

Chemical energetics: enthalpy changes and Hess's law (AS Chemistry notes)

These notes cover the AS part of the Chemical energetics topic in Cambridge International AS and A Level Chemistry (9701). You will learn what an enthalpy change is, how to tell exothermic from endothermic reactions, the standard definitions examiners expect word for word, how to work out enthalpy changes from experiments, how to use Hess's law with formation and combustion data, and how to use bond energies. Learn the boxed definitions exactly, then practise the worked examples.

Throughout, numerical data are given in each example or question. In the exam, bond energies come from the Data Booklet supplied with the paper, and other values (such as enthalpy changes of formation or combustion) are given in the question. The data used here are typical values; small differences from the Data Booklet do not change the method.

1. Enthalpy change, exothermic and endothermic reactions

1.1 What enthalpy change means

Every substance stores chemical energy in its bonds and in the arrangement of its particles. We cannot measure this total energy directly, but we can measure how much heat energy is transferred to or from the surroundings when a reaction happens at constant pressure. This heat energy transfer is called the **enthalpy change**, symbol ΔH , measured in kJ mol^{-1} .

Enthalpy change, ΔH : the heat energy transferred between a chemical system and its surroundings during a reaction carried out at constant pressure.

The "system" is the reacting chemicals. The "surroundings" are everything else: the solvent, the container and the air.

1.2 Exothermic reactions

In an **exothermic** reaction, heat energy is transferred from the system to the surroundings. The products have less enthalpy than the reactants, so ΔH is **negative**. The temperature of the surroundings (for example the solution in a calorimeter) rises.

Examples: combustion of fuels, neutralisation of an acid by an alkali, the reaction of reactive metals with acids or water, respiration, and the formation of most compounds from their elements.

1.3 Endothermic reactions

In an **endothermic** reaction, heat energy is transferred from the surroundings to the system. The products have more enthalpy than the reactants, so ΔH is **positive**. The temperature of the surroundings falls.

Examples: thermal decomposition of calcium carbonate, photosynthesis, dissolving ammonium nitrate in water, and breaking any chemical bond (such as atomising an element).

Exam tip: always write the sign of ΔH . An answer of " 56 kJ mol^{-1} " for a neutralisation will lose the mark because the correct answer is -56 kJ mol^{-1} . Put a + sign in front of positive values too, for



example $+178 \text{ kJ mol}^{-1}$.

1.4 Bond breaking and bond making

Energy changes in reactions come from bonds. Breaking a bond always **needs** energy (endothermic) because work must be done to pull the atoms apart against the attraction between them. Making a bond always **releases** energy (exothermic).

- If more energy is released making the new bonds in the products than is needed to break the bonds in the reactants, the reaction is exothermic overall.
- If more energy is needed to break the bonds in the reactants than is released making bonds in the products, the reaction is endothermic overall.

1.5 Reaction pathway diagrams and activation energy

A reaction pathway diagram (energy profile) plots enthalpy on the vertical axis against the progress of the reaction on the horizontal axis.

- For an exothermic reaction, the products line is **below** the reactants line. ΔH is drawn as a downward arrow from reactants to products.
- For an endothermic reaction, the products line is **above** the reactants line. ΔH is drawn as an upward arrow.
- In both cases the curve rises to a peak between reactants and products. The height of this peak above the reactants is the activation energy, E_a .

Activation energy, E_a : the minimum energy that colliding particles must have for a reaction to occur.

Activation energy explains why some very exothermic reactions, such as methane burning in air, do not start until a spark or flame is supplied.

2. Standard conditions and standard enthalpy changes

2.1 Why we need standard conditions

The size of an enthalpy change depends on the temperature, the pressure, the concentrations of solutions and the physical states of the substances. For example, burning hydrogen to make liquid water releases more energy than burning it to make steam, because energy is also released when steam condenses. To compare values fairly, chemists quote enthalpy changes under agreed standard conditions.

Standard conditions: a temperature of 298 K (25 °C) and a pressure of 101 kPa, with any solutions at a concentration of 1 mol dm^{-3} , and each substance in its standard state (its normal physical state under these conditions).

An enthalpy change measured under standard conditions is shown with the standard symbol, written $\Delta H^\ominus$ (said "delta H standard"). A subscript shows which type of change it is: $\Delta H_f^\ominus$ for formation, $\Delta H_c^\ominus$ for combustion, and so on. The standard state of carbon is graphite, of oxygen is $\text{O}_2(\text{g})$, of bromine is $\text{Br}_2(\text{l})$ and of water is $\text{H}_2\text{O}(\text{l})$.

2.2 Standard enthalpy change of reaction

Standard enthalpy change of reaction, $\Delta H_r^\ominus$: the enthalpy change when the amounts of reactants shown in the balanced equation react together under standard conditions, with all substances in their standard states.

Because ΔH_r refers to the equation as written, doubling the equation doubles ΔH , and reversing the equation reverses the sign of ΔH . Always quote the equation with a ΔH_r value.

2.3 Standard enthalpy change of formation

Standard enthalpy change of formation, $\Delta H_f^\ominus$: the enthalpy change when one mole of a compound is formed from its elements under standard conditions, with all reactants and products in their standard states.

Key points:

- Exactly one mole of product is formed, so fractions are often needed in the equation. For water: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$.
- The reactants must be elements in their standard states. For ethanol: $2\text{C}(\text{s}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$.
- The enthalpy change of formation of an element in its standard state is zero by definition, because forming the element from itself involves no change. So $\Delta H_f^\ominus$ of $\text{O}_2(\text{g})$, $\text{H}_2(\text{g})$, $\text{C}(\text{s, graphite})$ and $\text{Fe}(\text{s})$ are all 0.
- Many formation reactions cannot be carried out directly in a laboratory (you cannot make methane by mixing carbon and hydrogen), so their values are found by Hess's law.

2.4 Standard enthalpy change of combustion

Standard enthalpy change of combustion, $\Delta H_c^\ominus$: the enthalpy change when one mole of a substance is burned completely in excess oxygen under standard conditions, with all reactants and products in their standard states.

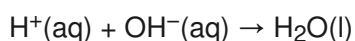
Key points:

- One mole of the substance being burned, so the oxygen may have a fractional coefficient. For ethane: $\text{C}_2\text{H}_6(\text{g}) + 3\frac{1}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$.
- "Completely" means all carbon ends up as CO_2 and all hydrogen as H_2O . Water is a liquid under standard conditions, so write $\text{H}_2\text{O}(\text{l})$.
- Combustion enthalpies are always negative (combustion is always exothermic).
- Note that $\Delta H_c^\ominus$ of carbon (graphite) is the same reaction as $\Delta H_f^\ominus$ of CO_2 , and $\Delta H_c^\ominus$ of hydrogen is the same as $\Delta H_f^\ominus$ of $\text{H}_2\text{O}(\text{l})$.

2.5 Standard enthalpy change of neutralisation

Standard enthalpy change of neutralisation, $\Delta H_{\text{neut}}^\ominus$: the enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions.

For any strong acid with any strong alkali, the reaction is really the same ionic reaction:



so the value is almost the same each time, about -57 kJ mol^{-1} . With sulfuric acid, one mole of H_2SO_4 gives two moles of water, so the enthalpy change for the full equation is double, but ΔH_{neut} (per mole of water) is unchanged.

With a **weak** acid such as ethanoic acid, or a weak alkali such as ammonia, the value is slightly **less exothermic**. The weak acid is only partly ionised, and some energy is used to complete its ionisation as the H^+ ions are removed. This absorbs some of the energy released when water forms.

2.6 Enthalpy change of atomisation

Standard enthalpy change of atomisation, $\Delta H_{\text{at}}^\ominus$: the enthalpy change when one mole of gaseous atoms is formed from the element in its standard state under standard conditions.

Examples:

- $\text{Na}(\text{s}) \rightarrow \text{Na}(\text{g})$
- $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$
- $\frac{1}{2}\text{Br}_2(\text{l}) \rightarrow \text{Br}(\text{g})$
- $\text{C}(\text{s, graphite}) \rightarrow \text{C}(\text{g})$

Atomisation is always endothermic, because bonds (metallic or covalent) and any intermolecular forces must be overcome. Notice that the definition is per mole of **atoms** formed. For chlorine, ΔH_{at} is half of the $\text{Cl}-\text{Cl}$ bond energy, because breaking one mole of $\text{Cl}-\text{Cl}$ bonds gives two moles of Cl atoms. For bromine, ΔH_{at} also includes the energy needed to vaporise the liquid.

2.7 Bond energy

Bond energy (bond enthalpy): the energy needed to break one mole of a particular covalent bond in gaseous molecules, forming gaseous atoms.

For a diatomic molecule such as H_2 or HCl , there is only one kind of bond and the bond energy is an exact value for that molecule: $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$.

For bonds that appear in many different molecules, such as $\text{C}-\text{H}$ or $\text{C}-\text{C}$, the strength of the bond changes slightly with its environment. The $\text{C}-\text{H}$ bond in methane is not quite the same as the $\text{C}-\text{H}$ bond in ethanol. The Data Booklet therefore lists an **average bond energy**: the mean value for that bond over a range of compounds.

Average bond energy: the energy needed to break one mole of a particular type of covalent bond, averaged over a range of different gaseous compounds containing that bond.

Bond energies are always positive because breaking a bond is always endothermic. Multiple bonds are stronger than single bonds between the same atoms ($\text{C}\equiv\text{C} > \text{C}=\text{C} > \text{C}-\text{C}$), and bond energy generally falls as bond length increases (for example $\text{H}-\text{Cl} > \text{H}-\text{Br} > \text{H}-\text{I}$).

3. Measuring enthalpy changes by calorimetry

3.1 The equation $q = mc\Delta T$

In a calorimetry experiment the reaction heats (or cools) a known mass of water or solution. We measure the temperature change and calculate the heat energy transferred:

$$q = mc\Delta T$$

q = heat energy transferred, in J

m = mass of the water or solution being heated, in g

c = specific heat capacity, in $\text{J g}^{-1} \text{K}^{-1}$ ($4.18 \text{ J g}^{-1} \text{K}^{-1}$ for water and dilute aqueous solutions)

ΔT = temperature change, in K (a change of 1 K is the same as a change of 1°C)

Then the enthalpy change per mole is:

$$\Delta H = -q \div n$$

where n is the number of moles of the reactant that is fully used up (the limiting reactant) or of the product stated in the definition. Convert q from J to kJ by dividing by 1000. The minus sign is there because if the solution gets hotter (q positive) the reaction is exothermic (ΔH negative).

3.2 Assumptions for reactions in solution

- The density of the dilute solution is 1.00 g cm^{-3} , so 50.0 cm^3 of solution has a mass of 50.0 g .
- The specific heat capacity of the solution is the same as that of water, $4.18 \text{ J g}^{-1} \text{K}^{-1}$.
- All the heat released is absorbed by the solution: none is lost to the surroundings or absorbed by the cup.
- The mass of any solid added (for example zinc powder) is ignored because it is small and its heat capacity is small compared with the water.

A polystyrene cup with a lid is used because polystyrene is a good insulator and has a very low heat capacity. For more accurate work, a temperature-time graph is extrapolated back to the time of mixing to correct for heat loss.

Worked example 1: enthalpy change of neutralisation

50.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid was mixed with 50.0 cm^3 of 1.00 mol dm^{-3} sodium hydroxide in a polystyrene cup. The temperature rose by 6.8°C . Calculate the enthalpy change of neutralisation.

Step 1, mass of solution: $50.0 + 50.0 = 100.0 \text{ cm}^3$, so $m = 100.0 \text{ g}$.

Step 2, heat transferred: $q = 100.0 \times 4.18 \times 6.8 = 2842 \text{ J} = 2.842 \text{ kJ}$.

Step 3, moles of water formed: $n(\text{HCl}) = 1.00 \times 50.0/1000 = 0.0500 \text{ mol}$, $n(\text{NaOH}) = 0.0500 \text{ mol}$, so 0.0500 mol of H_2O forms.

Step 4, $\Delta H = -2.842 \div 0.0500 = -56.8 \text{ kJ mol}^{-1}$.

Note that the mass is the **total** volume of both solutions, because both are heated.

3.3 Measuring enthalpy changes of combustion

To measure ΔH_c of a liquid fuel such as an alcohol, a spirit burner containing the fuel is weighed, used

to heat a known mass of water in a metal can (copper or aluminium), and weighed again. The loss in mass gives the mass of fuel burned.

Worked example 2: enthalpy change of combustion of ethanol

Burning 0.920 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$, raised the temperature of 200 g of water by 25.0 °C. Calculate ΔH_c of ethanol. (M_r of ethanol = 46.0)

Step 1: $q = 200 \times 4.18 \times 25.0 = 20\,900 \text{ J} = 20.9 \text{ kJ}$.

Step 2: $n(\text{ethanol}) = 0.920 \div 46.0 = 0.0200 \text{ mol}$.

Step 3: $\Delta H_c = -20.9 \div 0.0200 = -1045 \text{ kJ mol}^{-1}$, which is $-1050 \text{ kJ mol}^{-1}$ to 3 significant figures.

Note that here m is the mass of **water**, not the mass of fuel. A common mistake is to use 0.920 g in $q = mc\Delta T$.

The experimental value is much less exothermic than the data book value (about $-1367 \text{ kJ mol}^{-1}$). The main reasons are:

- heat is lost to the surroundings (the air, the can and the clamp) instead of heating the water;
- incomplete combustion, producing carbon (soot) or carbon monoxide, which releases less energy;
- some fuel evaporates from the wick without burning, so the mass "burned" is overestimated;
- the water formed is a gas, not a liquid as in standard conditions, so the energy from condensation is not released.

4. Hess's law

4.1 Statement of Hess's law

Hess's law: the total enthalpy change for a chemical reaction is independent of the route by which the reaction takes place, provided the initial and final conditions are the same.

Hess's law is a consequence of the conservation of energy.

Hess's law lets us find enthalpy changes that cannot be measured directly, for example:

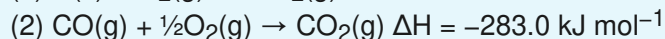
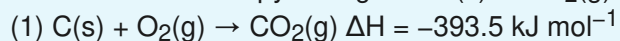
- reactions that are too slow, or that need a high activation energy, such as the formation of methane from carbon and hydrogen;
- reactions that give a mixture of products, such as burning carbon to make only carbon monoxide (some CO_2 always forms too);
- reactions that are hazardous or difficult to control.

4.2 Rules for manipulating equations

- If you reverse an equation, change the sign of ΔH .
- If you multiply an equation by a number, multiply ΔH by the same number.
- If you add equations together, add their ΔH values.

Worked example 3: combining given equations

Calculate the enthalpy change for $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$, given:



We need CO on the right, so reverse equation (2): $\text{CO}_2\text{(g)} \rightarrow \text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \quad \Delta H = +283.0 \text{ kJ mol}^{-1}$.

Add (1) and reversed (2): $\text{C(s)} + \text{O}_2\text{(g)} + \text{CO}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + \text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)}$.

Cancel CO_2 and $\frac{1}{2}\text{O}_2$ on both sides: $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$.

$$\Delta H = -393.5 + 283.0 = -110.5 \text{ kJ mol}^{-1}.$$

4.3 Hess cycles using enthalpy changes of formation

When you are given ΔH_f values, draw a triangle with the reactants at top left, the products at top right, and the **elements** at the bottom. Arrows go **up** from the elements to both the reactants and the products, because formation goes from elements to compounds.

Going round the cycle, the direct route (reactants $\rightarrow$ products) equals the indirect route (reactants $\rightarrow$ elements $\rightarrow$ products). Going from reactants down to elements is the reverse of formation, so its sign is changed. This gives the general result:

From formation data: $\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$

Remember to multiply each ΔH_f by the number of moles in the equation, and that ΔH_f of any element in its standard state is zero.

Worked example 4: using formation data

Calculate ΔH_r for the hydrogenation of ethene: $\text{C}_2\text{H}_4\text{(g)} + \text{H}_2\text{(g)} \rightarrow \text{C}_2\text{H}_6\text{(g)}$

Data: $\Delta H_f^\ominus(\text{C}_2\text{H}_4, \text{g}) = +52.3 \text{ kJ mol}^{-1}$, $\Delta H_f^\ominus(\text{C}_2\text{H}_6, \text{g}) = -84.7 \text{ kJ mol}^{-1}$.

Cycle: elements $2\text{C(s)} + 3\text{H}_2\text{(g)}$ at the bottom. Arrow up to reactants: $+52.3$ (H_2 is an element, contributes 0). Arrow up to products: -84.7 .

$$\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}) = (-84.7) - (+52.3 + 0) = -137.0 \text{ kJ mol}^{-1}.$$

Worked example 5: formation data with several moles

Calculate ΔH_r for: $\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$

Data (kJ mol^{-1}): $\Delta H_f(\text{CH}_4) = -74.8$, $\Delta H_f(\text{CO}_2) = -393.5$, $\Delta H_f(\text{H}_2\text{O, l}) = -285.8$.

$$\text{Products: } -393.5 + 2(-285.8) = -965.1$$

$$\text{Reactants: } -74.8 + 2(0) = -74.8$$

$$\Delta H_r = -965.1 - (-74.8) = -890.3 \text{ kJ mol}^{-1}. \text{ This is } \Delta H_c \text{ of methane.}$$

4.4 Hess cycles using enthalpy changes of combustion

When you are given ΔH_c values, draw the triangle with the reactants at top left, the products at top right and the **combustion products** (CO_2 and H_2O) at the bottom. Arrows go **down** from both reactants and products to the combustion products, because combustion goes from the substance to its oxides.

The direct route plus the route down from the products equals the route down from the reactants, which gives:

From combustion data: $\Delta H_r = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products})$

Note this is the opposite way round from the formation formula. Oxygen has no combustion enthalpy (it does not burn), and neither do CO_2 or H_2O .

Worked example 6: enthalpy change of formation of methane from combustion data

Calculate ΔH_f of methane: $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$

Data (kJ mol^{-1}): $\Delta H_c(\text{C, graphite}) = -393.5$, $\Delta H_c(\text{H}_2) = -285.8$, $\Delta H_c(\text{CH}_4) = -890.3$.

Cycle: $\text{C}(\text{s}) + 2\text{H}_2(\text{g})$ at top left, $\text{CH}_4(\text{g})$ at top right, $\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ at the bottom.

Reactants down: $-393.5 + 2(-285.8) = -965.1$

Products down: -890.3

$\Delta H_f = \sum \Delta H_c(\text{reactants}) - \sum \Delta H_c(\text{products}) = -965.1 - (-890.3) = -74.8 \text{ kJ mol}^{-1}$.

Exam tip for cycles: (1) write the target equation across the top, (2) put elements (formation data) or combustion products (combustion data) at the bottom, (3) draw arrows in the direction the data refer to, (4) multiply each value by its number of moles, (5) when you travel against an arrow, change its sign. Show the cycle in your working: it earns method marks even if the arithmetic goes wrong.

5. Calculations using bond energies

5.1 Method

Imagine a reaction happening in two steps: first all the bonds in the reactants are broken to give gaseous atoms (endothermic), then all the bonds in the products are formed from those atoms (exothermic). By Hess's law:

From bond energies: $\Delta H_r = \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds made})$

Equivalently: $\Delta H_r = \text{energy in to break bonds} - \text{energy out from making bonds}$.

Draw the displayed formula of every molecule so that you count every bond. It is often quicker to count only the bonds that actually change, but counting every bond on both sides always gives the right answer.

Worked example 7: combustion of methane

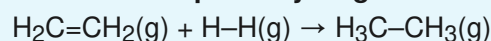
$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

Bond energies (kJ mol^{-1} , values for this example): C–H 410, O=O 496, C=O in CO_2 805, O–H 460.

Bonds broken: $4 \text{ C–H} + 2 \text{ O=O} = 4(410) + 2(496) = 1640 + 992 = 2632 \text{ kJ}$

Bonds made: $2 \text{ C=O} + 4 \text{ O–H} = 2(805) + 4(460) = 1610 + 1840 = 3450 \text{ kJ}$

$\Delta H_r = 2632 - 3450 = -818 \text{ kJ mol}^{-1}$.

Worked example 8: hydrogenation of ethene

 Bond energies (kJ mol^{-1}): C=C 610, H-H 436, C-C 350, C-H 410.

Only count the bonds that change. The four C-H bonds in ethene remain in ethane.

Bonds broken: C=C + H-H = 610 + 436 = 1046 kJ

Bonds made: C-C + 2 C-H = 350 + 2(410) = 1170 kJ

 $\Delta H_r = 1046 - 1170 = -124 \text{ kJ mol}^{-1}$.

5.2 Working backwards to find a bond energy

 If ΔH for a reaction is known, a single unknown bond energy can be found by rearranging the same equation.

Worked example 9: finding an unknown bond energy

 For $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$, $\Delta H = -103 \text{ kJ mol}^{-1}$. Given H-H = 436 and Br-Br = 193 kJ mol^{-1} , calculate the H-Br bond energy.

Bonds broken: 436 + 193 = 629 kJ

Bonds made: 2x

 $629 - 2x = -103$, so $2x = 732$ and $x = +366 \text{ kJ mol}^{-1}$.

Note that bromine must be gaseous here for the bond energy to apply directly.

5.3 Limits of bond-energy calculations

 Values from bond energies often differ from values found using enthalpies of formation or measured accurately in a calorimeter. In Worked example 7 the answer of -818 kJ mol^{-1} differs from the value of about -802 kJ mol^{-1} found from formation data for the same equation with $\text{H}_2\text{O}(\text{g})$. The reasons are:

- **Average values:** most bond energies in the Data Booklet are averages over many compounds. The actual strength of a bond in a particular molecule is slightly different from the average.
- **Gaseous state only:** bond energies apply to molecules in the gas phase. If any reactant or product is a liquid or solid, extra energy changes (for example vaporisation or condensation, which involve intermolecular forces) are not included. That is why Worked example 7 used $\text{H}_2\text{O}(\text{g})$: the standard ΔH_c of methane, with $\text{H}_2\text{O}(\text{l})$, is more exothermic (-890 kJ mol^{-1}) because energy is also released when the steam condenses.
- **Non-standard conditions:** bond energies do not refer to standard conditions in the same way as ΔH_f and ΔH_c .

 Values calculated from ΔH_f or ΔH_c data are therefore more reliable than values from average bond energies.

6. Summary of the key formulae

Situation	Formula	Watch out for
Calorimetry	$q = mc\Delta T$, then $\Delta H = -q \div n$	m is the mass of water or solution; convert J to kJ; give the sign

Formation data	$\Delta H_r = \Sigma \Delta H_f(\text{products}) - \Sigma \Delta H_f(\text{reactants})$	elements are zero; multiply by moles
Combustion data	$\Delta H_r = \Sigma \Delta H_c(\text{reactants}) - \Sigma \Delta H_c(\text{products})$	opposite order to formation; O_2 , CO_2 , H_2O have no ΔH_c
Bond energies	$\Delta H_r = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$	gases only; average values; draw displayed formulae
Combining equations	reverse: change sign; multiply: multiply ΔH ; add equations: add ΔH	check the final equation matches the target

Quick check

Answer all questions. Use $c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$ and assume dilute solutions have a density of 1.00 g cm^{-3} . Where bond energies are needed, use the values given in the question.

1. Define the term *standard enthalpy change of formation*. [3]
2. Write a balanced equation, with state symbols, for the reaction that represents the standard enthalpy change of formation of ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$. Then write the equation for the standard enthalpy change of combustion of ethanol. [3]
3. State the value of $\Delta H_f^\ominus$ of oxygen gas and explain your answer. [2]
4. Describe a reaction pathway diagram for an endothermic reaction, labelling ΔH and E_a . Explain, in terms of bond breaking and bond making, why the reaction is endothermic. [4]
5. 25.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid was added to 25.0 cm^3 of 2.00 mol dm^{-3} potassium hydroxide. The temperature rose by 13.4°C . Calculate the enthalpy change of neutralisation. [3]
6. Explain why the enthalpy change of neutralisation of ethanoic acid by sodium hydroxide is less exothermic than that of hydrochloric acid by sodium hydroxide. [2]
7. Burning 0.600 g of propan-1-ol, $\text{C}_3\text{H}_7\text{OH}$ ($M_r = 60.0$), raised the temperature of 150 g of water from 20.0°C to 47.5°C .
 - (a) Calculate the enthalpy change of combustion of propan-1-ol. [3]
 - (b) The data book value is about $-2020 \text{ kJ mol}^{-1}$. Suggest two reasons for the difference. [2]
8. Excess zinc powder was added to 50.0 cm^3 of $0.200 \text{ mol dm}^{-3}$ copper(II) sulfate solution. The temperature rose by 10.2°C .
 - (a) Calculate ΔH for $\text{Zn}(\text{s}) + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu}(\text{s})$. [3]
 - (b) Explain why zinc is added in excess. [1]
9. State Hess's law. [2]
10. Use the data to calculate ΔH_r for $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$.
 $\Delta H_f^\ominus / \text{kJ mol}^{-1}$: $\text{Fe}_2\text{O}_3(\text{s}) -824.2$; $\text{CO}(\text{g}) -110.5$; $\text{CO}_2(\text{g}) -393.5$. [3]
11. Use the combustion data to calculate the standard enthalpy change of formation of ethanol.
 $\Delta H_c^\ominus / \text{kJ mol}^{-1}$: $\text{C}(\text{s}) -393.5$; $\text{H}_2(\text{g}) -285.8$; $\text{C}_2\text{H}_5\text{OH}(\text{l}) -1367.3$. [3]
12. The enthalpy change for $\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$ cannot be measured directly.
 - (a) Explain why. [1]
 - (b) Use these data to calculate it: $\Delta H_c(\text{C}) = -393.5 \text{ kJ mol}^{-1}$; $\Delta H_c(\text{CO}) = -283.0 \text{ kJ mol}^{-1}$. [2]
13. Use bond energies to calculate ΔH for $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$.

Bond energies / kJ mol^{-1} : H–H 436; Cl–Cl 242; H–Cl 431. [2]

14. For $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, $\Delta H = -92 \text{ kJ mol}^{-1}$. Given $\text{N}\equiv\text{N} = 945 \text{ kJ mol}^{-1}$ and $\text{H–H} = 436 \text{ kJ mol}^{-1}$, calculate the N–H bond energy. [3]
15. (a) Define the term *standard enthalpy change of atomisation*. [2]
 (b) The Cl–Cl bond energy is 242 kJ mol^{-1} . Deduce $\Delta H_{\text{at}}^\ominus$ of chlorine and explain your answer. [2]
 (c) A student calculates ΔH_c of propane using average bond energies and gets a value different from the data book value. Give two reasons. [2]

Answers

1. The enthalpy change when one mole of a compound is formed from its elements [1], under standard conditions of 298 K and 101 kPa [1], with all reactants and products in their standard states [1].
2. Formation: $2\text{C}(\text{s}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$. One mole of ethanol from elements in standard states, so $\frac{1}{2}\text{O}_2$ is needed.
 Combustion: $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$. Check oxygen atoms: left $1 + 6 = 7$, right $4 + 3 = 7$.
3. $\Delta H_f^\ominus(\text{O}_2, \text{g}) = 0$. Oxygen gas is an element in its standard state, so forming it from itself involves no chemical change and no enthalpy change.
4. Enthalpy on the vertical axis, progress of reaction on the horizontal axis. The products line is higher than the reactants line. The curve rises from reactants to a peak and falls to products. E_a is an upward arrow from the reactants level to the top of the peak. ΔH is an upward arrow from the reactants level to the products level, labelled as positive. The reaction is endothermic because the energy needed to break the bonds in the reactants is greater than the energy released when the bonds in the products are made.
5. Total volume = 50.0 cm^3 , so $m = 50.0 \text{ g}$.
 $q = 50.0 \times 4.18 \times 13.4 = 2801 \text{ J} = 2.801 \text{ kJ}$.
 $n(\text{HCl}) = 2.00 \times 25.0/1000 = 0.0500 \text{ mol} = n(\text{KOH})$, so $0.0500 \text{ mol H}_2\text{O}$ forms.
 $\Delta H_{\text{neut}} = -2.801 \div 0.0500 = -56.0 \text{ kJ mol}^{-1}$.
6. Ethanoic acid is a weak acid and is only partly ionised in solution. As H^+ ions react, more acid molecules ionise, and this ionisation absorbs energy (it is endothermic). So less overall energy is released per mole of water formed.
7. (a) $\Delta T = 47.5 - 20.0 = 27.5 \text{ K}$.
 $q = 150 \times 4.18 \times 27.5 = 17\,243 \text{ J} = 17.24 \text{ kJ}$.
 $n(\text{propan-1-ol}) = 0.600 \div 60.0 = 0.0100 \text{ mol}$.
 $\Delta H_c = -17.24 \div 0.0100 = -1724 \text{ kJ mol}^{-1}$, which is $-1720 \text{ kJ mol}^{-1}$ to 3 significant figures.
 (b) Any two: heat lost to the surroundings (air, can, clamp); incomplete combustion producing carbon or carbon monoxide; evaporation of fuel from the wick so less fuel burned than the mass loss suggests; water produced as a gas, not a liquid; heat absorbed by the can is not included in the calculation.
8. (a) $q = 50.0 \times 4.18 \times 10.2 = 2132 \text{ J} = 2.132 \text{ kJ}$.
 $n(\text{CuSO}_4) = 0.200 \times 50.0/1000 = 0.0100 \text{ mol}$. Zinc is in excess, so copper(II) sulfate is limiting.
 $\Delta H = -2.132 \div 0.0100 = -213 \text{ kJ mol}^{-1}$.

(b) So that all the copper(II) ions react. Then the number of moles reacting is known exactly from the copper(II) sulfate solution.

9. The total enthalpy change for a reaction is independent of the route taken [1], provided the initial and final conditions are the same [1].

10. $\Delta H_r = \Sigma \Delta H_f(\text{products}) - \Sigma \Delta H_f(\text{reactants})$.

Products: $2(0) + 3(-393.5) = -1180.5 \text{ kJ}$ (Fe is an element).

Reactants: $-824.2 + 3(-110.5) = -824.2 - 331.5 = -1155.7 \text{ kJ}$.

$\Delta H_r = -1180.5 - (-1155.7) = -24.8 \text{ kJ mol}^{-1}$.

11. Target: $2\text{C(s)} + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH(l)}$. Cycle with $2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O(l)}$ at the bottom.

$\Delta H_f = \Sigma \Delta H_c(\text{reactants}) - \Sigma \Delta H_c(\text{products})$.

Reactants: $2(-393.5) + 3(-285.8) + 0 = -787.0 - 857.4 = -1644.4 \text{ kJ}$.

Products: -1367.3 kJ .

$\Delta H_f = -1644.4 - (-1367.3) = -277.1 \text{ kJ mol}^{-1}$.

12. (a) When carbon burns, some carbon dioxide always forms as well as carbon monoxide, so the reaction cannot be made to give only CO.

(b) $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ $\Delta H = -393.5$. Reverse the CO combustion: $\text{CO}_2(\text{g}) \rightarrow \text{CO(g)} + \frac{1}{2}\text{O}_2(\text{g})$ $\Delta H = +283.0$. Adding: $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}$, $\Delta H = -393.5 + 283.0 = -110.5 \text{ kJ mol}^{-1}$.

13. Bonds broken: $\text{H-H} + \text{Cl-Cl} = 436 + 242 = 678 \text{ kJ}$.

Bonds made: $2 \text{ H-Cl} = 2(431) = 862 \text{ kJ}$.

$\Delta H = 678 - 862 = -184 \text{ kJ mol}^{-1}$.

14. Bonds broken: $\text{N}\equiv\text{N} + 3 \text{ H-H} = 945 + 3(436) = 945 + 1308 = 2253 \text{ kJ}$.

Bonds made: 2NH_3 contain 6 N-H bonds, so $6x$.

$2253 - 6x = -92$, so $6x = 2345$ and $x = 391 \text{ kJ mol}^{-1}$ (390.8).

15. (a) The enthalpy change when one mole of gaseous atoms is formed from the element in its standard state [1], under standard conditions [1].

(b) $\Delta H_{\text{at}}^\ominus = +121 \text{ kJ mol}^{-1}$. Breaking one mole of Cl-Cl bonds (242 kJ) gives two moles of Cl atoms, but atomisation is defined per mole of atoms formed: $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl(g)}$, so the value is $242 \div 2 = +121 \text{ kJ mol}^{-1}$. Chlorine is already a gas, so no vaporisation energy is needed.

(c) Bond energies are average values over a range of compounds, so they are not exact for the bonds in propane, CO_2 and H_2O . Bond energies apply only to gases, but standard combustion produces liquid water, so the energy released on condensation is not included.