PEARSON
CHEMISTRY 12
WESTERN AUSTRALIA

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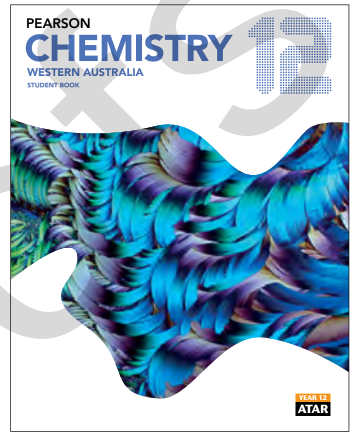

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How do chemicals swap protons?

AREA OF STUDY 3 OXIDATION AND REDUCTION

Where do chemicals find electrons?

Unit 4: Organic chemistry and chemical synthesis

How to use this book

Pearson Chemistry 12 Western Australia

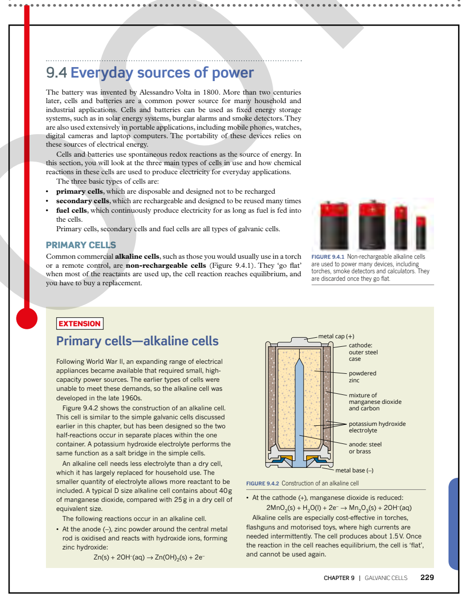
Pearson Chemistry 12 Western Australia has been written to the *WACE Chemistry ATAR Course, Year 12 Syllabus 2017.* Each chapter is clearly divided into manageable sections of work. Best practice literacy and instructional design are combined with high quality, relevant photos and illustrations. Explore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

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.

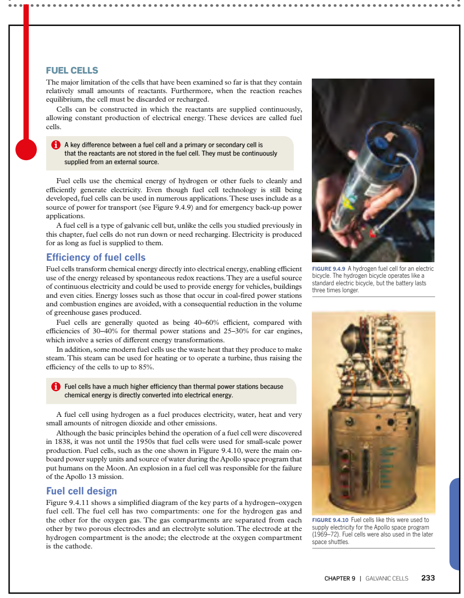


ChemFile

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

Highlight box

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



Chemistry in Action

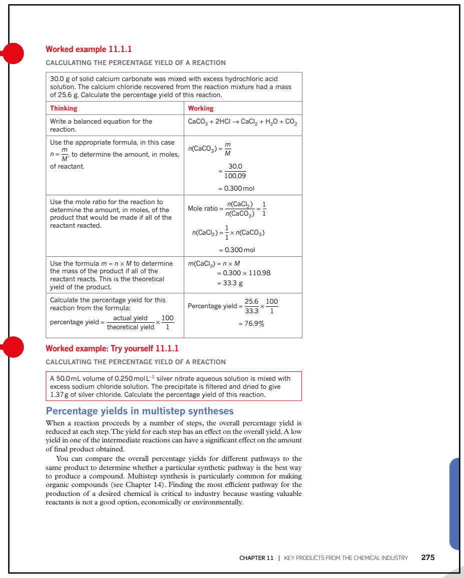
Chemistry in Action boxes place Chemistry in an applied situation or relevant context and encourages students to think about the development of chemistry and its use and influence of chemistry in society.

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.

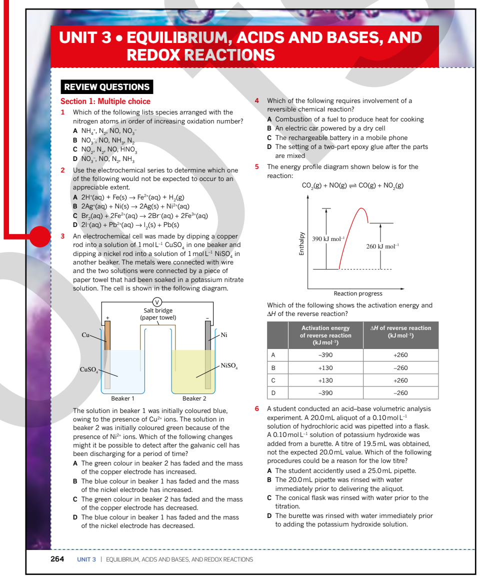
Each Worked example is followed by a Try Yourself: Worked example. This mirror problem allows students to immediately test their understanding.

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



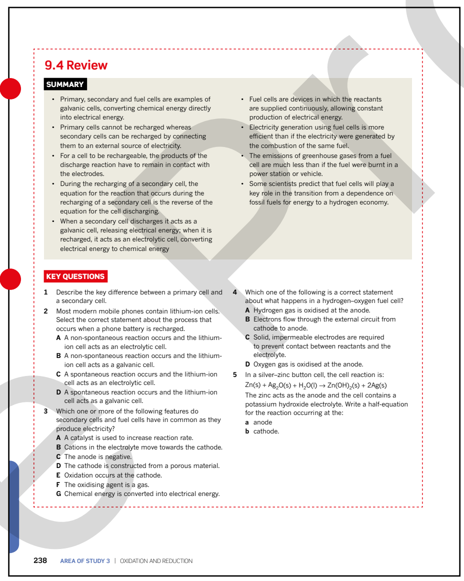
Unit Review

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.



Section summary

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



Section review questions

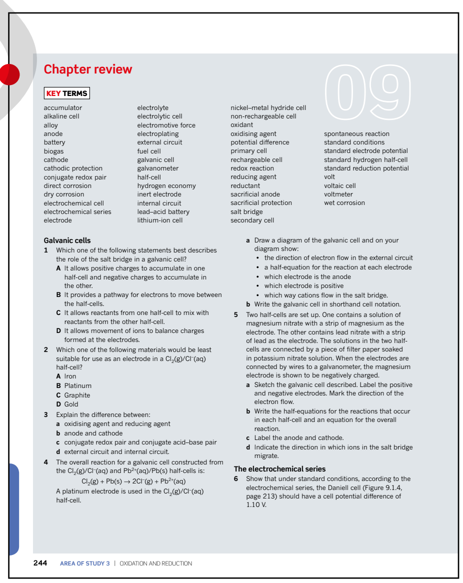
Each section finishes with questions to test students' understanding and ability to recall the key concepts of the section

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.

Chapter review

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



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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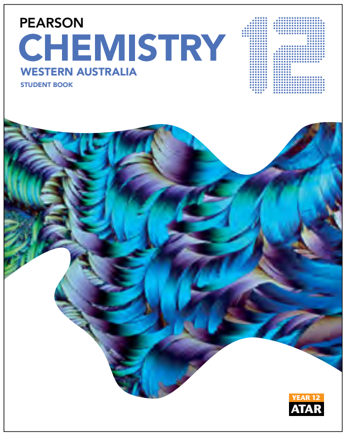
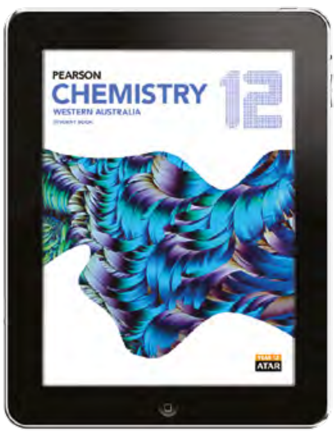


Student Book

Pearson Chemistry 12 Western Australia has been written to fully align with the *WACE Chemistry ATAR Course, Year 12 Syllabus 2016.* The series includes the very latest developments and applications of Chemistry and incorporates best practice literacy and instructional design to ensure the content and concepts are fully accessible to all students.



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UNIT 3 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.

CHAPTER 01

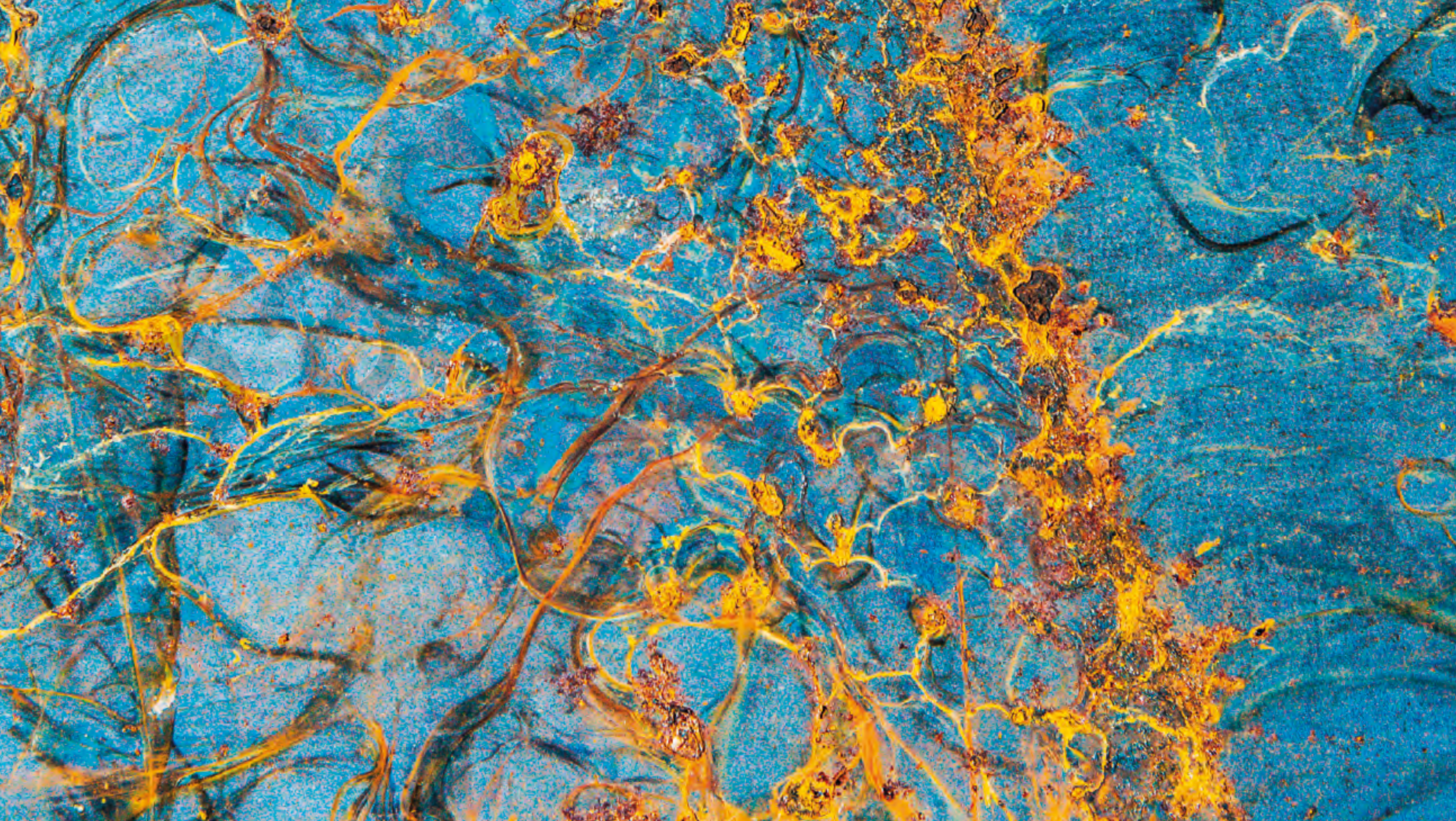
Rate of chemical reactions

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.

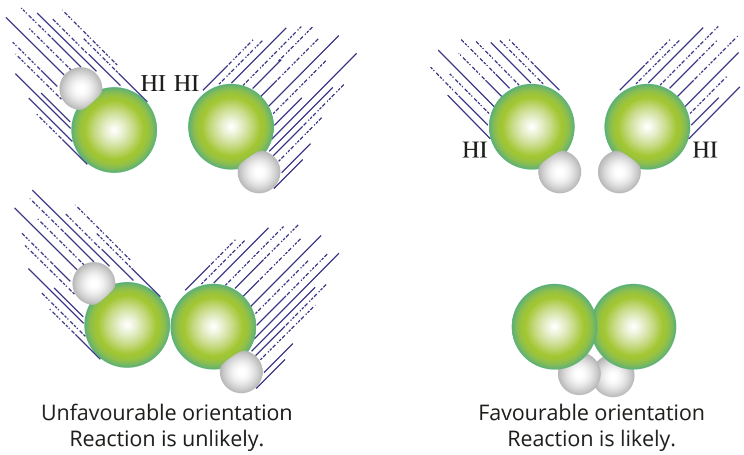
If either of these criteria is not met, the collision will not be successful and no chemical change will occur.

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.



$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

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.

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

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.

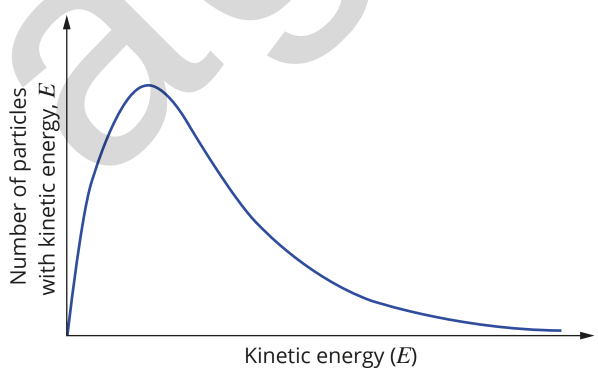


FIGURE 1.1.2 This Maxwell–Boltzmann curve shows the distribution of energies of particles in a sample at a particular temperature.

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**, $\boldsymbol{E_a}$.

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.

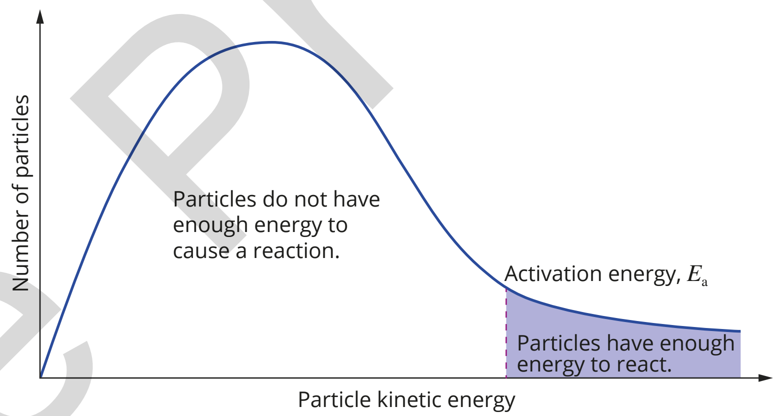


FIGURE 1.1.3 Only a small number of higher energy particles (represented by the shaded area) have sufficient energy to overcome the activation energy barrier.

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.

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 → reactants) is the sum of the activation energy 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.

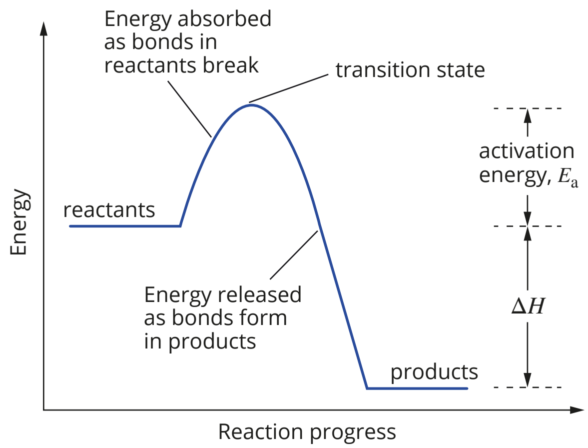


FIGURE 1.1.4 The energy profile diagram for an exothermic reaction such as the combustion of natural gas

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:

$$4C_3H_5N_3O_9(l) \rightarrow 12CO_2(g) + 10H_2O(g) + 6N_2(g) + O_2(g)$$

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).

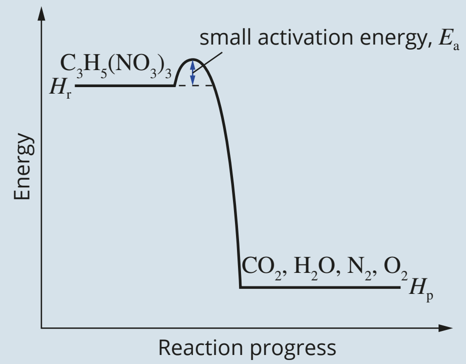


FIGURE 1.1.6 Nitroglycerin has a very low activation energy, making its rate of reaction very large.

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.

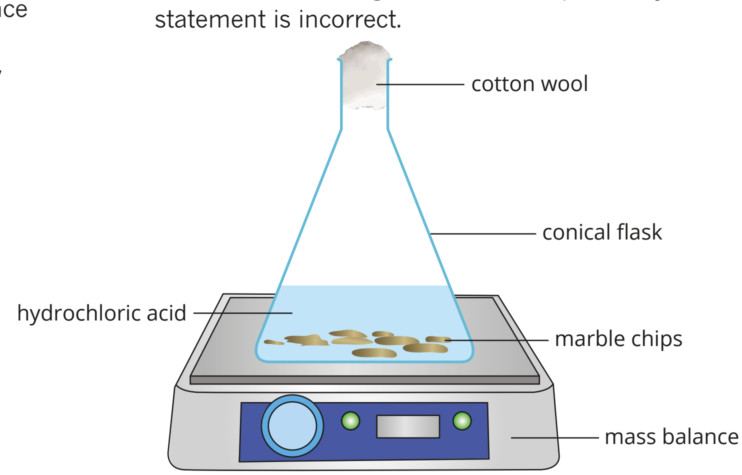


FIGURE 1.1.7 Measuring the rate of reaction between marble chips and hydrochloric acid

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.

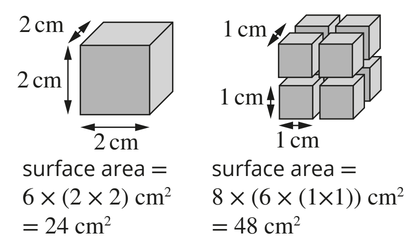


FIGURE 1.2.1 Given two samples of equal volume of a solid, it is clear that the sample with the smaller particle size has a greater total surface area.

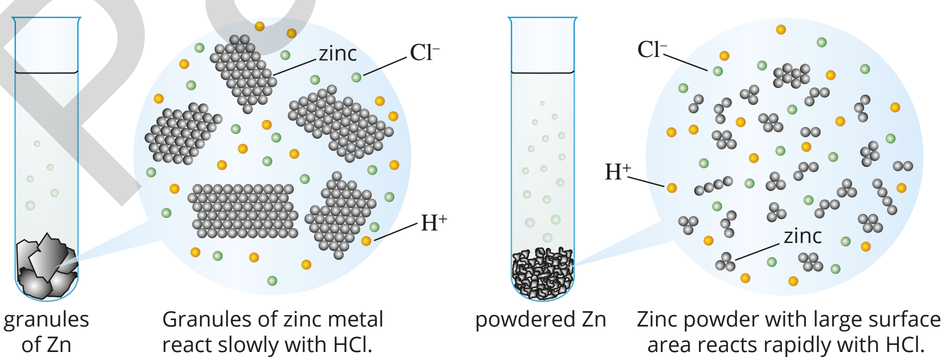


FIGURE 1.2.2 The reaction of hydrochloric acid and zinc. As the surface area of zinc increases, the rate of reaction with hydrochloric acid increases.

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.

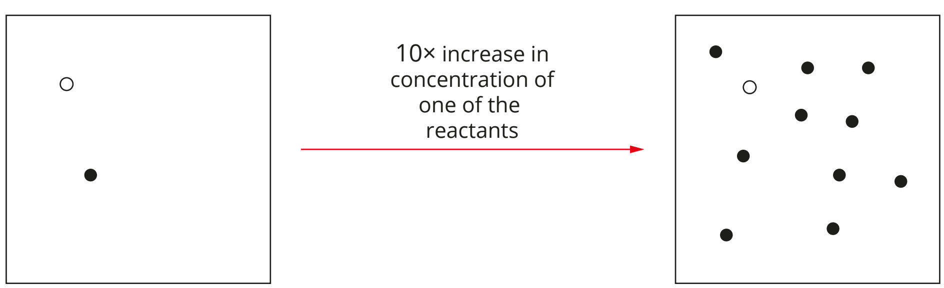


FIGURE 1.2.4 A greater number of reactant particles in the same volume will result in a greater number of collisions.

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.

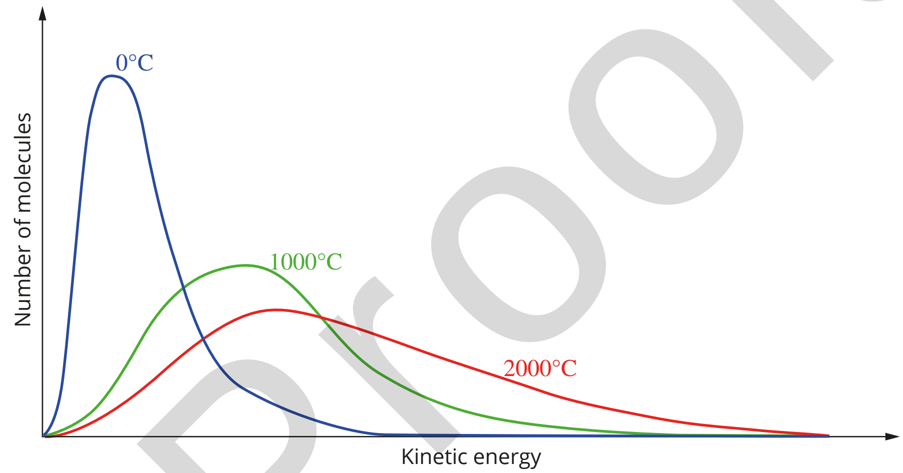


FIGURE 1.2.6 The Maxwell–Boltzmann distribution for a sample of gas at a range of temperatures. Note the reducing height of the maximum of each curve in the graph. This is to maintain the same area under the curve (which is equal to the total number of particles in the sample) as heating the gas does 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.

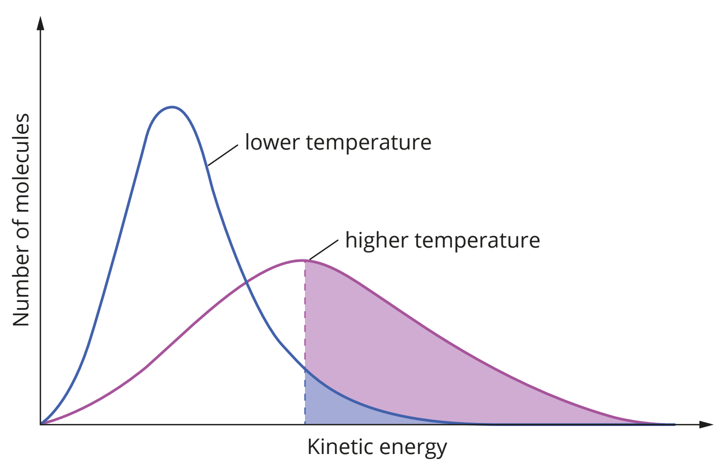


FIGURE 1.2.7 The proportion of particles that exceed the activation energy, E_a, is much greater for the sample at the higher temperature than the lower temperature.

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.

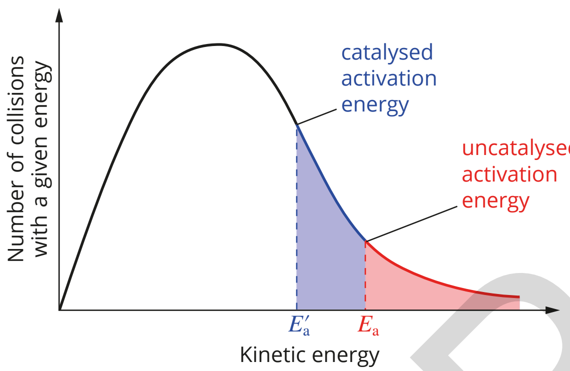


FIGURE 1.2.8 A catalyst provides an alternative reaction pathway with a low activation energy, increasing the proportion of collisions that exceed the activation energy and lead to a reaction.

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).

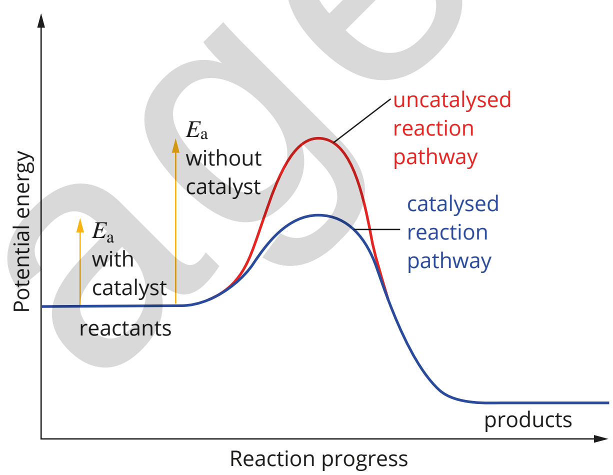


FIGURE 1.2.9 Energy profile diagrams with a catalysed and uncatalysed reaction. Note that the presence of a catalyst also reduces the activation energy for the reverse (products ⟶ reactants) reaction.

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.

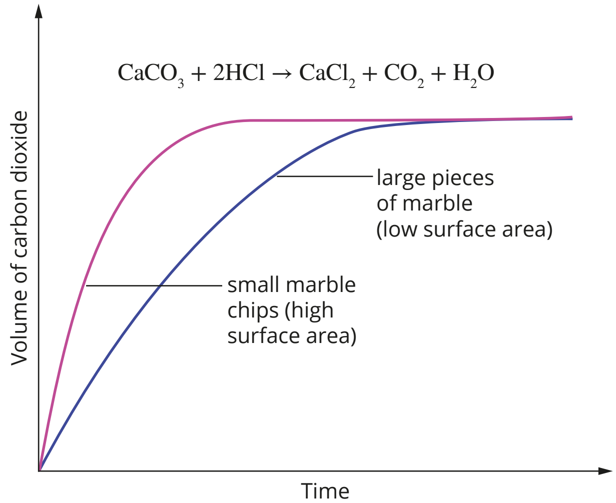


FIGURE 1.2.10 The volume of carbon dioxide produced by small and large marble chips over time

- **a** What does the steeper gradient of the small marble chips signify?
- **b** What does the region of zero gradient on the curve represent?
- **c** 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.

- **a** Write a balanced chemical equation for the reaction.
- **b** Calculate the value of the heat of reaction, ΔH, for the reaction.
- **c** 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:

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

This reaction has an activation energy of 167 kJ mol^{-1} and the heat of reaction, ΔH, is +28.0 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:

$$V(aq) + W(aq) \rightarrow X(aq) + Z(aq)$$

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

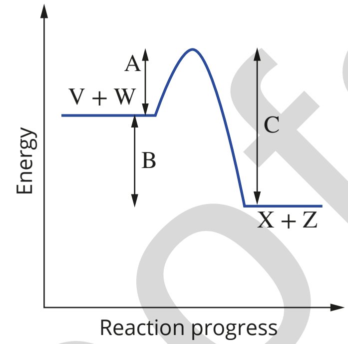


FIGURE 1.2.11 The energy profile diagram for the reaction between V(aq) and W(aq)

- **a** Is the reaction endothermic or exothermic?
- **b** What does the value marked A represent for the forward reaction?
- **c** What does the value marked B represent for the forward reaction?
- **d** What does the value marked B represent for the reverse of this reaction?
- **e** 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
activation energy
catalyst
collision theory
concentration
energy profile diagram
kinetic energy
kinetic energy distribution diagram
Maxwell–Boltzmann distribution curve
partial pressure
pressure
rate of reaction
reaction pathway
reverse reaction
surface area
temperature
transition state

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?
$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
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 $Cu^{2+}(aq)$ ions and powdered zinc is greater than with the large zinc pieces.
B The frequency of collisions between the $Cu^{2+}(aq)$ ions and powdered zinc is greater than with the large zinc pieces.
C The energy of collisions between the $Cu^{2+}(aq)$ ions and large zinc pieces is greater than with the powdered zinc.
D The frequency of collisions between the $Cu^{2+}(aq)$ 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.

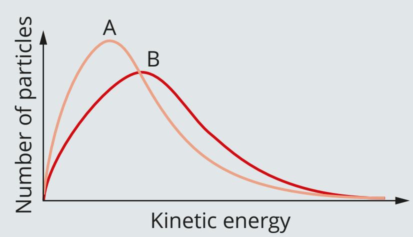


FIGURE 1.3.1 Energy profiles at 40°C and 60°C

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:

i collision frequency

ii 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?

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

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:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

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

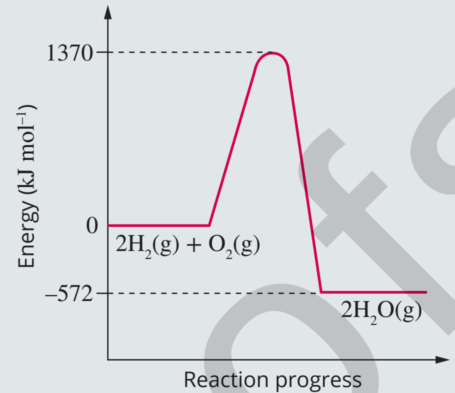


FIGURE 1.3.2 Energy changes for the reaction of hydrogen and oxygen

a What is the magnitude of the activation energy of this reaction?

b What is ΔH for this reaction?

c Several groups of scientists have claimed to have split water into hydrogen and oxygen using a molybdenum catalyst:

$$2H_2O(g) \xrightarrow{Mo} 2H_2(g) + O_2(g)$$

Sketch energy change graphs for this reaction with and without the presence of a catalyst.

d 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:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

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

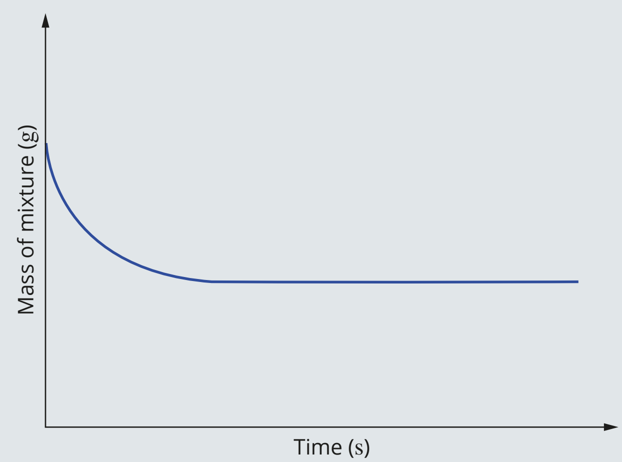


FIGURE 1.3.3 Mass of reaction mixture over time

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:

$$H_2(g) + I_2(s) \rightarrow 2HI(g)$$

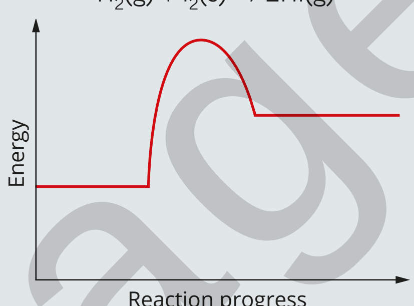


FIGURE 1.3.4 Energy profile diagram for the production of hydrogen iodide.

a Copy the diagram and label the following: $H_2(g)$ and $I_2(s)$; $HI(g)$; 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.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \quad (1)$$

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g) \quad (2)$$

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:

$$Fe(s) + H_2O(g) \rightarrow FeO(s) + H_2(g) \quad (3)$$

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.