Chemistry Units 3 & 4

Chapter 1 — Carbon-based fuels

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Theory

A **fuel** is a substance that stores chemical energy in a form that can be released in a controlled way to do useful work — most often as heat, and often also as light. In almost every fuel used for energy, that energy is released by **combustion**: the fuel reacts rapidly with oxygen from the air. Because the bonds formed in the products are more stable (lower in energy) than the bonds broken in the fuel and oxygen, energy is transferred to the surroundings. Combustion is therefore an **exothermic** reaction, one for which $\Delta H < 0$. The fuels of greatest importance are **carbon-based**: their molecules are built from carbon and hydrogen, and sometimes oxygen, so their complete combustion in plenty of oxygen produces carbon dioxide and water. For example, the methane in natural gas burns according to

$$\mathrm{CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)}$$

releasing energy to whatever surrounds the flame.

Fossil fuels. Fossil fuels formed over many millions of years from the buried remains of once-living organisms, altered by heat and pressure deep underground. The study design names three: **coal**, a carbon-rich *solid* formed from ancient land plants; **natural gas**, a *gas* that is mostly methane, $\mathrm{CH_4}$, formed from ancient marine micro-organisms; and **petrol**, a *liquid* mixture of hydrocarbons such as octane, $\mathrm{C_8H_{18}}$, separated from crude oil (petroleum) at a refinery. All three are drawn from finite underground deposits.

Biofuels. Biofuels are made from **biomass** — plant or animal matter that was alive very recently. The three named biofuels are **biogas**, mostly methane produced when bacteria break down organic waste in the absence of oxygen; **bioethanol**, which is ethanol, $\mathrm{C_2H_5OH}$, made by fermenting the sugars in crops such as sugar cane and then distilling the product; and **biodiesel**, made from plant oils or animal fats. Because a biofuel is grown rather than mined, a fresh supply can be produced within a single growing season.

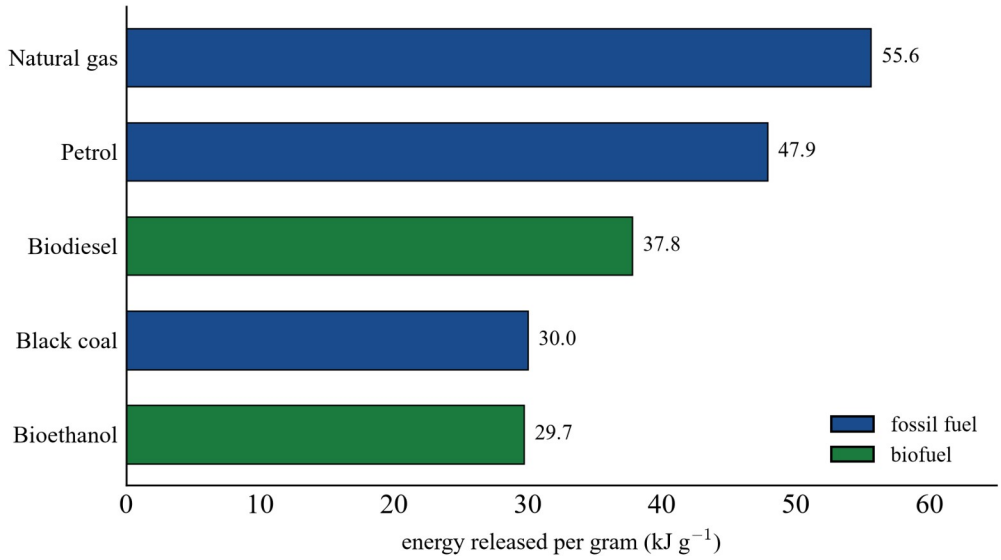
Renewability. A **renewable** resource is one that can be replaced by natural processes within a relatively short period of time. Biofuels are renewable: the crops or wastes they come from can be regrown or regenerated within months to a few years. Fossil fuels are **non-renewable**: although natural processes still form them, they do so over millions of years — far more slowly than they are consumed — so on any human timescale the supply is effectively fixed. The key idea is the *rate of replacement* compared with the rate of use, not simply whether a resource will one day run out. Notice that the same molecule can belong to either class: the methane in biogas is renewable because it is regenerated continuously from waste, while the chemically identical methane in natural gas is non-renewable because its deposit took millions of years to form.

Greenhouse-gas emissions. Every carbon-based fuel releases carbon dioxide, a **greenhouse gas**, when it burns. What differs is the *origin* of that carbon. Burning a fossil fuel moves carbon that has been locked underground for millions of years into the atmosphere, adding to the total there. Burning a biofuel releases $\mathrm{CO_2}$ that the source plants had removed from the atmosphere only recently by photosynthesis; if the crop is replanted, that $\mathrm{CO_2}$ is taken up again, so a biofuel can be close to **carbon neutral** over its whole life cycle. This is only approximate — growing, processing and transporting a biofuel still uses energy — but the *net* addition of $\mathrm{CO_2}$ to the atmosphere is much smaller than for a fossil fuel of the same energy output.

Comparing fuels. No single fuel is best for every purpose, so fuels are judged against several criteria at once:

- **energy content**, the energy released per gram (in $\mathrm{kJ\ g^{-1}}$) — a higher value delivers more energy for the same mass, which matters most where the fuel must be carried, as in transport;
- **renewability** — whether the resource can be replaced within a short time;
- **greenhouse-gas emissions on combustion** — the net amount of $\mathrm{CO_2}$ added to the atmosphere for the energy obtained;
- **physical state and ease of handling** — solids, liquids and gases differ in how easily they are stored, moved and burned (a liquid is convenient to pump and store; a gas must be compressed or liquefied into pressurised tanks; a solid is bulky and cannot be pumped);
- **source and availability** — whether the fuel comes from a finite deposit or from a resource that can be renewed.

The energy released per gram of a pure fuel is found by dividing the magnitude of its molar enthalpy of combustion by its molar mass, $|\Delta H_c| / M$. On this basis the light hydrocarbon fuels release the most energy per gram: natural gas (methane) releases about $55.6\ \text{kJ g}^{-1}$ and petrol (octane) about $47.9\ \text{kJ g}^{-1}$, whereas bioethanol releases about $29.7\ \text{kJ g}^{-1}$ — so a larger mass of bioethanol is needed to obtain the same energy.



Worked examples

Worked Example 1 — For each of the following fuels, state whether it is a fossil fuel or a biofuel, and whether it is renewable or non-renewable, giving a brief reason: (i) black coal, (ii) biogas, (iii) petrol, (iv) biodiesel.

Working	Comment
(i) black coal — fossil fuel, non-renewable	A carbon-rich solid formed from land plants buried for millions of years; replaced far more slowly than it is mined.
(ii) biogas — biofuel, renewable	Mostly methane made by bacteria decomposing organic waste; the waste is produced continuously, so the fuel is replaced within a short time.
(iii) petrol — fossil fuel, non-renewable	A liquid mixture of hydrocarbons refined from crude oil, a finite deposit that took millions of years to form.
(iv) biodiesel — biofuel, renewable	Made from plant oils or animal fats grown or reared within months to a few years.

Worked Example 2 — Natural gas is essentially methane, CH_4 ($M = 16.0\ \text{g mol}^{-1}$, $\Delta H_c = -890\ \text{kJ mol}^{-1}$); bioethanol is ethanol, $\text{C}_2\text{H}_5\text{OH}$ ($M = 46.0\ \text{g mol}^{-1}$, $\Delta H_c = -1367\ \text{kJ mol}^{-1}$). Calculate the energy released per gram by each fuel, and hence state which delivers more energy per gram and by roughly what factor.

Working	Comment
methane: $\dfrac{890}{16.0} = 55.6\ \text{kJ g}^{-1}$	The *magnitude* of ΔH_c (890) is divided by the molar mass; energy released is a positive quantity.
ethanol: $\dfrac{1367}{46.0} = 29.7\ \text{kJ g}^{-1}$	Same method applied to the second fuel.
$55.6\ \text{kJ g}^{-1} > 29.7\ \text{kJ g}^{-1}$	A direct two-way comparison of the two values.
$\dfrac{55.6}{29.7} = 1.87 \approx 1.9$	Methane releases about **1.9 times** as much energy per gram as bioethanol.

Worked Example 3 — Butane, C_4H_{10}, is a fuel obtained from natural gas and crude oil and is stored as a liquid under pressure in gas bottles. (a) Write a balanced thermochemical equation, with states, for the complete combustion

of butane, given $\Delta H_c = -2877\ \text{kJ mol}^{-1}$. (b) Classify butane as a fossil fuel or a biofuel, and as renewable or non-renewable.

(a) Quoting the molar enthalpy of combustion means writing the equation for **one mole** of butane, so a fractional oxygen coefficient is used (this is standard practice):

$$\text{C}_4\text{H}_{10}(\text{g}) + 13/2\,\text{O}_2(\text{g}) \rightarrow 4\,\text{CO}_2(\text{g}) + 5\,\text{H}_2\text{O}(\text{l}),\ \Delta H = -2877\ \text{kJ mol}^{-1}$$

Checking: 4 C and 10 H on each side; oxygen is $13/2 \times 2 = 13$ on the left and $4 \times 2 + 5 = 13$ on the right.

(b) Butane is separated from natural gas and petroleum — fossil deposits that formed over millions of years.

∴ butane is a **fossil fuel** and is **non-renewable**.

Worked Example 4 — A transport operator is choosing between petrol (octane, a fossil fuel, energy value $47.9\ \text{kJ g}^{-1}$) and bioethanol (a biofuel, energy value $29.7\ \text{kJ g}^{-1}$) for its vehicles. Compare the two fuels with reference to renewability, greenhouse-gas emissions and energy released per gram, and recommend the more sustainable choice.

Renewability. Bioethanol is renewable — it is fermented from crops that are regrown each season, so the resource is replaced within a short time — whereas petrol is non-renewable, being refined from finite crude oil.

Greenhouse-gas emissions. Both fuels release CO_2 when they burn, but the CO_2 from bioethanol was absorbed from the atmosphere by the crop only recently and is taken up again when the crop is replanted, so its *net* (life-cycle) emissions are much lower, approaching carbon neutral. Petrol adds carbon that had been stored underground for millions of years, a net increase in atmospheric CO_2.

Energy per gram. Petrol delivers more energy per gram (47.9 against $29.7\ \text{kJ g}^{-1}$), so a smaller mass of petrol supplies a given amount of energy. To match the energy of $1.00\ \text{g}$ of petrol, a vehicle must burn $\frac{47.9}{29.7} = 1.61\ \text{g}$ of bioethanol, and therefore carry more fuel.

∴ bioethanol is the more sustainable choice because it is renewable and close to carbon neutral, even though its lower energy value means a greater mass of fuel must be carried, and growing the crop requires cropland and water.

Practice questions

Question 1 — Consider natural gas and bioethanol.

a. Classify natural gas as a fossil fuel or a biofuel, and as renewable or non-renewable.
b. Classify bioethanol in the same two ways.
c. State the original source of each fuel.

Question 2 — Combustion reactions release the energy stored in fuels.

a. Write a balanced equation, with states, for the complete combustion of methane, $\text{CH}_4(\text{g})$.
b. Write a balanced equation, with states, for the complete combustion of ethane, $\text{C}_2\text{H}_6(\text{g})$.
c. Explain what is meant by describing combustion as *exothermic*.

Question 3 — Two liquid fuels are to be compared on an equal-mass basis.

a. Propane, C_3H_8 ($M = 44.0\ \text{g mol}^{-1}$), has $\Delta H_c = -2220\ \text{kJ mol}^{-1}$. Calculate the energy released per gram of propane.
b. Methanol, CH_3OH ($M = 32.0\ \text{g mol}^{-1}$), has $\Delta H_c = -726\ \text{kJ mol}^{-1}$. Calculate the energy released per gram of methanol.
c. State which of the two fuels delivers more energy per gram.

Question 4 — Renewability distinguishes biofuels from fossil fuels.

a. Define what is meant by a *renewable* resource.
b. Explain why biodiesel is classified as renewable, whereas the diesel refined from crude oil is not.
c. Biogas and natural gas are both mainly methane. Explain why one is renewable and the other is not.

Question 5 — Coal (a solid, energy value about $30\,\text{kJ g}^{-1}$) and natural gas (a gas, energy value about $55.6\,\text{kJ g}^{-1}$) are both fossil fuels burned to generate heat.

a. State which fuel releases more energy per gram.
b. Compare the two fuels with respect to their physical state and ease of handling and transport.
c. Both release CO_2 on combustion. Explain why burning either adds to atmospheric CO_2 in a way that burning a biofuel does not.

Question 6 — Bioethanol is increasingly blended into petrol (for example, as "E10" fuel) as a step toward more sustainable transport.

a. State what is meant by describing bioethanol as a *renewable* fuel.
b. Bioethanol has a lower energy value ($29.7\,\text{kJ g}^{-1}$) than petrol ($47.9\,\text{kJ g}^{-1}$). State one practical disadvantage this creates for a vehicle.
c. With reference to the green chemistry principle of using renewable feedstocks, explain one environmental advantage of replacing some petrol with bioethanol.

Question 7 — Classify each of the following as a fossil fuel or a biofuel, and as renewable or non-renewable: black coal, biogas, petrol, biodiesel, natural gas, bioethanol.

Question 8 — Fuels differ in how quickly their supply can be replaced.

a. Define a *non-renewable* fuel.
b. Choosing from the fuels named in the study design, give one renewable and one non-renewable example and justify each classification.

Question 9 — Petrol can be represented by octane, $\text{C}_8\text{H}_{18}(\text{l})$. Write a balanced thermochemical equation, with states, for the complete combustion of octane, given $\Delta H_c = -5460\,\text{kJ mol}^{-1}$.

Question 10 — Coal can be modelled as carbon.

a. Write a balanced equation, with states, for the complete combustion of carbon, $\text{C}(\text{s})$.
b. Name the greenhouse gas produced, and explain why burning coal raises the level of atmospheric CO_2 more lastingly than burning a biofuel does.

Question 11 — Ethane, C_2H_6 ($M = 30.0\,\text{g mol}^{-1}$, $\Delta H_c = -1560\,\text{kJ mol}^{-1}$), is a minor component of natural gas.

a. Calculate the energy released per gram of ethane.
b. State whether ethane is renewable, and justify your answer.

Question 12 — Explain why the carbon dioxide released when bioethanol is burned is often described as approximately "carbon neutral", whereas that released when petrol is burned is not. Set out the reasoning as a clear chain.

Question 13 — Butane, C_4H_{10} ($M = 58.0\,\text{g mol}^{-1}$), releases $2877\,\text{kJ mol}^{-1}$ on complete combustion.

a. Calculate the energy released per gram of butane.
b. State whether this is greater or smaller than the energy value of bioethanol ($29.7\,\text{kJ g}^{-1}$).

Question 14 — Natural gas is a gas, petrol is a liquid and coal is a solid at room temperature. Explain how the physical state of each fuel affects how it is stored and transported for use.

Question 15 — A student claims: "Biofuels are completely carbon neutral and release no greenhouse gases at all." Evaluate this claim.

Question 16 — Compare petrol and coal on an equal-mass basis.

a. Petrol can be modelled as octane, $\mathrm{C_8H_{18}}$ ($M = 114.0\,\mathrm{g\ mol^{-1}}$, $\Delta H_c = -5460\,\mathrm{kJ\ mol^{-1}}$). Calculate the energy released per gram of octane.
b. Coal can be modelled as carbon, C ($M = 12.0\,\mathrm{g\ mol^{-1}}$, $\Delta H_c = -394\,\mathrm{kJ\ mol^{-1}}$). Calculate the energy released per gram of carbon.
c. State which of petrol or coal delivers more energy per gram.

Question 17 — Methanol, $\mathrm{CH_3OH(l)}$, can be manufactured either from biomass ("bio-methanol") or from natural gas.

a. Write a balanced thermochemical equation, with states, for the complete combustion of methanol, given $\Delta H_c = -726\,\mathrm{kJ\ mol^{-1}}$.
b. Explain why methanol may be classified as either renewable or non-renewable, depending on how it is made.

Question 18 — A regional council is deciding whether to run its bus fleet on diesel (a fossil fuel, energy value $45.8\,\mathrm{kJ\ g^{-1}}$) or on biodiesel produced from used cooking oil (a biofuel, energy value $37.8\,\mathrm{kJ\ g^{-1}}$).

a. State one green chemistry principle that supports using biodiesel made from waste cooking oil.
b. Evaluate the two fuels as a choice of transport fuel. In your response, compare them with reference to at least **two** of renewability, greenhouse-gas emissions and energy released per gram, and finish with a concluding recommendation.

Answers

1 a natural gas — fossil fuel, non-renewable; b bioethanol — biofuel, renewable; c natural gas comes from fossil deposits (ancient marine micro-organisms, as crude oil / gas fields); bioethanol comes from recently grown crops (fermented sugars). **2** a $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; b $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$; c the reaction releases chemical energy to the surroundings as heat ($\Delta H < 0$). **3** a $50.5\,kJ\,g^{-1}$; b $22.7\,kJ\,g^{-1}$; c propane. **4** a a resource that can be replaced by natural processes within a relatively short period of time; b biodiesel is made from oils and fats of crops/animals grown within a few years (renewable), whereas crude-oil diesel comes from a finite deposit that took millions of years to form (non-renewable); c biogas methane is regenerated continuously from waste (renewable), while natural-gas methane took millions of years to form and is not replaced on a human timescale (non-renewable). **5** a natural gas; b coal is a bulky solid that must be moved by truck or rail and cannot be pumped, whereas natural gas flows through pipes but must be compressed or liquefied for storage/transport; c the CO_2 from both fossil fuels is carbon that was buried for millions of years, a net addition to the atmosphere, unlike a biofuel whose CO_2 was recently absorbed by its crop. **6** a it is made from crops that can be regrown within a season, so the resource is replaced within a short time; b a larger mass (and volume) of bioethanol is needed for the same energy, so vehicles travel a shorter distance per tank / need refuelling more often; c using a renewable feedstock reduces reliance on finite crude oil and lowers the net CO_2 added to the atmosphere. **7** fossil fuels (non-renewable): black coal, petrol, natural gas. Biofuels (renewable): biogas, biodiesel, bioethanol. **8** a a fuel whose supply is not replaced by natural processes within a short time (it forms over millions of years, far more slowly than it is used); b e.g. renewable — bioethanol (fermented from regrown crops); non-renewable — coal (formed over millions of years from buried plants). **9** $C_8H_{18}(l) + 25/2\,O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$, $\Delta H = -5460\,kJ\,mol^{-1}$. **10** a $C(s) + O_2(g) \rightarrow CO_2(g)$; b carbon dioxide; burning coal releases carbon locked underground for millions of years, a net addition to atmospheric CO_2, whereas a biofuel's CO_2 was recently removed from the air by its crop and is reabsorbed when the crop regrows. **11** a $52.0\,kJ\,g^{-1}$; b non-renewable — ethane is a component of natural gas, a fossil fuel formed over millions of years. **12** the CO_2 from bioethanol was absorbed from the atmosphere by the crop shortly beforehand and is reabsorbed when the crop is replanted, so the net addition is close to zero; the CO_2 from petrol comes from carbon buried underground for millions of years and is a net increase in atmospheric CO_2. **13** a $49.6\,kJ\,g^{-1}$; b greater than the energy value of bioethanol ($49.6 > 29.7$). **14** natural gas (a gas) has a low density and must be compressed or liquefied into pressurised tanks, or moved by pipeline; petrol (a liquid) is easily pumped and stored in tanks; coal (a solid) is bulky, cannot be pumped, and is transported in trucks, trains or ships. **15** the claim overstates the case: biofuels still release CO_2 when burned, and are only *approximately* carbon neutral because that CO_2 was recently taken up by the source crop; growing, processing and transporting the fuel also uses energy (often from fossil sources), so net emissions are low but not zero. **16** a $47.9\,kJ\,g^{-1}$; b $32.8\,kJ\,g^{-1}$; c petrol (octane). **17** a $CH_3OH(l) + 3/2\,O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$, $\Delta H = -726\,kJ\,mol^{-1}$; b it is renewable if made from biomass that can be regrown, but non-renewable if made from natural gas, a fossil fuel — the classification depends on the source of the carbon. **18** a e.g. the use of renewable feedstocks, or the prevention of waste (re-using waste cooking oil); b evaluation — biodiesel is renewable and close to carbon neutral and re-uses a waste material, but diesel has the higher energy value (45.8 against $37.8\,kJ\,g^{-1}$); recommend biodiesel as the more sustainable fuel despite the modestly greater mass required.

Fully-worked solutions

Question 1 a. Natural gas is a **fossil fuel** and is **non-renewable**: it is drawn from an underground deposit that took millions of years to form and is used much faster than it is replaced. b. Bioethanol is a **biofuel** and is **renewable**: it is produced from crops that can be regrown within a single season. c. Natural gas forms from ancient marine micro-organisms buried and altered over geological time (found with crude oil and in gas fields); bioethanol is produced by fermenting the sugars of recently grown crops such as sugar cane, followed by distillation.

Question 2 a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$. Check: 1 C, 4 H and $2 \times 2 = 4$ O atoms on each side. b. $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$. Check: 4 C, 12 H and $7 \times 2 = 14$ O atoms on each side ($4 \times 2 + 6 = 14$). c. An *exothermic* reaction releases chemical energy to the surroundings, so the surroundings warm up

and $\Delta H < 0$. In combustion the bonds formed in the products (CO_2 and H_2O) are more stable and lower in energy than those broken in the fuel and oxygen, and the difference is released as heat.

Question 3 a. $\frac{|\Delta H_c|}{M} = \frac{2220}{44.0} = 50.5\ \text{kJ g}^{-1}$. b. $\frac{|\Delta H_c|}{M} = \frac{726}{32.0} = 22.7\ \text{kJ g}^{-1}$. c. $50.5\ \text{kJ g}^{-1} > 22.7\ \text{kJ g}^{-1}$, so **propane** delivers more energy per gram.

Question 4 a. A renewable resource is one that can be replaced by natural processes within a relatively short period of time — short compared with the rate at which it is used. b. Biodiesel is made from the oils and fats of plants and animals, which can be grown or reared again within months to a few years, so the resource is replaced quickly. Diesel from crude oil comes from a finite underground deposit that took millions of years to form and is not replaced on any human timescale, so it is non-renewable. c. Renewability depends on the *source*, not the molecule. The methane in biogas is generated continuously by bacteria acting on organic waste, so it is replaced within days to weeks (renewable). The methane in natural gas formed over millions of years and is consumed far faster than it is replaced (non-renewable).

Question 5 a. Natural gas: $55.6\ \text{kJ g}^{-1} > 30\ \text{kJ g}^{-1}$, so it releases more energy per gram than coal. b. Coal is a solid: it is bulky, cannot be pumped, and is handled and transported in trucks, trains or ships. Natural gas is a gas: it has a low density, flows conveniently through pipelines, but for storage or road transport it must be compressed or liquefied into pressurised tanks. c. The carbon in both coal and natural gas was buried underground for millions of years. Releasing it as CO_2 is therefore a *net* addition to the carbon in the atmosphere. A biofuel's carbon was absorbed from the atmosphere by its source crop only recently and is taken up again when the crop regrows, so it does not add to the long-term atmospheric total in the same way.

Question 6 a. Bioethanol is renewable because it is fermented from crops that can be regrown within a single season, so the resource is replaced within a short period of time. b. Because bioethanol releases less energy per gram, a vehicle needs a larger mass (and volume) of it for the same energy — it travels less far on a full tank and must be refuelled more often. c. Using a renewable feedstock (the crop) in place of finite crude oil means less fossil carbon is taken from underground; the CO_2 released by the bioethanol was recently absorbed by the crop, so replacing part of the petrol lowers the *net* CO_2 added to the atmosphere.

Question 7 Fossil fuels, all non-renewable: **black coal, petrol, natural gas**. Biofuels, all renewable: **biogas, biodiesel, bioethanol**. (Fossil fuels come from deposits formed over millions of years; biofuels come from recently living biomass that can be regrown.)

Question 8 a. A non-renewable fuel is one whose supply is not replaced by natural processes within a short time: it forms over millions of years, far more slowly than it is consumed, so on a human timescale it is effectively finite. b. Renewable — **bioethanol**: fermented from crops (e.g. sugar cane) that are regrown each season. Non-renewable — **coal**: formed from plant matter buried and compressed over millions of years, and not replaced as it is mined. (Other valid pairs: biogas or biodiesel as renewable; petrol or natural gas as non-renewable.)

Question 9 Quoting a molar ΔH_c means writing the equation for one mole of octane, so a fractional oxygen coefficient is used:

$$C_8H_{18}(l) + 25/2\,O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(l), \Delta H = -5460\ \text{kJ mol}^{-1}$$

Check: 8 C and 18 H on each side; oxygen is $25/2 \times 2 = 25$ on the left and $8 \times 2 + 9 = 25$ on the right.

Question 10 a. $C(s) + O_2(g) \rightarrow CO_2(g)$. Check: 1 C and 2 O atoms on each side. b. The greenhouse gas is **carbon dioxide**. The carbon in coal was locked underground for millions of years, so burning it transfers that carbon into the atmosphere as a *net* increase. A biofuel's carbon was removed from the atmosphere by its crop only recently and is reabsorbed when the crop is regrown, so it does not raise the long-term atmospheric CO_2 level in the same lasting way.

Question 11 a. $\frac{|\Delta H_c|}{M} = \frac{1560}{30.0} = 52.0\ \text{kJ g}^{-1}$. b. Ethane is **non-renewable**: it is a component of natural gas, a fossil fuel that formed over millions of years and is used far faster than it is replaced.

Question 12 When bioethanol burns it releases CO_2; however, the carbon in that CO_2 was taken from the atmosphere only recently, during the growth of the crop by photosynthesis. When the crop is replanted, an equal amount of CO_2 is absorbed again, so over the life cycle the *net* addition to the atmosphere is close to zero — hence "approximately carbon neutral". Petrol also releases CO_2, but its carbon had been buried underground for millions of years; releasing it is a *net* increase in atmospheric CO_2 that is not balanced by any recent uptake, so petrol is not carbon neutral.

Question 13 a. $\frac{|\Delta H_c|}{M} = \frac{2877}{58.0} = 49.6\ \text{kJ g}^{-1}$. b. $49.6\ \text{kJ g}^{-1} > 29.7\ \text{kJ g}^{-1}$, so butane's energy value is **greater** than that of bioethanol.

Question 14 - Natural gas (a **gas**) has a very low density, so a useful mass occupies a large volume; it is moved efficiently through pipelines, but for vehicles or storage it must be compressed to high pressure or cooled to a liquid and kept in strong, sealed tanks. - Petrol (a **liquid**) is dense and easily poured and pumped; it is stored and transported conveniently in tanks and drums at ordinary pressure, which is one reason it is so widely used in transport. - Coal (a **solid**) is bulky and cannot be pumped or piped; it is handled and transported in large quantities by truck, train or ship, and must be fed mechanically into a furnace.

Question 15 The claim is an over-statement. Burning any biofuel *does* release CO_2, a greenhouse gas, so it is not true that "no greenhouse gases at all" are produced. Biofuels are only *approximately* carbon neutral: the CO_2 released was recently absorbed from the atmosphere by the source crop, and is taken up again if the crop is replanted, so the *net* emission is low. But growing, harvesting, processing and transporting the fuel all use energy — often from fossil sources — and clearing land for crops can release stored carbon. A fair statement is that biofuels have much lower *net* greenhouse emissions than fossil fuels, but are not perfectly carbon neutral and do release CO_2 on combustion.

Question 16 a. Octane: $\frac{|\Delta H_c|}{M} = \frac{5460}{114.0} = 47.9\ \text{kJ g}^{-1}$. b. Carbon: $\frac{|\Delta H_c|}{M} = \frac{394}{12.0} = 32.8\ \text{kJ g}^{-1}$. (Real coal is impure carbon, so its energy value, about $30\ \text{kJ g}^{-1}$, is a little lower than that of pure carbon.) c. $47.9\ \text{kJ g}^{-1} > 32.8\ \text{kJ g}^{-1}$, so **petrol** delivers more energy per gram than coal.

Question 17 a. Writing the equation for one mole of methanol (fractional oxygen coefficient) to match the molar ΔH_c:

$$\text{CH}_3\text{OH(l)} + 3/2\,\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\,\text{H}_2\text{O(l)}, \Delta H = -726\ \text{kJ mol}^{-1}$$

Check: 1 C and 4 H on each side; oxygen is $1 + 3/2 \times 2 = 4$ on the left and $2 + 2 = 4$ on the right. b. The classification depends on the *source* of the carbon. Made from biomass that can be regrown, methanol is renewable, because its feedstock is replaced within a short time. Made from natural gas — a fossil fuel formed over millions of years — the same molecule is non-renewable. The chemistry of the fuel is identical; only the origin of its carbon differs.

Question 18 a. Using a **renewable feedstock** — or the **prevention of waste**, since the used cooking oil would otherwise be discarded — is a green chemistry principle that supports making biodiesel from waste oil. b. *Renewability:* biodiesel from used cooking oil is renewable, drawing on a continually produced waste material, whereas diesel is refined from finite crude oil and is non-renewable. *Greenhouse-gas emissions:* both fuels release CO_2 when burned, but the carbon in biodiesel was recently absorbed from the atmosphere by the crops that produced the oil, so its net emissions are much lower, approaching carbon neutral; re-using waste oil also avoids the emissions and disposal problems of discarding it. *Energy per gram:* diesel has the higher energy value ($45.8\ \text{kJ g}^{-1}$ against $37.8\ \text{kJ g}^{-1}$), so a slightly greater mass of biodiesel is needed for the same energy. *Conclusion:* on balance biodiesel from used cooking oil is the more sustainable choice, because it is renewable, re-uses a waste material and has much lower net greenhouse emissions; the only real cost is the modestly greater mass of fuel required.

Chapter 1 Carbon-based fuels — 1B Fuels, photosynthesis and cellular respiration

Theory

Almost all of the energy that powers living things — and much of the energy stored in the fuels we use — can be traced back to the Sun. Green plants, algae and some bacteria capture a small fraction of the sunlight that reaches them and lock its energy into chemical bonds through **photosynthesis**. The glucose they make is the starting point for the food we eat and for biofuels such as bioethanol, so the Sun is the ultimate source of this chemical energy.

Photosynthesis. Photosynthesis is the process that converts **light energy into chemical energy**, storing it in molecules of glucose. Using the pigment chlorophyll, plants combine carbon dioxide and water to make glucose and oxygen:

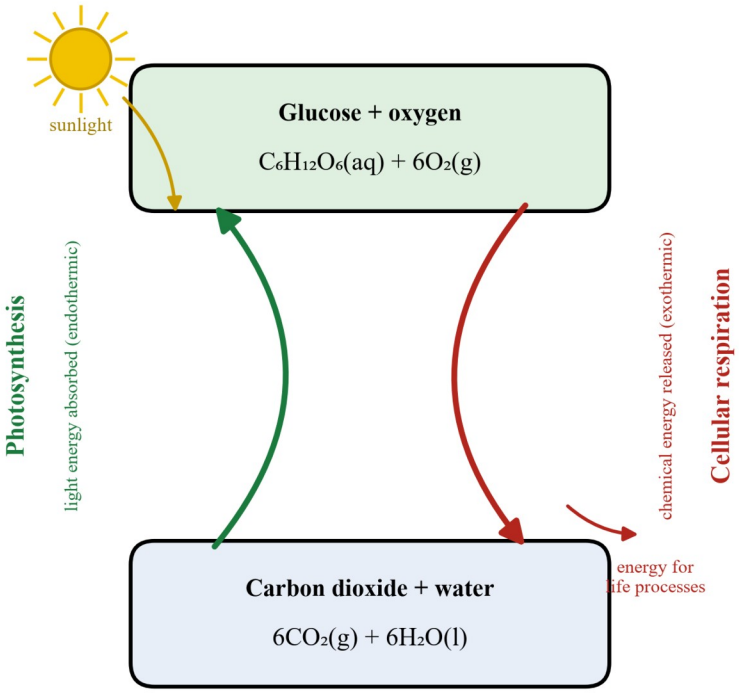
$$6\,CO_2(g) + 6\,H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6\,O_2(g)$$

Because it can only proceed by absorbing energy from sunlight, photosynthesis is **endothermic** ($\Delta H > 0$). It is the source of both the glucose and the oxygen on which respiration in living things depends.

Cellular respiration. Living cells recover the stored energy by **oxidising glucose** — essentially the reverse chemical change. In cellular respiration, glucose reacts with oxygen to release energy, carbon dioxide and water:

$$C_6H_{12}O_6(aq) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)$$

Respiration is **exothermic** ($\Delta H < 0$): it releases the chemical energy that photosynthesis stored, making it available for movement, growth and warmth. Glucose is a carbohydrate, and its oxidation is the body's **primary carbohydrate energy source**. Notice that the respiration equation is exactly the **reverse** of the photosynthesis equation — the products of one process are the reactants of the other. Together they form a cycle in which carbon and energy pass continually between the atmosphere and living things.



Bioethanol — a fuel grown from sunlight. The glucose made by photosynthesis can also be turned into a liquid fuel. In **fermentation**, enzymes in yeast break glucose down, in the absence of oxygen, into ethanol and carbon dioxide:

$$C_6H_{12}O_6(aq) \rightarrow 2\,C_2H_5OH(aq) + 2\,CO_2(g)$$

The dilute ethanol solution that forms is then concentrated by **distillation** to give **bioethanol**, which can be blended with petrol or used alone as a transport fuel. Bioethanol is regarded as a **more sustainable** fuel than petrol for two

main reasons. First, its feedstock is **renewable**: the sugar and starch crops it is made from are replaced within a single growing season by photosynthesis, whereas crude oil takes millions of years to form. Second, the carbon dioxide released when bioethanol is made and later burned was only recently removed from the atmosphere by the crop during photosynthesis, so over the whole cycle little *net* carbon dioxide is added — the fuel is described as close to **carbon-neutral**. (It is not perfectly carbon-neutral, because fossil-fuel energy is still used to grow, harvest and distil the crop.)

Fuel sources for the body. The energy a food supplies to the body is measured in kilojoules per gram, kJ g^{-1}, and depends on which of the three main food groups it contains. Their average energy values are:

- carbohydrates: $16\,\text{kJ g}^{-1}$
- proteins: $17\,\text{kJ g}^{-1}$
- lipids (fats and oils): $37\,\text{kJ g}^{-1}$

Carbohydrates such as glucose and starch are the body's main everyday fuel, oxidised through cellular respiration. Proteins are used chiefly for growth and repair, but can be oxidised for energy when needed. **Fats and oils (lipids) release more than twice as much energy per gram** as carbohydrates or proteins. This is because the carbon atoms in a fat are, on average, in a **lower (less oxidised) state** than those in a carbohydrate: a fat is built largely from energy-rich C–H and C–C bonds and contains proportionally less oxygen, so more energy is released when it is fully oxidised to carbon dioxide and water. The energy available from a food is found by multiplying the mass of each food group by its energy value and adding the contributions.

Worked examples

Worked Example 1 — A breakfast bar contains 30.0 g of carbohydrate, 6.0 g of protein and 10.0 g of fat. Using the food energy values carbohydrate $16\,\text{kJ g}^{-1}$, protein $17\,\text{kJ g}^{-1}$ and fat $37\,\text{kJ g}^{-1}$, calculate the total energy the bar supplies and the percentage of that energy that comes from fat.

Working	Comment
carbohydrate: $30.0 \times 16 = 480\,\text{kJ}$	Mass of each group × its energy value.
protein: $6.0 \times 17 = 102\,\text{kJ}$	Proteins supply $17\,\text{kJ g}^{-1}$.
fat: $10.0 \times 37 = 370\,\text{kJ}$	Fats are the most energy-dense group.
total $= 480 + 102 + 370 = 952\,\text{kJ}$	Sum of the three contributions.
% from fat $= \dfrac{370}{952} \times 100 = 38.9\,\%$	Fat's share of the total energy (3 sig figs).

Worked Example 2 — A vat at a bioethanol plant is charged with 90.0 g of glucose ($M = 180.0\,\text{g mol}^{-1}$), which is completely fermented according to $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) \rightarrow 2\,\text{C}_2\text{H}_5\text{OH}(\text{aq}) + 2\,\text{CO}_2(\text{g})$. Calculate the mass of ethanol ($M = 46.0\,\text{g mol}^{-1}$) and the mass of carbon dioxide ($M = 44.0\,\text{g mol}^{-1}$) produced.

Working	Comment
$n(\text{glucose}) = \dfrac{90.0}{180.0} = 0.500\,\text{mol}$	Amount of glucose, $n = m / M$.
$n(\text{ethanol}) = 2 \times 0.500 = 1.00\,\text{mol}$	Mole ratio of glucose to ethanol is $1:2$.
$m(\text{ethanol}) = 1.00 \times 46.0 = 46.0\,\text{g}$	Mass of ethanol, $m = n\,M$.
$n(\text{CO}_2) = 2 \times 0.500 = 1.00\,\text{mol}$	Mole ratio of glucose to CO_2 is $1:2$.
$m(\text{CO}_2) = 1.00 \times 44.0 = 44.0\,\text{g}$	Mass of carbon dioxide produced.

Worked Example 3 — Photosynthesis and cellular respiration are often described as complementary processes. Write a balanced equation, with states, for each; state whether each is exothermic or endothermic; and explain the energy relationship between them.

Photosynthesis stores energy captured from sunlight:

$$6\,CO_2(g) + 6\,H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6\,O_2(g)$$

It is **endothermic** ($\Delta H > 0$) because it can only proceed by absorbing light energy, which is converted into chemical energy stored in glucose.

Cellular respiration releases that stored energy by oxidising glucose:

$$C_6H_{12}O_6(aq) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)$$

It is **exothermic** ($\Delta H < 0$) because it releases chemical energy for the organism to use.

The second equation is the exact reverse of the first: the products of photosynthesis (glucose and oxygen) are the reactants of respiration, and the products of respiration (carbon dioxide and water) are the reactants of photosynthesis. Because the equations are reversed, their enthalpy changes are equal in magnitude and opposite in sign. ∴ energy that originates in sunlight is stored in glucose by photosynthesis and later released by respiration, while carbon cycles continuously between the atmosphere and living things.

Worked Example 4 — Bioethanol made by fermenting the glucose in sugar cane is used as a transport fuel. Write a balanced equation for the fermentation step, and explain, with reference to two green chemistry principles, why bioethanol is considered a more sustainable and close to carbon-neutral fuel than petrol.

Fermentation of glucose (catalysed by enzymes in yeast, in the absence of oxygen), after which the ethanol is concentrated by distillation:

$$C_6H_{12}O_6(aq) \rightarrow 2\,C_2H_5OH(aq) + 2\,CO_2(g)$$

Against the principle of **using renewable feedstocks**, bioethanol is made from the sugars in crops such as sugar cane, which are regrown within a single season by photosynthesis; petrol, by contrast, is refined from crude oil, a finite fossil resource that cannot be replaced on a human timescale.

Against the principle of **catalysis**, the fermentation step is brought about by enzymes in yeast — biological catalysts. They allow the glucose to be converted into ethanol at about 30 °C and atmospheric pressure, so little energy has to be supplied to the reaction itself, and because enzymes are highly specific almost all of the glucose ends up as ethanol and carbon dioxide rather than as unwanted by-products that would have to be separated and treated. Refining crude oil into petrol, by contrast, requires the crude to be heated to several hundred degrees Celsius.

Bioethanol is also close to **carbon-neutral**: the carbon dioxide released when it is produced and burned was recently taken up from the atmosphere by the growing crop (in $6\,CO_2 \rightarrow$ glucose), so over the full cycle little *net* carbon dioxide is added, whereas burning petrol releases carbon that has been locked underground for millions of years. (Carbon neutrality is evidence of bioethanol's lower net emissions; it is a consequence of the renewable feedstock, not a green chemistry principle in its own right.)

∴ because its feedstock is renewable and its production is enzyme-catalysed under mild conditions, bioethanol is more sustainable than petrol, and because its combustion carbon dioxide is largely offset by photosynthetic uptake it is close to carbon-neutral. (It is not perfectly carbon-neutral, since fossil-fuel energy is still used to grow, harvest and distil the crop.)

Practice questions

Question 1 — Photosynthesis is the process that begins the flow of energy through living things.

a. Write a balanced equation, with states, for photosynthesis.
b. State the form of energy that is converted, and the form it is converted into, during photosynthesis.
c. Name the two products of photosynthesis, and state which of them is the energy-storage molecule.

Question 2 — Cellular respiration supplies the energy that cells need.

a. Write a balanced equation, with states, for the complete oxidation of glucose in cellular respiration.
b. State whether respiration is exothermic or endothermic, and give a reason.
c. Explain the relationship between the respiration equation and the photosynthesis equation.

Question 3 — Use the food energy values carbohydrate $16\ \text{kJ g}^{-1}$, protein $17\ \text{kJ g}^{-1}$ and fat $37\ \text{kJ g}^{-1}$. A serving of yoghurt contains 18.0 g of carbohydrate, 9.0 g of protein and 5.0 g of fat.

a. Calculate the energy available from the carbohydrate.
b. Calculate the total energy available from the serving.
c. Calculate the percentage of the total energy that comes from fat.

Question 4 — The fermentation of glucose is $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) \rightarrow 2\,\text{C}_2\text{H}_5\text{OH}(\text{aq}) + 2\,\text{CO}_2(\text{g})$. A vat contains 45.0 g of glucose ($M = 180.0\ \text{g mol}^{-1}$).

a. Calculate the amount, in mol, of glucose.
b. Calculate the mass of ethanol ($M = 46.0\ \text{g mol}^{-1}$) produced by complete fermentation.
c. Calculate the mass of carbon dioxide ($M = 44.0\ \text{g mol}^{-1}$) released.

Question 5 — A bioethanol plant ferments a glucose solution in a sealed vat and then treats the liquid drawn off.

a. State the role of the yeast added to the vat.
b. Explain why air is excluded from the vat.
c. The liquid drawn from the vat is a dilute aqueous solution of ethanol. Name the process used to concentrate it, and explain how that process separates ethanol from water.

Question 6 — Use the food energy values carbohydrate $16\ \text{kJ g}^{-1}$, protein $17\ \text{kJ g}^{-1}$ and fat $37\ \text{kJ g}^{-1}$.

a. State which of the three food groups provides the most energy per gram.
b. Calculate the energy released by oxidising 20.0 g of fat and by oxidising 20.0 g of carbohydrate, and find the difference between them.
c. Calculate the mass of fat that would supply the same energy as 20.0 g of carbohydrate.

Question 7 — A packaged sandwich supplies 1240 kJ of energy and contains 40.0 g of carbohydrate and 7.0 g of protein. Using the food energy values (carbohydrate 16, protein 17, fat $37\ \text{kJ g}^{-1}$), calculate the mass of fat it contains.

Question 8 — A meal contains 55.0 g of carbohydrate, 20.0 g of protein and 30.0 g of fat. Using the food energy values (carbohydrate 16, protein 17, fat $37\ \text{kJ g}^{-1}$), calculate the total energy the meal provides.

Question 9 — A 250 mL sports drink provides 520 kJ of energy, all of it from carbohydrate ($16\ \text{kJ g}^{-1}$). Calculate the mass of carbohydrate the drink contains.

Question 10 — Explain why carbohydrates, rather than proteins, are described as the body's primary energy source. Refer to the oxidation of glucose in your answer.

Question 11 — Glucose is fermented to ethanol and carbon dioxide. Calculate the mass of ethanol that can be obtained from 1.00 kg of glucose ($M = 180.0\ \text{g mol}^{-1}$; ethanol $M = 46.0\ \text{g mol}^{-1}$), assuming complete conversion.

Question 12 — During photosynthesis a plant produces 90.0 g of glucose ($M = 180.0\ \text{g mol}^{-1}$). Using $6\,\text{CO}_2(\text{g}) + 6\,\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) + 6\,\text{O}_2(\text{g})$, calculate (a) the mass of carbon dioxide consumed ($M = 44.0\ \text{g mol}^{-1}$) and (b) the mass of oxygen released ($M = 32.0\ \text{g mol}^{-1}$).

Question 13 — Cellular respiration and photosynthesis have opposite enthalpy changes. State the sign of ΔH for each process, and justify each answer by referring to whether energy is absorbed or released.

Question 14 — Explain why fats and oils release more energy per gram than carbohydrates and proteins. Refer to the average oxidation state of the carbon atoms and to the bonding and composition of a fat molecule in your answer.

Question 15 — A muesli contains 62.0 g of carbohydrate, 11.0 g of protein and 8.0 g of fat per 100 g serving. Using the food energy values (carbohydrate 16, protein 17, fat $37\ \text{kJ g}^{-1}$), calculate (a) the energy content of one 100 g serving and (b) the average energy content per gram of the muesli.

Question 16 — With reference to the green chemistry principle of catalysis, explain one advantage of using yeast to carry out the conversion of glucose into ethanol.

Question 17 — A distillery ferments glucose ($M = 180.0\ \text{g mol}^{-1}$) and obtains 230 g of ethanol ($M = 46.0\ \text{g mol}^{-1}$). Calculate the minimum mass of glucose that must have been fermented, assuming complete conversion.

Question 18 — Bioethanol, produced by fermenting the glucose in sugar cane, is blended with petrol and sold as a transport fuel. Evaluate bioethanol as a more sustainable transport fuel than petrol. In your response:

- write a balanced equation, with states, for the fermentation of glucose;
- refer to two green chemistry principles; and
- give a concluding statement.

Answers

1 a $6\,CO_2(g)+6\,H_2O(l)\rightarrow C_6H_{12}O_6(aq)+6\,O_2(g)$; b light energy → chemical energy; c glucose and oxygen — glucose stores the chemical energy. **2** a $C_6H_{12}O_6(aq)+6\,O_2(g)\rightarrow 6\,CO_2(g)+6\,H_2O(l)$; b exothermic — it releases stored chemical energy; c respiration is the exact reverse of photosynthesis (products of one are the reactants of the other). **3** a $288\,kJ$; b $626\,kJ$; c $29.6\,\%$. **4** a $0.250\,mol$; b $23.0\,g$; c $22.0\,g$. **5** a the yeast supplies enzymes — biological catalysts — that catalyse the breakdown of glucose into ethanol and carbon dioxide; b fermentation is anaerobic: with oxygen present the yeast would instead oxidise the glucose completely to CO_2 and water, leaving no ethanol; c distillation — ethanol boils at about 78 °C and water at 100 °C, so on heating the vapour is much richer in ethanol and is condensed and collected. **6** a fats and oils (lipids); b fat $740\,kJ$, carbohydrate $320\,kJ$, difference $420\,kJ$; c $8.65\,g$. **7** $13.0\,g$. **8** $2330\,kJ$. **9** $32.5\,g$. **10** carbohydrates (glucose) are readily oxidised in respiration for immediate energy; proteins are used mainly for growth and repair and are oxidised for energy only when needed. **11** $511\,g$ ($0.511\,kg$). **12** a $132\,g$; b $96.0\,g$. **13** photosynthesis $\Delta H>0$ (endothermic — absorbs light energy); respiration $\Delta H<0$ (exothermic — releases energy); equal magnitude, opposite sign because the equations are reversed. **14** a fat has carbon atoms in a lower (less oxidised) average state, with more energy-rich C–H and C–C bonds and proportionally less oxygen, so full oxidation to CO_2 and H_2O releases more energy per gram. **15** a $1475\,kJ$; b $14.8\,kJ\,g^{-1}$. **16** the enzymes in yeast are catalysts, so the conversion runs at about 30 °C and atmospheric pressure — little energy need be supplied — and their specificity means almost all the glucose becomes ethanol and CO_2 rather than by-products, so there is less waste. **17** $450\,g$. **18** evaluation (fermentation equation + two green chemistry principles + conclusion) — see solutions.

Fully-worked solutions

Question 1 a. $6\,CO_2(g)+6\,H_2O(l)\rightarrow C_6H_{12}O_6(aq)+6\,O_2(g)$. b. Light (radiant) energy from the Sun is converted into chemical energy, which is stored in the bonds of glucose. c. The products are glucose, $C_6H_{12}O_6$, and oxygen, O_2. Glucose is the energy-storage molecule; the oxygen is released as a by-product.

Question 2 a. $C_6H_{12}O_6(aq)+6\,O_2(g)\rightarrow 6\,CO_2(g)+6\,H_2O(l)$. b. Exothermic: respiration releases the chemical energy stored in glucose (as heat and usable energy for the organism), so $\Delta H<0$. c. The respiration equation is the exact reverse of the photosynthesis equation. Glucose and oxygen — the products of photosynthesis — are the reactants of respiration, and carbon dioxide and water — the products of respiration — are the reactants of photosynthesis. Photosynthesis stores solar energy in glucose; respiration releases it.

Question 3 a. Carbohydrate energy $=18.0\times16=288\,kJ$. b. Protein $=9.0\times17=153\,kJ$; fat $=5.0\times37=185\,kJ$. Total $=288+153+185=626\,kJ$. c. From fat $=\dfrac{185}{626}\times100=29.6\,\%$.

Question 4 a. $n(\text{glucose})=\dfrac{45.0}{180.0}=0.250\,mol$. b. Glucose : ethanol $=1:2$, so $n(\text{ethanol})=2\times0.250=0.500\,mol$; $m(\text{ethanol})=0.500\times46.0=23.0\,g$. c. Glucose : $CO_2=1:2$, so $n(CO_2)=0.500\,mol$; $m(CO_2)=0.500\times44.0=22.0\,g$.

Question 5 a. The yeast supplies the **enzymes** that catalyse the fermentation reaction. Enzymes are biological catalysts: they bring about the breakdown of glucose into ethanol and carbon dioxide, and are not consumed by the reaction, so only a small quantity of yeast is needed. b. Fermentation is an **anaerobic** process — it proceeds only in the absence of oxygen. If air were admitted, the yeast would oxidise the glucose completely to carbon dioxide and water by cellular respiration instead, releasing the energy stored in the glucose and leaving little or no ethanol. Sealing the vat keeps oxygen out, so the glucose follows the fermentation pathway and its carbon is retained in ethanol.
c. **Distillation.** Fermentation stops once the mixture reaches roughly 12–15% ethanol, because the yeast cannot survive above that concentration, so the liquid drawn off is mostly water and holds too little ethanol to serve as a fuel. Ethanol boils at about 78 °C and water at 100 °C, so when the mixture is heated the vapour produced is much richer in ethanol than the liquid it came from; condensing and collecting that vapour gives a far more concentrated ethanol, leaving most of the water behind.

Question 6 a. Fats and oils (lipids), at $37\ \text{kJ g}^{-1}$. b. Fat: $20.0 \times 37 = 740\ \text{kJ}$; carbohydrate: $20.0 \times 16 = 320\ \text{kJ}$; difference $= 740 - 320 = 420\ \text{kJ}$. c. From part b, 20.0 g of carbohydrate supplies $320\ \text{kJ}$. The mass of fat that supplies the same energy is

$$m(\text{fat}) = \frac{320}{37} = 8.65\ \text{g}$$

i.e. less than half the mass, because fat is the more energy-dense fuel.

Question 7 Energy from carbohydrate $= 40.0 \times 16 = 640\ \text{kJ}$; energy from protein $= 7.0 \times 17 = 119\ \text{kJ}$. Energy from fat $= 1240 - (640 + 119) = 481\ \text{kJ}$. $m(\text{fat}) = \frac{481}{37} = 13.0\ \text{g}$.

Question 8 $E = (55.0 \times 16) + (20.0 \times 17) + (30.0 \times 37) = 880 + 340 + 1110 = 2330\ \text{kJ}$.

Question 9 $m = \frac{E}{\text{energy value}} = \frac{520}{16} = 32.5\ \text{g}$.

Question 10 Carbohydrates, such as glucose, are readily oxidised in cellular respiration ($C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$) to release energy quickly for immediate use, so the body draws on them first for its everyday energy needs. Proteins are used chiefly to build and repair tissue (growth and repair); they are oxidised for energy only when carbohydrate and fat supplies run low, and doing so also produces nitrogen-containing waste. ∴ carbohydrates, not proteins, are the body's primary energy source.

Question 11 $n(\text{glucose}) = \frac{1000}{180.0} = 5.556\ \text{mol}$. Glucose : ethanol $= 1:2$, so $n(\text{ethanol}) = 2 \times 5.556 = 11.11\ \text{mol}$. $m(\text{ethanol}) = 11.11 \times 46.0 = 511\ \text{g}$ (i.e. $0.511\ \text{kg}$).

Question 12 $n(\text{glucose}) = \frac{90.0}{180.0} = 0.500\ \text{mol}$. a. Glucose : $CO_2 = 1:6$, so $n(CO_2) = 6 \times 0.500 = 3.00\ \text{mol}$; $m(CO_2) = 3.00 \times 44.0 = 132\ \text{g}$. b. Glucose : $O_2 = 1:6$, so $n(O_2) = 6 \times 0.500 = 3.00\ \text{mol}$; $m(O_2) = 3.00 \times 32.0 = 96.0\ \text{g}$.

Question 13 Photosynthesis: $\Delta H > 0$ (endothermic). It cannot proceed without an input of light energy, which it absorbs and stores as chemical energy in glucose. Respiration: $\Delta H < 0$ (exothermic). It releases the chemical energy stored in glucose for the organism to use. Because respiration is the reverse reaction of photosynthesis, the two enthalpy changes are equal in magnitude but opposite in sign.

Question 14 Fats and oils release more energy per gram (about $37\ \text{kJ g}^{-1}$, more than double the $16\ \text{kJ g}^{-1}$ of carbohydrate) because their carbon atoms are, on average, in a lower (less oxidised) state. A fat molecule is built largely from energy-rich C–H and C–C bonds and contains proportionally less oxygen than a carbohydrate, so when it is fully oxidised to CO_2 and H_2O a greater amount of energy is released for each gram of fuel.

Question 15 a. $E = (62.0 \times 16) + (11.0 \times 17) + (8.0 \times 37) = 992 + 187 + 296 = 1475\ \text{kJ}$. b. Average energy per gram $= \frac{1475}{100} = 14.75 \approx 14.8\ \text{kJ g}^{-1}$.

Question 16 The principle of **catalysis** is that catalysts should be chosen so that the same desired product is obtained with less waste and using less energy and fewer reagents. The enzymes in yeast are biological catalysts, and they allow glucose to be converted into ethanol at about 30 °C and atmospheric pressure, so very little energy has to be supplied to the reaction itself. Enzymes are also highly specific, so almost all of the glucose is converted into ethanol and carbon dioxide rather than into a mixture of unwanted by-products that would have to be separated and treated — that is, less waste is generated. The yeast is not consumed by the reaction, so only a small quantity is required.

Question 17 $n(\text{ethanol}) = \frac{230}{46.0} = 5.00\ \text{mol}$. Glucose : ethanol $= 1:2$, so $n(\text{glucose}) = \frac{5.00}{2} = 2.50\ \text{mol}$. $m(\text{glucose}) = 2.50 \times 180.0 = 450\ \text{g}$.

Question 18 Fermentation of the glucose (by enzymes in yeast, in the absence of oxygen), the ethanol then being concentrated by distillation:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

Renewable feedstocks. Bioethanol is made from the sugars in sugar cane, a crop that is regrown within a single season by photosynthesis; its feedstock is therefore renewable. Petrol is refined from crude oil, a finite fossil resource that forms over millions of years and cannot be replaced on a human timescale, so bioethanol reduces reliance on a depleting resource.

Catalysis. The fermentation step is catalysed by the enzymes in yeast. These biological catalysts allow glucose to be converted into ethanol at about 30 °C and atmospheric pressure, so little energy has to be supplied to the reaction itself, and their specificity means almost all of the glucose becomes ethanol and carbon dioxide rather than by-products that would have to be separated and treated. Turning crude oil into petrol, by contrast, requires the crude to be heated to several hundred degrees Celsius for fractional distillation and cracking.

Supporting evidence — carbon neutrality. The carbon dioxide released both when the glucose is fermented and when the ethanol is later burned was recently removed from the atmosphere by the sugar cane during photosynthesis. Over the whole cycle little *net* carbon dioxide is added, so bioethanol is close to carbon-neutral, whereas burning petrol releases fossil carbon that has been locked underground for millions of years and adds to atmospheric carbon dioxide. (This follows from the renewable feedstock; it is evidence of lower net emissions rather than a green chemistry principle of its own.)

Concluding statement. Because its feedstock is renewable, its production is enzyme-catalysed under mild conditions, and its combustion carbon dioxide is largely offset by photosynthetic uptake, bioethanol is the more sustainable transport fuel; the main trade-off is that growing, harvesting and distilling the crop still uses some energy, land and water, so bioethanol is not perfectly carbon-neutral.

Chapter 1 Carbon-based fuels — 1C Exothermic and endothermic reactions

Theory

Every chemical reaction rearranges the bonds within the reactants into the new bonds of the products. Bonds do not break or form for free: **breaking a bond always absorbs energy**, because energy must be supplied to pull the bonded atoms apart, while **making a bond always releases energy**, as the atoms settle into a lower-energy arrangement. Whether a reaction as a whole gives out energy or takes it in depends on the **balance** between the energy absorbed to break all the reactant bonds and the energy released when all the product bonds form.

Exothermic and endothermic reactions. A reaction that releases energy to its surroundings overall is **exothermic**; the surroundings warm up. A reaction that absorbs energy from its surroundings overall is **endothermic**; the surroundings cool down. The energy exchanged at constant pressure is the **enthalpy change**, $\Delta H = H_{\text{products}} - H_{\text{reactants}}$. The sign of ΔH records the direction of energy flow:

- **exothermic**: energy released, products lie *below* reactants in energy, $\Delta H < 0$;
- **endothermic**: energy absorbed, products lie *above* reactants in energy, $\Delta H > 0$.

Units of enthalpy change. The same physical change can be quoted three ways. The enthalpy change **for a reaction as written** is a number of kJ. The **molar** enthalpy change — the value per mole of a specified substance — is quoted in kJ mol^{-1}; this is the form used for a molar enthalpy of combustion or of solution. For a **mixture** whose molar mass is not defined, such as a fuel blend or a food, the enthalpy change is quoted per gram, in kJ g^{-1}. Converting between them uses the amount and the molar mass: $\Delta H\,(\text{kJ mol}^{-1}) = \Delta H\,(\text{kJ}) / n$, and the per-gram value $= \Delta H\,(\text{kJ mol}^{-1}) / M$.

The sign lives only on ΔH. When a molar enthalpy is used to find the heat released by a given amount, or is converted to a per-gram value, work with the **magnitude** and re-attach the sign at the end. Energy released is a positive quantity of heat; carrying a negative sign into a heat or mass calculation produces a meaningless negative energy.

Estimating ΔH from bond enthalpies. The average **bond enthalpy** is the energy needed to break one mole of a particular covalent bond in the gas phase. Because bond breaking absorbs energy and bond making releases it, the enthalpy change of a gas-phase reaction can be estimated as

$$\Delta H = \Sigma(\text{bond enthalpies of bonds broken}) - \Sigma(\text{bond enthalpies of bonds formed})$$

counting the **number and type** of every bond in the reactants (broken) and in the products (formed). A negative result means more energy is released forming the product bonds than is absorbed breaking the reactant bonds — the reaction is exothermic; a positive result is endothermic. The values are averages, so this method gives an **estimate** of ΔH. (Average bond enthalpies were removed from the 2026 Data Book, so any values needed are supplied in the question.)

Energy profile diagrams. An energy profile plots the energy of the reacting system against the progress of the reaction. It shows the **reactant** level, the **product** level, and a peak — the **activated complex** — between them. Three quantities are read from it:

- the **enthalpy change** ΔH: the difference between the product and reactant levels (negative if the products are lower);
- the **forward activation energy** E_a: the height of the peak above the *reactant* level — the energy that must be absorbed to begin breaking the reactant bonds;
- the **reverse activation energy**: the height of the peak above the *product* level.

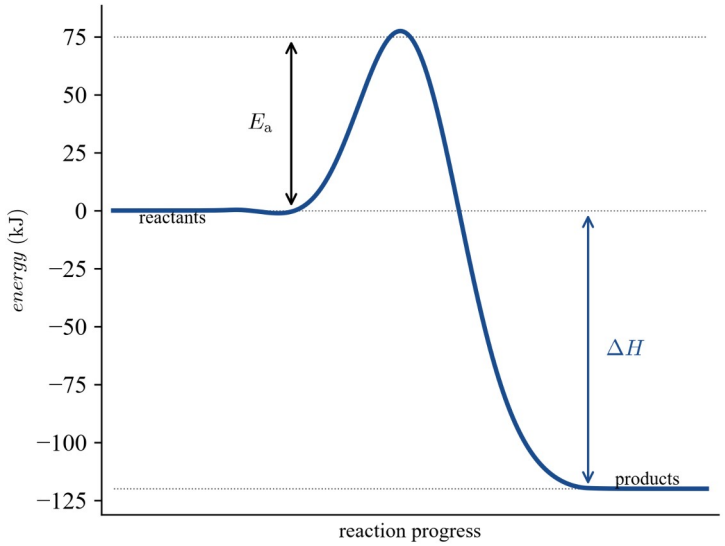
Because both activation energies are measured from the same peak, they are linked to the enthalpy change by

$$\Delta H = E_a(\text{forward}) - E_a(\text{reverse})$$

For an exothermic reaction the peak is closer to the reactants, so the forward activation energy is *smaller* than the reverse; for an endothermic reaction the forward activation energy is the *larger* of the two.

Worked examples

Worked Example 1 — The energy profile below is for a gas-phase reaction. Use it to determine the forward activation energy, the enthalpy change and the reverse activation energy, and classify the reaction.

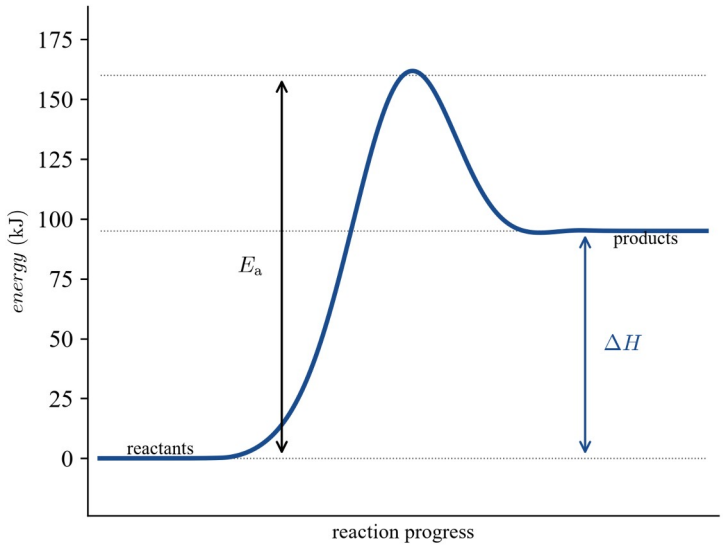


Working	Comment
Reactants at 0; peak (activated complex) at $+75\,\text{kJ}$; products at $-120\,\text{kJ}$	Read the three energy levels from the diagram.
$E_a(\text{forward}) = 75 - 0 = 75\,\text{kJ}$	Height of the peak above the reactant level.
$\Delta H = -120 - 0 = -120\,\text{kJ}$	Products lie below reactants, so ΔH is negative.
$E_a(\text{reverse}) = 75 - (-120) = 195\,\text{kJ}$	Height of the peak above the product level.
$\Delta H < 0 \Rightarrow$ **exothermic**	Energy is released; the surroundings warm. Check: $E_a(\text{fwd}) - E_a(\text{rev}) = 75 - 195 = -120\,\text{kJ} = \Delta H$.

Worked Example 2 — Estimate ΔH for the hydrogenation of ethene, $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$, using the average bond enthalpies (in kJ mol^{-1}): C=C 614, C–H 413, H–H 436, C–C 347. Classify the reaction and account for the sign.

Working	Comment
Bonds broken: $1(\text{C=C}) + 4(\text{C–H}) + 1(\text{H–H})$	Every bond in the reactants: ethene has one C=C and four C–H; hydrogen has one H–H.
$= 614 + 4(413) + 436 = 2702\,\text{kJ mol}^{-1}$	Energy absorbed breaking the reactant bonds.
Bonds formed: $1(\text{C–C}) + 6(\text{C–H})$	Ethane has one C–C and six C–H bonds.
$= 347 + 6(413) = 2825\,\text{kJ mol}^{-1}$	Energy released forming the product bonds.
$\Delta H = 2702 - 2825 = -123\,\text{kJ mol}^{-1}$	$\Delta H = \Sigma(\text{broken}) - \Sigma(\text{formed})$.
$\Delta H < 0 \Rightarrow$ **exothermic**	More energy is released forming the product bonds than is absorbed breaking the reactant bonds.

Worked Example 3 — The energy profile below is for the decomposition of a gaseous compound. Determine the forward activation energy, the enthalpy change and the reverse activation energy, and classify the reaction.



From the diagram, the reactants lie at 0, the activated complex at $+160\,\text{kJ}$ and the products at $+95\,\text{kJ}$. Hence

$$E_a(\text{forward}) = 160 - 0 = 160\,\text{kJ}$$

$$\Delta H = +95 - 0 = +95\,\text{kJ}$$

$$E_a(\text{reverse}) = 160 - 95 = 65\,\text{kJ}$$

The products lie *above* the reactants, so energy is absorbed. As a check, $E_a(\text{fwd}) - E_a(\text{rev}) = 160 - 65 = 95\,\text{kJ} = \Delta H$. $\therefore$ the reaction is **endothermic**, $\Delta H = +95\,\text{kJ}$, and its forward activation energy ($160\,\text{kJ}$) is the larger of the two barriers.

Worked Example 4 — When $2.00\,\text{mol}$ of a compound Z ($M = 40.0\,\text{g mol}^{-1}$) reacts completely, $360\,\text{kJ}$ of energy is released. Calculate the molar enthalpy change and the enthalpy change per gram.

The reaction releases energy, so it is exothermic and $\Delta H < 0$; work with the magnitude and attach the sign at the end. The **molar** enthalpy change is the energy per mole of Z:

$$\Delta H = -\frac{q}{n} = -\frac{360}{2.00} = -180\,\text{kJ mol}^{-1}$$

The mass of Z is $m = n \times M = 2.00 \times 40.0 = 80.0\,\text{g}$, so the enthalpy change **per gram** is

$$\Delta H = -\frac{360}{80.0} = -4.50\,\text{kJ g}^{-1}$$

$\therefore$ the molar enthalpy change is $-180\,\text{kJ mol}^{-1}$ and the enthalpy change per gram is $-4.50\,\text{kJ g}^{-1}$; both are negative because the process is exothermic, releasing $180\,\text{kJ}$ for every mole — or $4.50\,\text{kJ}$ for every gram — of Z.

Practice questions

Question 1 — Two reactions have $\Delta H = -642\,\text{kJ mol}^{-1}$ and $\Delta H = +112\,\text{kJ mol}^{-1}$ respectively.

a. Classify the first reaction as exothermic or endothermic, and state whether its surroundings warm or cool.
b. Do the same for the second reaction.
c. Explain, in terms of bond breaking and bond making, why the first reaction is exothermic.

Question 2 — An energy profile for a gas-phase reaction shows the reactants at $220\,\text{kJ}$, the activated complex at $305\,\text{kJ}$ and the products at $150\,\text{kJ}$.

a. Determine the forward activation energy.
b. Determine ΔH and classify the reaction.
c. Determine the reverse activation energy.

Question 3 — Hydrogen reacts with bromine: $\mathrm{H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)}$. Use the average bond enthalpies (in $\mathrm{kJ\ mol^{-1}}$): H–H 436, Br–Br 193, H–Br 366.

a. Calculate the total energy absorbed breaking the reactant bonds.
b. Calculate the total energy released forming the product bonds.
c. Calculate ΔH and classify the reaction.

Question 4 — A fuel G has a molar enthalpy of combustion $\Delta H = -3250\ \mathrm{kJ\ mol^{-1}}$ and a molar mass $M = 72.0\ \mathrm{g\ mol^{-1}}$.

a. Calculate the energy released per gram of G.
b. Calculate the enthalpy change when $0.150\ \mathrm{mol}$ of G burns.
c. Calculate the heat released when $18.0\ \mathrm{g}$ of G burns completely.

Question 5 — In one reaction the beaker becomes warm to the touch; in another the beaker becomes cold.

a. State the sign of ΔH for the first reaction and classify it.
b. State the sign of ΔH for the second reaction and classify it.
c. Explain, in terms of bond breaking and bond making, why an endothermic reaction draws energy from its surroundings.

Question 6 — A reaction has $\Delta H = +55\ \mathrm{kJ\ mol^{-1}}$ and a forward activation energy of $120\ \mathrm{kJ\ mol^{-1}}$.

a. Classify the reaction.
b. Determine the reverse activation energy.
c. Sketch the energy profile, labelling the reactants, the products, the forward activation energy and ΔH.

Question 7 — Classify each of the following as exothermic or endothermic: (i) a reaction with $\Delta H = -802\ \mathrm{kJ\ mol^{-1}}$; (ii) a reaction with $\Delta H = +178\ \mathrm{kJ\ mol^{-1}}$; (iii) a reaction whose surroundings cool during the change; (iv) a reaction in which the products store more chemical energy than the reactants.

Question 8 — In an energy profile the reactants lie at $120\ \mathrm{kJ}$, the activated complex at $410\ \mathrm{kJ}$ and the products at $300\ \mathrm{kJ}$. Determine ΔH, the forward activation energy and the reverse activation energy, and classify the reaction.

Question 9 — Write a balanced equation, with states, for the formation of ammonia from nitrogen gas and hydrogen gas. Then, using the average bond enthalpies (in $\mathrm{kJ\ mol^{-1}}$) N≡N 945, H–H 436 and N–H 391, estimate ΔH for the reaction and classify it.

Question 10 — For the complete combustion of methane, $\mathrm{CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)}$, use the average bond enthalpies (in $\mathrm{kJ\ mol^{-1}}$) C–H 413, O=O 498, C=O 805 and O–H 463 to estimate ΔH. (Note that each $\mathrm{CO_2}$ molecule contains two C=O bonds and each $\mathrm{H_2O}$ molecule two O–H bonds.)

Question 11 — A biofuel has a molar enthalpy of combustion of $-1580\ \mathrm{kJ\ mol^{-1}}$ and a molar mass of $60.0\ \mathrm{g\ mol^{-1}}$. Calculate the energy released per gram, in $\mathrm{kJ\ g^{-1}}$.

Question 12 — A fuel blend releases $42.0\ \mathrm{kJ\ g^{-1}}$ on combustion. Calculate the heat released when $25.0\ \mathrm{g}$ of the blend is burned completely.

Question 13 — A reaction has $\Delta H = -312\ \mathrm{kJ\ mol^{-1}}$. Calculate the enthalpy change, in kJ, when $0.400\ \mathrm{mol}$ of reactant is consumed.

Question 14 — The forward reaction $\mathrm{A \rightarrow B}$ has $\Delta H = -210\ \mathrm{kJ\ mol^{-1}}$. State the value and sign of ΔH for the reverse reaction $\mathrm{B \rightarrow A}$, classify the reverse reaction, and explain your reasoning in terms of the bonds involved.

Question 15 — Hydrogen burns in oxygen according to $2\,H_2(g)+O_2(g) \rightarrow 2\,H_2O(g)$, releasing heat. Using the average bond enthalpies (in $kJ\ mol^{-1}$) H–H 436, O=O 498 and O–H 463, and supporting your answer with a calculation, explain in terms of the bonds broken and the bonds formed why this reaction is exothermic.

Question 16 — A reaction has a forward activation energy of $60\,kJ\ mol^{-1}$ and a reverse activation energy of $145\,kJ\ mol^{-1}$. Determine ΔH, classify the reaction, and sketch the energy profile, labelling the reactants, the products, the forward activation energy and ΔH.

Question 17 — At the high temperatures inside an engine, nitrogen and oxygen combine: $N_2(g)+O_2(g) \rightarrow 2\,NO(g)$. Using the average bond enthalpies (in $kJ\ mol^{-1}$) N≡N 945, O=O 498 and 630 for the bond in NO, estimate ΔH and classify the reaction.

Question 18 — For the gas-phase reaction $X_2+3\,Y_2 \rightarrow 2\,XY_3$, the total energy absorbed breaking the reactant bonds is $2660\,kJ\ mol^{-1}$ and the total energy released forming the product bonds is $2810\,kJ\ mol^{-1}$. Calculate ΔH, classify the reaction, and state whether the products lie above or below the reactants on an energy profile.

Question 19 — Ethene burns completely according to $C_2H_4(g)+3\,O_2(g) \rightarrow 2\,CO_2(g)+2\,H_2O(g)$. Use the average bond enthalpies (in $kJ\ mol^{-1}$) C=C 614, C–H 413, O=O 498, C=O 805 and O–H 463.

a. Calculate the total energy absorbed breaking the reactant bonds.
b. Calculate the total energy released forming the product bonds.
c. Calculate ΔH and state whether the reaction is exothermic or endothermic.
d. Explain, in terms of the bonds broken and formed, why ΔH has the sign found in part c.
e. Sketch the energy profile for the reaction, labelling the reactants, the products and ΔH.

Answers

1 a exothermic — surroundings warm; b endothermic — surroundings cool; c more energy is released forming the product bonds than is absorbed breaking the reactant bonds, so $\Delta H < 0$. **2** a $85\,\text{kJ}$; b $\Delta H = -70\,\text{kJ}$, exothermic; c $155\,\text{kJ}$. **3** a $629\,\text{kJ mol}^{-1}$; b $732\,\text{kJ mol}^{-1}$; c $\Delta H = -103\,\text{kJ mol}^{-1}$, exothermic. **4** a $45.1\,\text{kJ g}^{-1}$; b $-488\,\text{kJ}$; c $813\,\text{kJ}$ released. **5** a $\Delta H < 0$, exothermic; b $\Delta H > 0$, endothermic; c the energy absorbed breaking the reactant bonds exceeds the energy released forming the product bonds, so the net shortfall is drawn from the surroundings. **6** a endothermic; b $65\,\text{kJ mol}^{-1}$; c profile with products above reactants, peak $120\,\text{kJ mol}^{-1}$ above reactants, $\Delta H = +55\,\text{kJ mol}^{-1}$ upward. **7** (i) exothermic; (ii) endothermic; (iii) endothermic; (iv) endothermic. **8** $\Delta H = +180\,\text{kJ}$; $E_a(\text{fwd}) = 290\,\text{kJ}$; $E_a(\text{rev}) = 110\,\text{kJ}$; endothermic. **9** $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta H = -93\,\text{kJ mol}^{-1}$, exothermic. **10** $\Delta H = -814\,\text{kJ mol}^{-1}$ (exothermic). **11** $26.3\,\text{kJ g}^{-1}$. **12** $1050\,\text{kJ}$. **13** $-125\,\text{kJ}$. **14** $\Delta H = +210\,\text{kJ mol}^{-1}$, endothermic; the same bonds are involved but broken and formed in the opposite roles, so the magnitude is unchanged and the sign reverses. **15** $\Delta H = -482\,\text{kJ mol}^{-1}$; exothermic because the $1852\,\text{kJ mol}^{-1}$ released forming the product bonds exceeds the $1370\,\text{kJ mol}^{-1}$ absorbed breaking the reactant bonds. **16** $\Delta H = -85\,\text{kJ mol}^{-1}$, exothermic; profile with products below reactants. **17** $\Delta H = +183\,\text{kJ mol}^{-1}$, endothermic. **18** $\Delta H = -150\,\text{kJ mol}^{-1}$, exothermic; products below reactants. **19** a $3760\,\text{kJ mol}^{-1}$; b $5072\,\text{kJ mol}^{-1}$; c $\Delta H = -1312\,\text{kJ mol}^{-1}$, exothermic; d,e see solutions.

Fully-worked solutions

Question 1 a. $\Delta H < 0$, so the reaction is **exothermic**; it releases energy, and its surroundings warm. b. $\Delta H > 0$, so the reaction is **endothermic**; it absorbs energy, and its surroundings cool. c. Breaking the reactant bonds absorbs energy and forming the product bonds releases energy. In the first reaction the energy released when the product bonds form is greater than the energy absorbed to break the reactant bonds, so there is a net release of energy to the surroundings and ΔH is negative.

Question 2 a. $E_a(\text{forward}) = 305 - 220 = 85\,\text{kJ}$. b. $\Delta H = 150 - 220 = -70\,\text{kJ}$; the products lie below the reactants, so the reaction is **exothermic**. c. $E_a(\text{reverse}) = 305 - 150 = 155\,\text{kJ}$. (Check: $E_a(\text{fwd}) - E_a(\text{rev}) = 85 - 155 = -70\,\text{kJ} = \Delta H$.)

Question 3 a. Bonds broken $= (\text{H–H}) + (\text{Br–Br}) = 436 + 193 = 629\,\text{kJ mol}^{-1}$. b. Bonds formed $= 2(\text{H–Br}) = 2 \times 366 = 732\,\text{kJ mol}^{-1}$. c. $\Delta H = 629 - 732 = -103\,\text{kJ mol}^{-1}$; $\Delta H < 0$, so the reaction is **exothermic**.

Question 4 a. Energy released per gram $= \dfrac{|\Delta H|}{M} = \dfrac{3250}{72.0} = 45.1\,\text{kJ g}^{-1}$. b. $\Delta H = -3250 \times 0.150 = -488\,\text{kJ}$ (i.e. $488\,\text{kJ}$ released). c. $n = \dfrac{18.0}{72.0} = 0.250\,\text{mol}$; heat released $= 0.250 \times 3250 = 813\,\text{kJ}$.

Question 5 a. The beaker warms, so the reaction releases energy: it is **exothermic** and $\Delta H < 0$. b. The beaker cools, so the reaction absorbs energy: it is **endothermic** and $\Delta H > 0$. c. In an endothermic reaction the energy needed to break the reactant bonds is greater than the energy released when the product bonds form. The extra energy required is taken in from the surroundings, so the surroundings lose energy and cool, and ΔH is positive.

Question 6 a. $\Delta H > 0$, so the reaction is **endothermic**. b. $E_a(\text{reverse}) = E_a(\text{forward}) - \Delta H = 120 - 55 = 65\,\text{kJ mol}^{-1}$. c. The sketch shows the reactant level, a peak $120\,\text{kJ mol}^{-1}$ above it (the forward activation energy), and the product level $55\,\text{kJ mol}^{-1}$ *above* the reactants; the upward arrow from reactants to products is labelled $\Delta H = +55\,\text{kJ mol}^{-1}$.

Question 7 (i) $\Delta H < 0 \Rightarrow$ **exothermic**. (ii) $\Delta H > 0 \Rightarrow$ **endothermic**. (iii) the surroundings cool, so energy is absorbed $\Rightarrow$ **endothermic**. (iv) the products store more chemical energy than the reactants, so energy has been absorbed $\Rightarrow$ **endothermic**.

Question 8 $\Delta H = 300 - 120 = +180\,\text{kJ}$; the products lie above the reactants, so the reaction is **endothermic**. $E_a(\text{forward}) = 410 - 120 = 290\,\text{kJ}$; $E_a(\text{reverse}) = 410 - 300 = 110\,\text{kJ}$. (Check: $290 - 110 = 180 = \Delta H$.)

Question 9 Balanced equation: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. Bonds broken $= (N{\equiv}N) + 3(H{-}H) = 945 + 3(436) = 2253\ \text{kJ mol}^{-1}$. Bonds formed $= 2 \times 3(N{-}H) = 6 \times 391 = 2346\ \text{kJ mol}^{-1}$ (each NH_3 has three N–H bonds). $\Delta H = 2253 - 2346 = -93\ \text{kJ mol}^{-1}$; $\Delta H < 0$, so the reaction is **exothermic**.

Question 10 Bonds broken $= 4(C{-}H) + 2(O{=}O) = 4(413) + 2(498) = 1652 + 996 = 2648\ \text{kJ mol}^{-1}$. Bonds formed $= 2(C{=}O \text{ in } CO_2) + 4(O{-}H \text{ in } 2H_2O) = 2(805) + 4(463) = 1610 + 1852 = 3462\ \text{kJ mol}^{-1}$.
$\Delta H = 2648 - 3462 = -814\ \text{kJ mol}^{-1}$ (**exothermic**).

Question 11 Energy per gram $= \dfrac{|\Delta H|}{M} = \dfrac{1580}{60.0} = 26.3\ \text{kJ g}^{-1}$.

Question 12 Heat released $= 42.0\ \text{kJ g}^{-1} \times 25.0\ \text{g} = 1050\ \text{kJ}$.

Question 13 $\Delta H = -312\ \text{kJ mol}^{-1} \times 0.400\ \text{mol} = -125\ \text{kJ}$ (i.e. $125\ \text{kJ}$ released).

Question 14 The reverse reaction breaks the bonds that were formed in the forward reaction and re-forms the bonds that were broken, so exactly the same bonds are involved with their roles swapped. The magnitude of ΔH is therefore unchanged and only the sign reverses: $\Delta H(\text{reverse}) = +210\ \text{kJ mol}^{-1}$, which is **endothermic**.

Question 15 Bonds broken $= 2(H{-}H) + 1(O{=}O) = 2(436) + 498 = 872 + 498 = 1370\ \text{kJ mol}^{-1}$ (energy absorbed). Bonds formed $= 4(O{-}H) = 4 \times 463 = 1852\ \text{kJ mol}^{-1}$ (energy released; the two H_2O molecules contain four O–H bonds in total). $\Delta H = 1370 - 1852 = -482\ \text{kJ mol}^{-1}$. The reaction is exothermic because the energy **released** when the four O–H bonds form ($1852\ \text{kJ mol}^{-1}$) is greater than the energy **absorbed** to break the two H–H bonds and one O=O bond ($1370\ \text{kJ mol}^{-1}$). The net energy, $482\ \text{kJ mol}^{-1}$, is released to the surroundings, so ΔH is negative.

Question 16 $\Delta H = E_a(\text{forward}) - E_a(\text{reverse}) = 60 - 145 = -85\ \text{kJ mol}^{-1}$; $\Delta H < 0$, so the reaction is **exothermic**. The sketch shows the reactant level, a peak $60\ \text{kJ mol}^{-1}$ above it, and the product level $85\ \text{kJ mol}^{-1}$ *below* the reactants, with the downward arrow labelled $\Delta H = -85\ \text{kJ mol}^{-1}$.

Question 17 Bonds broken $= (N{\equiv}N) + (O{=}O) = 945 + 498 = 1443\ \text{kJ mol}^{-1}$. Bonds formed $= 2 \times 630 = 1260\ \text{kJ mol}^{-1}$ (two NO molecules). $\Delta H = 1443 - 1260 = +183\ \text{kJ mol}^{-1}$; $\Delta H > 0$, so the reaction is **endothermic**.

Question 18 $\Delta H = \Sigma(\text{broken}) - \Sigma(\text{formed}) = 2660 - 2810 = -150\ \text{kJ mol}^{-1}$; $\Delta H < 0$, so the reaction is **exothermic**, and the products lie **below** the reactants on an energy profile.

Question 19 a. Bonds broken $= (C{=}C) + 4(C{-}H) + 3(O{=}O) = 614 + 4(413) + 3(498) = 614 + 1652 + 1494 = 3760\ \text{kJ mol}^{-1}$. b. Bonds formed $= 4(C{=}O) + 4(O{-}H) = 4(805) + 4(463) = 3220 + 1852 = 5072\ \text{kJ mol}^{-1}$ (two CO_2 contribute four C=O bonds; two H_2O contribute four O–H bonds). c. $\Delta H = 3760 - 5072 = -1312\ \text{kJ mol}^{-1}$; $\Delta H < 0$, so the reaction is **exothermic**. d. The energy released when the four C=O and four O–H bonds of the products form ($5072\ \text{kJ mol}^{-1}$) is greater than the energy absorbed to break the C=C, four C–H and three O=O bonds of the reactants ($3760\ \text{kJ mol}^{-1}$). The net release of $1312\ \text{kJ mol}^{-1}$ makes ΔH negative. e. The sketch shows the reactant level with a peak above it, the product level well below the reactants, and a large downward arrow from the reactant level to the product level labelled $\Delta H = -1312\ \text{kJ mol}^{-1}$.