Chemistry Units 3 & 4

Chapter 2 — Measuring energy changes

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Chapter 2 Measuring energy changes — 2A Combustion and greenhouse gases

Theory

Combustion is the rapid reaction of a fuel with oxygen that releases energy as heat and light. Because the bonds formed in the products are stronger — they release more energy on forming — than the bonds broken in the reactants, every combustion reaction is **exothermic**: it transfers heat to the surroundings and its enthalpy change is negative, $\Delta H < 0$. The organic fuels considered here contain carbon and hydrogen, and sometimes oxygen; when they burn, both the carbon and the hydrogen are oxidised.

Complete combustion. When a fuel burns in a plentiful supply of oxygen, **complete combustion** occurs: every carbon atom is oxidised fully to carbon dioxide, $\mathrm{CO_2}$, and every hydrogen atom to water, $\mathrm{H_2O}$. For a fuel built only from carbon, hydrogen and oxygen the *only* products are $\mathrm{CO_2}$ and $\mathrm{H_2O}$. Complete combustion releases the most energy per mole of fuel and produces neither soot nor carbon monoxide. For example,

$$\mathrm{C_4H_{10}(g) + 13/2\,O_2(g) \rightarrow 4\,CO_2(g) + 5\,H_2O(l)}$$

Incomplete combustion. When the oxygen supply is limited, **incomplete combustion** occurs and the carbon is only partly oxidised. The carbon-containing products are then **carbon monoxide**, $\mathrm{CO(g)}$, and/or **carbon** (soot), $\mathrm{C(s)}$, in place of some or all of the $\mathrm{CO_2}$; water is still formed. The less oxygen that is available, the further the products shift from $\mathrm{CO_2}$ towards CO and then to $\mathrm{C(s)}$. Incomplete combustion releases **less energy per mole of fuel** than complete combustion, because the carbon is not fully oxidised — the CO and $\mathrm{C(s)}$ formed still hold chemical energy that could be released by further oxidation. It also produces the toxic gas carbon monoxide and fine sooty particulates. Two incomplete-combustion equations for propane are

$$\mathrm{C_3H_8(g) + 7/2\,O_2(g) \rightarrow 3\,CO(g) + 4\,H_2O(l)}$$

$$\mathrm{C_3H_8(g) + 2\,O_2(g) \rightarrow 3\,C(s) + 4\,H_2O(l)}$$

Thermochemical equations and the molar convention. A **thermochemical equation** is a balanced equation written together with its enthalpy change, with a state symbol on every species. The ΔH quoted belongs to the coefficients exactly as written. To state a **molar enthalpy of combustion**, ΔH_c — the heat released per mole of fuel — the equation is written with **one mole of fuel**, which often requires a fractional oxygen coefficient. This is standard and acceptable:

$$\mathrm{C_4H_{10}(g) + 13/2\,O_2(g) \rightarrow 4\,CO_2(g) + 5\,H_2O(l)}, \Delta H = -2877\ \mathrm{kJ\ mol^{-1}}$$

Doubling the equation to clear the fraction would double the enthalpy change — to $-5754\ \mathrm{kJ}$ for two mole of butane — so the fraction is kept whenever a per-mole value is required.

Heat released from the molar enthalpy of combustion. When ΔH_c is known, the heat released on burning a given amount of fuel is the amount in mole multiplied by the *magnitude* of ΔH_c:

$$q = n \times |\Delta H_c|$$

The heat released, q, is a positive quantity; the negative sign lives only on ΔH_c and is never carried into the arithmetic. The amount of fuel comes from its mass, $n = \dfrac{m}{M}$, or, for a gaseous fuel measured by volume, from the molar gas volume below.

Stoichiometry at standard laboratory conditions. Every calculation in this subtopic is carried out at **standard laboratory conditions (SLC): 25 °C and 100 kPa**, where the molar volume of *any* gas is $V_m = 24.8\ \mathrm{L\ mol^{-1}}$. The amount of a gas is found from its volume by $n = \dfrac{V}{V_m}$, and the amount of any substance from its mass by $n = \dfrac{m}{M}$. A balanced equation links the amounts of reactants and products through their **mole ratio**, which supports three kinds of calculation:

- **mass–mass:** mass of fuel → mole of fuel → mole of product → mass of product ($m = n \times M$);
- **mass–volume:** mass of fuel → mole → mole of a gas → volume of that gas at SLC ($V = n \times V_m$);
- **volume–volume:** for gases at the same temperature and pressure, **Avogadro's law** makes the volume ratio equal to the mole ratio, so gas volumes are compared directly without ever finding moles.

Limiting reagent. When the amounts of two reactants are both fixed — for instance a set mass of fuel together with a set volume of oxygen — one reactant is usually consumed first: the **limiting reagent**. To identify it, compare the actual mole ratio of the reactants with the ratio required by the equation; the reactant present in *smaller* proportion than the equation demands is limiting, and it alone fixes the maximum amount of every product. The other reactant is **in excess** and some of it remains unreacted.

Greenhouse gases. The complete combustion of any carbon-based fuel releases **carbon dioxide**, a greenhouse gas that absorbs outgoing infrared radiation and so contributes to the enhanced greenhouse effect. The three major greenhouse gases named in this study are $\mathrm{CO_2}$, **methane** $\mathrm{CH_4}$ (the main component of natural gas, and a far more potent greenhouse gas per molecule than $\mathrm{CO_2}$), and **water vapour** $\mathrm{H_2O}$. Stoichiometry lets the **net mass or volume** of a greenhouse gas released by a given quantity of fuel be calculated: convert the mole of fuel to mole of $\mathrm{CO_2}$ through the balanced equation, then to a mass ($m = n \times M$) or a volume at SLC ($V = n \times V_m$). Burning methane rather than releasing it converts a stronger greenhouse gas into the weaker $\mathrm{CO_2}$; incomplete combustion, although it releases less $\mathrm{CO_2}$, produces toxic carbon monoxide and soot instead.

Worked examples

Worked Example 1 — Butane, $\mathrm{C_4H_{10}}$ ($M = 58.0\ \mathrm{g\ mol^{-1}}$), is the fuel in a portable camping stove and undergoes complete combustion with $\Delta H_c = -2877\ \mathrm{kJ\ mol^{-1}}$. Write a balanced thermochemical equation, with states, for the complete combustion of butane, and calculate the heat released when 5.80 g of butane burns completely.

Working	Comment
$\mathrm{C_4H_{10}(g) + 13/2\,O_2(g) \rightarrow 4\,CO_2(g) + 5\,H_2O(l)}$, $\Delta H = -2877\ \mathrm{kJ\ mol^{-1}}$	One mole of fuel, so a fractional $\mathrm{O_2}$ coefficient is used; states on every species.
$n(\mathrm{C_4H_{10}}) = \dfrac{m}{M} = \dfrac{5.80}{58.0} = 0.100\ \mathrm{mol}$	Amount of fuel from its mass.
$q = n \times \lvert\Delta H_c\rvert = 0.100 \times 2877 = 287.7\ \mathrm{kJ}$	Use the *magnitude* of ΔH_c; heat released is positive.
$q = 288\ \mathrm{kJ}$	Heat released (3 sig figs).

Worked Example 2 — In a poorly ventilated engine, octane, $\mathrm{C_8H_{18}}$ ($M = 114.0\ \mathrm{g\ mol^{-1}}$), undergoes incomplete combustion in which carbon monoxide and water are the only products; for this reaction $\Delta H = -3206\ \mathrm{kJ\ mol^{-1}}$. Write the balanced thermochemical equation, with states, and determine — for the incomplete combustion of 11.4 g of octane — the volume of carbon monoxide produced at SLC and the heat released.

Working	Comment
$\mathrm{C_8H_{18}(l) + 17/2\,O_2(g) \rightarrow 8\,CO(g) + 9\,H_2O(l)}$, $\Delta H = -3206\ \mathrm{kJ\ mol^{-1}}$	Carbon is only part-oxidised to CO; check O: $17/2 \times 2 = 17 = 8 + 9$.
$n(\mathrm{C_8H_{18}}) = \dfrac{11.4}{114.0} = 0.100\ \mathrm{mol}$	Amount of fuel.
$n(\mathrm{CO}) = 8 \times 0.100 = 0.800\ \mathrm{mol}$	Mole ratio fuel : CO is $1:8$.
$V(\mathrm{CO}) = n \times V_m = 0.800 \times 24.8 = 19.84\ \mathrm{L} = 19.8\ \mathrm{L}$	Volume of gas at SLC ($V_m = 24.8\ \mathrm{L\ mol^{-1}}$).
$q = 0.100 \times 3206 = 320.6 \approx 321\ \mathrm{kJ}$	Heat released, using the magnitude of ΔH.

Worked Example 3 — Natural gas is essentially methane, $\mathrm{CH_4}$, with $\Delta H_c = -890\ \mathrm{kJ\ mol^{-1}}$. In a burner, 6.00 L of methane, measured at SLC, undergoes complete combustion. Determine the volume of oxygen required and the volume of carbon dioxide produced (both at SLC), and the heat released.

The thermochemical equation is

$$\mathrm{CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)},\ \Delta H = -890\ \mathrm{kJ\ mol^{-1}}$$

At SLC equal volumes of gas contain equal amounts (Avogadro's law), so the volume ratio equals the mole ratio $\mathrm{CH_4 : O_2 : CO_2} = 1:2:1$:

$$V(\mathrm{O_2}) = 2 \times 6.00 = 12.0\ \mathrm{L},\ V(\mathrm{CO_2}) = 1 \times 6.00 = 6.00\ \mathrm{L}$$

The heat needs the amount of methane: $n(\mathrm{CH_4}) = \dfrac{V}{V_m} = \dfrac{6.00}{24.8} = 0.2419\ \mathrm{mol}$, so

$$q = 0.2419 \times 890 = 215.3\ \mathrm{kJ}$$

∴ 12.0 L of oxygen is required, 6.00 L of carbon dioxide is produced, and 215 kJ of heat is released.

Worked Example 4 — A rigid flask holds 5.60 g of ethene, $\mathrm{C_2H_4}$ ($M = 28.0\ \mathrm{g\ mol^{-1}}$), together with 12.4 L of oxygen measured at SLC. The mixture is ignited and ethene undergoes complete combustion. Determine the limiting reagent and hence the mass of carbon dioxide produced.

$$\mathrm{C_2H_4(g) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(l)}$$

The amounts present are

$$n(\mathrm{C_2H_4}) = \frac{5.60}{28.0} = 0.200\ \mathrm{mol},\ n(\mathrm{O_2}) = \frac{V}{V_m} = \frac{12.4}{24.8} = 0.500\ \mathrm{mol}$$

Complete combustion of 0.200 mol of ethene would require $3 \times 0.200 = 0.600\ \mathrm{mol}$ of oxygen, but only 0.500 mol is available, so **oxygen is the limiting reagent** and fixes the amount of product. From the mole ratio $\mathrm{O_2 : CO_2} = 3:2$,

$$n(\mathrm{CO_2}) = \frac{2}{3} \times 0.500 = 0.3333\ \mathrm{mol},\ m(\mathrm{CO_2}) = 0.3333 \times 44.0 = 14.67\ \mathrm{g}$$

∴ oxygen is limiting and 14.7 g of carbon dioxide is produced.

Practice questions

Question 1 — Pentane, $\mathrm{C_5H_{12}}$ ($M = 72.0\ \mathrm{g\ mol^{-1}}$), undergoes complete combustion with $\Delta H_c = -3509\ \mathrm{kJ\ mol^{-1}}$.

a. Write a balanced thermochemical equation, with states, for the complete combustion of pentane.
b. Calculate the heat released when 7.20 g of pentane burns completely.
c. Name the two products, and identify which of them are greenhouse gases.

Question 2 — Ethane, $\mathrm{C_2H_6}$ ($M = 30.0\ \mathrm{g\ mol^{-1}}$), can burn incompletely.

a. Write a balanced equation, with states, for the incomplete combustion of ethane in which carbon monoxide and water are the only products.
b. Write a balanced equation, with states, for the incomplete combustion of ethane in which carbon (soot) and water are the only products.
c. Using the equation in part a, calculate the mass of carbon monoxide produced when 9.00 g of ethane burns.

Question 3 — Butan-1-ol, $\mathrm{C_4H_{10}O}$ ($M = 74.0\ \mathrm{g\ mol^{-1}}$), is used as a solvent and fuel and undergoes complete combustion with $\Delta H_c = -2676\ \mathrm{kJ\ mol^{-1}}$.

a. Write a balanced thermochemical equation, with states, for the complete combustion of butan-1-ol.
b. Calculate the volume of carbon dioxide, measured at SLC, produced when 3.70 g of butan-1-ol burns completely.
c. Calculate the heat released.

Question 4 — Ethyne (acetylene), C_2H_2, is burned completely in an oxy-acetylene torch. 4.00 L of ethyne, measured at SLC, is burned.

a. Write a balanced equation, with states, for the complete combustion of ethyne.
b. Determine the volume of oxygen, at SLC, required to burn the ethyne completely.
c. Determine the volume of carbon dioxide, at SLC, produced.

Question 5 — A rigid container holds 13.2 g of propane, C_3H_8 ($M = 44.0\,\text{g mol}^{-1}$), and 40.0 g of oxygen ($M = 32.0\,\text{g mol}^{-1}$). The mixture is ignited and propane undergoes complete combustion where possible.

a. Calculate the amount, in mole, of propane and of oxygen present.
b. Determine the limiting reagent.
c. Calculate the mass of carbon dioxide produced.

Question 6 — A laboratory burner uses hexane, C_6H_{14} ($M = 86.0\,\text{g mol}^{-1}$), which undergoes complete combustion with $\Delta H_c = -4163\,\text{kJ mol}^{-1}$.

a. Write a balanced thermochemical equation, with states, for the complete combustion of hexane.
b. Calculate the heat released when 4.30 g of hexane burns completely.
c. Calculate the mass of carbon dioxide released in part b.

Question 7 — Heptane, C_7H_{16} ($M = 100.0\,\text{g mol}^{-1}$), undergoes complete combustion with $\Delta H_c = -4817\,\text{kJ mol}^{-1}$. Calculate the heat released when 25.0 g of heptane burns completely.

Question 8 — Write a balanced thermochemical equation, including states, for the complete combustion of propan-1-ol, C_3H_8O, given that its molar enthalpy of combustion is $-2021\,\text{kJ mol}^{-1}$.

Question 9 — Write a balanced equation, including states, for the incomplete combustion of pentane, C_5H_{12}, in which carbon monoxide and water are the only products.

Question 10 — Butane, C_4H_{10} ($M = 58.0\,\text{g mol}^{-1}$), undergoes complete combustion. Calculate the volume of carbon dioxide, measured at SLC, produced when 14.5 g of butane burns completely.

Question 11 — In a gas heater, 6.00 L of propane, C_3H_8, measured at SLC undergoes complete combustion. Determine the volume of oxygen consumed and the volume of carbon dioxide produced, both at SLC.

Question 12 — A rigid vessel holds 8.40 g of propene, C_3H_6 ($M = 42.0\,\text{g mol}^{-1}$), and 25.0 L of oxygen measured at SLC. The mixture is ignited and propene undergoes complete combustion. Determine the limiting reagent and the mass of carbon dioxide produced.

Question 13 — When natural gas burns with a very restricted air supply, methane can burn to give carbon (soot) and water only. Write the balanced equation, with states, for this reaction, and calculate the mass of carbon produced when 4.00 g of methane, CH_4 ($M = 16.0\,\text{g mol}^{-1}$), burns in this way.

Question 14 — A car burns 1.14 kg of octane, C_8H_{18} ($M = 114.0\,\text{g mol}^{-1}$), on a trip, undergoing complete combustion. Calculate the mass of carbon dioxide greenhouse gas released.

Question 15 — Glucose, $C_6H_{12}O_6$ ($M = 180.0\,\text{g mol}^{-1}$), undergoes complete combustion with $\Delta H_c = -2803\,\text{kJ mol}^{-1}$. For the complete combustion of 9.00 g of glucose, calculate:

a. the heat released;
b. the volume of carbon dioxide produced at SLC.

Question 16 — Butane, C_4H_{10} ($M = 58.0\,\text{g mol}^{-1}$), can burn completely ($\Delta H = -2877\,\text{kJ mol}^{-1}$) or incompletely to carbon monoxide and water ($\Delta H = -1750\,\text{kJ mol}^{-1}$).

a. Calculate the heat released when 2.90 g of butane burns completely.

b. Calculate the heat released when 2.90 g of butane burns incompletely to carbon monoxide and water.
c. Explain, in terms of the products, why incomplete combustion releases less energy per mole of fuel.

Question 17 — Cyclohexane, C_6H_{12} ($M = 84.0\,\text{g mol}^{-1}$), undergoes complete combustion. For the complete combustion of 21.0 g of cyclohexane, calculate:

a. the mass of oxygen required;
b. the mass of carbon dioxide produced.

Question 18 — A biogas sample of volume 50.0 L at SLC is 80.0% methane, CH_4, by volume, the remainder being carbon dioxide.

a. Calculate the volume of methane in the sample.
b. Calculate the volume of oxygen, at SLC, needed to completely combust this methane.
c. Explain why burning the methane, rather than releasing the biogas unburned, reduces the sample's overall greenhouse impact.

Question 19 — 7.00 L of propane, C_3H_8, and 25.0 L of oxygen, both measured at SLC, are mixed and ignited; complete combustion occurs.

a. Determine the limiting reagent.
b. Calculate the volume of carbon dioxide produced at SLC.
c. Calculate the volume of excess reactant gas remaining (the water condenses and may be ignored).

Question 20 — Two fuels are compared for heating: methane, CH_4 ($\Delta H_c = -890\,\text{kJ mol}^{-1}$, $M = 16.0\,\text{g mol}^{-1}$), and a coal modelled as pure carbon, C ($\Delta H_c = -394\,\text{kJ mol}^{-1}$, $M = 12.0\,\text{g mol}^{-1}$). Both burn completely.

a. Write balanced thermochemical equations, with states, for the complete combustion of each fuel.
b. For each fuel, calculate the mass of carbon dioxide released per megajoule (1 MJ = 1000 kJ) of heat.
c. Using your answers to part b and the green chemistry principles, evaluate which fuel is the better choice for reducing greenhouse emissions per unit of energy, and give a concluding statement.

Question 21 — A car engine burns octane, C_8H_{18} ($M = 114.0\,\text{g mol}^{-1}$), completely, with $\Delta H_c = -5470\,\text{kJ mol}^{-1}$. On one journey it consumes 570 g of octane.

a. Calculate the amount, in mole, of octane burned.
b. Calculate the total heat released, in kJ.
c. Calculate the mass of carbon dioxide released.
d. Calculate the volume of carbon dioxide, at SLC, released.

Answers

1 a $C_5H_{12}(l)+8O_2(g)\rightarrow 5CO_2(g)+6H_2O(l)$, $\Delta H=-3509\,\text{kJ mol}^{-1}$; b 351 kJ; c carbon dioxide and water; both CO_2 and water vapour are greenhouse gases. **2** a $C_2H_6(g)+5/2\,O_2(g)\rightarrow 2CO(g)+3H_2O(l)$; b $C_2H_6(g)+3/2\,O_2(g)\rightarrow 2C(s)+3H_2O(l)$; c 16.8 g. **3** a $C_4H_{10}O(l)+6O_2(g)\rightarrow 4CO_2(g)+5H_2O(l)$, $\Delta H=-2676\,\text{kJ mol}^{-1}$; b 4.96 L; c 134 kJ. **4** a $C_2H_2(g)+5/2\,O_2(g)\rightarrow 2CO_2(g)+H_2O(l)$; b 10.0 L; c 8.00 L. **5** a $n(C_3H_8)=0.300\,\text{mol}$, $n(O_2)=1.25\,\text{mol}$; b oxygen; c 33.0 g. **6** a $C_6H_{14}(l)+19/2\,O_2(g)\rightarrow 6CO_2(g)+7H_2O(l)$, $\Delta H=-4163\,\text{kJ mol}^{-1}$; b 208 kJ; c 13.2 g. **7** 1.20×10^3 kJ (1200 kJ). **8** $C_3H_8O(l)+9/2\,O_2(g)\rightarrow 3CO_2(g)+4H_2O(l)$, $\Delta H=-2021\,\text{kJ mol}^{-1}$. **9** $C_5H_{12}(l)+11/2\,O_2(g)\rightarrow 5CO(g)+6H_2O(l)$. **10** 24.8 L. **11** $V(O_2)=30.0\,\text{L}$; $V(CO_2)=18.0\,\text{L}$. **12** oxygen is in excess, so propene is limiting; $m(CO_2)=26.4\,\text{g}$. **13** $CH_4(g)+O_2(g)\rightarrow C(s)+2H_2O(l)$; $m(C)=3.00\,\text{g}$. **14** 3.52 kg (3520 g). **15** a 140 kJ; b 7.44 L. **16** a 144 kJ; b 87.5 kJ; c the carbon is oxidised only to CO, not fully to CO_2, so the fuel is not fully oxidised and less energy is released. **17** a 72.0 g; b 66.0 g. **18** a 40.0 L; b 80.0 L; c methane is a far more potent greenhouse gas than CO_2, so converting it to CO_2 by combustion lowers the sample's greenhouse impact. **19** a oxygen; b 15.0 L; c 2.00 L of propane remains. **20** a $CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l)$, $\Delta H=-890\,\text{kJ mol}^{-1}$; $C(s)+O_2(g)\rightarrow CO_2(g)$, $\Delta H=-394\,\text{kJ mol}^{-1}$; b methane 49.4 g MJ^{-1}, carbon 112 g MJ^{-1}; c methane (lower CO_2 per unit energy) — see solution. **21** a 5.00 mol; b 2.74×10^4 kJ (27 350 kJ); c 1760 g (1.76 kg); d 992 L.

Fully-worked solutions

Question 1 a. Each carbon → CO_2, each hydrogen → H_2O; balance oxygen last (needs 8 O_2): $C_5H_{12}(l)+8O_2(g)\rightarrow 5CO_2(g)+6H_2O(l)$, $\Delta H=-3509\,\text{kJ mol}^{-1}$. b. $n=\dfrac{7.20}{72.0}=0.100\,\text{mol}$; $q=n\times|\Delta H_c|=0.100\times3509=351\,\text{kJ}$. c. The products are carbon dioxide and water. Both are greenhouse gases: CO_2, and water when present as vapour.

Question 2 a. Carbon is oxidised only to CO: $C_2H_6(g)+5/2\,O_2(g)\rightarrow 2CO(g)+3H_2O(l)$ (O: $5/2\times2=5=2+3$). b. Carbon is left as soot: $C_2H_6(g)+3/2\,O_2(g)\rightarrow 2C(s)+3H_2O(l)$ (O: $3/2\times2=3=3$).

c. $n(C_2H_6)=\dfrac{9.00}{30.0}=0.300\,\text{mol}$; ratio $C_2H_6:CO=1:2$, so $n(CO)=0.600\,\text{mol}$; $m(CO)=0.600\times28.0=16.8\,\text{g}$.

Question 3 a. $C_4H_{10}O(l)+6O_2(g)\rightarrow 4CO_2(g)+5H_2O(l)$, $\Delta H=-2676\,\text{kJ mol}^{-1}$ (O: $1+12=13=8+5$). b. $n(\text{fuel})=\dfrac{3.70}{74.0}=0.0500\,\text{mol}$; $n(CO_2)=4\times0.0500=0.200\,\text{mol}$; $V(CO_2)=0.200\times24.8=4.96\,\text{L}$.

c. $q=0.0500\times2676=133.8\approx134\,\text{kJ}$.

Question 4 a. $C_2H_2(g)+5/2\,O_2(g)\rightarrow 2CO_2(g)+H_2O(l)$ (O: $5/2\times2=5=4+1$). b. At SLC the volume ratio equals the mole ratio. $C_2H_2:O_2=1:5/2$, so $V(O_2)=5/2\times4.00=10.0\,\text{L}$. c. $C_2H_2:CO_2=1:2$, so $V(CO_2)=2\times4.00=8.00\,\text{L}$.

Question 5 a. $n(C_3H_8)=\dfrac{13.2}{44.0}=0.300\,\text{mol}$; $n(O_2)=\dfrac{40.0}{32.0}=1.25\,\text{mol}$. b. $C_3H_8(g)+5O_2(g)\rightarrow 3CO_2(g)+4H_2O(l)$. Complete combustion of 0.300 mol of propane needs $5\times0.300=1.50\,\text{mol}$ of O_2, but only 1.25 mol is present, so **oxygen is the limiting reagent**. c. From $O_2:CO_2=5:3$, $n(CO_2)=\dfrac{3}{5}\times1.25=0.750\,\text{mol}$; $m(CO_2)=0.750\times44.0=33.0\,\text{g}$.

Question 6 a. $C_6H_{14}(l)+19/2\,O_2(g)\rightarrow 6CO_2(g)+7H_2O(l)$, $\Delta H=-4163\,\text{kJ mol}^{-1}$ (O: $19/2\times2=19=12+7$). b. $n=\dfrac{4.30}{86.0}=0.0500\,\text{mol}$; $q=0.0500\times4163=208.15\approx208\,\text{kJ}$. c. $n(CO_2)=6\times0.0500=0.300\,\text{mol}$; $m(CO_2)=0.300\times44.0=13.2\,\text{g}$.

Question 7 $n = \dfrac{25.0}{100.0} = 0.250\,\text{mol}$; $q = 0.250 \times 4817 = 1204 \approx 1.20 \times 10^3\,\text{kJ}$.

Question 8 Each of the 3 carbons $\rightarrow CO_2$, each pair of the 8 hydrogens $\rightarrow H_2O$ (4 waters); oxygen balanced last, with one O already in the fuel: $C_3H_8O(l) + 9/2\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$, $\Delta H = -2021\,\text{kJ mol}^{-1}$ (O: $1 + 9 = 10 = 6 + 4$).

Question 9 Carbon is oxidised only as far as CO: $C_5H_{12}(l) + 11/2\,O_2(g) \rightarrow 5\,CO(g) + 6\,H_2O(l)$ (O: $11/2 \times 2 = 11 = 5 + 6$).

Question 10 $n(C_4H_{10}) = \dfrac{14.5}{58.0} = 0.250\,\text{mol}$. From $C_4H_{10}(g) + 13/2\,O_2(g) \rightarrow 4\,CO_2(g) + 5\,H_2O(l)$, $n(CO_2) = 4 \times 0.250 = 1.00\,\text{mol}$; $V(CO_2) = 1.00 \times 24.8 = 24.8\,\text{L}$.

Question 11 $C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$. At SLC the volume ratio equals the mole ratio: $V(O_2) = 5 \times 6.00 = 30.0\,\text{L}$; $V(CO_2) = 3 \times 6.00 = 18.0\,\text{L}$.

Question 12 $n(C_3H_6) = \dfrac{8.40}{42.0} = 0.200\,\text{mol}$; $n(O_2) = \dfrac{25.0}{24.8} = 1.008\,\text{mol}$. From $C_3H_6(g) + 9/2\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$, 0.200 mol of propene needs $9/2 \times 0.200 = 0.900\,\text{mol}$ of O_2; since 1.008 mol is available, oxygen is in excess and **propene is the limiting reagent**. $n(CO_2) = 3 \times 0.200 = 0.600\,\text{mol}$; $m(CO_2) = 0.600 \times 44.0 = 26.4\,\text{g}$.

Question 13 $CH_4(g) + O_2(g) \rightarrow C(s) + 2\,H_2O(l)$ (O: $2 = 2$). $n(CH_4) = \dfrac{4.00}{16.0} = 0.250\,\text{mol}$; ratio $CH_4 : C = 1 : 1$, so $n(C) = 0.250\,\text{mol}$; $m(C) = 0.250 \times 12.0 = 3.00\,\text{g}$.

Question 14 $n(C_8H_{18}) = \dfrac{1140}{114.0} = 10.0\,\text{mol}$. From $C_8H_{18}(l) + 25/2\,O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(l)$, $n(CO_2) = 8 \times 10.0 = 80.0\,\text{mol}$; $m(CO_2) = 80.0 \times 44.0 = 3520\,\text{g} = 3.52\,\text{kg}$.

Question 15 $C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)$. $n = \dfrac{9.00}{180.0} = 0.0500\,\text{mol}$. a. $q = 0.0500 \times 2803 = 140.15 \approx 140\,\text{kJ}$. b. $n(CO_2) = 6 \times 0.0500 = 0.300\,\text{mol}$; $V(CO_2) = 0.300 \times 24.8 = 7.44\,\text{L}$.

Question 16 $n(C_4H_{10}) = \dfrac{2.90}{58.0} = 0.0500\,\text{mol}$. a. Complete: $q = 0.0500 \times 2877 = 143.85 \approx 144\,\text{kJ}$. b. Incomplete (to CO): $q = 0.0500 \times 1750 = 87.5\,\text{kJ}$. c. In complete combustion every carbon is oxidised fully to CO_2, the lowest-energy carbon product. In incomplete combustion the carbon is oxidised only as far as CO (or is left as soot), which is not fully oxidised and still contains chemical energy that could be released by burning further. Because that additional oxidation does not occur, less energy is released per mole of fuel.

Question 17 $n(C_6H_{12}) = \dfrac{21.0}{84.0} = 0.250\,\text{mol}$. Equation: $C_6H_{12}(l) + 9\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)$. a. $n(O_2) = 9 \times 0.250 = 2.25\,\text{mol}$; $m(O_2) = 2.25 \times 32.0 = 72.0\,\text{g}$. b. $n(CO_2) = 6 \times 0.250 = 1.50\,\text{mol}$; $m(CO_2) = 1.50 \times 44.0 = 66.0\,\text{g}$.

Question 18 a. $V(CH_4) = 0.800 \times 50.0 = 40.0\,\text{L}$. b. $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$; at SLC the volume ratio equals the mole ratio, so $V(O_2) = 2 \times 40.0 = 80.0\,\text{L}$. c. Methane is a much more potent greenhouse gas per molecule than carbon dioxide, so releasing the biogas unburned would let this strong greenhouse gas enter the atmosphere directly. Burning the methane converts each CH_4 molecule into one CO_2 molecule, which has a smaller greenhouse effect; the net greenhouse impact of the sample is therefore reduced.

Question 19 $C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$; at SLC volumes stand in the mole ratio. a. 7.00 L of propane would require $5 \times 7.00 = 35.0\,\text{L}$ of oxygen, but only 25.0 L is present, so **oxygen is the limiting reagent**. b.

Propane reacting $= \dfrac{25.0}{5} = 5.00\,\text{L}$; $V(\text{CO}_2) = 3 \times 5.00 = 15.0\,\text{L}$. c. Excess propane $= 7.00 - 5.00 = 2.00\,\text{L}$ remains unreacted.

Question 20 a. $\text{CH}_4(\text{g}) + 2\,\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\,\text{H}_2\text{O}(\text{l})$, $\Delta H = -890\,\text{kJ mol}^{-1}$; $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$, $\Delta H = -394\,\text{kJ mol}^{-1}$. b. Each fuel makes 1 mol of CO_2 (mass $44.0\,\text{g}$) per mole burned. Methane: per 890 kJ, $44.0\,\text{g}$ of CO_2; per MJ $= \dfrac{44.0}{890} \times 1000 = 49.4\,\text{g MJ}^{-1}$. Carbon: per 394 kJ, $44.0\,\text{g}$ of CO_2; per MJ $= \dfrac{44.0}{394} \times 1000 = 112\,\text{g MJ}^{-1}$. c. Methane releases far less carbon dioxide per unit of energy ($49.4\,\text{g MJ}^{-1}$) than the coal ($112\,\text{g MJ}^{-1}$), because methane has a high hydrogen-to-carbon ratio: much of its energy comes from oxidising hydrogen to water rather than carbon to CO_2. Judged against the green chemistry principle of *designing for energy efficiency*, methane delivers more useful heat for each gram of CO_2 emitted. Neither fuel, however, satisfies the principle of *using renewable feedstocks*, since both are finite fossil resources. Concluding statement: of these two, methane is the better choice for reducing greenhouse emissions per unit of energy, but a genuinely sustainable option would be a renewable fuel such as biogas or green hydrogen.

Question 21 a. $n(\text{C}_8\text{H}_{18}) = \dfrac{570}{114.0} = 5.00\,\text{mol}$. b. $q = 5.00 \times 5470 = 27\,350\,\text{kJ} \approx 2.74 \times 10^4\,\text{kJ}$. c. From $\text{C}_8\text{H}_{18}(\text{l}) + 25/2\,\text{O}_2(\text{g}) \rightarrow 8\,\text{CO}_2(\text{g}) + 9\,\text{H}_2\text{O}(\text{l})$, $n(\text{CO}_2) = 8 \times 5.00 = 40.0\,\text{mol}$; $m(\text{CO}_2) = 40.0 \times 44.0 = 1760\,\text{g}$ (1.76 kg). d. $V(\text{CO}_2) = 40.0 \times 24.8 = 992\,\text{L}$.

Chapter 2 Measuring energy changes — 2B Calorimetry

Theory

Calorimetry is the experimental measurement of the heat energy released or absorbed by a chemical reaction. Because heat cannot be measured directly, it is found from the **temperature change** it produces in a known mass of substance — almost always water, whose thermal behaviour is well known.

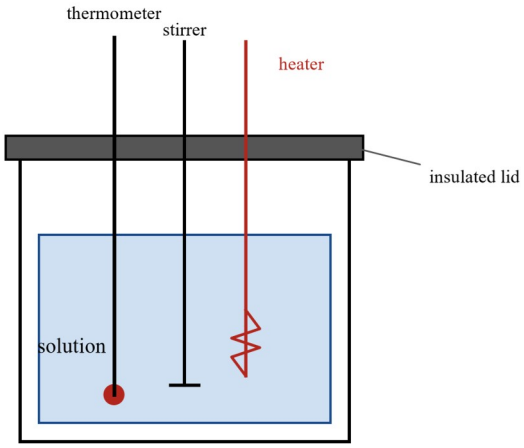
Heat and the specific heat capacity of water. The heat energy q needed to change the temperature of a mass m of water by ΔT is

$$q = m\,c\,\Delta T$$

where $c = 4.18\ \text{J g}^{-1}\,^{\circ}\text{C}^{-1}$ is the **specific heat capacity of water** — the energy required to raise 1 g of water by 1 °C. Because $\rho_{\text{water}} = 1.00\ \text{g mL}^{-1}$, a volume of water in millilitres equals its mass in grams (100.0 mL of water has a mass of 100.0 g). The temperature change $\Delta T = T_{\text{final}} - T_{\text{initial}}$ is the same number in °C or in K, so c may also be written $4.18\ \text{J g}^{-1}\,\text{K}^{-1}$.

A first estimate of the heat released by a burning fuel or food can be made by using its flame to warm a known mass of water and applying $q = m\,c\,\Delta T$. This approach always **underestimates** the true heat of combustion, because much of the heat is lost to the surroundings, the container and the escaping combustion gases rather than passing into the water.

Solution calorimetry. A more reliable method carries the reaction out *inside* an insulated container — a **solution calorimeter** — so that the reacting mixture and the calorimeter warm up together with little heat loss. A typical solution calorimeter has an insulated cup and lid, a thermometer, a stirrer to keep the temperature uniform, and an electrical heater used for calibration.



solution calorimeter

The calibration factor. Rather than assume the contents behave exactly like pure water, the whole calorimeter is **calibrated**: a measured quantity of electrical energy is supplied and the resulting temperature rise is recorded. The electrical energy delivered by a heater of voltage V carrying current I for time t is

$$Q = V\,I\,t$$

(in joules, when V is in volts, I in amperes and t in seconds). The **calibration factor** CF is the energy needed to raise the temperature of the whole calorimeter by 1 °C:

$$CF = \frac{V\,I\,t}{\Delta T}\left(\text{units J}\,^{\circ}\text{C}^{-1}\right)$$

Once CF is known, the heat released by a **reaction** carried out in the same calorimeter is found from its temperature change:

$$q = CF \times \Delta T$$

Temperature–time graphs and correcting for heat loss. Even a well-insulated calorimeter loses a little heat while the reaction proceeds, so the highest temperature actually recorded is slightly *lower* than the temperature the mixture would have reached instantaneously. The correction is made graphically. The temperature is recorded before mixing, at mixing, and for several minutes afterwards. After the peak, the temperature falls along a straight **cooling line**; this line is extrapolated back to the **time of mixing** to read the *corrected* maximum temperature. The corrected temperature change,

$$\Delta T = T_{\text{corrected max}} - T_{\text{initial}}$$

is larger than the change based on the observed peak, and gives the true heat of reaction (see Worked Example 3).

Molar enthalpy and the sign of ΔH. The quantity q found from $q = m\,c\,\Delta T$ or $q = C\,F \times \Delta T$ is always a **positive magnitude of heat**. The molar enthalpy change is obtained by dividing by the amount, in mole, of the substance reacting:

$$\Delta H = \pm \frac{q}{n} \left(\text{kJ mol}^{-1}\right)$$

The **sign** is assigned from the direction of the temperature change, and is written only on ΔH: an **exothermic** reaction releases heat, the temperature rises, and $\Delta H < 0$; an **endothermic** reaction absorbs heat, the temperature falls, and $\Delta H > 0$. A common and costly error is to carry the negative sign into a $q = m\,c\,\Delta T$ or $q = C\,F \times \Delta T$ calculation — this produces a meaningless negative heat or negative temperature change. Keep q positive throughout and attach the sign only at the final ΔH statement.

For a mixture whose molar mass is not defined (for example a solution of unknown composition), the enthalpy change is quoted per gram, in kJ g^{-1}: $\Delta H = \pm q / m$.

Calibration by a reaction of known enthalpy change. A calorimeter may also be calibrated *chemically*, by carrying out inside it a reaction whose molar enthalpy change is accurately known. If n mole of the limiting reactant is consumed and the accepted molar enthalpy change has magnitude $|\Delta H|$, the heat released is $q = n \times |\Delta H|$, so

$$C\,F = \frac{n \times |\Delta H|}{\Delta T}$$

Electrical calibration is the more common method, because V, I and t are measured precisely and no extra chemicals are consumed. Chemical calibration has the compensating advantage that the standard reaction is mixed and stirred in exactly the way the reaction under study will be.

What the calibration factor includes. $C\,F$ belongs to the calorimeter *together with its contents*: it covers the heat capacity of the solution and of the cup, lid, thermometer and stirrer. It is therefore always larger than $m\,c$ for the solution alone, and the difference

$$C_{\text{apparatus}} = C\,F - m\,c$$

is the heat capacity of the apparatus itself. Because the contents are part of $C\,F$, changing the volume or the identity of the solution changes $C\,F$, and the calorimeter **must be calibrated again**. Re-using an old calibration factor after refilling with a larger volume gives a value of q that is too small.

Solution vs bomb calorimetry (one-line contrast). Solution calorimetry — the examinable method above — measures reactions in solution at constant pressure; a **bomb calorimeter** instead burns a sample in excess oxygen inside a sealed vessel to measure a heat of combustion at constant volume.

Worked examples

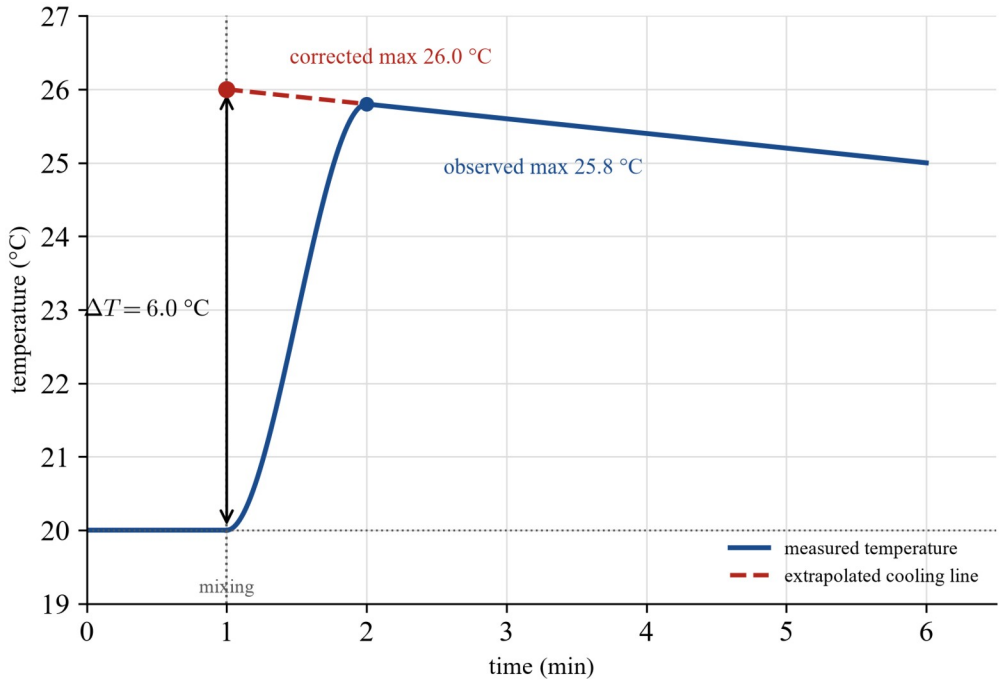
Worked Example 1 — A 1.20 g sample of propan-1-ol, $\text{C}_3\text{H}_7\text{OH}$ ($M = 60.0\ \text{g mol}^{-1}$), is burned completely in a spirit burner, and its flame heats 200.0 g of water in a metal can from 19.5 °C to 46.5 °C. Assuming all the heat released is absorbed by the water, calculate the heat gained by the water and the experimental molar enthalpy of combustion of propan-1-ol.

Working	Comment
$m = 200.0\,\text{g},\ \Delta T = 46.5 - 19.5 = 27.0\,^\circ\text{C}$	Mass of water; the temperature *rise* is a positive number.
$q = m c \Delta T = 200.0 \times 4.18 \times 27.0$	Substitute $c = 4.18\,\text{J g}^{-1}\,^\circ\text{C}^{-1}$; keep q positive.
$q = 22\,572\,\text{J} = 22.6\,\text{kJ}$	Heat gained by the water (3 sig figs).
$n = \dfrac{m}{M} = \dfrac{1.20}{60.0} = 0.0200\,\text{mol}$	Amount of fuel burned.
$\Delta H_c = -\dfrac{q}{n} = -\dfrac{22.572}{0.0200} = -1.13 \times 10^3\,\text{kJ mol}^{-1}$	The negative sign belongs on ΔH only, never inside $q = m c \Delta T$.
The magnitude is an **underestimate**	Heat lost to the can, the air and the escaping hot gases never reaches the water — which is why the calibrated calorimeter of Worked Example 2 is needed.

Worked Example 2 — A solution calorimeter is calibrated electrically by passing a current of 2.00 A at 5.00 V through its heater for 250 s, which raises the temperature by 1.25 °C. In the same calorimeter, 50.0 mL of $2.00\,\text{mol L}^{-1}$ hydrochloric acid is neutralised by 50.0 mL of $2.00\,\text{mol L}^{-1}$ sodium hydroxide solution, and the temperature rises by 2.85 °C. Determine the molar enthalpy of neutralisation.

Working	Comment
$Q = V I t = 5.00 \times 2.00 \times 250 = 2500\,\text{J}$	Electrical energy supplied during calibration.
$CF = \dfrac{V I t}{\Delta T} = \dfrac{2500}{1.25} = 2000\,\text{J}\,^\circ\text{C}^{-1}$	Calibration factor: energy to warm the whole calorimeter by 1 °C.
$q = CF \times \Delta T = 2000 \times 2.85 = 5700\,\text{J} = 5.70\,\text{kJ}$	Heat released by the neutralisation.
$n(\text{H}_2\text{O}) = c V = 2.00 \times 0.0500 = 0.100\,\text{mol}$	Acid and base react 1:1, so 0.100 mol of water forms.
$\Delta H = -\dfrac{q}{n} = -\dfrac{5.70}{0.100} = -57.0\,\text{kJ mol}^{-1}$	Negative sign attached because the mixture warmed (exothermic).
$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$	Balanced equation, with states.

Worked Example 3 — A solution calorimeter is calibrated electrically at 6.00 V and 2.50 A for 300 s, giving a temperature rise of 1.80 °C. In the same calorimeter, 0.250 mol of an anhydrous ionic solid is then dissolved in the water, and the temperature is monitored to give the graph below. Determine the molar enthalpy of solution, correcting for heat loss.



Calibration: $Q = V\,I\,t = 6.00 \times 2.50 \times 300 = 4500\ \text{J}$, so $CF = \dfrac{4500}{1.80} = 2500\ \text{J °C}^{-1}$.

The baseline temperature is 20.0 °C. The solid is added at the mixing time; the temperature rises to an *observed* peak of 25.8 °C, then falls along a straight cooling line. Extrapolating that cooling line back to the mixing time gives a **corrected** maximum of 26.0 °C (higher than the observed peak, because heat is lost to the surroundings while the solid dissolves). Hence the corrected temperature change is

$$\Delta T = 26.0 - 20.0 = 6.0\ \text{°C}$$

$$q = CF \times \Delta T = 2500 \times 6.0 = 15\,000\ \text{J} = 15.0\ \text{kJ}$$

$$\Delta H = -\frac{q}{n} = -\frac{15.0}{0.250} = -60.0\ \text{kJ mol}^{-1}$$

$\therefore$ the molar enthalpy of solution is $-60.0\ \text{kJ mol}^{-1}$ (exothermic). Had the *observed* peak of 25.8 °C been used ($\Delta T = 5.8\ \text{°C}$), the result would be only $-58.0\ \text{kJ mol}^{-1}$ — less exothermic — showing why the heat-loss correction matters.

Worked Example 4 — A solution calorimeter is calibrated *chemically*: 50.0 mL of $1.00\ \text{mol L}^{-1}$ hydrochloric acid is neutralised in it by 50.0 mL of $1.00\ \text{mol L}^{-1}$ sodium hydroxide solution, for which the accepted molar enthalpy of neutralisation is $-57.0\ \text{kJ mol}^{-1}$ of water formed, and the temperature rises by 1.50 °C. In the same calorimeter, 0.125 mol of an anhydrous salt is then dissolved and the temperature **falls** by 2.00 °C. Determine the molar enthalpy of solution of the salt.

Calibration — the acid and base react 1:1, so

$$n(\text{H}_2\text{O}) = c\,V = 1.00 \times 0.0500 = 0.0500\ \text{mol}$$

$$q = n \times |\Delta H| = 0.0500 \times 57.0 = 2.85\ \text{kJ} = 2850\ \text{J}$$

$$CF = \frac{q}{\Delta T} = \frac{2850}{1.50} = 1900\ \text{J °C}^{-1}$$

Dissolution — the same calibration factor now converts the temperature change into heat:

$$q = CF \times \Delta T = 1900 \times 2.00 = 3800\ \text{J} = 3.80\ \text{kJ}$$

$$\Delta H = +\frac{q}{n} = +\frac{3.80}{0.125} = +30.4\ \text{kJ mol}^{-1}$$

$\therefore$ the molar enthalpy of solution is $+30.4\ \text{kJ mol}^{-1}$ (endothermic). The temperature *fell*, so the dissolving salt absorbed heat from the mixture and ΔH is **positive** — but q and ΔT were both entered as positive magnitudes, exactly as in the exothermic examples; only the final ΔH carries the sign.

Practice questions

Question 1 — A 3.00 g pellet of a solid fuel of molar mass $120.0\ \text{g mol}^{-1}$ is burned and its flame heats 150.0 g of water from 18.0 °C to 41.4 °C. Assume all the heat is absorbed by the water.

a. Calculate the heat absorbed by the water, in kJ.
b. Calculate the experimental molar enthalpy of combustion of the fuel, including its sign.
c. State, with a reason, the sign of ΔH for the combustion.

Question 2 — A solution calorimeter is calibrated by passing 3.00 A at 4.00 V through its heater for 200 s, raising the temperature by 1.60 °C.

a. Calculate the calibration factor.
b. A reaction carried out in the same calorimeter raises the temperature by 3.20 °C. Calculate the heat released.

c. The reaction consumed 0.120 mol of the limiting reactant. Calculate ΔH for the reaction, including its sign.

Question 3 — A reaction is carried out in a solution calorimeter with calibration factor $1250\ \text{J °C}^{-1}$. The mixture's initial temperature is 22.0 °C. The reactants are mixed at $t = 1.0\ \text{min}$; after the peak the temperature falls linearly, reading 30.0 °C at $t = 3.0\ \text{min}$ and 29.2 °C at $t = 5.0\ \text{min}$.

a. By extrapolating the cooling line back to the mixing time, determine the corrected temperature change.
b. Calculate the heat released.
c. Given that 0.200 mol of reactant was consumed, calculate ΔH.

Question 4 — A solution calorimeter is calibrated chemically. In it, 25.0 mL of $1.60\ \text{mol L}^{-1}$ nitric acid is neutralised by 25.0 mL of $1.60\ \text{mol L}^{-1}$ potassium hydroxide solution, for which the accepted molar enthalpy of neutralisation is $-57.0\ \text{kJ mol}^{-1}$ of water formed. The temperature rises by 1.90 °C.

a. Calculate the amount, in mole, of water formed.
b. Calculate the calibration factor of the calorimeter.
c. A different reaction, carried out in the same calorimeter and consuming 0.0600 mol of the limiting reactant, raises the temperature by 2.50 °C. Calculate ΔH for that reaction, including its sign.

Question 5 — A solution calorimeter has a calibration factor of $1350\ \text{J °C}^{-1}$. When 0.0800 mol of a salt is dissolved in it, the temperature of the contents **falls** by 1.60 °C.

a. State whether the dissolution is exothermic or endothermic, and give the sign of ΔH.
b. Calculate the heat exchanged between the dissolving salt and the calorimeter contents.
c. Calculate the molar enthalpy of solution of the salt, including its sign.

Question 6 — Methanol, CH_3OH ($M = 32.0\ \text{g mol}^{-1}$), undergoes complete combustion with $\Delta H_c = -726\ \text{kJ mol}^{-1}$.

a. Write a balanced thermochemical equation for the complete combustion of methanol, including states.
b. Calculate the heat released when 4.80 g of methanol burns completely.
c. If all of this heat were absorbed by 1000.0 g (1.00 L) of water, calculate the temperature rise of the water.

Question 7 — Calculate the temperature rise produced when 250.0 g of water absorbs 20.9 kJ of heat.

Question 8 — A reaction releases 6.27 kJ of heat, raising the temperature of a water sample by 5.00 °C. Assuming all the heat is absorbed by the water, calculate the mass of water present.

Question 9 — During an electrical calibration, a heater passes 1.50 A at 8.00 V for 400 s and the calorimeter temperature rises by 2.00 °C. Calculate the calibration factor.

Question 10 — A reaction in a calorimeter of calibration factor $1800\ \text{J °C}^{-1}$ raises the temperature by 4.50 °C. If 0.150 mol of reactant is consumed, calculate the molar enthalpy of the reaction, including its sign.

Question 11 — The dissolution of a salt has $\Delta H = -52.0\ \text{kJ mol}^{-1}$. Predict the temperature change when 0.250 mol of the salt is dissolved in 200.0 g of water, assuming no heat loss, and state whether the temperature rises or falls.

Question 12 — When 5.00 g of an anhydrous solid ($M = 100.0\ \text{g mol}^{-1}$) dissolves in water, 4.20 kJ of heat is released. Calculate (i) the enthalpy change per gram and (ii) the molar enthalpy of solution, each with the correct sign.

Question 13 — In a solution calorimeter of calibration factor $1000\ \text{J °C}^{-1}$, a mixture begins at 24.0 °C and is mixed at $t = 1.0\ \text{min}$. On the cooling section the temperature reads 31.5 °C at $t = 4.0\ \text{min}$ and 31.1 °C at $t = 6.0\ \text{min}$. For 0.100 mol of reactant, determine the corrected temperature change and the molar enthalpy of the reaction.

Question 14 — A calorimeter of calibration factor $2100\ \text{J °C}^{-1}$ is to be re-calibrated electrically, using a 6.00 V heater run for 350 s to produce a temperature rise of 2.00 °C. Calculate the current the heater must carry.

Question 15 — A reaction is carried out in a solution calorimeter of calibration factor $1150\ \text{J °C}^{-1}$ that holds 250.0 g of solution. The reaction consumes 0.0750 mol of the limiting reactant and raises the temperature by 2.50 °C.

a. Calculate ΔH for the reaction using the calibration factor.
b. Calculate the value a student would obtain by assuming instead that the 250.0 g of solution absorbs all of the heat, and determine the percentage by which this assumption understates the magnitude of ΔH.

Question 16 — A solution calorimeter is calibrated electrically while it holds 100.0 mL of water, giving a calibration factor of $530\ \text{J °C}^{-1}$.

a. Calculate the heat capacity of the calorimeter apparatus alone — the cup, lid, thermometer and stirrer.
b. The calorimeter is emptied and refilled with 200.0 mL of water. Predict its new calibration factor.
c. Explain why a student who continued to use $530\ \text{J °C}^{-1}$ after refilling would calculate a heat that is too small.

Question 17 — Propane, C_3H_8 ($M = 44.0\ \text{g mol}^{-1}$), has $\Delta H_c = -2220\ \text{kJ mol}^{-1}$.

a. Write a balanced thermochemical equation for the complete combustion of propane, including states.
b. Calculate the heat released when 2.20 g of propane burns completely.

Question 18 — A student measures the molar enthalpy of neutralisation as $-54.0\ \text{kJ mol}^{-1}$, whereas the accepted value is $-57.0\ \text{kJ mol}^{-1}$.

a. Calculate the percentage difference between the measured and accepted values.
b. Explain why the measured value is *less* exothermic than the accepted value, referring to heat loss.

Question 19 — In a solution calorimetry experiment the temperature of the calorimeter is recorded for two minutes before the reactants are mixed, at the moment of mixing, and for five minutes afterwards, with the contents stirred throughout.

a. Explain why the temperature is recorded for several minutes *before* the reactants are mixed.
b. Explain why the contents must be stirred continuously while the temperature is recorded.
c. A second student repeats the experiment using twice the volume of solution but the same amount, in mole, of reactant, re-calibrating the calorimeter first. State, with a reason, the effect on (i) the temperature change recorded and (ii) the calculated molar enthalpy change.

Question 20 — A company must determine the molar enthalpy change of a newly developed reaction. One option is to run the reaction in a 20 L pilot reactor and estimate ΔH from the temperature rise of the contents; the other is to run 100 mL of the same mixture in an electrically calibrated solution calorimeter.

a. In one calibration of the solution calorimeter a heater at 6.00 V carried 3.50 A for 200 s and raised the temperature by 3.00 °C. Calculate the calibration factor.
b. With reference to two green chemistry principles, evaluate the small-scale calibrated calorimeter against the pilot-reactor trial as the method for determining ΔH, and give a concluding statement.

Question 21 — A solution calorimeter is calibrated electrically at 8.00 V and 2.00 A for 200 s, giving a temperature rise of 2.00 °C. A neutralisation is then carried out: the mixture begins at 22.0 °C, is mixed at $t = 1.0\ \text{min}$, and on the cooling line reads 28.8 °C at $t = 3.0\ \text{min}$ and 28.4 °C at $t = 5.0\ \text{min}$. The reaction forms 0.180 mol of water.

a. Calculate the calibration factor.
b. Determine the corrected temperature change by extrapolation.
c. Calculate ΔH for the neutralisation.
d. State one modification to the apparatus or method that would reduce heat loss.

Answers

1 a 14.7 kJ; b $-587\ \text{kJ mol}^{-1}$; c $\Delta H < 0$ (exothermic — the water warmed). **2** a $1500\ \text{J °C}^{-1}$; b 4.80 kJ; c $-40.0\ \text{kJ mol}^{-1}$. **3** a 8.80 °C; b 11.0 kJ; c $-55.0\ \text{kJ mol}^{-1}$. **4** a 0.0400 mol; b $1200\ \text{J °C}^{-1}$; c $-50.0\ \text{kJ mol}^{-1}$. **5** a endothermic, $\Delta H > 0$; b 2.16 kJ; c $+27.0\ \text{kJ mol}^{-1}$. **6** a $\text{CH}_3\text{OH(l)} + 3/2\,\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\,\text{H}_2\text{O(l)}$, $\Delta H = -726\ \text{kJ mol}^{-1}$; b 109 kJ; c 26.1 °C. **7** 20.0 °C. **8** 300 g. **9** $2400\ \text{J °C}^{-1}$. **10** $-54.0\ \text{kJ mol}^{-1}$. **11** +15.6 °C — the temperature rises (exothermic). **12** (i) $-0.840\ \text{kJ g}^{-1}$; (ii) $-84.0\ \text{kJ mol}^{-1}$. **13** $\Delta T = 8.10\ \text{°C}$; $\Delta H = -81.0\ \text{kJ mol}^{-1}$. **14** 2.00 A. **15** a $-38.3\ \text{kJ mol}^{-1}$; b $-34.8\ \text{kJ mol}^{-1}$, understated by 9.13 %. **16** a $112\ \text{J °C}^{-1}$; b $948\ \text{J °C}^{-1}$; c the true CF is now larger, so $q = CF \times \Delta T$ calculated with the old value is too small. **17** a $\text{C}_3\text{H}_8\text{(g)} + 5\,\text{O}_2\text{(g)} \rightarrow 3\,\text{CO}_2\text{(g)} + 4\,\text{H}_2\text{O(l)}$, $\Delta H = -2220\ \text{kJ mol}^{-1}$; b 111 kJ. **18** a 5.26 %; b heat lost to the surroundings makes the measured ΔT (and hence q and $|\Delta H|$) too small. **19** a to establish a steady baseline temperature and fix the mixing time for the extrapolation; b to keep the temperature uniform so the thermometer reads the whole mixture; c (i) smaller ΔT; (ii) unchanged ΔH. **20** a $1400\ \text{J °C}^{-1}$; b evaluation (prevention of waste and design for energy efficiency vs the scale-realism of the pilot trial). **21** a $1600\ \text{J °C}^{-1}$; b 7.20 °C; c $-64.0\ \text{kJ mol}^{-1}$; d e.g. add a fitted lid / better insulation / a smaller air gap.

Fully-worked solutions

Question 1 a. $\Delta T = 41.4 - 18.0 = 23.4\ \text{°C}$; $q = mc\Delta T = 150.0 \times 4.18 \times 23.4 = 14\,672\ \text{J} = 14.7\ \text{kJ}$. b. $n = \dfrac{3.00}{120.0} = 0.0250\ \text{mol}$; $\Delta H_c = -\dfrac{14.672}{0.0250} = -587\ \text{kJ mol}^{-1}$. c. $\Delta H < 0$: the reaction is exothermic because it released heat, raising the water temperature. The magnitude used in $q = mc\Delta T$ stays positive; the negative sign is placed only on ΔH.

Question 2 a. $CF = \dfrac{VIt}{\Delta T} = \dfrac{4.00 \times 3.00 \times 200}{1.60} = \dfrac{2400}{1.60} = 1500\ \text{J °C}^{-1}$. b. $q = CF \times \Delta T = 1500 \times 3.20 = 4800\ \text{J} = 4.80\ \text{kJ}$. c. $\Delta H = -\dfrac{q}{n} = -\dfrac{4.80}{0.120} = -40.0\ \text{kJ mol}^{-1}$ (negative — the temperature rose, so the reaction is exothermic).

Question 3 a. Cooling-line gradient $= \dfrac{29.2 - 30.0}{5.0 - 3.0} = -0.40\ \text{°C min}^{-1}$. Extrapolating to $t = 1.0\ \text{min}$: $T = 30.0 + (-0.40)(1.0 - 3.0) = 30.8\ \text{°C}$. Corrected $\Delta T = 30.8 - 22.0 = 8.80\ \text{°C}$. b. $q = CF \times \Delta T = 1250 \times 8.80 = 11\,000\ \text{J} = 11.0\ \text{kJ}$. c. $\Delta H = -\dfrac{11.0}{0.200} = -55.0\ \text{kJ mol}^{-1}$.

Question 4 a. The acid and base react 1:1, so $n(\text{H}_2\text{O}) = cV = 1.60 \times 0.0250 = 0.0400\ \text{mol}$. b. $q = n \times |\Delta H| = 0.0400 \times 57.0 = 2.28\ \text{kJ} = 2280\ \text{J}$; $CF = \dfrac{q}{\Delta T} = \dfrac{2280}{1.90} = 1200\ \text{J °C}^{-1}$. c. $q = CF \times \Delta T = 1200 \times 2.50 = 3000\ \text{J} = 3.00\ \text{kJ}$; $\Delta H = -\dfrac{3.00}{0.0600} = -50.0\ \text{kJ mol}^{-1}$ (negative — the temperature rose, so the reaction is exothermic).

Question 5 a. The temperature of the contents **fell**, so the dissolving salt absorbed heat from them: the dissolution is **endothermic** and $\Delta H > 0$. b. $q = CF \times \Delta T = 1350 \times 1.60 = 2160\ \text{J} = 2.16\ \text{kJ}$. Both CF and ΔT are entered as positive magnitudes. c. $\Delta H = +\dfrac{q}{n} = +\dfrac{2.16}{0.0800} = +27.0\ \text{kJ mol}^{-1}$. The positive sign is attached at this final step because the mixture cooled.

Question 6 a. $\text{CH}_3\text{OH(l)} + 3/2\,\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\,\text{H}_2\text{O(l)}$, $\Delta H = -726\ \text{kJ mol}^{-1}$. b. $n = \dfrac{4.80}{32.0} = 0.150\ \text{mol}$; $q = 0.150 \times 726 = 108.9 \approx 109\ \text{kJ}$. c. $\Delta T = \dfrac{q}{mc} = \dfrac{108\,900}{1000.0 \times 4.18} = 26.1\ \text{°C}$.

Question 7 $\Delta T = \dfrac{q}{m\,c} = \dfrac{20\,900}{250.0 \times 4.18} = \dfrac{20\,900}{1045} = 20.0\,^{\circ}\text{C}$.

Question 8 $m = \dfrac{q}{c\,\Delta T} = \dfrac{6270}{4.18 \times 5.00} = \dfrac{6270}{20.9} = 300\,\text{g}$ (300 mL of water).

Question 9 $CF = \dfrac{V\,I\,t}{\Delta T} = \dfrac{8.00 \times 1.50 \times 400}{2.00} = \dfrac{4800}{2.00} = 2400\,\text{J}\,^{\circ}\text{C}^{-1}$.

Question 10 $q = CF \times \Delta T = 1800 \times 4.50 = 8100\,\text{J} = 8.10\,\text{kJ}$; $\Delta H = -\dfrac{8.10}{0.150} = -54.0\,\text{kJ mol}^{-1}$ (exothermic).

Question 11 The negative sign of ΔH tells us the dissolution is exothermic; its **magnitude**, $52.0\,\text{kJ mol}^{-1}$, is the heat released. Do *not* substitute the negative sign into $q = m\,c\,\Delta T$. $q = n \times |\Delta H| = 0.250 \times 52.0 = 13.0\,\text{kJ} = 13\,000\,\text{J}$. $\Delta T = \dfrac{q}{m\,c} = \dfrac{13\,000}{200.0 \times 4.18} = 15.6\,^{\circ}\text{C}$. Because heat is released, the temperature **rises** by 15.6 °C.

Question 12 $n = \dfrac{5.00}{100.0} = 0.0500\,\text{mol}$. (i) Per gram: $\Delta H = -\dfrac{4.20}{5.00} = -0.840\,\text{kJ g}^{-1}$ (negative — heat released). (ii) Molar: $\Delta H = -\dfrac{4.20}{0.0500} = -84.0\,\text{kJ mol}^{-1}$.

Question 13 Cooling-line gradient $= \dfrac{31.1 - 31.5}{6.0 - 4.0} = -0.20\,^{\circ}\text{C min}^{-1}$. Extrapolating to $t = 1.0\,\text{min}$: $T = 31.5 + (-0.20)(1.0 - 4.0) = 32.1\,^{\circ}\text{C}$. Corrected $\Delta T = 32.1 - 24.0 = 8.10\,^{\circ}\text{C}$. $q = 1000 \times 8.10 = 8100\,\text{J} = 8.10\,\text{kJ}$; $\Delta H = -\dfrac{8.10}{0.100} = -81.0\,\text{kJ mol}^{-1}$.

Question 14 The electrical energy needed is the energy that raises the whole calorimeter by 2.00 °C: $Q = CF \times \Delta T = 2100 \times 2.00 = 4200\,\text{J}$. Rearranging $Q = V\,I\,t$: $I = \dfrac{Q}{V\,t} = \dfrac{4200}{6.00 \times 350} = \dfrac{4200}{2100} = 2.00\,\text{A}$.

Question 15 a. $q = CF \times \Delta T = 1150 \times 2.50 = 2875\,\text{J} = 2.875\,\text{kJ}$; $\Delta H = -\dfrac{2.875}{0.0750} = -38.3\,\text{kJ mol}^{-1}$. b. Assuming only the solution absorbs the heat: $q = m\,c\,\Delta T = 250.0 \times 4.18 \times 2.50 = 2612.5\,\text{J} = 2.6125\,\text{kJ}$, giving $\Delta H = -\dfrac{2.6125}{0.0750} = -34.8\,\text{kJ mol}^{-1}$. The assumption ignores the heat capacity of the cup, lid, thermometer and stirrer, so it understates the magnitude by $\dfrac{2875 - 2612.5}{2875} \times 100 = 9.13\,\%$.

Question 16 a. The water contributes $m\,c = 100.0 \times 4.18 = 418\,\text{J}\,^{\circ}\text{C}^{-1}$ (100.0 mL of water has a mass of 100.0 g), so the apparatus contributes $C_{\text{apparatus}} = CF - m\,c = 530 - 418 = 112\,\text{J}\,^{\circ}\text{C}^{-1}$. b. With 200.0 mL (200.0 g) of water the contents contribute $200.0 \times 4.18 = 836\,\text{J}\,^{\circ}\text{C}^{-1}$, and the apparatus is unchanged: $CF = 836 + 112 = 948\,\text{J}\,^{\circ}\text{C}^{-1}$. c. The calibration factor includes the heat capacity of the contents as well as of the apparatus, and doubling the volume of water almost doubles it ($530 \rightarrow 948\,\text{J}\,^{\circ}\text{C}^{-1}$). The refilled calorimeter therefore needs far more energy for each 1 °C of temperature rise. Using the old, smaller factor in $q = CF \times \Delta T$ credits the measured rise with too little energy, so the calculated q — and hence the magnitude of ΔH — comes out too small.

Question 17 a. $\text{C}_3\text{H}_8(\text{g}) + 5\,\text{O}_2(\text{g}) \rightarrow 3\,\text{CO}_2(\text{g}) + 4\,\text{H}_2\text{O}(\text{l})$, $\Delta H = -2220\,\text{kJ mol}^{-1}$. b. $n = \dfrac{2.20}{44.0} = 0.0500\,\text{mol}$; $q = 0.0500 \times 2220 = 111\,\text{kJ}$.

Question 18 a. Percentage difference $= \dfrac{57.0 - 54.0}{57.0} \times 100 = 5.26\,\%$. b. Some of the heat released by the reaction is lost to the surroundings (and to the calorimeter walls and any un-insulated parts) instead of raising the temperature of the solution. The measured temperature rise is therefore smaller than it should be, so the calculated $q = CF \times \Delta T$ is

too small, and dividing by n gives a ΔH whose magnitude is too small — that is, less exothermic than the accepted value.

Question 19 a. The reading before mixing establishes the **initial temperature** T_{initial} and shows that it is steady, so any drift caused by the room being warmer or cooler than the calorimeter can be seen and allowed for. It also fixes the **time of mixing** on the time axis, which is the point the cooling line must be extrapolated back to when the heat-loss correction is made. b. Stirring keeps the temperature **uniform** throughout the mixture. Without it the reactants mix slowly and warm (or cool) unevenly, so the thermometer records only the temperature of the liquid immediately around it — a reading that depends on where the probe sits and that misses the true maximum. A uniform temperature is also what the calibration assumed, so stirring keeps the measurement and the calibration comparable. c. (i) The temperature change is **smaller**. The same amount of reactant releases the same heat, but that heat now warms twice as much solution — a calorimeter with a much larger calibration factor — so $\Delta T = q / CF$ falls. (ii) The molar enthalpy change is **unchanged**. The larger CF exactly offsets the smaller ΔT, so $q = CF \times \Delta T$ is the same as before, and dividing by the same n gives the same ΔH. ΔH is a property of the reaction per mole, not of the scale on which it is run — which is why the calorimeter had to be re-calibrated for the new volume.

Question 20 a. $Q = V\,I\,t = 6.00 \times 3.50 \times 200 = 4200\ \text{J}$; $CF = \dfrac{Q}{\Delta T} = \dfrac{4200}{3.00} = 1400\ \text{J °C}^{-1}$. b. Against the green chemistry principle of **prevention of waste**, the calorimeter consumes only 100 mL of the reaction mixture, about one two-hundredth of the 20 L pilot charge; almost no reagent is committed to a measurement, and the small volume of product that results is far cheaper and safer to treat than a 20 L batch of an unknown mixture. Against the principle of **designing for energy efficiency**, the calorimeter needs only the few kilojoules of electrical energy used in the calibration, whereas the pilot reactor must be charged, stirred, heated to the starting temperature and afterwards cooled — energy that is spent on the vessel rather than on the measurement. The calibrated calorimeter is also the more *accurate* method: its calibration factor accounts for the heat capacity of the whole apparatus, while a pilot-reactor estimate must assume a heat capacity for a large vessel it cannot measure. Set against this, only the pilot trial shows how the reaction behaves at real operating scale — how fast the heat is released and whether the plant's cooling system can remove it — and a large vessel loses proportionally less heat through its surface. Concluding statement: the enthalpy change should be determined in the calibrated solution calorimeter, because it yields a more accurate molar ΔH while consuming a fraction of the reagents and energy; the pilot reactor should be reserved for the separate engineering question of removing that heat at full scale, once ΔH is known.

Question 21 a. $CF = \dfrac{V\,I\,t}{\Delta T} = \dfrac{8.00 \times 2.00 \times 200}{2.00} = \dfrac{3200}{2.00} = 1600\ \text{J °C}^{-1}$. b. Cooling-line gradient $= \dfrac{28.4 - 28.8}{5.0 - 3.0} = -0.20\ \text{°C min}^{-1}$. Extrapolating to $t = 1.0\ \text{min}$: $T = 28.8 + (-0.20)(1.0 - 3.0) = 29.2\ \text{°C}$. Corrected $\Delta T = 29.2 - 22.0 = 7.20\ \text{°C}$. c. $q = CF \times \Delta T = 1600 \times 7.20 = 11\,520\ \text{J} = 11.52\ \text{kJ}$; $\Delta H = -\dfrac{11.52}{0.180} = -64.0\ \text{kJ mol}^{-1}$. d. Any one of: fit a close-fitting insulated lid to reduce evaporative and convective loss; use a thicker-walled or double-walled (vacuum) insulated cup; reduce the air gap above the solution; or add the reactant more quickly and stir to shorten the time over which heat can escape.

Chapter 2 Measuring energy changes — 2C Energy content of food and fuels

Theory

Every fuel and every food releases energy when it is completely burned in oxygen. The **energy value** (or energy content) of a fuel or food is the quantity of heat energy released per gram of the substance, measured in kJ g^{-1}. Because it is quoted *per gram*, the energy value lets substances of quite different composition — a fuel, a fat, a carbohydrate — be compared on an equal-mass basis.

Estimating energy content by flame heating. A simple laboratory estimate of the energy value of a fuel or food is made by burning a known mass of it and using the flame to warm a known mass of water. The heat gained by the water is found from

$$q = m\,c\,\Delta T$$

where m is the mass of water in grams, $c = 4.18\ \text{J g}^{-1}\,^{\circ}\text{C}^{-1}$ is the specific heat capacity of water, and $\Delta T = T_{\text{final}} - T_{\text{initial}}$ is the temperature rise. Because $\rho_{\text{water}} = 1.00\ \text{g mL}^{-1}$, a volume of water in millilitres equals its mass in grams (250.0 mL of water has a mass of 250.0 g). The heat q is always used as a **positive magnitude**: the negative sign that marks an exothermic reaction belongs on ΔH only, never inside $q = m\,c\,\Delta T$. Dividing the heat delivered to the water by the mass of fuel burned gives the experimental energy value:

$$\text{energy value} = \frac{q}{m_{\text{fuel}}}\ (\text{kJ g}^{-1})$$

This flame-heating method always **underestimates** the true energy value, because much of the heat is lost to the surrounding air, to the container and to the escaping hot combustion gases rather than passing into the water; any incomplete combustion or evaporation of the fuel lowers the measured value further. (Obtaining a more accurate value requires an insulated, calibrated calorimeter — the method of subtopic 2B.)

Energy transformation efficiency. When a fuel is burned to do a useful job such as heating water, only part of the chemical energy stored in the fuel ends up where it is wanted. The **energy transformation efficiency** is the percentage of the chemical energy released by combustion that is converted to useful (absorbed) energy:

$$\text{efficiency} = \frac{\text{useful energy output}}{\text{chemical energy released}} \times 100\,\%$$

The chemical energy released is found from the amount of fuel burned and its molar enthalpy of combustion: for n mole of fuel it is $n \times |\Delta H_c|$, using the **magnitude** of ΔH_c. The useful output is the heat actually absorbed by the water, $q = m\,c\,\Delta T$. Efficiency is always below 100% because of heat lost to the surroundings, evaporation of water, and any incomplete combustion.

Energy content of foods. The energy the body obtains from food comes from three groups of nutrients. Their average energy values, as listed in the Data Book, are

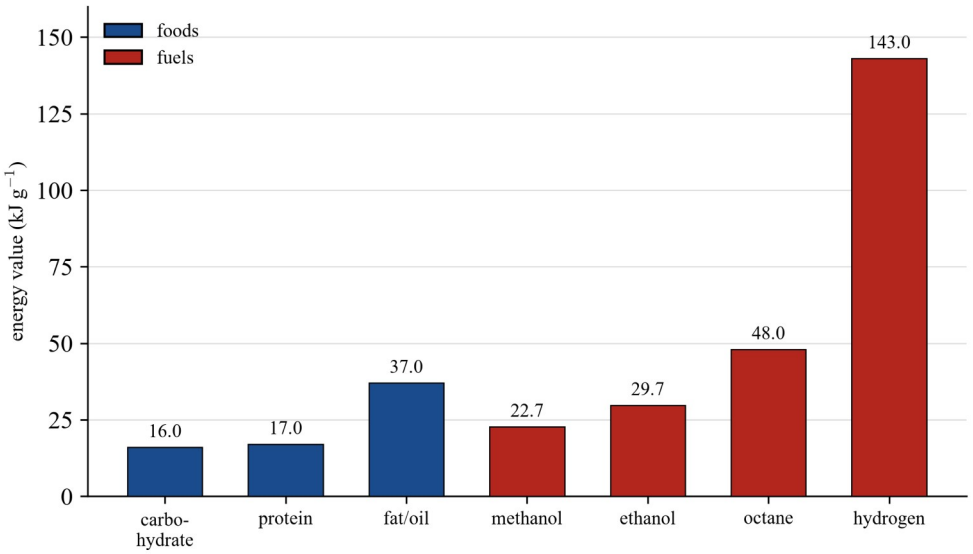
$$\text{carbohydrates } 16\ \text{kJ g}^{-1},\ \text{proteins } 17\ \text{kJ g}^{-1},\ \text{fats and oils } 37\ \text{kJ g}^{-1}.$$

The total energy available from a food is the sum of the energy from each group:

$$E = m_{\text{carb}} \times 16 + m_{\text{prot}} \times 17 + m_{\text{fat}} \times 37\ (\text{kJ})$$

Fats and oils release **more than twice** the energy per gram of carbohydrates or proteins. This is because the carbon atoms in a fat are the least oxidised: a fat has a high proportion of energy-rich C–H and C–C bonds and relatively little oxygen already bonded to its carbon, so there is further for its carbon and hydrogen to be oxidised when it burns completely to CO_2 and H_2O, and more energy is released.

Comparing fuels and foods. Ranking substances by energy value shows the same trend — the more highly reduced (hydrogen-rich, oxygen-poor) the molecule, the greater its energy per gram. The figure below ranks the three food groups against four common fuels. Hydrogen, with no carbon at all, has by far the highest energy value of any common fuel, at $143\ \text{kJ g}^{-1}$ — roughly three times that of octane, the hydrocarbon used to represent petrol.



The energy value is only one factor when a fuel is chosen: a fuel with a lower energy value per gram may still be preferred if it is renewable, burns more cleanly, or is safer to store. Bioethanol, for example, has a lower energy value than petrol but is made from a renewable feedstock — a comparison of energy value must be weighed against these other considerations.

Worked examples

Worked Example 1 — A 0.650 g piece of cashew nut is burned completely, and its flame heats 150.0 g of water in a metal can from 22.0 °C to 40.5 °C. Assuming all the heat released is absorbed by the water, calculate the heat gained by the water and the experimental energy value of the cashew in kJ g^{-1}.

Working	Comment
$m = 150.0\,\text{g},\ \Delta T = 40.5 - 22.0 = 18.5\,°\text{C}$	Mass of water; the temperature *rise* is a positive number.
$q = m c \Delta T = 150.0 \times 4.18 \times 18.5$	Substitute $c = 4.18\,\text{J g}^{-1}\,°\text{C}^{-1}$; keep q positive.
$q = 11\,600\,\text{J} = 11.6\,\text{kJ}$	Heat gained by the water (3 sig figs).
$\text{energy value} = \dfrac{11.60\,\text{kJ}}{0.650\,\text{g}} = 17.8\,\text{kJ g}^{-1}$	Heat delivered to the water per gram of cashew.
This is a *lower bound* on the true energy value	Heat lost to the surroundings means the true value is higher.

Worked Example 2 — Methanol, CH_3OH ($M = 32.0\,\text{g mol}^{-1}$, $\Delta H_c = -726\,\text{kJ mol}^{-1}$), is burned in a spirit burner. Burning 1.28 g of methanol raises the temperature of 220.0 g of water from 18.5 °C to 34.5 °C. Calculate the energy transformation efficiency of the heating.

Working	Comment
$n(\text{methanol}) = \dfrac{m}{M} = \dfrac{1.28}{32.0} = 0.0400\,\text{mol}$	Amount of fuel burned.
chemical energy $= n \times \lvert\Delta H_c\rvert = 0.0400 \times 726 = 29.04\,\text{kJ}$	Use the *magnitude* of ΔH_c; the sign stays on ΔH_c only.
$\Delta T = 34.5 - 18.5 = 16.0\,°\text{C}$	Temperature rise of the water.
$q = m c \Delta T = 220.0 \times 4.18 \times 16.0 = 14\,714\,\text{J} = 14.7\,\text{kJ}$	Useful heat absorbed by the water.
$\text{efficiency} = \dfrac{14.714}{29.04} \times 100 = 50.7\,\%$	Useful output as a percentage of chemical energy released.
$\text{CH}_3\text{OH}(\text{l}) + 3/2\,\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\,\text{H}_2\text{O}(\text{l})$	Balanced thermochemical equation, $\Delta H = -726\,\text{kJ mol}^{-1}$.

Worked Example 3 — A serving of mixed nuts contains 8.0 g of carbohydrate, 12.0 g of protein and 26.0 g of fat. Using the Data Book energy values (carbohydrate 16, protein 17, fat $37\ \text{kJ g}^{-1}$), calculate the total energy available from the serving, the percentage of that energy supplied by fat, and the average energy per gram of the three nutrients.

Total energy:

$$E = (8.0 \times 16) + (12.0 \times 17) + (26.0 \times 37) = 128 + 204 + 962 = 1294\ \text{kJ}$$

Percentage from fat:

$$\frac{962}{1294} \times 100 = 74.3\,\%$$

Average energy per gram of nutrient:

$$\frac{1294\ \text{kJ}}{(8.0 + 12.0 + 26.0)\ \text{g}} = \frac{1294}{46.0} = 28.1\ \text{kJ g}^{-1}$$

$\therefore$ although fat is only $26.0 / 46.0 = 57\,\%$ of the nutrient mass, it supplies 74.3% of the energy, because its energy value ($37\ \text{kJ g}^{-1}$) is more than double that of carbohydrate or protein.

Worked Example 4 — Compare hydrogen (H_2, $M = 2.0\ \text{g mol}^{-1}$, $\Delta H_c = -286\ \text{kJ mol}^{-1}$) and octane ($\text{C}_8\text{H}_{18}$, $M = 114.0\ \text{g mol}^{-1}$, $\Delta H_c = -5470\ \text{kJ mol}^{-1}$) by their energy values per gram.

$$\text{energy value } (\text{H}_2) = \frac{|\Delta H_c|}{M} = \frac{286}{2.0} = 143\ \text{kJ g}^{-1}$$

$$\text{energy value (octane)} = \frac{5470}{114.0} = 48.0\ \text{kJ g}^{-1}$$

$\therefore$ hydrogen releases about three times as much energy per gram as octane (143 versus $48.0\ \text{kJ g}^{-1}$), because it is entirely hydrogen with no carbon to carry oxygen. Its combustion, $\text{H}_2(\text{g}) + 1/2\,\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$, produces only water; the practical drawback is that a gas of such low density must be stored compressed or liquefied to carry a useful mass.

Practice questions

Question 1 — A 0.880 g fire-lighter cube is burned completely beneath a metal can, and its flame heats 200.0 g of water from 20.0 °C to 38.4 °C. Assume all the heat is absorbed by the water.

a. Calculate the heat absorbed by the water, in kJ.
b. Calculate the experimental energy value of the fuel in kJ g^{-1}.
c. State, with a reason, why this experimental energy value is likely to be lower than the fuel's true energy value.

Question 2 — A serving of breakfast cereal contains 27.0 g of carbohydrate, 4.0 g of protein and 3.0 g of fat. 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. Calculate the total energy available from the serving.
b. Calculate the percentage of this energy that comes from fat.
c. Explain why fats provide more energy per gram than carbohydrates.

Question 3 — Methanol, CH_3OH ($M = 32.0\ \text{g mol}^{-1}$, $\Delta H_c = -726\ \text{kJ mol}^{-1}$), is burned in a spirit burner. 1.60 g of methanol heats 250.0 g of water from 21.0 °C to 40.0 °C.

a. Calculate the chemical energy released by the methanol.
b. Calculate the heat absorbed by the water.
c. Calculate the energy transformation efficiency of the heating.

Question 4 — Two fuels are compared as cooking fuels: ethanol ($M = 46.0\ \text{g mol}^{-1}$, $\Delta H_c = -1367\ \text{kJ mol}^{-1}$) and propane ($M = 44.0\ \text{g mol}^{-1}$, $\Delta H_c = -2220\ \text{kJ mol}^{-1}$).

a. Calculate the energy value of ethanol in kJ g^{-1}.
b. Calculate the energy value of propane in kJ g^{-1}.
c. State which fuel delivers more energy per gram, and give one advantage of ethanol as a fuel.

Question 5 — A 1.10 g piece of cheese is burned completely and its flame raises the temperature of 100.0 g of water by 26.0 °C.

a. Calculate the energy delivered to the water, in kJ.
b. Determine the experimental energy value of the cheese in kJ g^{-1}.
c. The manufacturer lists the cheese's energy value as $15.0\ \text{kJ g}^{-1}$. State whether the experimental value is higher or lower than this, and suggest why.

Question 6 — A camping stove burns propane, C_3H_8 ($M = 44.0\ \text{g mol}^{-1}$, $\Delta H_c = -2220\ \text{kJ mol}^{-1}$), and transfers 45.0% of the chemical energy to the water it heats.

a. Calculate the chemical energy released when 5.50 g of propane burns completely.
b. Calculate the useful heat transferred to the water.
c. Calculate the temperature rise this produces in 2.00 kg of water.

Question 7 — A fuel's flame raises the temperature of 180.0 g of water by 32.0 °C. Calculate the heat energy, in kJ, delivered to the water.

Question 8 — Burning 0.750 g of a fuel delivers 18.6 kJ of heat to the water it warms. Calculate the experimental energy value of the fuel in kJ g^{-1}.

Question 9 — A burning fuel delivers 30.0 kJ of heat to a beaker of water, raising its temperature by 25.0 °C. Assuming all the heat is absorbed by the water, calculate the mass of water present.

Question 10 — 2.30 g of ethanol ($M = 46.0\ \text{g mol}^{-1}$, $\Delta H_c = -1367\ \text{kJ mol}^{-1}$) is burned and heats 400.0 g of water by 24.0 °C. Calculate the energy transformation efficiency of the heating.

Question 11 — A protein bar contains 20.0 g of carbohydrate, 15.0 g of protein and 7.0 g of fat. Using the food energy values (carbohydrate 16, protein 17, fat $37\ \text{kJ g}^{-1}$), calculate (a) the total energy content of the bar and (b) the percentage of the energy that comes from protein.

Question 12 — Two foods are analysed. Per 100 g, food X contains 5.0 g of carbohydrate, 25.0 g of protein and 15.0 g of fat; food Y contains 70.0 g of carbohydrate, 5.0 g of protein and 8.0 g of fat.

a. Calculate the energy content of 100 g of each food.
b. Hence state which food has the greater energy value per gram.

Question 13 — Butane, C_4H_{10} ($M = 58.0\ \text{g mol}^{-1}$), has $\Delta H_c = -2877\ \text{kJ mol}^{-1}$.

a. Write a balanced thermochemical equation for the complete combustion of butane, including states.
b. Calculate the energy value of butane in kJ g^{-1}.

Question 14 — Two students estimate the energy value of the same fuel, whose true energy value is $30.0\ \text{kJ g}^{-1}$, by burning it beneath a can of water. Student A burns 0.500 g of the fuel and delivers 6.00 kJ to the water. Student B fits a draught shield around the flame and a lid to the can, burns 0.500 g of the same fuel, and delivers 9.75 kJ to the water.

a. Calculate the experimental energy value obtained by each student, and the percentage of the fuel's chemical energy that each captured.

b. Explain why student B's apparatus gives a value closer to the true energy value, and why student B's value is still an underestimate.

Question 15 — A water heater must deliver 500 kJ of useful heat to water and operates at 40.0% energy efficiency using ethanol ($M = 46.0\ \text{g mol}^{-1}$, $\Delta H_c = -1367\ \text{kJ mol}^{-1}$) as its fuel. Calculate the mass of ethanol required.

Question 16 — Two breakfast options are compared. Option A contains 55.0 g of carbohydrate, 15.0 g of protein and 25.0 g of fat; option B contains 70.0 g of carbohydrate, 20.0 g of protein and 8.0 g of fat.

a. Calculate the total energy provided by each option.
b. A student wants a breakfast providing about 2000 kJ but low in fat. Evaluate the two options against these two goals, referring to the fat contributions, and give a concluding recommendation.

Question 17 — A school canteen cooks with LPG (treated as propane, energy value $50.5\ \text{kJ g}^{-1}$) and burns 12.0 kg of it each week. The school is offered a digester that would ferment the canteen's food scraps — which currently go to landfill — into biogas of energy value $22.0\ \text{kJ g}^{-1}$, supplying 20.0 kg of biogas each week.

a. Determine the percentage of the canteen's weekly energy demand that the biogas could supply.
b. With reference to two green chemistry principles, evaluate the biogas against LPG as the canteen's cooking fuel, and give a concluding statement.

Question 18 — A 0.920 g sample of a biofuel (which may be treated as ethanol, $M = 46.0\ \text{g mol}^{-1}$, $\Delta H_c = -1367\ \text{kJ mol}^{-1}$) is burned in a simple burner beneath a can holding 300.0 g of water. The water temperature rises from 19.0 °C to 34.0 °C.

a. Calculate the experimental energy value of the biofuel from the water data.
b. Calculate the true energy value of the biofuel from ΔH_c and M.
c. Hence calculate the energy transformation efficiency of the apparatus, and explain the difference between the two energy values.

Answers

1 a $15.4\ \text{kJ}$; b $17.5\ \text{kJ g}^{-1}$; c lower — heat is lost to the surroundings, so the measured value is a lower bound on the true value. **2** a $611\ \text{kJ}$; b 18.2%; c fats are the least-oxidised group, releasing more energy per gram on complete oxidation. **3** a $36.3\ \text{kJ}$; b $19.9\ \text{kJ}$; c 54.7%. **4** a $29.7\ \text{kJ g}^{-1}$; b $50.5\ \text{kJ g}^{-1}$; c propane delivers more energy per gram; ethanol is renewable (made by fermenting plant sugars). **5** a $10.9\ \text{kJ}$; b $9.88\ \text{kJ g}^{-1}$; c lower than $15.0\ \text{kJ g}^{-1}$ — heat lost to the surroundings (and any incomplete combustion) lowers the measured value. **6** a $277.5\ \text{kJ}$; b $124.9\ \text{kJ}$; c $14.9\ °\text{C}$. **7** $24.1\ \text{kJ}$. **8** $24.8\ \text{kJ g}^{-1}$. **9** $287\ \text{g}$. **10** 58.7%. **11** a $834\ \text{kJ}$; b 30.6%. **12** a food X $1060\ \text{kJ}$, food Y $1501\ \text{kJ}$ (per 100 g); b food Y ($15.0\ \text{kJ g}^{-1} > 10.6\ \text{kJ g}^{-1}$). **13** a $\text{C}_4\text{H}_{10}(\text{g}) + 13/2\,\text{O}_2(\text{g}) \rightarrow 4\,\text{CO}_2(\text{g}) + 5\,\text{H}_2\text{O}(\text{l})$, $\Delta H = -2877\ \text{kJ mol}^{-1}$; b $49.6\ \text{kJ g}^{-1}$. **14** a student A $12.0\ \text{kJ g}^{-1}$ (40.0%), student B $19.5\ \text{kJ g}^{-1}$ (65.0%); b the shield and lid cut the heat carried away by draughts, escaping hot gases and evaporation, so more of it reaches the water; heat is still lost to the can and the surroundings (and combustion may be incomplete), so the value stays below $30.0\ \text{kJ g}^{-1}$. **15** $42.1\ \text{g}$. **16** a option A $2060\ \text{kJ}$, option B $1756\ \text{kJ}$; b evaluation (A meets the energy target but 44.9% of its energy is fat; B is lower in energy but only 16.9% fat). **17** a 72.6%; b evaluation (prevention of wastes and use of renewable feedstocks vs an energy value less than half that of LPG, so the biogas cannot meet the whole demand). **18** a $20.4\ \text{kJ g}^{-1}$; b $29.7\ \text{kJ g}^{-1}$; c 68.8% — the difference is the chemical energy lost to the surroundings instead of the water.

Fully-worked solutions

Question 1 a. $\Delta T = 38.4 - 20.0 = 18.4\ °\text{C}$; $q = mc\,\Delta T = 200.0 \times 4.18 \times 18.4 = 15\,382\ \text{J} = 15.4\ \text{kJ}$. b. Energy value $= \dfrac{15.382\ \text{kJ}}{0.880\ \text{g}} = 17.5\ \text{kJ g}^{-1}$. c. The value is lower than the true energy value because much of the heat released by the burning fuel is lost to the surrounding air, the metal can and the escaping combustion gases instead of entering the water. The measured ΔT is therefore smaller than it would be if all the heat were captured, so q and the calculated energy value are too small.

Question 2 a. $E = (27.0 \times 16) + (4.0 \times 17) + (3.0 \times 37) = 432 + 68 + 111 = 611\ \text{kJ}$. b. From fat: $\dfrac{111}{611} \times 100 = 18.2\%$.

c. Complete combustion oxidises every carbon to CO_2 and every hydrogen to H_2O. The carbon atoms in a fat are less oxidised than those in a carbohydrate, and a fat has a greater proportion of energy-rich C–H and C–C bonds per gram, so more energy is released when it is fully oxidised — giving fat a higher energy value ($37\ \text{kJ g}^{-1}$ versus $16\ \text{kJ g}^{-1}$).

Question 3 a. $n = \dfrac{1.60}{32.0} = 0.0500\ \text{mol}$; chemical energy $= 0.0500 \times 726 = 36.3\ \text{kJ}$. b.
$q = mc\,\Delta T = 250.0 \times 4.18 \times (40.0 - 21.0) = 250.0 \times 4.18 \times 19.0 = 19\,855\ \text{J} = 19.9\ \text{kJ}$.
c. $\text{efficiency} = \dfrac{19.855}{36.3} \times 100 = 54.7\%$.

Question 4 a. Ethanol: energy value $= \dfrac{|\Delta H_c|}{M} = \dfrac{1367}{46.0} = 29.7\ \text{kJ g}^{-1}$. b. Propane: energy value $= \dfrac{2220}{44.0} = 50.5\ \text{kJ g}^{-1}$.

c. Propane delivers more energy per gram ($50.5 > 29.7\ \text{kJ g}^{-1}$). An advantage of ethanol is that it is renewable — it can be produced by fermenting plant sugars (bioethanol), whereas propane is obtained from finite fossil sources.

Question 5 a. $q = mc\,\Delta T = 100.0 \times 4.18 \times 26.0 = 10\,868\ \text{J} = 10.9\ \text{kJ}$. b. Energy value $= \dfrac{10.868\ \text{kJ}}{1.10\ \text{g}} = 9.88\ \text{kJ g}^{-1}$.

c. The experimental value ($9.88\ \text{kJ g}^{-1}$) is **lower** than the listed $15.0\ \text{kJ g}^{-1}$. In the open flame-heating apparatus, much of the heat is lost to the surroundings and the container, and combustion may be incomplete, so less heat reaches the water than the food's full energy content.

Question 6 a. $n = \dfrac{5.50}{44.0} = 0.125\ \text{mol}$; chemical energy $= 0.125 \times 2220 = 277.5\ \text{kJ}$. b. Useful heat
$= 0.450 \times 277.5 = 124.9\ \text{kJ}$. c. $\Delta T = \dfrac{q}{mc} = \dfrac{124\,875}{2000.0 \times 4.18} = \dfrac{124\,875}{8360} = 14.9\ °\text{C}$ (2.00 kg = 2000 g of water).

Question 7 $q = m\,c\,\Delta T = 180.0 \times 4.18 \times 32.0 = 24\,077\ \text{J} = 24.1\ \text{kJ}$.

Question 8 Energy value $= \dfrac{q}{m_{\text{fuel}}} = \dfrac{18.6\ \text{kJ}}{0.750\ \text{g}} = 24.8\ \text{kJ g}^{-1}$.

Question 9 $m = \dfrac{q}{c\,\Delta T} = \dfrac{30\,000}{4.18 \times 25.0} = \dfrac{30\,000}{104.5} = 287\ \text{g}$ (about 287 mL of water).

Question 10 $n = \dfrac{2.30}{46.0} = 0.0500\ \text{mol}$; chemical energy $= 0.0500 \times 1367 = 68.35\ \text{kJ}$.

$q = m\,c\,\Delta T = 400.0 \times 4.18 \times 24.0 = 40\,128\ \text{J} = 40.128\ \text{kJ}$. efficiency $= \dfrac{40.128}{68.35} \times 100 = 58.7\,\%$.

Question 11 a. $E = (20.0 \times 16) + (15.0 \times 17) + (7.0 \times 37) = 320 + 255 + 259 = 834\ \text{kJ}$. b. From protein: $\dfrac{255}{834} \times 100 = 30.6\,\%$.

Question 12 a. Food X: $E = (5.0 \times 16) + (25.0 \times 17) + (15.0 \times 37) = 80 + 425 + 555 = 1060\ \text{kJ}$ per 100 g. Food Y: $E = (70.0 \times 16) + (5.0 \times 17) + (8.0 \times 37) = 1120 + 85 + 296 = 1501\ \text{kJ}$ per 100 g. b. Per gram, food X $= 10.6\ \text{kJ g}^{-1}$ and food Y $= 15.0\ \text{kJ g}^{-1}$, so **food Y** has the greater energy value per gram — despite being carbohydrate-rich, its larger total mass of nutrients makes it the more energy-dense food.

Question 13 a. $\text{C}_4\text{H}_{10}(\text{g}) + 13/2\,\text{O}_2(\text{g}) \rightarrow 4\,\text{CO}_2(\text{g}) + 5\,\text{H}_2\text{O}(\text{l})$, $\Delta H = -2877\ \text{kJ mol}^{-1}$. b. Energy value $= \dfrac{|\Delta H_c|}{M} = \dfrac{2877}{58.0} = 49.6\ \text{kJ g}^{-1}$.

Question 14 a. Student A: energy value $= \dfrac{6.00\ \text{kJ}}{0.500\ \text{g}} = 12.0\ \text{kJ g}^{-1}$; captured $= \dfrac{12.0}{30.0} \times 100 = 40.0\,\%$. Student B: energy value $= \dfrac{9.75\ \text{kJ}}{0.500\ \text{g}} = 19.5\ \text{kJ g}^{-1}$; captured $= \dfrac{19.5}{30.0} \times 100 = 65.0\,\%$. b. The draught shield stops moving air from sweeping heat away from the flame and the can, and the lid keeps the hot combustion gases in contact with the can for longer while preventing heat loss by evaporation from the water surface. A greater share of the heat released therefore enters the water, giving a larger ΔT, a larger q and an energy value nearer the true one. It remains an underestimate because heat is still absorbed by the metal can and lost to the surrounding air, some hot gas still escapes, and combustion in an open flame may be incomplete (producing carbon monoxide and soot), so not all of the fuel's chemical energy is released to the water.

Question 15 Chemical energy required $= \dfrac{\text{useful energy}}{\text{efficiency}} = \dfrac{500}{0.400} = 1250\ \text{kJ}$. $n(\text{ethanol}) = \dfrac{1250}{1367} = 0.9144\ \text{mol}$; $m = n\,M = 0.9144 \times 46.0 = 42.1\ \text{g}$.

Question 16 a. Option A: $E = (55.0 \times 16) + (15.0 \times 17) + (25.0 \times 37) = 880 + 255 + 925 = 2060\ \text{kJ}$. Option B: $E = (70.0 \times 16) + (20.0 \times 17) + (8.0 \times 37) = 1120 + 340 + 296 = 1756\ \text{kJ}$. b. Against the energy target, option A (2060 kJ) is very close to the desired 2000 kJ, while option B (1756 kJ) falls a little short. Against the low-fat goal, however, option A obtains $\dfrac{925}{2060} \times 100 = 44.9\,\%$ of its energy from fat, whereas option B obtains only $\dfrac{296}{1756} \times 100 = 16.9\,\%$ from fat. The two goals conflict: A meets the energy need but is high in fat, while B is much lower in fat but supplies less energy. Recommendation: option B is the better choice for a low-fat breakfast, with the small energy shortfall made up by a carbohydrate-rich addition (such as fruit) rather than by fat.

Question 17 a. Weekly energy demand $= 1.20 \times 10^4\ \text{g} \times 50.5\ \text{kJ g}^{-1} = 6.06 \times 10^5\ \text{kJ}$. Energy available from the biogas $= 2.00 \times 10^4\ \text{g} \times 22.0\ \text{kJ g}^{-1} = 4.40 \times 10^5\ \text{kJ}$.

$$\frac{4.40\times10^{5}}{6.06\times10^{5}}\times100=72.6\,\%$$

b. Against the green chemistry principle of **prevention of wastes**, the food scraps currently go to landfill, where they decompose anaerobically and release methane — a far more potent greenhouse gas than CO_2 — straight to the atmosphere. The digester captures that methane and burns it to CO_2 and water, so a waste stream becomes the fuel itself rather than a problem to be cleaned up afterwards. Against the principle of **use of renewable feedstocks**, the scraps come from crops grown within the last season and are replenished every week the canteen operates, whereas LPG is a finite fossil fraction; the CO_2 released when the biogas burns was recently taken from the atmosphere by those crops, so its *net* carbon emissions are much lower. Set against this, the biogas has less than half the energy value of LPG (22.0 against $50.5\,\text{kJ g}^{-1}$), so a much greater mass must be burned for the same heat, and even all 20.0 kg of it meets only 72.6% of the canteen's demand — LPG would still be needed for the remaining 27.4%. Biogas is also a low-density gas that must be stored under pressure, and its energy value varies with the methane content of whatever is fed to the digester. Concluding statement: the digester should be installed and the canteen run on biogas with LPG as a top-up, because the waste-prevention and renewable-feedstock gains outweigh the lower energy value, which costs only a larger mass of fuel rather than any loss of heat delivered.

Question 18 a. $\Delta T = 34.0 - 19.0 = 15.0\,°\text{C}$; $q = m\,c\,\Delta T = 300.0\times4.18\times15.0 = 18\,810\,\text{J} = 18.81\,\text{kJ}$. Experimental energy value $= \dfrac{18.81\,\text{kJ}}{0.920\,\text{g}} = 20.4\,\text{kJ g}^{-1}$. b. True energy value $= \dfrac{|\Delta H_c|}{M} = \dfrac{1367}{46.0} = 29.7\,\text{kJ g}^{-1}$.

c. $n = \dfrac{0.920}{46.0} = 0.0200\,\text{mol}$; chemical energy $= 0.0200\times1367 = 27.34\,\text{kJ}$; $\text{efficiency} = \dfrac{18.81}{27.34}\times100 = 68.8\,\%$. The experimental energy value ($20.4\,\text{kJ g}^{-1}$) is smaller than the true value ($29.7\,\text{kJ g}^{-1}$) because only 68.8% of the chemical energy released reaches the water; the remaining 31.2% is lost to the surroundings, the container and the escaping combustion gases.