{-1} nitric acid. The equation for the reaction that occurred is:
- $$3\text{Cu}(\text{s}) + 8\text{HNO}_3(\text{aq}) \rightarrow 3\text{Cu}(\text{NO}_3)_2(\text{aq}) + 2\text{NO}(\text{g}) + 4\text{H}_2\text{O}(\text{l})$$

The changing mass of the mixture was observed for a period of time, and the graph in Figure 1.3.3 was obtained.

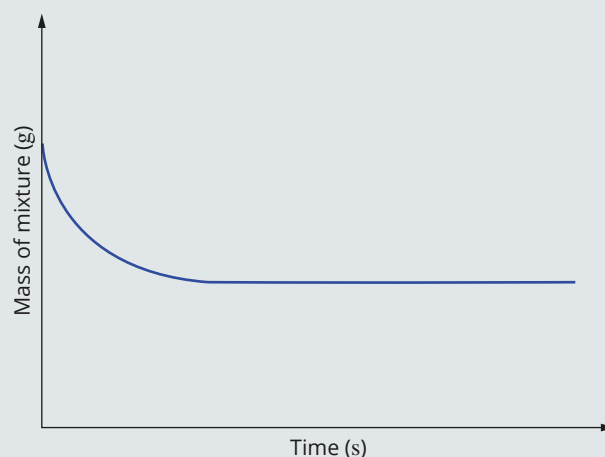


FIGURE 1.3.3 Mass of reaction mixture over time

- a Describe the rate of the reaction over the duration of the experiment and explain it using collision theory.
- b Explain why the graph levels out.
- c Redraw the graph in Figure 1.3.3, then sketch in the expected curve if an excess of 1.00 mol L^{-1} nitric acid had been used instead. Label your new graph line. Explain the difference in shape.
- d Redraw the graph, then sketch in the expected curve if 5.00 g of powdered copper was used instead. Label this new graph line. Explain the difference in shape.
- 17** Lumps of limestone, calcium carbonate, react readily with dilute hydrochloric acid. Four large lumps of limestone, mass 10.0 g , were reacted with 100 mL 0.100 mol L^{-1} acid.
- a Write a balanced equation to describe the reaction.
- b Use a calculation to prove that calcium carbonate is in excess.
- c Describe a technique that you could use in a school laboratory to measure the rate of the reaction.
- d 10.0 g of small lumps of limestone will react at a different rate from four large lumps. Will the reaction with the smaller lumps be faster or slower? Explain your answer in terms of collision theory.
- e List two other ways in which the rate of this reaction can be altered. Explain your answer in terms of collision theory.
- 18** The graph in Figure 1.3.4 shows the energy profile diagram for the reaction of hydrogen and iodine to form hydrogen iodide:

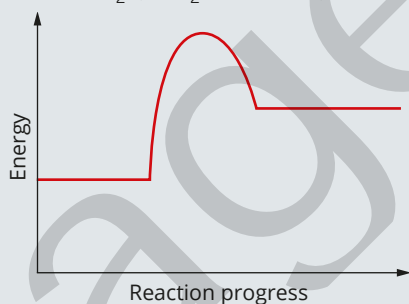
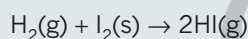


FIGURE 1.3.4 Energy profile diagram for the production of hydrogen iodide.

- a Copy the diagram and label the following: $\text{H}_2(\text{g})$ and $\text{I}_2(\text{s})$; $\text{HI}(\text{g})$; ΔH ; activation energy.
- b Is the reaction endothermic or exothermic?
- c On the diagram draw the energy profile that would result if a catalyst was used in the reaction.

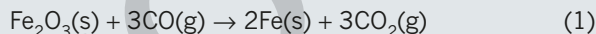
- 19** Read the article and answer the questions that follow.

Exploding iron

In 1996, while the Turkish ship *MV B. Onal* was riding at anchor in Delaware Bay, near Philadelphia in the USA, a 2-tonne hatch cover suddenly blew off. As the ship was carrying a cargo of iron, the surprised crew asked themselves, 'Can iron explode?'

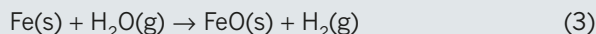
As you may be aware, traditionally iron oxide (Fe_2O_3) is reduced to molten iron in a blast furnace.

A new process that uses less energy has been developed. Iron oxide is converted directly to solid iron without having to heat the reactants to the melting point of iron. Iron oxide is heated to 550°C in the presence of carbon monoxide and hydrogen gas. The iron oxide is reduced to iron by both gases with the formation of carbon dioxide or water.



The pellets of pure iron that are formed are extremely porous and full of many tiny holes, in contrast to the solid formed when the molten iron from a blast furnace cools. Under the right conditions the iron pellets can be oxidised back to iron oxide.

In most cases, iron is oxidised slowly by oxygen back to iron oxide and the resulting heat can readily escape. If the pellets are more than 1 metre deep, as in the hold of a ship, the heat cannot escape quickly enough and the temperature rises. This speeds up the reaction rate. If the temperature increases sufficiently and water is present, another reaction occurs and the oxidation rate is speeded up 100-fold, with the release of more heat:



Any spark or fire will set off an explosion of hydrogen gas, and that is what happened on the *MV B. Onal*.

- a What is the main reason the new reduction process uses less energy than the old process?
- b Write equations showing the oxidation of iron by oxygen to form iron(II) oxide and iron(III) oxide.
- c If water is present, the oxidation reaction speeds up 100-fold. Is water acting as a catalyst? Explain your answer.
- d Is the reaction shown in equation 3 endothermic or exothermic?
- e List the factors that increased the rate of reaction in equation 3.
- f Firefighters were not able to use water to put out the fire in the cargo hold. Why not? Suggest how they could put out the fire.