

Before the invention of agriculture, a person in an early hunter-gatherer society used approximately 10 MJ of energy per day. Despite being less active than hunter-gatherers, a person in our modern industrial society uses, on average, nearly 1000 MJ per day. This figure is 100 times greater than the body's basic requirement. The bulk of our energy use comes from the combustion of fuels, which we use directly or indirectly. Some of our activities use small amounts of energy. Others, such as the launching of a space shuttle, use enormous amounts of energy.

In Chapter 1 you learned about the different fuels available to meet current transport, heating and cooking requirements across the globe. By the end of this chapter, you will have a greater understanding of the way in which energy changes that occur as a result of combustion of fuels can be represented when writing chemical equations and by drawing energy profile diagrams. You will also learn how the energy released by the combustion of different fuels can be measured.

### Key knowledge

- The comparison of exothermic and endothermic reactions including their enthalpy changes and representations in energy profile diagrams
- Combustion of fuels as exothermic reactions with reference to the use of the joule as the SI unit of energy and measurement of enthalpy change including symbol ( $\Delta H$ ) and common units ( $\text{kJ mol}^{-1}$ ,  $\text{kJ g}^{-1}$ ,  $\text{MJ/tonne}$ )
- The writing of balanced thermochemical equations, including states, for the complete and incomplete combustion of hydrocarbons, methanol and ethanol, using experimental data and data tables
- The use of the specific heat capacity of water to determine the approximate amount of heat energy released in the combustion of fuel

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## 2.1 Exothermic and endothermic reactions



**FIGURE 2.1.1** The energy released by the combustion of wood in a fire is easily seen and felt.

Chemical reactions occur when particles (atoms, molecules or ions) collide and are rearranged to form new particles. Chemical reactions involve energy changes. As the reactant particles are rearranged, the **chemical energy** of the reactants is also ‘rearranged’, although not in quite the same way.

In some chemical reactions, including the **combustion** of fuels, the rearrangement of atoms causes energy to be released to the surroundings. For example, the amount of energy released in the combustion of wood is large enough to be easily seen or felt (Figure 2.1.1).

In other chemical reactions, energy is absorbed from the surroundings as the chemical reaction takes place. The energy change in some reactions is very small and can only be determined with specialised equipment.

In this section, you will learn about the energy changes that occur during chemical reactions. You will also learn how to classify chemical reactions based on their energy changes.

### CHEMICAL ENERGY

There are many different forms of energy. You will be more familiar with some than others. For example, you are in contact with forms of heat (thermal energy), light (radiant energy), sound energy and electrical energy every day. You can probably see, hear or feel some of them as you are reading these pages.

All substances have a form of energy called chemical energy. It is stored in the bonds between atoms and molecules. This energy results from:

- attractions between electrons and protons in atoms
- repulsions between nuclei
- repulsions between electrons
- movement of electrons
- vibrations and rotations around bonds.

When you eat a meal, the bonds between the food molecules have stored energy that you can access to provide energy for other chemical and physical activities that take place in your body (Figure 2.1.2).



**FIGURE 2.1.2** When you eat food, you access the chemical energy stored in the food. This energy powers all of the chemical reactions and physical activities that take place in your body.

As you learned in Chapter 1, the SI unit for energy is the joule, J. Other units also used for quantifying energy are kilojoules, kJ, and megajoules, MJ.

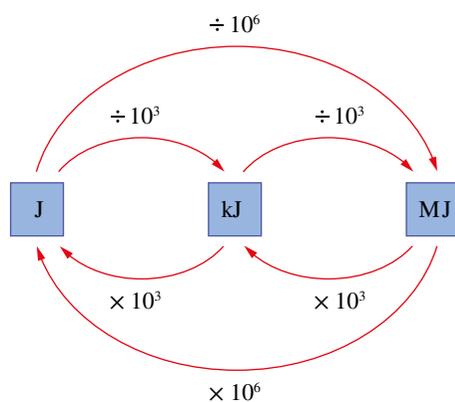
The relationship between joules and megajoules is:

$$1 \text{ J} = 10^{-3} \text{ kJ} = 10^{-6} \text{ MJ}$$

This can also be expressed as:

$$1 \text{ MJ} = 1000 \text{ kJ} = 1\,000\,000 \text{ J}$$

Figure 2.1.3 shows how you can convert between different units of energy.



**FIGURE 2.1.3** Converting between different energy units.

## ENERGY CONSERVATION

According to the **law of conservation of energy**, energy cannot be created or destroyed. However, it can change forms. When energy is transformed from one form to another, the total amount of energy remains the same.

### Systems and surroundings

When we talk about energy changes in chemical reactions, we often refer to a **system** and its **surroundings**.

In chemistry, the system is usually the chemical reaction. When we say that energy is released or absorbed by a system, we are referring to energy changes that occur as bonds are broken and formed between the atoms of the elements involved in the reaction.

The surroundings are usually regarded as everything else. For example, the walls of a container in which a reaction takes place in the gas phase, or the water in a solution in which a reaction takes place in the aqueous phase, can be regarded as the surroundings for the reaction. Energy leaves the system (the reaction) and enters the surroundings, or leaves the surroundings and enters the system.

### Energy changes during chemical reactions

The reactants in a chemical reaction have a certain amount of chemical energy stored in their bonds. The products that form as a result of the rearrangement of particles during the chemical reaction have different bonds and so have a different amount of chemical energy. Energy will be released or absorbed during the reaction depending on the relative energies of the bonds within the reactants and products. When fuels undergo combustion, they are able to release energy that can be used. This is what makes them fuels.

Often the energy released to or absorbed from the surroundings is in the form of heat (thermal energy). However, heat can be converted into other types of energy, including light, electricity and movement (kinetic energy).

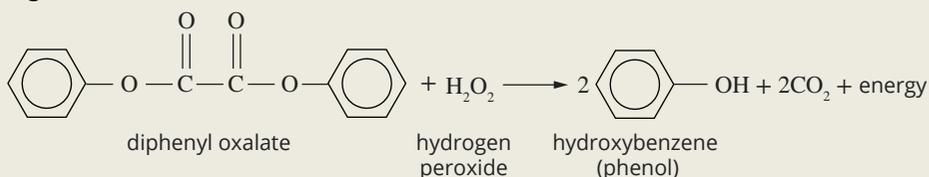
#### CHEMISTRY IN ACTION

### Glow-in-the-dark light sticks

You might have seen glow-in-the-dark hoops, necklaces and bracelets similar to those shown in Figure 2.1.4 at festivals or concerts, especially those held at night.

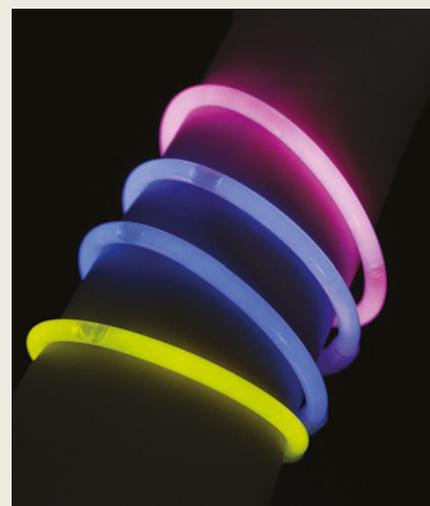
Glow-in-the-dark bracelets contain chemicals held in separate containers. When these bracelets are bent, the containers break and the chemicals combine. Light is produced through a process called **chemiluminescence**.

The chemistry of a glow stick is fairly straightforward. When the aqueous reactants (hydrogen peroxide in one area and diphenyl oxalate in another area) mix, energy is released from the reaction that occurs. This reaction is shown in Figure 2.1.5.



**FIGURE 2.1.5** This reaction occurs in a glow stick.

Instead of the energy from this reaction being released to the surroundings solely as heat, a carrier molecule transfers the energy to a **chemiluminescent** dye in the glow stick. The electrons in the dye are excited to higher energy levels. Light is emitted as these electrons return to their original lower energy levels. The light from the glow stick is simply the emission spectrum of the dye molecule.



**FIGURE 2.1.4** Glow-in-the-dark bracelets give off light that is the result of chemiluminescence.

## CHEMFILE

### Glow-worms

Glow-worms (Figure 2.1.6) apply similar chemical principles to chemiluminescence for their glow-in-the-dark **bioluminescence**. Three chemicals within the worm combine. However, they require oxygen to produce light. When the worm breathes, oxygen acts as the oxidising agent in the chemical reaction between the three reactants producing the bioluminescence. Worms are able to control the amount of 'glow' by breathing in more or less oxygen.



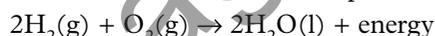
**FIGURE 2.1.6** A female glow-worm. The luminescent abdominal organs are visible.

## EXOTHERMIC AND ENDOTHERMIC SYSTEMS

When the total chemical energy of the products of a chemical reaction is less than the total chemical energy of the reactants, the excess energy is released to the surroundings. Energy 'exits' the reaction system and the chemical reaction is called an **exothermic** reaction.

The released energy can be shown in a chemical equation by writing 'energy' on the product side of the arrow.

For example, the production of water from the reaction between hydrogen and oxygen gas is an exothermic reaction. This can be represented by the equation:



Another example of an exothermic reaction is the combustion of methane gas:



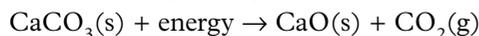
Heat is given off to the surroundings. All combustion reactions give off heat (energy) to the surroundings and are therefore exothermic reactions.

When the total chemical energy of the products of a chemical reaction is greater than the total chemical energy of the reactants, energy is absorbed from the surrounding environment. Energy 'enters' the reaction system and the chemical reaction is called an **endothermic** reaction.

If an endothermic reaction takes place in a container, the container may feel cold to the touch. This is because the reaction system is absorbing heat from the surroundings, leaving the environment cooler.

In a chemical equation of an endothermic reaction, the energy that is required can be written on the reactant side of the equation arrow.

For example, the **decomposition** of calcium carbonate is an endothermic process. This can be represented by the equation:



Endothermic reactions require the constant input of energy.

### Changes of state

Changes of state, such as a solid melting to form a liquid, are a type of physical change, rather than a chemical change. These changes also involve energy being absorbed or released.

For example, the melting of ice into water requires the absorption of energy, making it an endothermic process. The boiling of water to produce water vapour is also endothermic.

Conversely, condensing a gas to a liquid and freezing a liquid to form a solid both release heat to the surroundings and so are exothermic processes.

**i** If the total chemical energy of the products is *less* than the total energy of the reactants, energy will be released from the system into the surroundings. This is called an exothermic reaction.

If the total chemical energy of the products is *greater* than the total energy of the reactants, energy will be absorbed from the surroundings. This is called an endothermic reaction.

## CHEMFILE

### Instant cold packs

Instant cold packs are often carried in first aid kits at sporting events (Figure 2.1.7). One type of cold pack contains a sealed bag of water surrounded by solid ammonium nitrate. When the cold pack is squeezed, the water bag is broken and ammonium nitrate dissolves in the water. The process is endothermic, absorbing heat from the surroundings and quickly lowering the pack's temperature.



FIGURE 2.1.7 An endothermic reaction produces an instant cold pack.

## 2.1 Review

### SUMMARY

- Energy is measured in J, kJ or MJ:  
 $1 \text{ J} = 10^{-3} \text{ kJ} = 10^{-6} \text{ MJ}$
- Chemical energy is stored in the bonds between atoms and molecules.
- Energy is conserved during a chemical reaction; energy cannot be created or destroyed.
- Chemical reactions and changes of state involve energy changes.
- A chemical reaction that releases energy to the surroundings is called an exothermic reaction.
- A chemical reaction in which energy is absorbed from the surroundings is called an endothermic reaction.
- All combustion reactions are exothermic reactions.

### KEY QUESTIONS

- 1 Which of the following statements about combustion reactions is correct?
  - A Combustion reactions are usually exothermic, meaning energy is absorbed during the reaction.
  - B Combustion reactions are always exothermic, meaning energy is absorbed during the reaction.
  - C Combustion reactions are usually endothermic, meaning energy is absorbed by the system.
  - D Combustion reactions are always exothermic, meaning energy is released during the reaction.
- 2 Convert the following energy values to kJ.
  - a 0.180 MJ
  - b  $1.5 \times 10^6 \text{ J}$
  - c 10.0 J
  - d  $2.0 \times 10^{-3} \text{ J}$
- 3 Explain the difference between the terms 'system' and 'surroundings' in relation to a chemical reaction.
- 4 Explain the term 'endothermic' in relation to the total amount of chemical energy of the reactants and products.

## 2.2 Thermochemical equations and energy profile diagrams

When fuels undergo combustion, energy is released in the form of heat. As you saw in the previous section, the word ‘energy’ can be included in a combustion equation to show that energy is released. However, it is generally more useful for a chemist to be precise about the magnitude (size) of the energy change that takes place.

**Thermochemical equations** achieve this by including a sign and numerical value for the energy change that occurs in the reaction.

It is also useful for chemists to be able to show the energy changes that occur as a reaction proceeds. All reactions absorb some energy before they can proceed, even if energy is released overall. An **energy profile diagram** represents the energy changes that occur during the course of a reaction.

In this section, you will learn how to write and interpret thermochemical equations and draw energy profile diagrams. Although the focus for this section is on the combustion of fuels (which are exothermic reactions), you will also learn about writing and representing other equations, including endothermic reactions. These reactions are important for your understanding of some of the concepts that will be covered in later chapters.

### REPRESENTING ENERGY CHANGE IN A CHEMICAL EQUATION

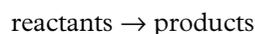
#### Enthalpy change

The chemical energy of a substance is sometimes called its **heat content** or **enthalpy**. It is given the symbol  $H$ . The enthalpy of the reactants in a chemical reaction is given the symbol  $H_r$  and the enthalpy of the products is given the symbol  $H_p$ .

Most chemical processes take place in open systems under a constant pressure (usually atmospheric). The exchange of heat energy between the system and its surroundings under constant pressure is referred to as the **enthalpy change**, or **heat of reaction**, and is given the symbol  $\Delta H$ . The capital delta symbol ( $\Delta$ ) is commonly used in chemistry to represent ‘change in’. For example,  $\Delta T$  is the symbol for change in temperature.

Fuels provide you with energy by undergoing exothermic combustion reactions. Knowing the precise enthalpy change per mole or gram that occurs during combustion of different fuels helps you to decide which fuel might be most suitable for a particular purpose.

For the general reaction:



the enthalpy change ( $\Delta H$ ) is calculated by:

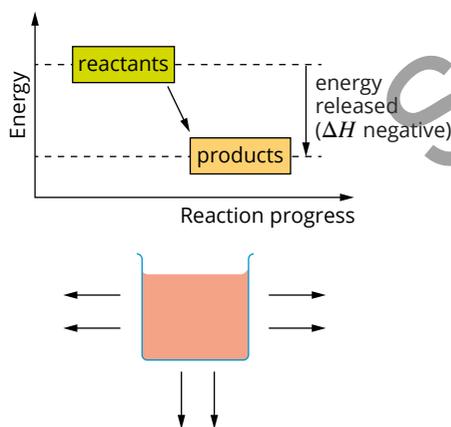
$$\Delta H = H_p - H_r$$

#### Enthalpy change in exothermic reactions

When  $H_p$  is less than  $H_r$ , energy is released from the system into the surroundings, so the reaction is exothermic. The system has lost energy, so  $\Delta H$  has a negative value.

Therefore, for combustion reactions (which are exothermic reactions),  $\Delta H < 0$  (see Figure 2.2.1).

**i** Enthalpy change is a measure of the amount of energy absorbed or released during chemical reactions. It is given the symbol  $\Delta H$  and is determined by subtracting the enthalpy of the reactants ( $H_r$ ) from the enthalpy of the products ( $H_p$ ).



**FIGURE 2.2.1** In the combustion of a fuel, the enthalpy of the reactants is greater than the enthalpy of the products, so energy is released to the surroundings during the reaction.

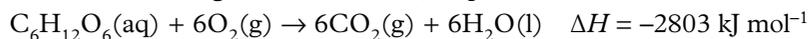
## Enthalpy change in endothermic reactions

When  $H_p$  is greater than  $H_r$ , energy must be absorbed from the surroundings, so the reaction is endothermic. The system has gained energy, so  $\Delta H$  has a positive value, i.e.  $\Delta H > 0$  (see Figure 2.2.2).

## Thermochemical equations

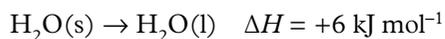
The enthalpy change can be shown by writing the  $\Delta H$  value to the right of the chemical equation. Such an equation is called a thermochemical equation. The  $\Delta H$  value in a thermochemical equation usually has the units  $\text{kJ mol}^{-1}$ . This means that the amount of energy (in kJ) signified by the  $\Delta H$  value corresponds to the mole amounts specified by the coefficients in the equation.

For example, respiration in most living things can be considered as a type of combustion reaction of glucose. Therefore, respiration is an exothermic reaction:

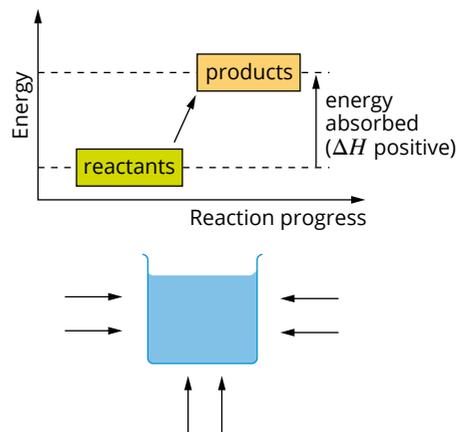


This thermochemical equation tells you that when 1 mole of glucose reacts with 6 moles of oxygen to produce 6 moles of carbon dioxide and 6 moles of water, 2803 kJ of energy is released.

Enthalpy changes also occur during physical changes, so thermochemical equations can be written for physical changes. Melting ice is an example of a physical change. It is an endothermic process, because heat must be applied to solid ice in order to convert it into liquid water. The thermochemical equation for this reaction is:



The  $\Delta H$  value is positive because this is an endothermic reaction.



**FIGURE 2.2.2** For an endothermic reaction, the enthalpy of the reactants is less than the enthalpy of the products so energy is absorbed during the reaction.

### CHEMISTRY IN ACTION

## Explosives—a blast of chemical energy

Humans have been using chemicals to make explosions since 919 BCE. Chinese people first mixed saltpetre (potassium nitrate), sulfur and charcoal with explosive results. They quickly realised that there were many uses for this mixture, which later became known as gunpowder. It was put to military use and eventually led to the development of bombs, cannons and guns.

Today, explosives are an essential tool for mining and other engineering works, such as road construction, tunnelling, building and demolition (see Figure 2.2.3).

Explosives transform chemical energy into large quantities of thermal energy very quickly. Although thermal energy is also released when fuels such as petrol and natural gas burn, the rate of combustion in these reactions is limited by the availability of oxygen gas to the fuel. In contrast, the compounds making up an explosive contain sufficient oxygen for a complete (or almost complete) reaction to occur very quickly.



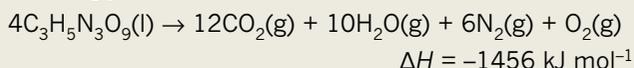
**FIGURE 2.2.3** An old bridge is demolished with the help of explosives.

## CHEMISTRY IN ACTION

### The chemistry behind an explosion

When chemical explosives, such as ammonium nitrate, trinitrotoluene (TNT) and nitroglycerine decompose, they release large amounts of energy and gaseous products very quickly.

This is the thermochemical equation for the decomposition of nitroglycerine:



Notice that 29 moles of gas (the total number of moles of all products) are produced from 4 moles of nitroglycerine. The negative  $\Delta H$  value indicates that this is an exothermic reaction. At atmospheric pressure, the reactant products would expand to fill a volume more than 10 000 times larger than the volume of the nitroglycerine! During a blast, this gas is usually produced within a small hole into which the explosive has been placed, creating huge pressures that shatter the surrounding rock or structure.

### THERMOCHEMICAL EQUATIONS AND MOLE RATIOS

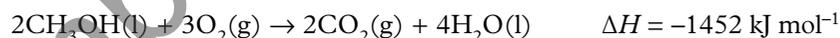
The  $\Delta H$  value in a thermochemical equation corresponds to the mole amounts specified by the equation. If the coefficients in the equation are changed, the  $\Delta H$  value will also change.

For example, the thermochemical equation for the combustion of methanol can be written as:

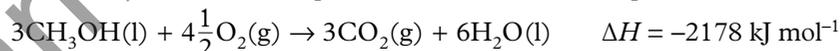


This means that 726 kJ of energy is released when 1 mole of methanol reacts with 1.5 moles of oxygen gas, to produce 1 mole of carbon dioxide and 2 moles of water.

If twice as much methanol were to react, then twice as much energy would be released. So, if the coefficients of the equation are doubled, the  $\Delta H$  value is also doubled:



If the mole amounts are tripled, the  $\Delta H$  value is also tripled:



### The importance of states

It is very important to always include state symbols in thermochemical equations. Physical changes involve an enthalpy change, so the state of the species in a chemical reaction affects the enthalpy change of the reaction.

For example, both of the following equations represent physical changes involving water. They have different  $\Delta H$  values because the states are different.

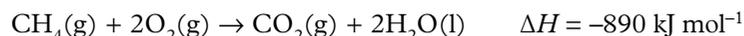


You can see that it requires more energy to boil water than it does to melt ice.

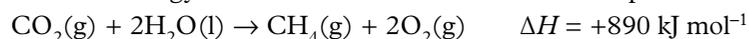
### Effect on $\Delta H$ of reversing a chemical reaction

Reversing a chemical equation changes the sign but not the magnitude of  $\Delta H$ .

For example, methane ( $\text{CH}_4$ ) reacts with oxygen gas to produce carbon dioxide gas and water in an exothermic reaction:



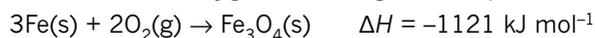
If this reaction is reversed, the magnitude of  $\Delta H$  remains the same because the enthalpies of the individual chemicals have not changed, but the sign changes to indicate that energy must be absorbed for this reaction to proceed.



## Worked example 2.2.1

### CALCULATING $\Delta H$ FOR ANOTHER EQUATION

Iron reacts with oxygen according to the equation:



Calculate  $\Delta H$  for the reaction represented by the equation:

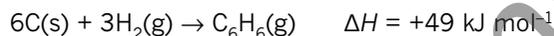


Thinking	Working
The reaction has been reversed in the second equation, so the sign for $\Delta H$ is changed to the opposite sign.	$\Delta H$ for the second equation is positive.
Identify how the mole amounts in the equation have changed.	The mole amount of $\text{Fe}_3\text{O}_4$ has changed from 1 to 2, $\text{O}_2$ has changed from 2 to 4 and Fe has changed from 3 to 6. They have all doubled.
Identify how the magnitude of $\Delta H$ will have changed for the second equation.	The mole amounts of the chemicals have all doubled, so $\Delta H$ will also have doubled.
Calculate the new <i>magnitude</i> of $\Delta H$ . (You will write the sign of $\Delta H$ in the next step.)	$2 \times 1121$ $= 2242$
Write $\Delta H$ for the second equation, including the sign.	$\Delta H = +2242 \text{ kJ mol}^{-1}$

## Worked example: Try yourself 2.2.1

### CALCULATING $\Delta H$ FOR ANOTHER EQUATION

Carbon reacts with hydrogen according to the equation:



Calculate  $\Delta H$  for the reaction represented by the equation:



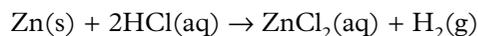
## Activation energy

The energy required to break the bonds of reactants so that a reaction can proceed is called the **activation energy**. The activation energy is an energy barrier that must be overcome before a reaction can get started. (The concept of activation energy is discussed in more detail in Chapter 7.)

**i** A reaction cannot proceed unless the bonds in the reactants are broken.

An activation energy barrier exists for both exothermic and endothermic reactions. If the activation energy for a reaction is very low, the chemical reaction can be initiated as soon as the reactants come into contact because the reactants already have sufficient energy for a reaction to take place. Special conditions are not always required for reactions to occur. An example of this can be seen in the reaction between zinc and hydrochloric acid on page 44.

The reaction between zinc and hydrochloric acid produces hydrogen gas:



As you can see in Figure 2.2.4, bubbles of hydrogen gas are vigorously produced as soon as zinc is added to the acid.



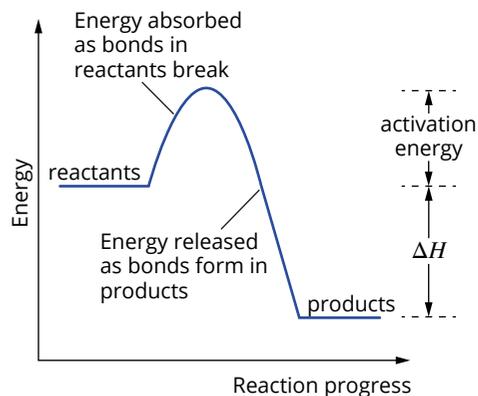
**FIGURE 2.2.4** When zinc comes into contact with hydrochloric acid, it reacts almost immediately. The reactants have sufficient energy to 'overcome' the activation energy barrier.

## ENERGY PROFILE DIAGRAMS

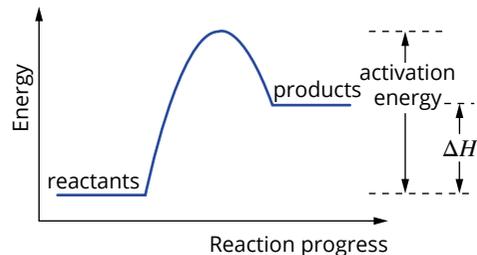
The energy changes that occur during the course of a chemical reaction can be shown on an energy profile diagram.

The energy profile diagram for an exothermic combustion reaction like the one shown in Figure 2.2.5 indicates that the enthalpy of the products is always less than the enthalpy of the reactants. Overall, energy is released and so the  $\Delta H$  value is negative. The energy profile also shows that, even in exothermic reactions, the activation energy must first be absorbed to start the reaction.

The energy profile diagram for an endothermic reaction (Figure 2.2.6) shows that the enthalpy of the products is greater than the enthalpy of the reactants. Overall, energy is absorbed and so the  $\Delta H$  value is positive. The energy profile also shows the absorption of the activation energy before the release of energy as bonds form in the products.



**FIGURE 2.2.5** The characteristic shape of an energy profile diagram for an exothermic reaction.



**FIGURE 2.2.6** The characteristic shape of an energy profile diagram for an endothermic reaction.

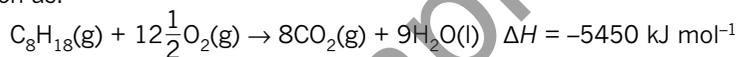
## 2.2 Review

### SUMMARY

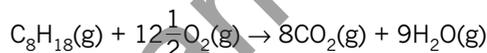
- Thermochemical equations include a  $\Delta H$  value for a chemical reaction. The unit of  $\Delta H$  is usually  $\text{kJ mol}^{-1}$ .
- The value of  $\Delta H$  indicates the magnitude of the energy change and whether the energy is absorbed (a positive value) or released (a negative value).
- Reversing an equation causes the sign of  $\Delta H$  to change, as the reaction changes from exothermic to endothermic, or vice versa.
- Doubling the coefficients in a chemical reaction causes the  $\Delta H$  value to also double, as twice as many reactants react to produce or absorb twice as much energy.
- States of matter must be included in thermochemical equations because changes of state involve enthalpy changes.
- Activation energy is the energy that must be absorbed to break the bonds in the reactants so that a chemical reaction can proceed. Both endothermic and exothermic reactions require activation energy.
- Energy profile diagrams show energy changes over the course of a reaction. They show the relative enthalpies of reactants and products and the activation energy.
- Combustion reactions are always exothermic and so always have a negative  $\Delta H$  value.

### KEY QUESTIONS

- 1 Explain what a negative  $\Delta H$  value indicates about a chemical reaction, in terms of the relative enthalpies of the reactants and products.
- 2 When 1 mole of methane gas undergoes combustion in oxygen to produce carbon dioxide and water, 890 kJ of energy is released. Write a balanced thermochemical equation for this reaction.
- 3 The combustion of octane to form carbon dioxide and liquid water can be written as:

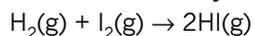


The combustion of octane to form carbon dioxide and steam can be written as:

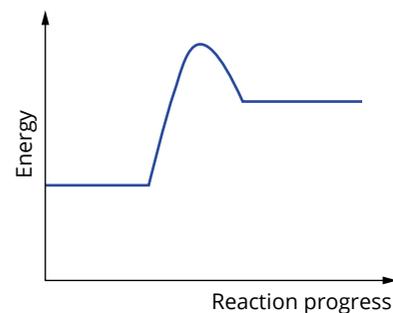


How would the energy released by the combustion of 1 mole of octane to form steam compare with the energy released by 1 mole of octane to form liquid water?

- 4 The energy profile diagram in Figure 2.2.7 shows the energy changes during the reaction of hydrogen and iodine to form hydrogen iodide:



- a Is the reaction exothermic or endothermic?
  - b Describe the relative enthalpies of the reactants and products.
  - c Comment on the size of the activation energy compared with  $\Delta H$ .
- 5 The reaction for photosynthesis is the opposite to the reaction for respiration shown on page 41. Write a thermochemical equation for photosynthesis.



**FIGURE 2.2.7** Energy profile of the reaction between hydrogen and iodine to form hydrogen iodide.

## 2.3 Energy from combustion

### Review

#### The mole

The **mole** is a unit used by chemists for counting particles. One mole of any type of particle is a standard **amount** of substance, which contains the same number of specified particles as there are atoms in exactly 12 g of carbon-12.

The symbol for the amount of substance is  $n$ . The unit is **mole**, which is abbreviated to mol.

Because atoms are very small, chemists have defined the mole so that it represents a very large number. There are  $6.02 \times 10^{23}$  particles in 1 mole. This number is called **Avogadro's number** and has the symbol  $N_A$ .

A useful relationship links the amount of a substance ( $n$ ), in mol, Avogadro's number ( $N_A$ ) and the number of particles in a substance ( $N$ ):

$$n = \frac{N}{N_A}$$

Where needed, this relationship can be rearranged to:

$$N = n \times N_A$$

#### Mass

Chemists often use mass, measured in grams, to measure an exact number of mole of an element or compound.

The **molar mass** of an element or compound is the mass of 1 mole of the element or compound. Molar mass is derived from the relative atomic mass, relative molecular mass or relative formula mass. A useful relationship links the amount of a substance ( $n$ ), in mol, its molar mass ( $M$ ), in  $\text{g mol}^{-1}$ , and the given mass of the substance ( $m$ ), in g:

$$n = \frac{m}{M}$$

Where needed, this relationship can be rearranged to:

$$m = n \times M \quad \text{or} \quad M = \frac{m}{n}$$

Fire heats our homes, powers our cars and entertains us with firework displays. Bushfires can destroy homes and lives, devastating huge areas of bush and damaging the habitat of many animals. However, a bushfire can also be an agent of regrowth and renewal in land management.

Ancient cultures, such as the Ancient Greeks and Ancient Japanese, described fire as one of the fundamental elements, along with air, earth and water (see Figure 2.3.1).

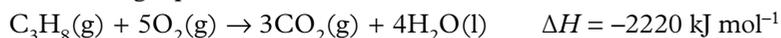
Fire results from the combustion of substances. Combustion reactions need three things:

- fuel to burn
- oxygen for the fuel to burn in
- energy to get the process started.

Fire can be understood and controlled by applying your knowledge of chemistry. In this section, you will look at combustion reactions and their importance to the world in more detail.

### COMBUSTION AS A CHEMICAL PROCESS

Combustion reactions are exothermic reactions in which the reactant combines with oxygen to produce oxides. This type of reaction is often referred to as an **oxidation** reaction. The combustion of a hydrocarbon produces carbon dioxide and water, provided there is enough oxygen present. An example is the combustion of propane ( $\text{C}_3\text{H}_8$ ), a major component of LPG (liquefied petroleum gas), shown in the following equation:



Note the following important features of this thermochemical equation.

- No atoms are created or destroyed in the reaction, so the numbers of atoms of each element are balanced on the two sides of the equation.



**FIGURE 2.3.1** According to the Ancient Greeks, the classical four elements were fire, earth, air and water.

- The balanced equation tells you the number of molecules of oxygen that are required for the combustion of each molecule of propane.
- The enthalpy change for the reaction is negative, indicating that this is an exothermic reaction.
- The enthalpy change is given in  $\text{kJ mol}^{-1}$ . It tells you the energy released, in kJ, according to the coefficients given in the equation.
- State symbols show the state of each reactant and product. (Although in a combustion reaction, water is released as water vapour, the enthalpy change of this thermochemical equation shows the energy change if liquid water is formed.)

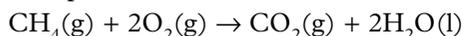
**i** In redox reactions that involve oxygen as a reactant, oxidation can be defined as the addition of oxygen to form oxides, such as in a combustion reaction.

## Complete and incomplete combustion

Combustion reactions can be described as complete or incomplete. The difference between the two is due to the amount of oxygen available to react with the fuel.

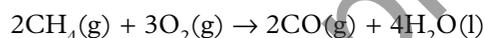
**Complete combustion** occurs when oxygen is plentiful. The only products are carbon dioxide and water.

An example is the complete combustion of methane:



When the oxygen supply is limited, **incomplete combustion** occurs. As less oxygen is available, not all of the carbon can be converted into carbon dioxide. Carbon monoxide and/or carbon are produced instead. The hydrocarbon burns with a yellow, smoky or sooty flame, due to the presence of glowing carbon particles. Figure 2.3.2 shows the appearance of the different flames of a Bunsen burner due to incomplete and complete combustion.

The equation for the incomplete combustion of methane to form carbon monoxide is:



### CHEMFILE

#### Carbon monoxide poisoning

Carbon monoxide is a highly poisonous gas. It combines readily with haemoglobin, the oxygen carrier in blood. When attached to carbon monoxide, haemoglobin cannot transport oxygen around the body, which leads to oxygen starvation of tissues. (You can read more about the chemistry of carbon monoxide poisoning in Chapter 8, page 219.)

Even at concentrations as low as 10 parts per million (ppm), carbon monoxide can cause drowsiness, dizziness and headaches. At about 200 ppm, carbon monoxide can lead to death. The average carbon monoxide concentration in large cities, mostly due to incomplete combustion of fuels in cars (Figure 2.3.3), is now 7 ppm, but it can be as high as 120 ppm at busy intersections in heavy traffic.



**FIGURE 2.3.2** The yellow flame of a Bunsen burner is due to incomplete combustion and produces carbon as a product. The blue flame is a hotter flame that occurs when the collar hole is open and more oxygen is allowed into the reaction. Complete combustion can then occur.



**FIGURE 2.3.3** Car exhaust gases can contain high levels of carbon monoxide as a result of incomplete combustion of fuels.

**i** The complete combustion of hydrocarbons occurs when there is sufficient oxygen for the fuel to burn. The products of complete combustion are carbon dioxide and water. When oxygen is not plentiful, incomplete combustion occurs. The products of incomplete combustion are carbon monoxide and/or carbon and water.

## WRITING EQUATIONS FOR COMPLETE COMBUSTION OF FUELS

It is important to write chemical equations correctly because they tell you a lot about chemical reactions. Writing equations for the complete combustion reactions of fuels containing carbon and hydrogen is relatively straightforward, because the products are always carbon dioxide and water.

Perhaps the most important of all combustion reactions involving fuels are those that occur when petrol is burnt. Petrol is a mixture of hydrocarbons, including octane.

The combustion reactions of octane ( $C_8H_{18}$ ) and the other hydrocarbons in petrol power the internal combustion engines in most of Australia's 17.6 million motor vehicles.

### Worked example 2.3.1

#### WRITING EQUATIONS FOR COMPLETE COMBUSTION OF HYDROCARBON FUELS

Write the equation, including state symbols, for the complete combustion of butane ( $C_4H_{10}$ ).

Thinking	Working
Add oxygen as a reactant and carbon dioxide and water as the products.	$C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$
Balance carbon and hydrogen atoms, based on the formula of the hydrocarbon.	$C_4H_{10} + O_2 \rightarrow 4CO_2 + 5H_2O$
Find the total number of oxygen atoms on the product side.	Total O $= (4 \times 2) + 5$ $= 13$
If this is an odd number, multiply all of the coefficients in the equation by two, except for the coefficient of oxygen.	$2C_4H_{10} + O_2 \rightarrow 8CO_2 + 10H_2O$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$
Add state symbols.	$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

### Worked example: Try yourself 2.3.1

#### WRITING EQUATIONS FOR COMPLETE COMBUSTION OF HYDROCARBON FUELS

Write the equation, including state symbols, for the complete combustion of hexane ( $C_6H_{14}$ ).

A similar series of steps can also be used to write the combustion equations for other carbon-based fuels that contain oxygen; for example, alcohols.

### Worked example 2.3.2

#### WRITING EQUATIONS FOR COMBUSTION REACTIONS OF ALCOHOLS

Write the equation, including state symbols, for the complete combustion of liquid ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ).

Thinking	Working
Add oxygen as a reactant and carbon dioxide and water as the products.	$\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
Balance carbon and hydrogen atoms, based on the formula of the alcohol.	$\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
Find the total number of oxygen atoms on the product side. Then subtract the one oxygen atom in the alcohol molecule from the total number of oxygen atoms on the product side.	Total O on product side $= (2 \times 2) + 3$ $= 7$ Total O on product side – 1 in alcohol $= 7 - 1 = 6$
If this is an odd number, multiply all the coefficients in the equation by two, except for the coefficient of oxygen.	$\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
Add state symbols.	$\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$

### Worked example: Try yourself 2.3.2

#### WRITING EQUATIONS FOR COMBUSTION REACTIONS OF ALCOHOLS

Write the equation, including state symbols, for the complete combustion of liquid methanol ( $\text{CH}_3\text{OH}$ ).

#### WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

When the supply of oxygen is insufficient, incomplete combustion of fuels occurs. Equations can also be written to represent this. In general, for the incomplete combustion of hydrocarbons, as well as carbon-based fuels that contain oxygen, the products are carbon monoxide and/or carbon and water.

### Worked example 2.3.3

#### WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

Write an equation, including state symbols, for the incomplete combustion of ethane gas ( $\text{C}_2\text{H}_6$ ) to form carbon monoxide and water vapour.

Thinking	Working
Add oxygen as a reactant and carbon monoxide and water as the products.	$\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$
Balance the carbon and hydrogen atoms, based on the formula of the hydrocarbon.	$\text{C}_2\text{H}_6 + \text{O}_2 \rightarrow 2\text{CO} + 3\text{H}_2\text{O}$
Balance oxygen by adding the appropriate coefficient to the reactant side of the equation.	$\text{C}_2\text{H}_6 + \frac{5}{2}\text{O}_2 \rightarrow 2\text{CO} + 3\text{H}_2\text{O}$
If oxygen gas has a coefficient that is half of a whole number, multiply all of the coefficients in the equation by two.	$2\text{C}_2\text{H}_6 + 5\text{O}_2 \rightarrow 4\text{CO} + 6\text{H}_2\text{O}$
Add state symbols.	$2\text{C}_2\text{H}_6(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{CO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

### Worked example: Try yourself 2.3.3

#### WRITING EQUATIONS FOR INCOMPLETE COMBUSTION OF FUELS

Write an equation, including state symbols, for the incomplete combustion of liquid methanol ( $\text{CH}_3\text{OH}$ ) to form carbon monoxide and water vapour.

### HEAT OF COMBUSTION

The **heat of combustion** of a fuel is defined as the enthalpy change that occurs when a specified amount (e.g. 1 g, 1 L, 1 mol) of the fuel burns completely in oxygen. It is usually measured at conditions of 298 K and 100 kPa, which means that the water produced should be shown in the liquid state. The heat of combustion can be given the symbol  $\Delta H_c$ .

- i** The heat of combustion is usually measured at conditions of 298 K and 100 kPa. This means that the water produced should be shown in the liquid state.

Many fuels, including wood, coal and kerosene, are mixtures of chemicals and do not have a specific chemical formula or molar mass. This means their heat of combustion cannot be expressed in  $\text{kJ mol}^{-1}$ . Therefore, it is measured only as  $\text{kJ g}^{-1}$ ,  $\text{kJ L}^{-1}$  or  $\text{MJ/tonne}$ .

- i** Only fuels that exist as pure substances can have their heat of combustion measured in  $\text{kJ mol}^{-1}$ .

The heats of combustion for some common elements and compounds present in fuels are listed in Table 2.3.1. Heat energy is released during combustion, so  $\Delta H_c$  always has a negative value.

**TABLE 2.3.1** Heats of combustion for some common elements and compounds

Substance	Heat of combustion, $\Delta H_c$ (kJ mol <sup>-1</sup> )
Methane	-890
Ethane	-1560
Propane	-2220
Butane	-2886
Octane	-5450
Methanol	-725
Ethanol	-1367
Hydrogen	-286
Carbon (graphite)	-394

As you learned in Chapter 1, when these fuels are burnt, not all the energy is released as heat energy, and not all of the heat energy liberated can be harnessed for a particular purpose, such as powering a vehicle or producing electricity. However, even if the energy transformation process is not 100% efficient, you can still use these values to compare the energy released from combustion of different compounds.

As Worked Example 2.3.4 shows, you can use the data in Table 2.3.1 to calculate the energy released on combustion of a specified mass of one of the fuels. The energy released when  $n$  mol of a fuel burns is given by the equation:

$$\text{Energy} = n \times \Delta H_c$$

### Worked example 2.3.4

#### CALCULATING ENERGY RELEASED BY A SPECIFIED MASS OF A PURE FUEL

Calculate the amount of energy released when 3.60 kg of butane (C<sub>4</sub>H<sub>10</sub>) is burnt in an unlimited supply of oxygen.

Thinking	Working
Calculate the number of moles of the compound using: $n = \frac{m \text{ (in grams)}}{M}$	$n(\text{C}_4\text{H}_{10}) = \frac{m}{M}$ $= \frac{3.60 \times 10^3}{58.0}$ $= 62.1 \text{ mol}$
Multiply the number of moles by the heat of combustion.	$\text{Energy} = n \times \Delta H_c$ $= 62.1 \times 2886$ $= 1.79 \times 10^5 \text{ kJ}$

### Worked example: Try yourself 2.3.4

#### CALCULATING ENERGY RELEASED BY A SPECIFIED MASS OF A PURE FUEL

Calculate the amount of energy released when 5.40 kg of propane (C<sub>3</sub>H<sub>8</sub>) is burnt in an unlimited supply of oxygen.

## Energy content per gram

The energy content of a fuel is often expressed in units of kilojoules per gram.

For a pure substance, the heat of combustion per gram can be calculated by simply dividing the heat of combustion per mole ( $\text{kJ mol}^{-1}$ ) by the molar mass of the substance.

For example, for ethanol (which is being burnt in a spirit burner in Figure 2.3.4):

$$\text{Heat of combustion per mole} = -1367 \text{ kJ mol}^{-1}$$

$$\text{Molar mass} = 46.0 \text{ g mol}^{-1}$$

$$\text{Heat of combustion per gram} = \frac{-1367}{46.0} = -29.7 \text{ kJ g}^{-1}$$

For fuels that are mixtures, approximate values for the heat of combustion per gram are shown in Table 2.3.2.

**TABLE 2.3.2** Approximate heat of combustion values for some fuel mixtures

Substance	Heat of combustion ( $\text{kJ g}^{-1}$ ) (approx.)
Wood, dried	-18
Peat, dried	-25
Brown coal, dried	-30
Black coal, dried	-35

## Energy content per tonne

The quantities of fuel consumed and the amount of energy produced are often so large that the unit megajoules per tonnes, MJ/tonne, is a more useful way of expressing the heat of combustion. For example, the Hazelwood power station consumes about 13 million tonnes of coal in 1 year. It is more useful to consider the energy released per tonne, rather than per gram of coal.

$$1 \text{ kJ} = 10^{-3} \text{ MJ}$$

$$1 \text{ g} = 10^{-6} \text{ tonne}$$

$$\text{Therefore, } 1 \text{ kJ g}^{-1} = 10^{-3} \text{ MJ}/10^{-6} \text{ t.}$$

$$\text{This can be simplified to } 1 \text{ kJ g}^{-1} = 10^3 \text{ MJ/tonne.}$$

### EXTENSION

## Energy density

Liquid fuels, such as petrol, are normally sold by **volume** rather than by mass. For these fuels, it is often convenient to refer to the heat of combustion per litre. Table 2.3.3 shows some heats of combustion per litre for common liquid fuels. The energy released per litre of fuel is often called the fuel's **energy density**.

**TABLE 2.3.3** Energy densities for some common liquid fuels

Substance	Energy density ( $\text{kJ L}^{-1}$ )
Petrol (unleaded 91)	-34 200
Kerosene	-36 500
Diesel fuel	-38 000
Heating oil	-38 500
Ethanol	-23 400



**FIGURE 2.3.4** Ethanol burning in a spirit burner. Combustion of 1 gram of ethanol releases almost 30 kJ of energy.

## 2.3 Review

### SUMMARY

- Combustion reactions are exothermic reactions that can be represented by balanced thermochemical equations.
- The products of the complete combustion of hydrocarbons and carbon-based fuels containing oxygen are carbon dioxide and water.
- Incomplete combustion, resulting in the production of carbon monoxide and/or carbon, occurs when hydrocarbons and carbon-based fuels containing oxygen undergo combustion in a limited supply of oxygen.
- Heats of combustion,  $\Delta H_c$ , indicate the maximum amount of energy that can be released when a specified amount of fuel undergoes complete combustion. Common units are  $\text{kJ mol}^{-1}$ ,  $\text{kJ g}^{-1}$  and MJ/tonne.
- The amount of energy released by different fuels can be compared by referring to heats of combustion.
- For a pure fuel with a heat of combustion,  $\Delta H_c$ , measured in  $\text{kJ mol}^{-1}$ , the energy released when  $n$  mol of the fuel burns is given by the equation:  
Energy =  $n \times \Delta H_c$

### KEY QUESTIONS

- 1 Write a balanced equation for the complete combustion of liquid benzene ( $\text{C}_6\text{H}_6$ ).
- 2 Information about two hydrocarbon fuels, propane and octane, is given in Table 2.3.4.

TABLE 2.3.4

Characteristic	Propane ( $\text{C}_3\text{H}_8$ )	Octane ( $\text{C}_8\text{H}_{18}$ )
Heat of combustion ( $\text{kJ mol}^{-1}$ )	-2220	-5450
Molar mass ( $\text{g mol}^{-1}$ )	44.0	114.0

Calculate the heat of combustion of each fuel in  $\text{kJ g}^{-1}$  and use your answer to state which fuel produces more energy per kilogram.

- 3 Write a balanced equation for the incomplete combustion of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) when carbon monoxide is formed.
- 4 Using the information in Tables 2.3.1 and 2.3.2, calculate the amount of energy released when the following amounts of each fuel undergo complete combustion.
  - a 250 g of methane
  - b 9.64 kg of propane
  - c 403 kg of ethanol
  - d 573 t of dried brown coal

---

## 2.4 Determining the heat of combustion of fuels

Knowing the energy released by similar quantities of different fuels helps you to compare fuels and determine their suitability for specific purposes. For example, the fuel used to power an aeroplane (Figure 2.4.1) is different from the fuel used to power a car or bus.



**FIGURE 2.4.1** F15 jets being refuelled by a Boeing 707. The type of fuel suitable for use in aircraft is different from the type of fuel suitable for use in cars or buses.

In previous sections, you learned two ways of representing the energy change for fuels involved in combustion reactions.

- The heat of combustion of a fuel gives the amount of energy released when a specified amount of the fuel burns in oxygen.
- A thermochemical equation includes a  $\Delta H$  value, which shows the amount of heat released when a fuel undergoes combustion. The value of  $\Delta H$  is based on the stoichiometric ratios in the equation.

In this section, you will learn how knowledge of the specific heat capacity of water can be used to obtain an experimental estimate of the energy released in the combustion of a fuel.

### SPECIFIC HEAT CAPACITY OF WATER

The **specific heat capacity** of a substance is a measure of the amount of energy (usually in joules) needed to increase the temperature of a specific quantity of that substance (usually 1 gram) by  $1^{\circ}\text{C}$ .

Specific heat capacity is given the symbol  $C$  and is usually expressed in joules per gram per degrees Celsius, i.e.  $\text{J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ . It can also be expressed in joules per grams per kelvin, i.e.  $\text{J g}^{-1} \text{ K}^{-1}$  (an increase of  $1^{\circ}\text{C}$  is the same as an increase of 1 K).

The specific heat capacities of some common substances are listed in Table 2.4.1. You can see that the value for water is relatively high.

**TABLE 2.4.1** Specific heat capacities of common substances

Substance	Specific heat capacity (J g <sup>-1</sup> °C <sup>-1</sup> )
Water	4.18
Glycerine	2.43
Ethanol	2.46
Sand	0.48
Copper	0.39
Lead	0.16

The specific heat capacity of a substance is a reflection of the types of bonds holding the molecules, ions or atoms together in the substance.

Water has a specific heat capacity of 4.18 J g<sup>-1</sup> °C<sup>-1</sup>. This means that 4.18 joules of heat energy are needed to increase the temperature of 1 gram of water by 1°C. This relatively high value is due to the hydrogen bonds between the water molecules. The higher the specific heat capacity, the more effectively a material stores heat energy.

When a substance is being heated, its temperature rises. The temperature of 1 g of water increases by 1°C when it is supplied with 4.18 J of heat energy. In comparison, 2.43 J of heat energy is required to increase the temperature of 1 g of glycerine by 1°C. The effect of the different specific heat capacities of water and glycerine on their temperatures when heated can be seen in Figure 2.4.2.

**i** Water is distinguished by its very high heat capacity, which is a consequence of the hydrogen bonding between its molecules. The special properties of water are described in *Heinemann Chemistry 1*.

### Calculations using specific heat capacity

The specific heat capacity of water can be used to calculate the heat energy in joules needed to increase the temperature of a given mass of water by a particular amount. Heat energy is given the symbol  $q$ .

A useful equation can be written:

$$\text{Heat energy} = \text{specific heat capacity} \times \text{mass} \times \text{temperature change}$$

Using symbols, the equation can be written as:

$$q = C \times m \times \Delta T$$

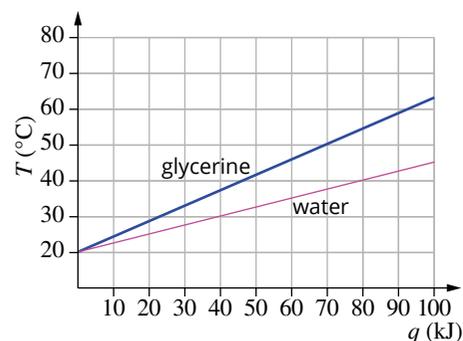
where  $q$  is the amount of heat energy (in J),  $C$  is the specific heat capacity (in J g<sup>-1</sup> °C<sup>-1</sup>),  $m$  is the mass (in g) and  $\Delta T$  is the temperature change (in °C).

**i** The heat energy required to increase the temperature of a given mass of water by a particular amount can be calculated using the equation:

$$q = C \times m \times \Delta T$$

where  $q$  is the amount of heat energy (in J),  $C$  is the specific heat capacity (in J g<sup>-1</sup> °C<sup>-1</sup>),  $m$  is the mass (in g) and  $\Delta T$  is the temperature change (in °C).

**i** The specific heat capacity of a substance is the amount of energy required to increase the temperature of 1 g of the substance by 1°C. Specific heat capacity is frequently written using the units J g<sup>-1</sup> °C<sup>-1</sup>.



**FIGURE 2.4.2** A comparison of the effect of the different specific heat capacities of water and glycerine on the increase in temperature ( $T$ ). Water has a very high heat capacity so it requires more heat energy ( $q$ ) to increase its temperature by 1°C.

### Worked example 2.4.1

#### CALCULATING THE AMOUNT OF ENERGY REQUIRED TO HEAT A SPECIFIED MASS OF WATER USING SPECIFIC HEAT CAPACITY

Calculate the heat energy, in kJ, needed to increase the temperature of 500 mL of water by 15°C.

Thinking	Working
Change the volume of water, in mL, to mass of water, in g. Remember that 1 mL of water has a mass of 1 g.	1 mL of water has a mass of 1 g, so 500 mL of water has a mass of 500 g.
Find the specific heat capacity of water from the data in Table 2.4.1.	The specific heat capacity of water is 4.18 J g <sup>-1</sup> °C <sup>-1</sup> .
To calculate the quantity of heat energy in joules, use the formula: $q = C (\text{J g}^{-1} \text{ °C}^{-1}) \times m (\text{g}) \times \Delta T (\text{°C})$	$q = 4.18 \times 500 \times 15$ $= 3.14 \times 10^4 \text{ J}$
Express the quantity of energy in kJ. Remember that to convert from J to kJ, you multiply by 10 <sup>-3</sup> .	$q = 3.14 \times 10^4 \times 10^{-3}$ $= 31.4 \text{ kJ}$

### Worked example: Try yourself 2.4.1

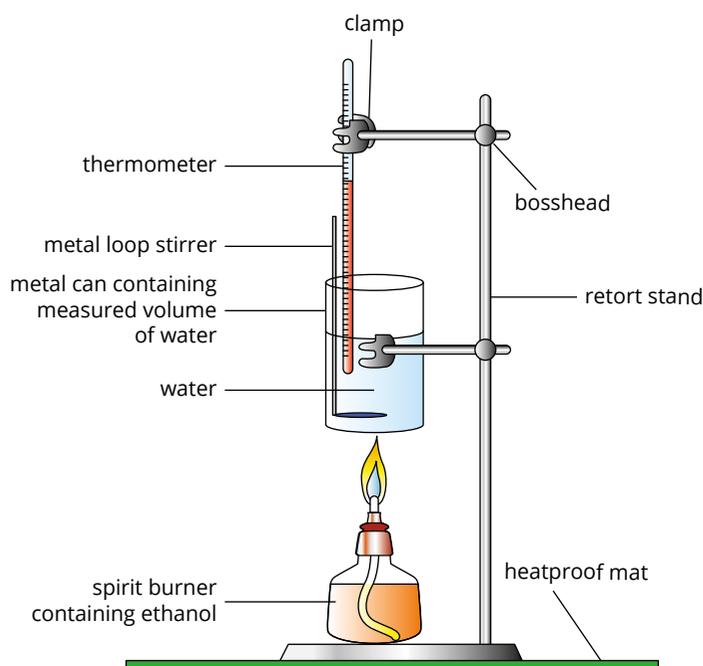
#### CALCULATING THE AMOUNT OF ENERGY REQUIRED TO HEAT A SPECIFIED MASS OF WATER USING SPECIFIC HEAT CAPACITY

Calculate the heat energy, in kJ, needed to increase the temperature of 375 mL of water by 45°C.

### EXPERIMENTAL DETERMINATION OF HEAT OF COMBUSTION

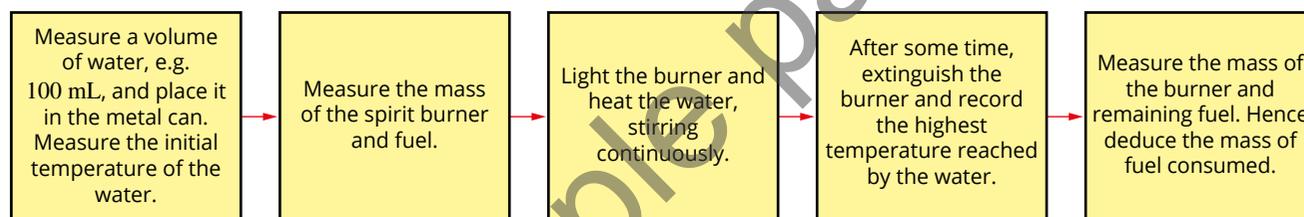
When a combustion reaction takes place, chemical energy is converted to thermal energy. You can use the thermal energy released by a specific quantity of fuel as it undergoes combustion to heat a measured volume of water. If you measure the temperature change of the water, it can be used to determine the approximate amount of energy released by the fuel.

An experimental arrangement for estimating the heat of combustion of a liquid fuel, such as ethanol, is shown in Figure 2.4.3.



**FIGURE 2.4.3** Apparatus for measuring heat of combustion of a fuel (for example, ethanol). A metal can containing a measured volume of water is held above the wick of a spirit burner.

Figure 2.4.4 summarises the steps followed in this experiment.



**FIGURE 2.4.4** Flowchart of the steps followed when using the specific heat capacity of water to determine the heat of combustion of a fuel.

Three key pieces of information collected from this procedure are the:

- mass of water (because the density of water is  $1.00 \text{ g mL}^{-1}$ , the volume of water, measured in mL, is equal to its mass, in g)
- change in temperature of the water,  $\Delta T$
- mass of fuel consumed,  $m$ .

This data can be used to determine the heat of combustion of the fuel, as shown in Worked Example 2.4.2.

Note that when performing these calculations, it is assumed that all of the energy released by the combustion of the fuel is used to heat the water. In reality, some of the energy heats the metal can as well as being lost to the surroundings.

For this reason, measurements of heats of combustion from these experiments only give approximate values. More accurate measurements are obtained using bomb calorimetry, which is discussed in Chapter 17.

### Worked example 2.4.2

#### CALCULATING THE HEAT OF COMBUSTION OF A FUEL FROM EXPERIMENTAL DATA

0.355 g of methanol ( $\text{CH}_3\text{OH}$ ) undergoes complete combustion in a spirit burner. The heat energy released is used to heat 100 mL of water. The temperature of the water rose from  $20.24^\circ\text{C}$  to  $37.65^\circ\text{C}$ . Calculate the heat of combustion of methanol in  $\text{kJ mol}^{-1}$ .

Thinking	Working
Calculate the temperature change of the water.	$\Delta T = 37.65 - 20.24$ $= 17.41^\circ\text{C}$
Use the specific heat capacity of water to determine the energy used to heat the water. Use the formula: $q = C \times m \times \Delta T$ ( $m$ in this formula is the mass of water.)	$q = 4.18 \times 100 \times 17.41$ $= 7277 \text{ J}$
Express the quantity of energy in kJ. Remember that to convert from J to kJ, you multiply by $10^{-3}$ .	$q = 7277 \times 10^{-3}$ $= 7.277 \text{ kJ}$
Calculate the amount, in moles, of methanol using the formula: $n = \frac{m}{M}$	$n = \frac{0.355}{32.0}$ $= 0.0111 \text{ mol}$
Determine the heat of combustion of methanol, in $\text{kJ mol}^{-1}$ . Heat of combustion = $\frac{\text{heat energy released by sample}}{\text{amount of sample (in mol)}}$	Heat of combustion = $\frac{-7.277}{0.0111}$ $= -656 \text{ kJ mol}^{-1}$ (Note: The negative sign indicates the reaction released energy, causing the temperature to rise.)

### Worked example: Try yourself 2.4.2

#### CALCULATING THE HEAT OF COMBUSTION OF A FUEL FROM EXPERIMENTAL DATA

0.295 g of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) undergoes complete combustion in a spirit burner. The heat energy released is used to heat 100 mL of water. The temperature of the water rose from  $19.56^\circ\text{C}$  to  $38.85^\circ\text{C}$ . Calculate the heat of combustion of ethanol in  $\text{kJ mol}^{-1}$ .

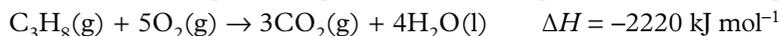
## DETERMINING THE $\Delta H$ VALUE FOR THERMOCHEMICAL EQUATIONS

Experimentally determined heats of combustion for different elements and compounds used as fuels can be listed in a data table, such as that shown in Table 2.4.2.

**TABLE 2.4.2** Experimentally determined heats of combustion of various fuels

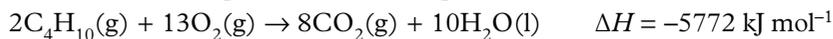
Fuel	Heat of combustion, $\Delta H_c$ ( $\text{kJ mol}^{-1}$ )
Octane	-5450
Butane	-2886
Propane	-2220
Ethane	-1560
Ethanol	-1367
Methane	-890
Methanol	-725
Carbon (graphite)	-394
Hydrogen	-286

This data can be used to write thermochemical equations for the combustion of these fuels. For example, the equation for the complete combustion of propane is:



In this equation, the coefficient of propane is 1 so the  $\Delta H$  value is the same as the heat of combustion.

If the coefficient of the fuel in the combustion equation is 2 or more, the heat of combustion must be multiplied by this number to determine  $\Delta H$ . For example, the thermochemical equation for the complete combustion of butane is written as:



$\Delta H$  in this case is twice the heat of combustion,  $2 \times -2886 = -5772 \text{ kJ mol}^{-1}$ .

Note that heats of combustion measured in  $\text{kJ g}^{-1}$  should be converted to units of  $\text{kJ mol}^{-1}$  for use in thermochemical equations. Combustion reactions are always exothermic, so the enthalpy change always has a negative sign.

### Worked example 2.4.3

#### WRITING A THERMOCHEMICAL EQUATION USING HEAT OF COMBUSTION DATA

Write a thermochemical equation for the complete combustion of octane ( $\text{C}_8\text{H}_{18}$ ).

Thinking	Working
Add oxygen as a reactant and carbon dioxide and water as the products in the equation.	$\text{C}_8\text{H}_{18} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
Balance the carbon, hydrogen then oxygen atoms. Add states.	$2\text{C}_8\text{H}_{18}(\text{g}) + 25\text{O}_2(\text{g}) \rightarrow 16\text{CO}_2(\text{g}) + 18\text{H}_2\text{O}(\text{l})$
Obtain the heat of combustion, in $\text{kJ mol}^{-1}$ , from Table 2.4.2.	The heat of combustion of octane is $-5450 \text{ kJ mol}^{-1}$ .
Determine $\Delta H$ for the thermochemical equation by multiplying the heat of combustion by the coefficient of the fuel in the balanced equation.	$\Delta H = 2 \times -5450 = -10900 \text{ kJ mol}^{-1}$
Write the thermochemical equation.	$2\text{C}_8\text{H}_{18}(\text{g}) + 25\text{O}_2(\text{g}) \rightarrow 16\text{CO}_2(\text{g}) + 18\text{H}_2\text{O}(\text{l})$ $\Delta H = -10900 \text{ kJ mol}^{-1}$

### Worked example: Try yourself 2.4.3

#### WRITING A THERMOCHEMICAL EQUATION USING HEAT OF COMBUSTION DATA

Write a thermochemical equation for the complete combustion of ethane ( $\text{C}_2\text{H}_6$ ).

## 2.4 Review

### SUMMARY

- The specific heat capacity of a substance measures the quantity of energy (usually in joules) needed to increase the temperature of a specified quantity of that substance (usually 1 gram) by 1°C.
- The specific heat capacity of water is  $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ .
- The heat energy required to increase the temperature of a given mass of water by a particular amount can be calculated using the equation:  
 $q = C \times m \times \Delta T$   
where  $q$  is heat energy (in J),  $C$  is the specific heat capacity (in  $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$ ),  $m$  is mass (in g) and  $\Delta T$  is the temperature change (in  $^\circ\text{C}$ ).
- Heat of combustion is the energy released when a specified quantity of a substance (usually 1 mole, 1 gram or 1 litre) is burnt.
- The specific heat capacity of water can be used in the experimental determination of the approximate amount of heat energy released in the combustion of a fuel.
- Heat of combustion data can be used to determine the enthalpy change,  $\Delta H$ , in a thermochemical equation.

### KEY QUESTIONS

- 1 Calculate the heat energy, in kJ, needed to increase the temperature of 1.00 kg of water by  $25.0^\circ\text{C}$ .
- 2 What assumptions are made when making calculations relating to the heat of combustion of fuels using experimental data obtained from the apparatus shown in Figure 2.4.3 (on page 57)?
- 3 A temperature rise of  $1.78^\circ\text{C}$  was observed when  $1.00 \times 10^{-3}$  mol of propane gas was burnt and used to heat 300 mL of water. Calculate the heat of combustion for propane in  $\text{kJ mol}^{-1}$ , assuming all the heat released was used to heat the water.
- 4 A temperature rise of  $11.5^\circ\text{C}$  was observed when 0.500 g of butane gas ( $\text{C}_4\text{H}_{10}$ ) was burnt and used to heat 500 mL of water. Calculate the heat of combustion, in  $\text{kJ g}^{-1}$ , for butane, assuming all the heat released is used to heat the water.
- 5 The heat of combustion of methane is  $-890 \text{ kJ mol}^{-1}$ .
  - a Write a thermochemical equation for the complete combustion of methane.
  - b Determine the mass of methane, in g, which has to be burnt in order to heat 500 mL of water from  $20.0^\circ\text{C}$  to boiling. Assume all the heat released was used to heat the water.

# Chapter review

## KEY TERMS

activation energy  
bioluminescence  
chemical energy  
chemiluminescence  
chemiluminescent  
complete combustion  
decomposition

endothermic  
energy density  
energy profile diagram  
enthalpy  
enthalpy change  
exothermic  
heat content

heat of combustion  
incomplete combustion  
law of conservation  
of energy  
oxidation  
SI units  
specific heat capacity

02  
surroundings  
system  
thermochemical equation  
volume

## Exothermic and endothermic reactions

- Convert the following units of energy to the unit given (to 3 significant figures).
  - 2205 J to kJ
  - 0.152 kJ to J
  - 1 890 000 J to MJ
  - 0.0125 MJ to kJ
- Decide whether the following processes are exothermic or endothermic. Give reasons for your answers.
  - burning of wood
  - melting of ice
  - recharging of a car battery
  - decomposition of plants in a compost heap
- What is the difference between 'bioluminescence' and 'chemiluminescence'? Give an example in your answer.

## Thermochemical equations and energy profile diagrams

- Which one of the following is correct about the energy profile diagrams of both endothermic and exothermic reactions?
  - There is always less energy absorbed than released.
  - The enthalpy of the products is always less than the energy of the reactants.
  - Some energy is always absorbed to break bonds in the reactants.
  - The  $\Delta H$  value is the difference between the enthalpy of the reactants and the highest energy point reached on the energy profile.
- Identify whether each of the following statements related to activation energy is true or false.
  - Activation energy is the energy required to break bonds in the reactants.
  - Reactions that start immediately do not have an activation energy.

- Reactions that release energy overall do not need to absorb activation energy.
  - The match used to light a fire is providing activation energy.
- The combustion reaction of ethyne gas that occurs in a welding machine can be represented by the thermochemical equation:  
$$2\text{C}_2\text{H}_2(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$$
$$\Delta H = -2619 \text{ kJ mol}^{-1}$$
    - Is this reaction endothermic or exothermic?
    - What would be the new value of  $\Delta H$  if the equation was now written as follows?  
$$4\text{C}_2\text{H}_2(\text{g}) + 10\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$$
  - Explain why reversing a chemical reaction reverses the sign of  $\Delta H$ .
  - The combustion of butane gas in portable stoves can be represented by the thermochemical equation:  
$$2\text{C}_4\text{H}_{10}(\text{g}) + 13\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 10\text{H}_2\text{O}(\text{l})$$
$$\Delta H = -5772 \text{ kJ mol}^{-1}$$
    - How does the overall energy of the bonds in the reactants compare with the overall energy of the bonds in the products?
    - Draw an energy profile diagram for the reaction, labelling  $\Delta H$  and activation energy.

## Energy from combustion

- Write a balanced equation for the complete combustion of butanol ( $\text{C}_4\text{H}_9\text{OH}$ ), a commonly used biofuel.
- Write a balanced equation for the incomplete combustion of butane ( $\text{C}_4\text{H}_{10}$ ) where carbon monoxide is formed.
- Calculate the energy released when 5.00 kg of methane ( $\text{CH}_4$ ) is burnt in an unlimited supply of oxygen. The heat of combustion of methane is  $-890 \text{ kJ mol}^{-1}$ . (Give your answer in megajoules, MJ.)

- 12 a** Use the data from Table 2.3.1 on page 51 to calculate the energy available from 1 kg of each of the following fuels.
- Octane
  - Butane
  - Hydrogen
- b** Use the results of your calculations in part **a** to list octane, butane and hydrogen in order of most energy produced per kilogram to least energy produced per kilogram.

### Determining the heat of combustion of fuels

- 13** Calculate the energy needed to heat:
- 100 mL of water from 20.0°C to 80.0°C
  - 250 mL of water from 25.0°C to 100.0°C
  - 1.5 kg of water from 20.0°C to 30.0°C
  - 2300 g of water from 18.0°C to 100.0°C
  - 300 g of cooking oil from 18.0°C to 100.0°C ( $C(\text{cooking oil}) = 2.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ ).
- 14** A 200 mL beaker of water at a temperature of 21.0°C is heated with 10.0 kJ of energy. Calculate the temperature reached by the beaker of water.
- 15** 0.254 g of black coal was burnt and used to heat 300 mL of water. The temperature of the water rose from 18.25°C to 24.92°C. Calculate the heat of combustion, in  $\text{kJ g}^{-1}$ , of the coal. Assume all of the heat released during combustion was used to heat the water.
- 16** The heat of combustion of hydrogen is  $-286 \text{ kJ mol}^{-1}$ . Write a thermochemical equation for the complete combustion of hydrogen.

### Connecting the main ideas

- 17** In a steelworks, carbon monoxide present in the exhaust gases of the blast furnace can be used as a fuel elsewhere in the plant. It reacts according to the equation:
- $$\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \quad \Delta H = -283 \text{ kJ mol}^{-1}$$
- Which has the greater total enthalpy: 1 mol of  $\text{CO(g)}$  and 0.5 mol of  $\text{O}_2\text{(g)}$  or 1 mol of  $\text{CO}_2\text{(g)}$ ?
  - Write the value of  $\Delta H$  for the following equations:
    - $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$
    - $2\text{CO}_2\text{(g)} \rightarrow 2\text{CO(g)} + \text{O}_2\text{(g)}$
- 18** A temperature rise of 5.52°C was observed when 0.0450 g of ethane ( $\text{C}_2\text{H}_6$ ) was burnt and used to heat 100.0 mL of water. Use this information to write a balanced thermochemical equation for the complete combustion of ethane.
- 19** A 500 mL volume of water in a beaker was heated using the energy released by the combustion of a 3.00 g piece of wood. The observed temperature rise was 22.9°C.
- Calculate the heat of combustion of wood in  $\text{kJ g}^{-1}$  and in MJ/tonne.
  - Would the heat of combustion you calculated in part **a** be higher or lower than the actual heat of combustion of the wood. Give reasons for your answer.