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IB DIPLOMA CHEMISTRY · FIRST ASSESSMENT 2025

Reactivity 1.2
Energy Cycles in Reactions

Booklet 2 · Understandings 1.2.1 – 1.2.2

Bond enthalpy: why breaking bonds absorbs energy and making bonds releases it, calculating ΔH from average bond enthalpies, and Hess's law with equations, cycles and energy level diagrams

Complete revision notes, worked examples, model answers & practice questions · Standard Level & Higher Level

How the level tags work in this booklet

SL + HL Understandings 1.2.1 (bond enthalpy) and 1.2.2 (Hess's law) are common to both levels. Every student must know this booklet.

HL The additional higher level understandings 1.2.3 – 1.2.5 (standard enthalpies of formation and combustion in cycles, and Born–Haber cycles) follow in **Booklet 3**. ★ marks harder, multi-step practice questions.

Inside this booklet

1. What the syllabus actually asks of you
2. 1.2.1 — Bond breaking, bond making and bond enthalpy
3. 1.2.1 — Calculating ΔH from bond enthalpies
4. 1.2.2 — Hess's law
5. 1.2.2 — Hess's law method 1: combining equations
6. 1.2.2 — Hess's law method 2: cycles and level diagrams
7. 1.2.2 — Hess's law in the laboratory
8. Key points to memorise
9. Check yourself
10. Answers

1 What the syllabus actually asks of you

Booklet 1 showed how to *measure* an enthalpy change. This booklet shows how to *predict* one without doing the experiment. There are two routes. The first goes through the bonds: a reaction breaks some bonds and makes others, and the balance between the two decides the sign and size of ΔH. The second goes through the law of conservation of energy: because energy cannot be created or destroyed, the enthalpy change between two states does not depend on the route, so known enthalpy changes can be added together to find unknown ones. Both routes appear in every Paper 1 and Paper 2.

Understanding	What it says	What you must be able to do	Level
1.2.1 Bond enthalpy	Bond-breaking absorbs and bond-forming releases energy.	Calculate the enthalpy change of a reaction from given average bond enthalpy data. Explain why bond enthalpy data are **average** values and may differ from those measured experimentally. Average bond enthalpies are given in the data booklet.	SL+HL
1.2.2 Hess's law	Hess's law states that the enthalpy change for a reaction is independent of the pathway between the initial and final states.	Apply Hess's law to calculate enthalpy changes in multistep reactions, by combining thermochemical equations or by using energy cycles and energy level diagrams.	SL+HL
1.2.3 – 1.2.5	Standard enthalpies of combustion and formation in cycles; Born–Haber cycles.	Covered in Booklet 3.	HL

Linking questions and connections for 1.2.1 – 1.2.2

- **Structure 2.2:** how would you expect bond enthalpy to relate to bond length and polarity? → section 2.4
- **Structure 1.3:** E = hν links the energy of a photon to the energy needed to break a bond. → section 2.5 (ozone)
- **Reactivity 1.1:** exothermic means the products are more stable; this booklet explains *why* in terms of bonds. Calorimetry data are combined with Hess's law in section 7.
- **Reactivity 2.2:** activation energy is needed because some bonds must break before new ones form. → section 3.5
- **Reactivity 3.4:** how does the strength of a carbon–halogen bond affect the rate of nucleophilic substitution? → section 3.5

What the data booklet gives you — and what it does not

The data booklet gives a table of **average bond enthalpies** (in kJ mol^{-1}, at 298 K) and a table of **standard enthalpies of combustion**. It does not give the equation ΔH = ΣE(bonds broken) − ΣE(bonds formed), the rules for combining equations, or any enthalpies of vaporization. Those you must learn or be given in the question. Always use the values from your data booklet or from the question; different textbooks quote slightly different averages.

2 Reactivity 1.2.1 — Bond breaking, bond making and bond enthalpy

SL + HL

2.1 Breaking bonds is endothermic; making bonds is exothermic

A covalent bond is the electrostatic attraction between a shared pair of electrons and the positive nuclei of the two bonded atoms (Structure 2.2). To pull the atoms apart, work must be done against this attraction, so energy must be **supplied**. Bond breaking is therefore always **endothermic**:

$$Cl_2(g) \rightarrow 2Cl(g) \quad \Delta H^{\ominus} = +242 \text{ kJ mol}^{-1}$$

When the same atoms come together and the bond forms, exactly the same amount of energy is **released**, so bond making is always **exothermic**:

$$H(g) + H(g) \rightarrow H_2(g) \quad \Delta H^{\ominus} = -436 \text{ kJ mol}^{-1}$$

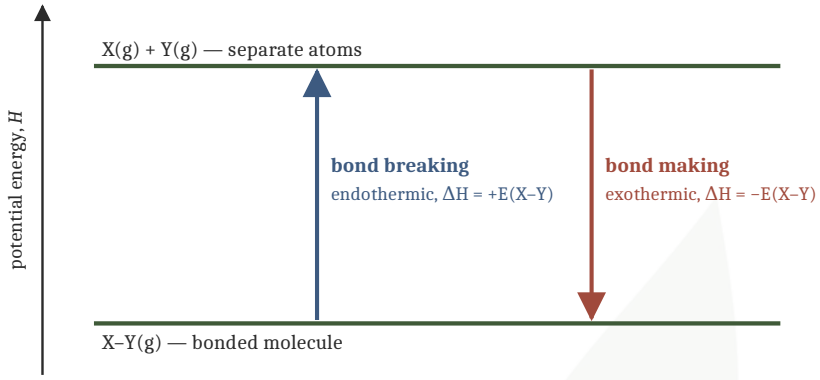


Figure 1 — The same energy, E(X–Y), is absorbed when a bond breaks and released when it forms. Only the sign changes.

> **Definition to learn**
>
> The **bond enthalpy** is the energy needed to break **one mole** of a particular covalent bond in **gaseous** molecules under standard conditions. It is always positive.

Notice the word *gaseous*. The definition only concerns the bond itself: if the substance were a liquid or solid, extra energy would also be needed to overcome the intermolecular forces, and that energy is not part of the bond enthalpy.

2.2 Why bond enthalpies are averages

The energy needed to break a given bond depends slightly on its environment in the molecule. Breaking the two O–H bonds in water one at a time needs different amounts of energy:

Step	$\Delta H^{\ominus}$ / kJ mol^{-1}
$H_2O(g) \rightarrow H(g) + OH(g)$ (first O–H bond)	+502
$OH(g) \rightarrow H(g) + O(g)$ (second O–H bond)	+427
$H_2O(g) \rightarrow 2H(g) + O(g)$ (both): average E(O–H) = (502 + 427)/2	**+464.5**

The O–H bond in ethanol, C_2H_5OH, needs a slightly different energy again. For bonds that occur in many different molecules, data tables therefore give an **average bond enthalpy**, measured across a range of similar compounds. The data booklet value of E(O–H), 463 kJ mol^{-1}, is such an average. For bonds found in only one molecule (H–H, Cl–Cl, H–Cl, O=O) the value is exact for that molecule.

> **Definition to learn**
>
> The **average bond enthalpy** is the energy needed to break one mole of a bond in gaseous molecules under standard conditions, **averaged over similar compounds**.

2.3 Values used in this booklet

These are the average bond enthalpies and bond lengths given in the IB data booklet. You will use them throughout sections 3 and 9.

Bond	E / kJ mol^{-1}	Length / pm	Bond	E / kJ mol^{-1}	Length / pm	Bond	E / kJ mol^{-1}	Length / pm
H–H	436	74	C–F	492	138	H–I	298	160
C–C	346	154	H–F	567	92	O–O	144	148
C=C	614	134	Cl–Cl	242	199	O=O	498	121
C–H	414	108	C–Cl	324	177	C=O	804	122
O–H	463	97	H–Cl	431	128	N≡N	945	110
C–O	358	143	Br–Br	193	228	N–H	391	101
F–F	159	142	H–Br	366	141	N–N	158	145
C≡C	839	120	I–I	151	267			

2.4 Patterns in bond enthalpies

Multiple bonds. More shared electrons mean a stronger attraction between the nuclei and the bonding electrons, so bond enthalpy increases and bond length decreases from single to double to triple: C–C 346, C=C 614, C≡C 839 kJ mol^{-1} (154, 134, 120 pm). A double bond is *not* twice as strong as a single bond, because the second (π) bond is weaker than the first (σ) bond.

Atomic size. Down group 17 the atoms get larger, the bonding pair is further from the nuclei, and the attraction weakens: Cl–Cl > Br–Br > I–I, and H–Cl > H–Br > H–I. Longer bonds are generally weaker.

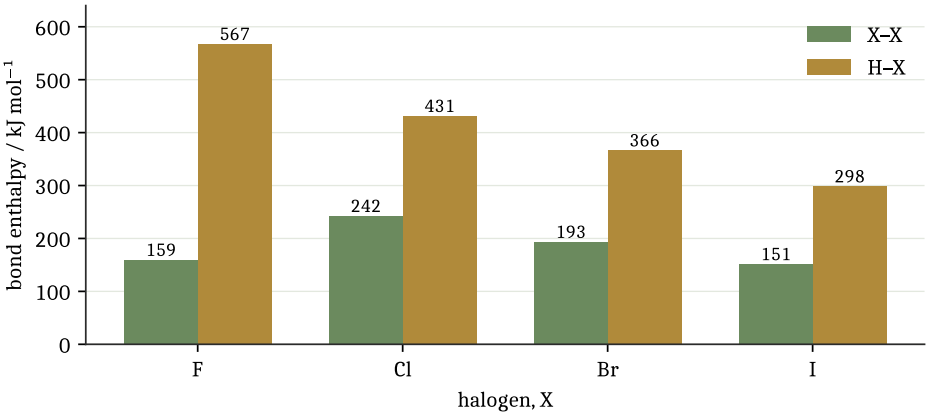


Figure 2 — Bond enthalpies of the halogens (X–X) and hydrogen halides (H–X). F–F breaks the trend.

The fluorine anomaly. F–F (159 kJ mol^{-1}) is much weaker than Cl–Cl (242 kJ mol^{-1}). Fluorine atoms are so small that, in the short F–F bond, the non-bonding (lone) pairs on the two atoms are close together and repel each other strongly, which weakens the bond. This weak bond is one reason fluorine is so reactive.

Polarity. If a bond between different atoms X and Y were purely covalent, we might expect its enthalpy to be the average of E(X–X) and E(Y–Y). Polar bonds are stronger than this:

X	average of E(H–H) and E(X–X) / kJ mol^{-1}	E(H–X) / kJ mol^{-1}	difference / kJ mol^{-1}
Cl	(436 + 242)/2 = 339	431	**92**
Br	(436 + 193)/2 = 314.5	366	**51.5**
I	(436 + 151)/2 = 293.5	298	**4.5**

The extra strength is greatest for the most polar bond, H–Cl, and almost zero for H–I, where hydrogen and iodine have very similar electronegativities. The partial charges in a polar bond add an extra electrostatic attraction. In general, a polar X–Y bond is stronger than the average of the non-polar X–X and Y–Y bonds. (Pauling used exactly these differences to build his electronegativity scale; you do not need the details.)

2.5 Bond enthalpy and light: oxygen and ozone

The O–O bond in ozone, O_3, has a bond enthalpy of 363 kJ mol^{-1}: between the O–O single bond (144) and the O=O double bond (498). This is because the two oxygen–oxygen bonds in ozone are identical, each intermediate between a single and a double bond (bond order 1.5, resonance in Structure 2.2). Because the bond in ozone is weaker, it can be broken by ultraviolet light of **lower energy, longer wavelength** than the light needed to break O_2. That is how the ozone layer absorbs harmful UV radiation that O_2 alone would let through.

Worked example — the longest wavelength that can break a bond ★

Q. Calculate the longest wavelength of light that can break the O=O bond (498 kJ mol^{-1}). Use h = 6.63 × 10^{-34} J s, c = 3.00 × 10^{8} m s^{-1}, N_A = 6.02 × 10^{23} mol^{-1}.

energy per bond: E = 498 000 J mol^{-1} / 6.02 × 10^{23} mol^{-1} = 8.27 × 10^{-19} J

λ = hc / E = (6.63 × 10^{-34} × 3.00 × 10^{8}) / 8.27 × 10^{-19} = 2.40 × 10^{-7} m = **240 nm**

For the bond in ozone (363 kJ mol^{-1}) the same method gives **330 nm**: a longer wavelength, lower-energy UV photon is enough.

Remember to convert kJ to J and to divide by N_A: one photon breaks **one** bond, not one mole of bonds.

Model answer: "Explain why bond enthalpy data are average values and why bond-making is exothermic." (3 marks)

The energy needed to break a particular bond varies with its environment in different molecules **[1]**, so tabulated values are averaged over a range of similar compounds **[1]**. When a bond forms, the nuclei and the shared pair of electrons are brought together by electrostatic attraction, so energy is released **[1]**.

Examiner traps in 1.2.1 (theory)

- Leaving "gaseous" or "one mole" out of the bond enthalpy definition.
- Writing the bond enthalpy equation with elements in their standard states, e.g. HBr(g) → ½H_2(g) + ½Br_2(l). Bond enthalpy produces **gaseous atoms**: HBr(g) → H(g) + Br(g).
- "Breaking bonds releases energy" (a very common slip). Breaking absorbs; making releases.
- Explaining the F–F anomaly by electronegativity. The reason is lone-pair repulsion between the small atoms.

3 Reactivity 1.2.1 — Calculating ΔH from bond enthalpies SL + HL

3.1 The idea

Imagine the reaction happening in two steps: first **all** the bonds in the reactants break to give gaseous atoms (endothermic), then the atoms join up to make **all** the bonds in the products (exothermic). The overall enthalpy change is the difference between the two. A reaction is exothermic when the bonds formed are stronger, in total, than the bonds broken.

$$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$$

"break minus make" · valid when all reactants and products are gases

Method — five steps

1. Write the balanced equation and draw the **displayed formula** of every species, so that no bond is missed.
2. List the bonds broken in the reactants and the bonds formed in the products, multiplying by the **coefficients** in the equation.
3. Look up each bond enthalpy and add up the totals for broken and for formed.
4. ΔH = total broken − total formed. Give the sign and units, kJ mol^{-1}.
5. Shortcut (optional): bonds that appear unchanged on both sides can be left out of both columns.

3.2 Worked examples

Worked example 1 — hydrogen and chlorine

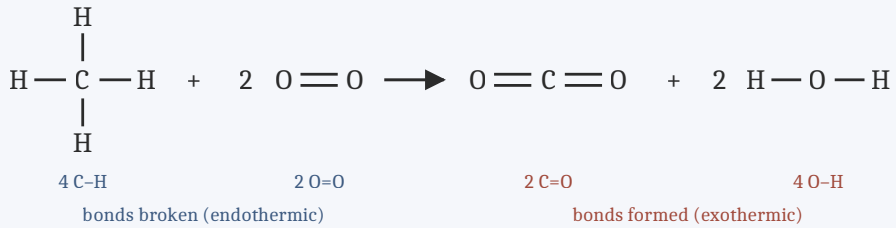
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

broken: 1 H–H + 1 Cl–Cl = 436 + 242 = 678 kJ

formed: 2 H–Cl = 2 × 431 = 862 kJ

ΔH = 678 − 862 = **−184 kJ mol^{-1}**

Worked example 2 — combustion of methane



Bonds broken	Energy absorbed / kJ	Bonds formed	Energy released / kJ
4 C–H	4 × 414 = 1656	2 C=O	2 × 804 = 1608
2 O=O	2 × 498 = 996	4 O–H	4 × 463 = 1852
Total	**2652**	**Total**	**3460**

ΔH = 2652 − 3460 = **−808 kJ mol^{-1}**

The data booklet value of $\Delta H_c^{\ominus}(CH_4)$ is −891 kJ mol^{-1}. The calculation is reliable in sign and order of magnitude, but not exact, for the reasons in section 3.4.

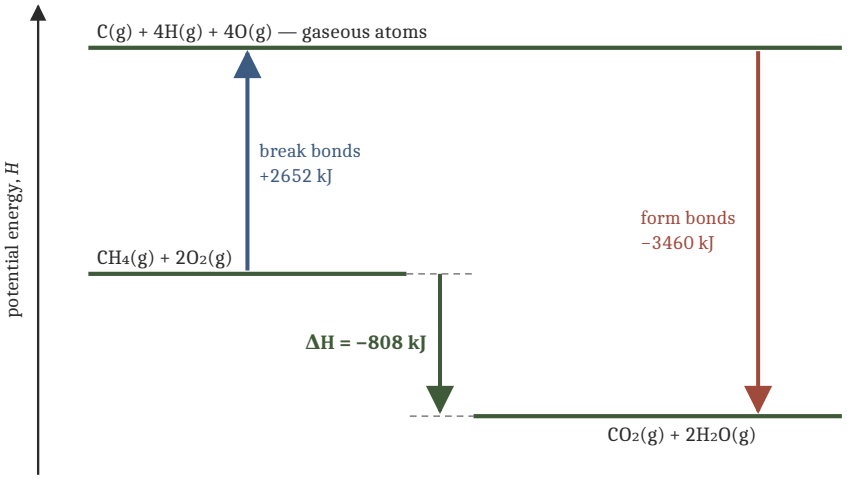


Figure 3 — The bond enthalpy calculation as an energy level diagram. Breaking every bond takes the system up to gaseous atoms; making the product bonds brings it further down than where it started.

Worked example 3 — ethanol, and what to do when species are not gases

Q. (a) Use bond enthalpies to estimate ΔH for $C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$. (b) Ethanol is actually a liquid (ΔH_{vap} = +42 kJ mol^{-1}) and in the standard combustion the water is also liquid (ΔH_{vap} = +44 kJ mol^{-1}). Estimate $\Delta H_c^{\ominus}$ and compare with the data booklet value, −1367 kJ mol^{-1}.

(a) Ethanol, $CH_3–CH_2–O–H$, contains 5 C–H, 1 C–C, 1 C–O and 1 O–H.

broken: 5(414) + 346 + 358 + 463 + 3(498) = 2070 + 346 + 358 + 463 + 1494 = 4731 kJ

formed: 4 C=O + 6 O–H = 4(804) + 6(463) = 3216 + 2778 = 5994 kJ

ΔH = 4731 − 5994 = **−1263 kJ mol^{-1}**

(b) The liquid ethanol must first be vaporized (+42 kJ), and condensing 3 mol of steam releases 3 × 44 = 132 kJ:

ΔH ≈ +42 − 1263 − 132 = **−1353 kJ mol^{-1}**, within about 1 % of −1367 kJ mol^{-1}.

Most of the difference between a “bond enthalpy” answer and a data booklet value comes from states: bond enthalpies apply only to gases, so the energy of intermolecular forces in liquids and solids is missing.

3.3 Working backwards: finding an unknown bond enthalpy

If ΔH for a reaction is known, the same equation can be rearranged to find one unknown bond enthalpy.

Worked example 4 — the average N–H bond enthalpy in ammonia

Q. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, $\Delta H^{\ominus}$ = −92 kJ mol^{-1}. Calculate the average N–H bond enthalpy, using E(N≡N) = 945 and E(H–H) = 436 kJ mol^{-1}.

broken: 945 + 3(436) = 2253 kJ; formed: 6 N–H = 6E(N–H)

−92 = 2253 − 6E(N–H) ⇒ 6E(N–H) = 2345 ⇒ E(N–H) = **391 kJ mol^{-1}**

There are **six** N–H bonds formed, because two molecules of NH_3 each have three.

3.4 Why bond enthalpy answers differ from experimental values

Two reasons to give, in this order

1. **Average values.** The bond enthalpies are averages over many compounds, not the actual values for the bonds in these particular molecules.
2. **States.** Bond enthalpies refer to the gaseous state. If any reactant or product is a liquid or solid under standard conditions (water in combustion is $H_2O(l)$), the energy associated with intermolecular forces is not included.

Calculations using ΔH_f or ΔH_c data (Hess's law, section 5 onwards and Booklet 3) are more accurate because those values are measured for the specific substances.

3.5 Bond enthalpy, activation energy and rate

Bond enthalpies also help explain the **activation energy** met in Reactivity 1.1: before new bonds can form, some existing bonds must start to break, and the stronger those bonds, the higher the energy barrier tends to be. A clear example comes in Reactivity 3.4. The carbon–halogen bond gets weaker from C–F (492 kJ mol^{-1}) through C–Cl (324 kJ mol^{-1}) down to C–I, so iodoalkanes undergo substitution fastest and fluoroalkanes hardly react at all.

Model answer: "The enthalpy of combustion of methane calculated from bond enthalpies is −808 kJ mol^{-1}. Explain why it differs from the data booklet value of −891 kJ mol^{-1}." (2 marks)

The bond enthalpies used are average values from a range of compounds, not the specific values for the bonds in methane, carbon dioxide and water **[1]**. Bond enthalpies refer to gaseous species, but under standard conditions water is a liquid, so the energy released when steam condenses is not included **[1]**.

Examiner traps in bond enthalpy calculations

- Using "formed − broken". It is always **broken − formed**, the opposite way round to the ΔH_f formula you will meet in Booklet 3.
- Forgetting the coefficients: $2O_2$ means 2 O=O bonds; $2H_2O$ means 4 O–H bonds.
- Counting CO_2 as having one C=O. It has **two**: O=C=O.
- Missing the C–C, C–O or O–H bonds in an alcohol. Always draw the displayed formula.
- Writing the units as kJ when the question asks for kJ mol^{-1}, or dropping the sign.

4 Reactivity 1.2.2 — Hess's law SL + HL

4.1 The law and why it must be true

Definition to learn

Hess's law: the enthalpy change for a reaction is independent of the route (pathway) taken, provided the initial and final conditions, reactants and products are the same.

Suppose A can be converted into C either directly, or indirectly through an intermediate B:

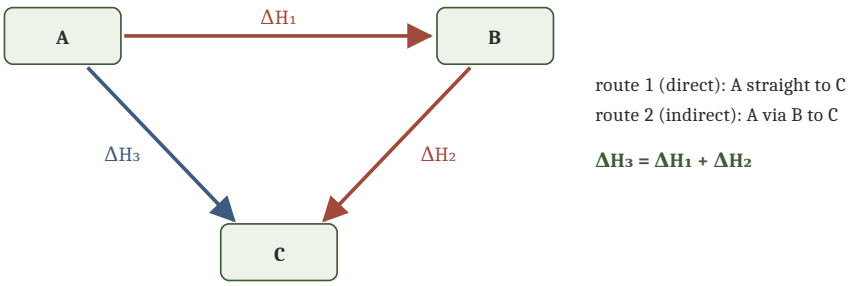


Figure 4 — Two routes from A to C. Hess's law: both routes have the same total enthalpy change.

Go round the cycle clockwise, A → B → C and then back from C to A. You finish where you started, so by the law of conservation of energy the total enthalpy change must be zero: $\Delta H_1 + \Delta H_2 - \Delta H_3 = 0$, which gives $\Delta H_3 = \Delta H_1 + \Delta H_2$. If this were not true, you could go round the cycle in one direction for ever and create energy from nothing, a perpetual motion machine. **Hess's law is a consequence of the law of conservation of energy.**

4.2 Why Hess's law is so useful

Many enthalpy changes cannot be measured directly. Carbon and hydrogen do not combine to give propane in the laboratory; thermal decompositions such as $CaCO_3 \rightarrow CaO + CO_2$ need continuous strong heating, so the heat transferred cannot be measured in a calorimeter; and some reactions produce a mixture of products. Hess's law lets us calculate these enthalpy changes from other reactions that *can* be measured, even if the intermediate steps are hypothetical. The only requirement is that every equation in the cycle balances.

You met one Hess cycle already in Booklet 1 (Figure 3): $H_2 + O_2 \rightarrow H_2O_2$ (−188 kJ) followed by $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$ (−98 kJ) has the same total, −286 kJ, as burning hydrogen directly to water.

There are three equivalent ways of applying the law: **combining equations** (section 5), drawing an **energy cycle**, and drawing an **energy level diagram** (section 6). They always give the same answer, so use whichever you find most reliable, but be ready to draw a cycle or a level diagram when asked.

5 Reactivity 1.2.2 — Hess's law method 1: combining equations SL + HL

5.1 The three rules

Operation on an equation	Effect on ΔH	Example
Reverse it	change the sign	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, −891 becomes $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$, +891
Multiply it by a number	multiply ΔH by the same number	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, −286, becomes $2H_2 + O_2 \rightarrow 2H_2O$, −572
Add two equations	add their ΔH values	species that appear on both sides cancel, just as in algebra

Strategy — work from the target equation

1. Write the **target equation** at the top of your working.
2. For each substance in the target, find a given equation that contains it (ideally only once).
3. **Reverse** that equation if the substance is on the wrong side; **multiply** it so the coefficient matches the target.
4. Add the adjusted equations; check that everything not in the target cancels; add the adjusted ΔH values.

Worked example 5 — the enthalpy change of formation of methane

Q. Calculate ΔH for $C(graphite) + 2H_2(g) \rightarrow CH_4(g)$, which cannot be measured directly, from:

(1) $C(graphite) + O_2(g) \rightarrow CO_2(g)$	$\Delta H = -394\ kJ\ mol^{-1}$
(2) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	$\Delta H = -286\ kJ\ mol^{-1}$
(3) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	$\Delta H = -891\ kJ\ mol^{-1}$

Target species	What to do	Adjusted equation	ΔH / kJ
C on the left, ×1	use (1) as given	$C + O_2 \rightarrow CO_2$	−394
$2H_2$ on the left	(2) × 2	$2H_2 + O_2 \rightarrow 2H_2O$	2(−286) = −572
CH_4 on the right	**reverse** (3)	$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$	+891
Add: $2O_2$, CO_2 and $2H_2O$ cancel		**$C + 2H_2 \rightarrow CH_4$**	**−75**

$\Delta H = -394 - 572 + 891 =$ **$-75\ kJ\ mol^{-1}$**

Worked example 6 — graphite into diamond

Q. $C(graphite) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -393.5\ kJ\ mol^{-1}$; $C(diamond) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -395.4\ kJ\ mol^{-1}$. Calculate ΔH for $C(graphite) \rightarrow C(diamond)$ and deduce which allotrope is more stable.

Keep the graphite equation; reverse the diamond equation: $CO_2 \rightarrow C(diamond) + O_2$, +395.4

$\Delta H = -393.5 + 395.4 =$ **$+1.9\ kJ\ mol^{-1}$**. Graphite has the lower enthalpy, so it is the more stable allotrope.

This links back to Booklet 1: diamond is energetically unstable relative to graphite, yet the very high activation energy means it does not change at an observable rate.

6 Reactivity 1.2.2 — Hess's law method 2: cycles and level diagrams

SL + HL

6.1 Energy cycles

An energy cycle shows the target reaction along the top and an alternative route underneath, through a common set of substances. When combustion data are given, the alternative route is almost always **through the combustion products**.

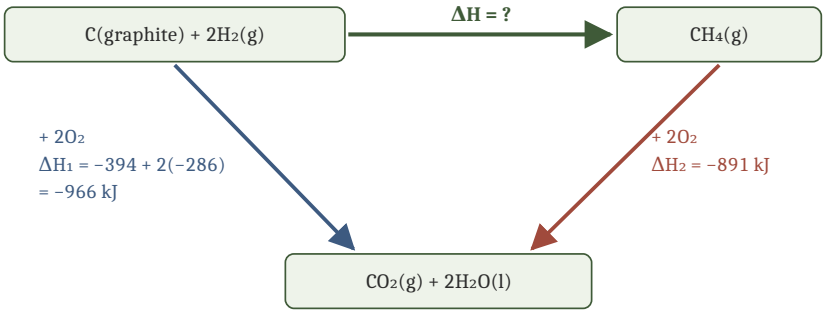


Figure 5 — The same calculation as worked example 5, drawn as a cycle. Both routes start at C(graphite) + $2H_2(g)$ and finish at $CO_2(g)$ + $2H_2O(l)$. The $2O_2$ added on each side is the same, so it does not affect the answer.

Rules for using a cycle

- Direct route = indirect route. Follow the arrows from start to finish along each route.
- If your route goes **against** the direction of an arrow, **change the sign** of that ΔH.
- Multiply each ΔH by the number of moles shown in the box it comes from (here 2 × ΔH for H_2).

From Figure 5: $\Delta H_1 = \Delta H + \Delta H_2$, so $\Delta H = \Delta H_1 - \Delta H_2 = -966 - (-891) =$ **-75 kJ mol^{-1}**, as before.

6.2 Energy level diagrams

An energy level diagram shows the same information with a vertical enthalpy axis, so you can see at once which substances are most stable. Downward arrows are exothermic, upward arrows endothermic.

Worked example 7 — the enthalpy change of formation of propane

Q. Use ΔH_c values (C(graphite) −394, $H_2(g)$ −286, $C_3H_8(g)$ −2219 kJ mol^{-1}) to calculate ΔH for 3C(graphite) + $4H_2(g) \rightarrow C_3H_8(g)$, and show it on an energy level diagram.

Route via combustion products: burn 3C and $4H_2$: $3(-394) + 4(-286) = -1182 - 1144 = -2326$ kJ

Direct route: ΔH then burn the propane: ΔH + (−2219)

$\Delta H - 2219 = -2326 \Rightarrow \Delta H =$ **-107 kJ mol^{-1}**

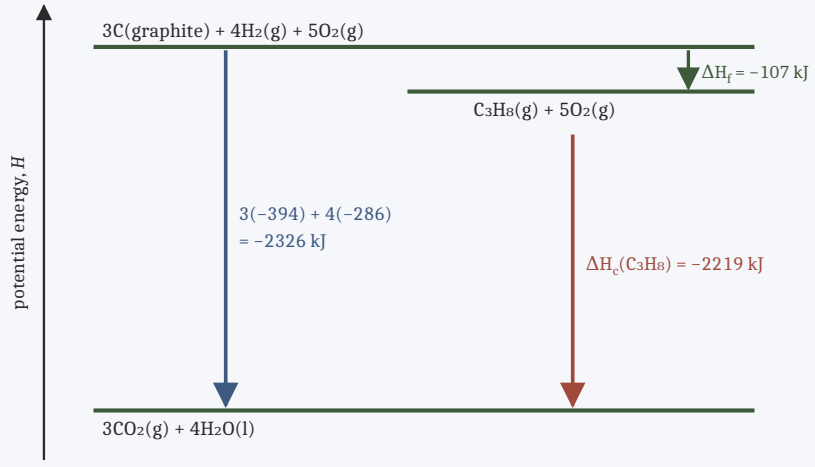


Figure 6 — Energy level diagram for the formation of propane. Propane lies only 107 kJ below its elements, but 2219 kJ above its combustion products.

Model answer: "State Hess's law and explain why it is a consequence of the law of conservation of energy." (3 marks)

The enthalpy change for a reaction is independent of the route taken, provided the initial and final states are the same **[1]**. Energy cannot be created or destroyed, so going round a closed cycle back to the starting substances must give a total enthalpy change of zero **[1]**. If two routes had different enthalpy changes, going one way and returning the other would create or destroy energy, which is impossible **[1]**.

Examiner traps in Hess's law

- Reversing an equation but forgetting to change the sign of ΔH (the commonest single error).
- Multiplying the equation but not the ΔH, or the other way round.
- Going against an arrow in a cycle without changing its sign.
- Not checking that the adjusted equations actually add up to the target equation. Always write the cancelled sum.
- Ignoring state symbols: $H_2O(g)$ and $H_2O(l)$ are different substances with different enthalpies.

7 Reactivity 1.2.2 — Hess's law in the laboratory SL + HL

Hess's law is also an experimental tool. When a reaction cannot be followed in a calorimeter, find two reactions that *can* be measured and that connect the same start and finish.

7.1 The enthalpy change of hydration of copper(II) sulfate

Adding water to white anhydrous copper(II) sulfate gives blue hydrated crystals and releases a lot of heat, but the solid gets wet unevenly and the heat cannot be measured reliably. Instead, each salt is dissolved separately in excess water: both give the same solution, so they share a common end point.

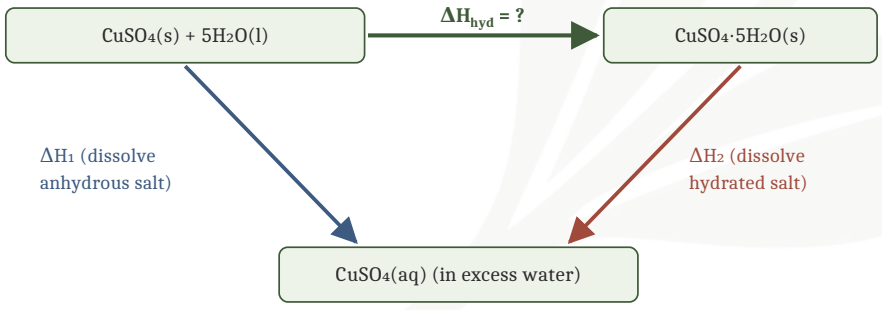


Figure 7 — $\Delta H_{hyd} = \Delta H_1 - \Delta H_2$. The hydration step itself is never carried out.

Worked example 8 — combining calorimetry with Hess's law

Q. 3.99 g of anhydrous $CuSO_4$ (M = 159.62 g mol^{-1}) dissolved in 50.0 g of water raised the temperature by 7.9 K. 6.24 g of $CuSO_4 \cdot 5H_2O$ (M = 249.72 g mol^{-1}) dissolved in 50.0 g of water lowered the temperature by 1.4 K. Calculate ΔH_{hyd} for $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 \cdot 5H_2O(s)$.

ΔH_1: Q = 50.0 × 4.18 × 7.9 = 1651 J; n = 3.99/159.62 = 0.0250 mol; ΔH_1 = −1.651/0.0250 = −66.1 kJ mol^{-1}

ΔH_2: Q = 50.0 × 4.18 × 1.4 = 293 J; n = 6.24/249.72 = 0.0250 mol; ΔH_2 = +0.293/0.0250 = +11.7 kJ mol^{-1} (temperature fell)

$\Delta H_{hyd} = \Delta H_1 - \Delta H_2 = -66.1 - 11.7 =$ **−77.8 kJ mol^{-1}**

The anhydrous route goes along ΔH_1; the target route goes along ΔH_{hyd} then ΔH_2. So $\Delta H_1 = \Delta H_{hyd} + \Delta H_2$.

7.2 Thermal decomposition

The decomposition of a metal carbonate, such as $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, is handled in the same way: react the carbonate and, separately, the oxide with excess dilute hydrochloric acid. Both give the same products ($CaCl_2(aq) + H_2O(l)$), and the difference between the two measured enthalpy changes is the enthalpy of decomposition (question 21).

8 Key points to memorise

Everything below is either wording that examiners look for or knowledge you must carry into the exam yourself.

A Definitions — near-verbatim

- **Bond enthalpy:** the energy needed to break one mole of a bond in gaseous molecules under standard conditions.
- **Average bond enthalpy:** the same, averaged over a range of similar compounds.
- **Hess's law:** the enthalpy change for a reaction is independent of the route, provided the initial and final states are the same. It follows from the law of conservation of energy.

B Equations and rules

- Bond breaking is endothermic (+); bond making is exothermic (−).
- $\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$: gases only; multiply by coefficients; draw displayed formulae.
- Reverse an equation → change the sign of ΔH. Multiply an equation → multiply ΔH. Add equations → add ΔH values.
- In a cycle: direct route = indirect route; going against an arrow changes its sign.

C Explanations you will be asked for

- Bond enthalpy answers differ from experimental values because the values are **averages** and because they apply only to **gaseous** species.
- Multiple bonds are stronger and shorter than single bonds. Larger atoms give longer, weaker bonds.
- F–F is anomalously weak because of repulsion between lone pairs on the small atoms. Polar bonds are stronger than the average of the corresponding non-polar bonds.
- Ozone's weaker O–O bond (bond order 1.5) is broken by lower-energy, longer-wavelength UV than O=O.
- Hess's law gives enthalpy changes that cannot be measured directly: formation from elements, thermal decomposition, hydration of salts.

9 Check yourself

Use the bond enthalpies in section 2.3 unless a question gives other values. Marks are shown in brackets; allow roughly 1.2 minutes per mark. Full answers with mark-scheme wording are in section 10.

Part A — Multiple choice SL + HL

1. Which processes are endothermic?

I. $Cl_2(g) \rightarrow 2Cl(g)$ II. $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ III. $H_2O(l) \rightarrow H_2O(g)$

A I and II only **B** I and III only **C** II and III only **D** I, II and III

2. Which equation represents the bond enthalpy of the H–Br bond?

A $HBr(g) \rightarrow H(g) + Br(g)$ **B** $HBr(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Br_2(l)$

C $HBr(aq) \rightarrow H^+(aq) + Br^-(aq)$ **D** $HBr(g) \rightarrow H^+(g) + Br^-(g)$

3. Which shows the bonds in order of **increasing** bond enthalpy?

A I–I < F–F < Cl–Cl < H–Cl **B** F–F < I–I < Cl–Cl < H–Cl

C I–I < Cl–Cl < F–F < H–Cl **D** H–Cl < Cl–Cl < F–F < I–I

4. What is ΔH, in kJ mol^{-1}, for $H_2(g) + F_2(g) \rightarrow 2HF(g)$?

A −539 **B** +539 **C** +28 **D** −1134

5. What is ΔH, in kJ mol^{-1}, for $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$?

A −93 **B** +93 **C** +1080 **D** −2346

6. Why does ΔH calculated from bond enthalpies often differ from an experimental value?

A Average bond enthalpies are used, which are not exact for the bonds in the particular molecules.

B Bond enthalpies are measured at high temperatures.

C Bond enthalpy calculations can only be used for exothermic reactions.

D Hess's law does not apply to bond breaking.

7. Which statement about carbon–carbon bonds is correct?

A The C≡C bond is the shortest and has the highest bond enthalpy.

B The C–C bond is the strongest because it is the longest.

C The C=C bond enthalpy is exactly twice the C–C bond enthalpy.

D All three bonds have the same length but different strengths.

8. Which is a statement of Hess's law?

A The enthalpy change of a reaction depends only on the initial and final states, not on the route.

B Energy is always released when a reaction takes place.

C The enthalpy change of a reaction equals the sum of the bond enthalpies of the products.

D The rate of a reaction is independent of the route taken.

9. For A → B, $\Delta H = \Delta H_1$; for B → C, $\Delta H = \Delta H_2$. What is ΔH for C → A?

A $\Delta H_1 + \Delta H_2$ **B** $\Delta H_1 - \Delta H_2$ **C** $-\Delta H_1 - \Delta H_2$ **D** $\Delta H_2 - \Delta H_1$

10. $2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$, $\Delta H = -790$ kJ; $S(s) + O_2(g) \rightarrow SO_2(g)$, $\Delta H = -297$ kJ. What is ΔH for $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$?

A −196 kJ **B** −1384 kJ **C** +196 kJ **D** −493 kJ

11. $C(graphite) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -394$ kJ; $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$, $\Delta H = -283$ kJ. What is ΔH for $C(graphite) + \frac{1}{2}O_2(g) \rightarrow CO(g)$?

A −111 kJ **B** +111 kJ **C** −677 kJ **D** +677 kJ

12. ★ $W \rightarrow X$, $\Delta H = -120$ kJ; $X \rightarrow Z$, $\Delta H = +35$ kJ; $Y \rightarrow Z$, $\Delta H = -60$ kJ. What is ΔH for $W \rightarrow Y$?

A −25 kJ **B** −145 kJ **C** +25 kJ **D** −215 kJ

Part B — Structured questions SL + HL

13. (a) Define the term *average bond enthalpy*. [2]

(b) Explain why bond enthalpies always have positive values. [1]

(c) The first and second O–H bonds in water require +502 and +427 kJ mol^{-1} to break. Calculate the average and comment on the data booklet value of 463 kJ mol^{-1}. [1]

14. (a) Explain the trend in bond enthalpy from Cl–Cl to Br–Br to I–I. [1]

(b) Explain why the F–F bond is weaker than the Cl–Cl bond. [1]

(c) Explain why E(H–Cl) is greater than the average of E(H–H) and E(Cl–Cl). [1]

(d) Identify the hydrogen halide with the weakest bond and state one consequence. [1]

15. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

(a) Use bond enthalpies to calculate ΔH for this reaction, showing the bonds broken and formed. [3]

(b) The data booklet gives $\Delta H_c^{\ominus}(C_3H_8) = -2219$ kJ mol^{-1}. Suggest two reasons for the difference. [2]

16. ★ Hydrazine is a rocket fuel: $N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$, $\Delta H = -579$ kJ mol^{-1}. Hydrazine has the structure $H_2N–NH_2$.

(a) Calculate the N–N bond enthalpy in hydrazine. [3]

(b) Compare your answer with the data booklet value and suggest why they differ. [1]

17. The value of ΔH for $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is −92 kJ mol^{-1}. Calculate the average N–H bond enthalpy in ammonia without using the data booklet value. [3]

18. Consider the hydrogenation of ethene: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$.

(a) Use these equations to calculate ΔH for the hydrogenation. [3]

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$	−1411 kJ mol^{-1}
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	−286 kJ mol^{-1}
$C_2H_6(g) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$	−1561 kJ mol^{-1}

(b) ★ Use your answer to (a) and bond enthalpies for C–C, C–H and H–H to calculate the C=C bond enthalpy. [2]

(c) Suggest why your answer to (b) differs from the data booklet value of 614 kJ mol^{-1}. [1]

19. Glucose is fermented: $C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$. Using ΔH_c values of −2803 kJ mol^{-1} (glucose) and −1367 kJ mol^{-1} (ethanol), draw an energy cycle and calculate ΔH for the fermentation. [3]

20. $N_2(g) + O_2(g) \rightarrow 2NO(g)$, $\Delta H = +181$ kJ; $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, $\Delta H = -114$ kJ.

(a) Calculate ΔH for $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$. [1]

(b) Hence calculate ΔH for $\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$. [1]

(c) Deduce whether NO_2 is more or less stable than its elements. [1]

21. The enthalpy change for $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ cannot easily be measured directly.

(a) Suggest why. [1]

(b) In separate experiments with excess HCl(aq):

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g) \quad \Delta H_1 = -15$ kJ mol^{-1}

$CaO(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) \quad \Delta H_2 = -194$ kJ mol^{-1}

Construct an energy cycle and calculate the enthalpy change of decomposition of $CaCO_3$. [3]

(c) State the law you have used. [1]

22. A student found the enthalpy change of hydration of magnesium sulfate, $MgSO_4(s) + 7H_2O(l) \rightarrow MgSO_4{\cdot}7H_2O(s)$.

Experiment 1: 2.41 g of $MgSO_4$ ($M = 120.38$ g mol^{-1}) in 50.0 g of water; temperature **rose** by 8.6 K.

Experiment 2: 4.93 g of $MgSO_4{\cdot}7H_2O$ ($M = 246.52$ g mol^{-1}) in 50.0 g of water; temperature **fell** by 1.5 K.

(a) Calculate the enthalpy change of solution of anhydrous $MgSO_4$. [2]

(b) Calculate the enthalpy change of solution of $MgSO_4{\cdot}7H_2O$. [2]

(c) Calculate the enthalpy change of hydration. [1]

(d) Explain why the hydration cannot be measured directly. [1]

23. ★ (a) Explain why the oxygen–oxygen bond enthalpy in ozone (363 kJ mol^{-1}) lies between those of O–O and O=O. [1]

(b) Calculate the longest wavelength, in nm, of light that can break one O–O bond in ozone ($h = 6.63 \times 10^{-34}$ J s, $c = 3.00 \times 10^8$ m s^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}). [2]

(c) Use your answer to explain how the ozone layer protects living things. [1]

24. ★ The bond enthalpy estimate for the combustion of methane is −808 kJ mol^{-1}, assuming $H_2O(g)$ forms. Given that $H_2O(g) \rightarrow H_2O(l)$ has $\Delta H = -44$ kJ mol^{-1}, show that most of the difference from the data booklet value (−891 kJ mol^{-1}) is caused by the state of the water. [2]

Part A: 12 marks · Part B: 49 marks · Total: 61 marks

10 Answers

Part A

1. B. I breaks a bond and III overcomes intermolecular forces; both absorb energy. II forms an ionic lattice and releases energy.

2. A. Bond enthalpy forms gaseous *atoms* from one mole of gaseous molecules. D breaks the bond heterolytically into ions.

3. A. I–I 151 < F–F 159 < Cl–Cl 242 < H–Cl 431 kJ mol^{-1}.

4. A. (436 + 159) − 2(567) = 595 − 1134 = −539. C forgets that two H–F bonds form.

5. A. broken 945 + 3(436) = 2253; formed 6(391) = 2346; $\Delta H = -93$. C counts only three N–H bonds.

6. A. Averages are not exact for specific molecules. (The other common reason, non-gaseous states, is not offered here.)

7. A. More shared electron pairs give a shorter, stronger bond. C=C (614) is less than twice C–C (346 × 2 = 692).

8. A.

9. C. A → C is $\Delta H_1 + \Delta H_2$; reversing it changes the sign.

10. A. Use the first equation as given and reverse 2 × the second: −790 − 2(−297) = −790 + 594 = −196 kJ.

11. A. Use the first equation and reverse the second: −394 + 283 = −111 kJ.

12. A. W → X → Z → Y: −120 + 35 + 60 = −25 kJ (Y → Z reversed, so +60).

Part B

13. (a) The energy needed to break one mole of a bond in gaseous molecules under standard conditions **[1]**, averaged over a range of similar compounds **[1]**.
(b) Breaking a bond always requires energy to overcome the attraction between the nuclei and the shared electrons, so the process is endothermic **[1]**.
(c) (502 + 427)/2 = 464.5 kJ mol^{-1}; the data booklet value of 463 kJ mol^{-1} is slightly different because it is averaged over O–H bonds in many compounds, not only water **[1]**.

14. (a) The atoms get larger, so the bonding pair is further from the nuclei and the bond is longer and weaker **[1]**.
(b) Fluorine atoms are very small, so the lone pairs on the two atoms are close together and repel strongly, weakening the bond **[1]**.
(c) The H–Cl bond is polar; the partial charges add extra electrostatic attraction, making it stronger than a purely covalent bond **[1]**.
(d) H–I (298 kJ mol^{-1}); for example, HI decomposes into its elements most easily on heating (or is the strongest acid of the hydrogen halides) **[1]**.

15. (a) broken: 2 C–C + 8 C–H + 5 O=O = 2(346) + 8(414) + 5(498) = 692 + 3312 + 2490 = 6494 kJ **[1]**; formed: 6 C=O + 8 O–H = 6(804) + 8(463) = 4824 + 3704 = 8528 kJ **[1]**; ΔH = 6494 − 8528 = **-2034 kJ mol^{-1}** **[1]**.
(b) Bond enthalpies are averages, not exact values for these molecules **[1]**; the data booklet value forms $H_2O(l)$, whereas the calculation forms $H_2O(g)$, so the heat released on condensing is missing (4 × 44 = 176 kJ, giving −2210 kJ mol^{-1}) **[1]**.

16. (a) broken: 4 N–H + N–N + O=O = 4(391) + E + 498 = 2062 + E **[1]**; formed: N≡N + 4 O–H = 945 + 4(463) = 2797 kJ **[1]**; −579 = 2062 + E − 2797, so E(N–N) = **156 kJ mol^{-1} [1]**.
(b) Close to the data booklet value of 158 kJ mol^{-1}; the difference arises because the other bond enthalpies used are averages **[1]**.

17. broken: 945 + 3(436) = 2253 kJ **[1]**; −92 = 2253 − 6E(N–H) **[1]**; E(N–H) = 2345/6 = **391 kJ mol^{-1} [1]**.

18. (a) Keep the C_2H_4 and H_2 equations; reverse the C_2H_6 equation **[1]**; ΔH = −1411 + (−286) + 1561 **[1]** = **−136 kJ mol^{-1} [1]**.
(b) broken: C=C + H–H; formed: C–C + 2 C–H (the other four C–H bonds are unchanged) **[1]**; −136 = E + 436 − 346 − 2(414), so E(C=C) = **602 kJ mol^{-1} [1]**.
(c) The C–C, C–H and C=C data booklet values are averages over many compounds, not the exact values for ethene and ethane **[1]**.

19. Cycle: glucose → $2C_2H_5OH + 2CO_2$ on top; both sides burn to $6CO_2 + 6H_2O(l)$ underneath **[1]**. −2803 = ΔH + 2(−1367) **[1]**; ΔH = −2803 + 2734 = **−69 kJ mol^{-1} [1]**.

20. (a) +181 + (−114) = **+67 kJ [1]**.
(b) +67/2 = **+33.5 kJ mol^{-1} [1]**.
(c) Less stable: ΔH is positive, so NO_2 has a higher enthalpy than N_2 and O_2 **[1]**.

21. (a) The reaction needs continuous strong heating, so the heat transferred by the reaction cannot be separated from the heat supplied (or measured in a calorimeter) **[1]**.
(b) Cycle with $CaCO_3$ → $CaO + CO_2$ on top and both reacting with 2HCl to give $CaCl_2(aq) + H_2O(l)$ (+ CO_2) **[1]**; $\Delta H_1 = \Delta H + \Delta H_2$ **[1]**; ΔH = −15 − (−194) = **+179 kJ mol^{-1} [1]**.
(c) Hess's law: the enthalpy change is independent of the route taken **[1]**.

22. (a) Q = 50.0 × 4.18 × 8.6 = 1797 J; n = 2.41/120.38 = 0.0200 mol **[1]**; ΔH = −1.797/0.0200 = **−89.8 kJ mol^{-1} [1]**.
(b) Q = 50.0 × 4.18 × 1.5 = 314 J; n = 4.93/246.52 = 0.0200 mol **[1]**; ΔH = **+15.7 kJ mol^{-1}** (positive because the temperature fell) **[1]**.
(c) ΔH_{hyd} = −89.8 − 15.7 = **−105.5 kJ mol^{-1}** (accept −106) **[1]**.
(d) Water cannot be added to the anhydrous solid in a controlled way: the solid would not hydrate evenly or completely, and some would dissolve, so the heat for the hydration alone cannot be measured **[1]**.

23. (a) The two bonds in ozone are identical and intermediate between single and double bonds (bond order 1.5, resonance) **[1]**.
(b) E per bond = 363 000 / 6.02 × 10^{23} = 6.03 × 10^{-19} J **[1]**; λ = hc/E = (6.63 × 10^{-34} × 3.00 × 10^{8}) / 6.03 × 10^{-19} = 3.30 × 10^{-7} m = **330 nm [1]**.
(c) Ozone absorbs UV of wavelength up to about 330 nm, longer than O_2 can absorb (up to about 240 nm), so it removes harmful UV radiation that would otherwise reach the surface **[1]**.

24. Two moles of $H_2O(g)$ condense: 2 × (−44) = −88 kJ **[1]**; −808 − 88 = −896 kJ mol^{-1}, within 5 kJ (about 0.6 %) of −891 kJ mol^{-1}, so the state of the water accounts for most of the original 83 kJ difference **[1]**.

Where this fits in Reactivity 1

- **Booklet 1** — Reactivity 1.1.1 to 1.1.4: heat, exothermic and endothermic reactions, energy profiles and calorimetry.
- **Booklet 2** (this booklet) — Reactivity 1.2.1 to 1.2.2: bond enthalpies and Hess's law.
- **Booklet 3** — HL Reactivity 1.2.3 to 1.2.5: standard enthalpies of formation and combustion in cycles ($\Delta H = \Sigma \Delta H_f(\text{products}) - \Sigma \Delta H_f(\text{reactants})$), and Born–Haber cycles.
- Links forward: **Reactivity 1.3** (energy from fuels), **Reactivity 2.2** (activation energy), **Reactivity 3.4** (carbon–halogen bond strength).

These notes are a free resource, shared for any IB student who finds them useful.

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