MEGA LECTURE

IB DP CHEMISTRY

Reactivity 1: What Drives Chemical Reactions?

Reactivity 1.2 Energy Cycles in Reactions

Revision Notes · Standard and Higher Level

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What the syllabus requires

Reactivity 1.2 asks a simple question with powerful consequences: if we cannot measure an enthalpy change directly, can we *calculate* it from data we already have? The answer is yes, because enthalpy is a state function. Use this checklist before the exam.

Understanding	You should be able to...
Hess's law	State that the enthalpy change of a reaction is independent of the route taken, and use energy cycles to exploit this.
Enthalpies of formation	Calculate ΔH°_r from standard enthalpies of formation of reactants and products.
Enthalpies of combustion	Calculate ΔH°_r from standard enthalpies of combustion of reactants and products.
Hess cycles	Combine given equations (reversing and scaling as needed) to reach a target equation and its enthalpy change.
Bond enthalpies	Estimate ΔH° of a gas-phase reaction from average bond enthalpies of bonds broken and made.
Born–Haber cycles (HL)	Construct a Born–Haber cycle and determine an unknown step such as lattice enthalpy or electron affinity.
Enthalpy of solution (HL)	Relate ΔH°_{sol} to lattice enthalpy and hydration enthalpies, and account for trends in hydration enthalpy.

> **Exam note:** Hess cycles, formation, combustion and bond enthalpies are **SL and HL**. Born–Haber cycles and the solution/hydration cycle are **HL only** (flagged with "(HL)" below). All numerical data in an exam is supplied — you are marked on the cycle and the arithmetic.

1. Hess's law and state functions

Enthalpy, *H*, is a **state function**: its value depends only on the current state of the system (temperature, pressure, amount and identity of substances), not on how that state was reached. It follows that the change in enthalpy between reactants and products, ΔH°, depends only on the initial and final states — not on the pathway.

Hess's law: the total enthalpy change for a reaction is the same whether the reaction takes place in one step or in several steps.

This is a direct consequence of the conservation of energy: if a route from reactants to products and back released or absorbed net energy, we could build a perpetual-motion machine. Because we cannot, every route must give the same ΔH°.

Energy cycle diagrams

An energy cycle draws the direct reaction as one arrow and an indirect route (through intermediates such as elements, or gaseous ions, or combustion products) as a chain of arrows. Because both routes start and finish at the same states, their enthalpy changes are equal:

$$\textbf{reactants} \rightarrow \textbf{products}\ \ (\textbf{direct, } \Delta H^\circ_1) \ = \ \textbf{reactants} \rightarrow \textbf{intermediates} \rightarrow \textbf{products}\ \ (\Delta H^\circ_2 + \Delta H^\circ_3)$$

The whole of this topic is the same three moves applied to different intermediates: (1) draw the two routes, (2) equate them, (3) rearrange for the unknown. The only rules are that **reversing** a step changes the sign of its ΔH°, and **scaling** an equation by a factor scales its ΔH° by the same factor.

> **Standard conditions:** A standard enthalpy change ΔH° (note the degree sign) is measured at 100 kPa and a stated temperature, usually 298 K, with all substances in their standard states. Always keep state symbols — they change the value (for example water as liquid versus gas).

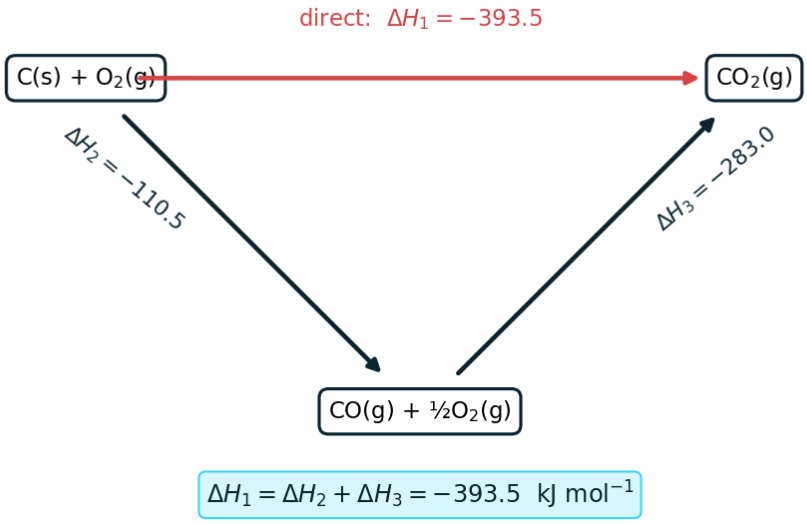

Figure 1. Hess's law cycle: the direct enthalpy change ΔH_1 equals the indirect route $\Delta H_2 + \Delta H_3$. Here $-393.5 = (-110.5) + (-283.0)$ kJ mol^{-1}.

2. Using enthalpies of formation

The **standard enthalpy of formation**, ΔH°_f, is the enthalpy change when **one mole** of a compound forms from its elements in their standard states. By definition, ΔH°_f of any element in its standard state is **zero** (for example O_2(g), C(graphite), Na(s)).

Imagine breaking all reactants down into their elements and then building the products from those elements. The elements are the shared intermediate, so:

$$\Delta H^\circ_r = \Sigma \Delta H^\circ_f(\text{products}) - \Sigma \Delta H^\circ_f(\text{reactants})$$

Multiply each ΔH°_f by the stoichiometric coefficient of that species in the balanced equation. “Products minus reactants” is the direction that comes straight from the cycle: down from elements to products, up (reversed) from reactants to elements.

Worked example 1 — combustion of methane from formation data

Find ΔH°_r for $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$.

Data / kJ mol^{-1}: $\Delta H^\circ_f[CH_4] = -74.8$; $\Delta H^\circ_f[CO_2] = -393.5$; $\Delta H^\circ_f[H_2O(l)] = -285.8$; $\Delta H^\circ_f[O_2] = 0$.

$\Delta H^\circ_r = [(-393.5) + 2(-285.8)] - [(-74.8) + 2(0)]$

$= [-393.5 - 571.6] - [-74.8] = -965.1 + 74.8 = \mathbf{-890.3\ kJ\ mol^{-1}}$ (exothermic).

Worked example 2 — combustion of ethanol from formation data

Find ΔH°_r for $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$.

Data / kJ mol^{-1}: $\Delta H^\circ_f[C_2H_5OH(l)] = -277.7$; $\Delta H^\circ_f[CO_2] = -393.5$; $\Delta H^\circ_f[H_2O(l)] = -285.8$.

$\Delta H^\circ_r = [2(-393.5) + 3(-285.8)] - [(-277.7) + 3(0)]$

$= [-787.0 - 857.4] + 277.7 = -1644.4 + 277.7 = \mathbf{-1366.7\ kJ\ mol^{-1}}$.

Watch the coefficients: the ×2 and ×3 are the commonest place to drop marks.

3. Using enthalpies of combustion

The **standard enthalpy of combustion**, ΔH°_c, is the enthalpy change when **one mole** of a substance burns completely in oxygen under standard conditions. Here the shared intermediate is the set of combustion products (CO_2 and H_2O). Burning the reactants and burning the products must reach the same place, so:

$$\Delta H^\circ_r = \Sigma \Delta H^\circ_c(\text{reactants}) - \Sigma \Delta H^\circ_c(\text{products})$$

Notice the direction is **reversed** relative to the formation equation (reactants minus products). The reason is geometric: on a combustion cycle the arrows point *down* from both reactants and products to the common combustion products, so building the target means going down the reactant arrow and *up* the product arrow.

Worked example 3 — enthalpy of formation of methane from combustion data

Find $\Delta H^\circ_f[CH_4]$ for $C(s) + 2H_2(g) \rightarrow CH_4(g)$.

Data / kJ mol^{-1}: $\Delta H^\circ_c[C] = -393.5$; $\Delta H^\circ_c[H_2] = -285.8$; $\Delta H^\circ_c[CH_4] = -890.3$.

$\Delta H^\circ_r = \Sigma \Delta H^\circ_c(\text{reactants}) - \Sigma \Delta H^\circ_c(\text{products}) = [(-393.5) + 2(-285.8)] - [(-890.3)]$

$= [-393.5 - 571.6] + 890.3 = -965.1 + 890.3 = \mathbf{-74.8\ kJ\ mol^{-1}}$.

This is the reverse calculation of Worked example 1 — combustion and formation data are two ways into the same cycle.

> **Why the signs differ:** Formation uses "products − reactants"; combustion uses "reactants − products". Do not memorise them blindly — sketch the cycle and the direction falls out every time. Elements have $\Delta H^\circ_f = 0$ but a non-zero ΔH°_c (e.g. carbon burns).

4. Constructing Hess cycles from given equations

Often you are handed two or three thermochemical equations and asked for the ΔH° of a target equation that is some combination of them. Treat the equations like algebra: add, subtract, reverse and scale them until the species cancel to leave the target. Apply the identical operations to the ΔH° values.

- **Reverse** an equation → change the sign of ΔH°.
- **Multiply** an equation by *n* → multiply ΔH° by *n*.
- **Add** equations → add their ΔH° values; species on opposite sides cancel.

Worked example 4 — target by subtraction

Find ΔH° for $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$, given:

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H^\circ = -393.5$ kJ mol^{-1}

(2) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$, $\Delta H^\circ = -283.0$ kJ mol^{-1}

Target = (1) − (2): reverse (2) and add. $C + O_2$ gives CO_2; then CO_2 gives $CO + \frac{1}{2}O_2$. CO_2 and $\frac{1}{2}O_2$ cancel to leave $C + \frac{1}{2}O_2 \rightarrow CO$.

$\Delta H^\circ = (-393.5) - (-283.0) = \mathbf{-110.5\ kJ\ mol^{-1}}$. (This step cannot be measured directly — some CO_2 always forms — which is exactly why Hess's law is needed.)

Worked example 5 — target by addition and scaling

Find ΔH° for $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$, given:

(1) $N_2(g) + O_2(g) \rightarrow 2NO(g)$, $\Delta H^\circ = +180.5$ kJ mol^{-1}

(2) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, $\Delta H^\circ = -114.1$ kJ mol^{-1}

Add (1) + (2): the 2NO produced in (1) is consumed in (2) and cancels, leaving $N_2 + 2O_2 \rightarrow 2NO_2$.

$\Delta H^\circ = (+180.5) + (-114.1) = \mathbf{+66.4\ kJ\ mol^{-1}}$ (endothermic).

5. Bond enthalpies

The **average bond enthalpy** is the energy needed to break one mole of a given type of bond in the **gaseous** state, averaged over a range of molecules. Breaking bonds is always **endothermic** (+); making bonds is always **exothermic** (−). Treat a reaction as breaking every bond in the reactants and remaking every bond in the products:

$$\Delta H^\circ \approx \Sigma\text{(bonds broken)} - \Sigma\text{(bonds made)}$$

The relation is **approximate** and carries a "≈" for two reasons: the values are averages that ignore the specific molecular environment, and the equation is only valid when every species is a **gas** (bond enthalpies say nothing about the energy of forming a liquid or solid). If a reactant or product is a liquid or solid, bond enthalpies alone will not give an accurate answer.

Worked example 6 — hydrogenation of ethene

Estimate $\Delta H°$ for $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$.

Bond enthalpies / kJ mol^{-1}: C=C 614, C−C 346, C−H 414, H−H 436.

Net change: break one C=C and one H−H; make one C−C and two new C−H (the four original C−H bonds are unchanged and cancel).

$\Delta H° = [614 + 436] - [346 + 2(414)] = 1050 - 1174 =$ **-124 kJ mol^{-1}**.

The experimental value is about −137 kJ mol^{-1}; the ~13 kJ mol^{-1} gap is the price of using *average* bond enthalpies.

Worked example 7 — combustion of methane (gaseous water)

Estimate $\Delta H°$ for $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$.

Bond enthalpies / kJ mol^{-1}: C−H 414, O=O 498, C=O (in CO_2) 804, O−H 463.

Broken: 4 C−H + 2 O=O = 4(414) + 2(498) = 1656 + 996 = 2652.

Made: 2 C=O + 4 O−H = 2(804) + 4(463) = 1608 + 1852 = 3460.

$\Delta H° = 2652 - 3460 =$ **-808 kJ mol^{-1}**.

This differs from the −890 kJ mol^{-1} of Worked example 1 because bond enthalpies require **gaseous** water; condensing $2H_2O(g)$ to $2H_2O(l)$ would release a further ~88 kJ mol^{-1}.

Ozone / resonance trap: Use the specific value quoted (e.g. C=O in CO_2 is 804 kJ mol^{-1}, not the general ~745 for a carbonyl). Always count *every* bond, including all the C−H bonds you might be tempted to ignore.

6. Born−Haber cycles (HL)

A Born−Haber cycle is a Hess cycle for the formation of an ionic compound. It builds the compound by two routes: directly from the elements ($\Delta H°_f$), or the long way round — atomising the elements, ionising the gaseous atoms, then bringing the gaseous ions together to form the lattice.

The steps for a compound $M^+X^-(s)$ are:

Step	Process	Sign
Atomisation, $\Delta H°_{at}$	Element → gaseous atoms (e.g. Na(s) → Na(g); ½Cl_2 → Cl)	endothermic (+)
Ionisation energy, IE	Gaseous atom → gaseous cation + e^-	endothermic (+)

Step	Process	Sign
Electron affinity, EA	Gaseous atom + e^- → gaseous anion	usually exothermic (−)
Lattice enthalpy, $\Delta H°_{lat}$	Gaseous ions → ionic solid (formation of lattice)	strongly exothermic (−)
Formation, $\Delta H°_f$	Elements → ionic solid (the direct route)	usually exothermic (−)

Equating the direct route with the long route gives the master equation:

$$\Delta H°_f = \Delta H°_{at}(\text{metal}) + IE + \Delta H°_{at}(\text{non-metal}) + EA + \Delta H°_{lat}$$

Any one unknown — most often the lattice enthalpy, which cannot be measured directly — is found by rearrangement.

Worked example 8 — lattice enthalpy of sodium chloride

Find the lattice enthalpy (of formation) $\Delta H°_{lat}$ for NaCl, given / kJ mol^{-1}:

$\Delta H°_f[NaCl] = -411$; $\Delta H°_{at}[Na] = +107$; $IE_1[Na] = +496$; $\Delta H°_{at}[Cl] = +121$ (= ½ × 242); $EA_1[Cl] = -349$.

Rearrange: $\Delta H°_{lat} = \Delta H°_f - [\Delta H°_{at}(Na) + IE + \Delta H°_{at}(Cl) + EA]$.

Bracket = 107 + 496 + 121 + (−349) = +375.

$\Delta H°_{lat} = (-411) - (+375) = \mathbf{-786\ kJ\ mol^{-1}}$ (lattice dissociation = +786 kJ mol^{-1}).

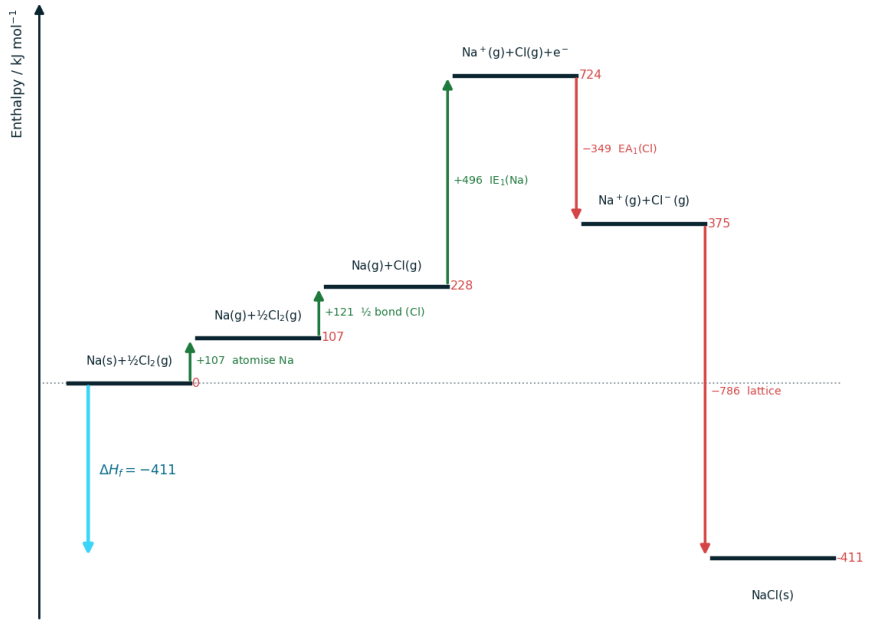

Figure 2. Born−Haber cycle for NaCl (HL): the direct formation $\Delta H°_f$ (−411 kJ mol^{-1}) equals the long route (atomise, ionise, electron affinity, lattice). Solving gives lattice enthalpy −786 kJ mol^{-1}; the sum around the cycle is 0.

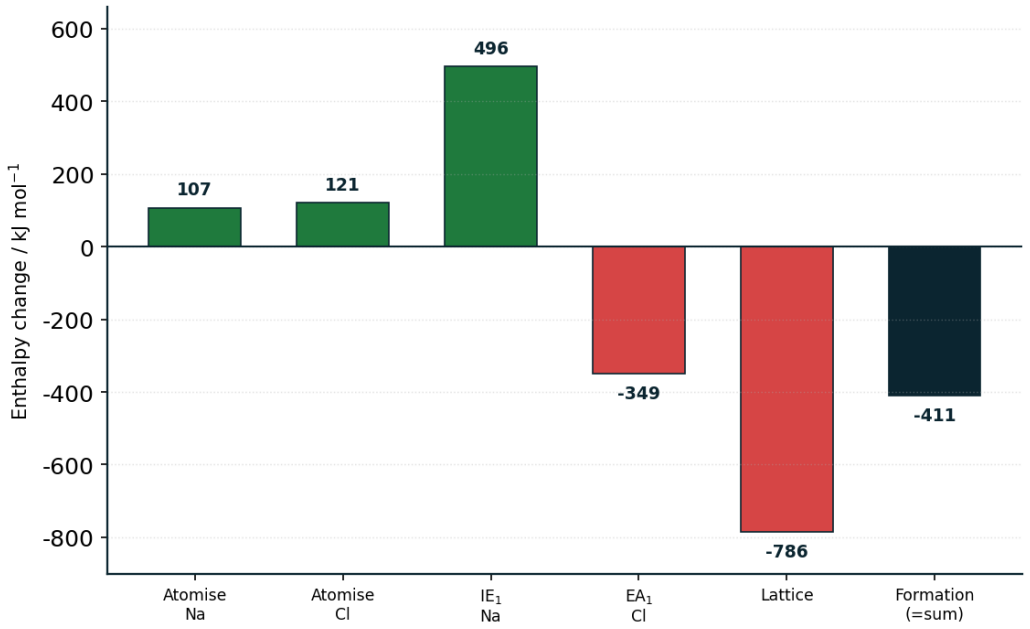

Figure 3. Signed component enthalpies of the NaCl Born–Haber cycle (green endothermic, red exothermic). The five steps sum to the formation enthalpy $\Delta H^\circ_f = -411$ kJ mol^{-1}.

Comparing ionic compounds

Lattice enthalpy becomes more exothermic (larger magnitude) as the **ionic charges increase** and as the **ionic radii decrease**, because the electrostatic attraction between ions rises. So the magnitude of the lattice enthalpy follows MgO > NaCl, and NaF > NaCl > NaBr > NaI. A large lattice enthalpy is why MgO is so much harder to melt than NaCl.

> **Sign discipline (HL):** Data booklets usually list **lattice dissociation** enthalpies as positive (solid → gaseous ions). If your cycle is built with gaseous ions → solid, you need the negative (formation) value. State which one you are using and keep it consistent — a wrong sign here is the classic HL error.

7. Enthalpy of solution and hydration (HL)

When an ionic solid dissolves in water, the lattice must first be pulled apart into gaseous ions (endothermic, = the lattice dissociation enthalpy), and those gaseous ions are then surrounded and stabilised by water molecules (exothermic, = the hydration enthalpies). The **enthalpy of solution**, ΔH°_{sol}, is the sum:

$$\mathbf{\Delta H^\circ_{sol} = -\Delta H^\circ_{lat} + \Sigma \Delta H^\circ_{hyd}}$$

Here ΔH°_{lat} is the (negative) lattice enthalpy of formation, so "$-\Delta H^\circ_{lat}$" is the positive energy needed to break the lattice; each ΔH°_{hyd} (for the cation and the anion) is negative. The **hydration enthalpy** is the enthalpy change when one mole of gaseous ions is dissolved in water to give an infinitely dilute solution: $X^{n\pm}(g) \rightarrow X^{n\pm}(aq)$.

Worked example 9 — enthalpy of solution of sodium chloride

Find $\Delta H^\circ_{sol}[NaCl]$ given / kJ mol^{-1}: lattice dissociation $-\Delta H^\circ_{lat} = +786$; $\Delta H^\circ_{hyd}[Na^+] = -406$; $\Delta H^\circ_{hyd}[Cl^-] = -378$.

$\Delta H^\circ_{sol} = +786 + (-406) + (-378) = +786 - 784$

= **+2 kJ mol^{-1}** — very slightly endothermic, which is why a NaCl solution cools almost imperceptibly as it dissolves.

The two large numbers (breaking the lattice, hydrating the ions) nearly cancel, so ΔH°_{sol} is a small difference of large quantities — round carefully.

Trends in hydration enthalpy

Hydration enthalpy becomes more exothermic (larger magnitude) as the **ionic charge increases** and as the **ionic radius decreases**, because a smaller, more highly charged ion has a greater charge density and attracts the polar water molecules more strongly.

Ion	Radius trend	Hydration enthalpy / kJ mol^{-1}	Comment
Li^+	smallest	−519	most exothermic of the group 1 cations
Na^+	larger	−406	charge density falls down the group
K^+	larger still	−322	least exothermic shown
Mg^{2+}	small, 2+	−1920	high charge, small radius → very exothermic

Same logic, twice: Both lattice enthalpy and hydration enthalpy are governed by the **same** two factors — ionic charge and ionic radius. Higher charge and smaller radius make *both* more exothermic, which is why ΔH°_{sol} (a small difference between them) is hard to predict by inspection.

8. Common pitfalls

- **Direction in a cycle:** formation uses products − reactants; combustion uses reactants − products. Sketch the cycle rather than guessing.
- **Forgetting to reverse a sign:** reversing an equation flips the sign of ΔH°; scaling multiplies it. Do both to the equation and to ΔH° together.
- **Coefficients:** multiply each ΔH°_f, ΔH°_c or bond enthalpy by the number of moles in the balanced equation (the ×2, ×3 traps).
- **Average vs exact:** bond-enthalpy answers are estimates (≈); formation/combustion answers are, in principle, exact. Never quote a bond-enthalpy result as if it were exact.
- **States:** bond enthalpies apply to **gases only**; $H_2O(l)$ and $H_2O(g)$ give different answers. Keep state symbols throughout.
- **Lattice-enthalpy sign (HL):** decide up front whether you are using the dissociation (+) or formation (−) value and stay consistent.

- **Elements:** ΔH°_f of an element = 0, but its ΔH°_c is not zero. Do not set combustion enthalpies of elements to zero.

9. Quick reference

Tool	Equation	Use when...
Formation data	$\Delta H^\circ_r = \Sigma \Delta H^\circ_f(\text{prod}) - \Sigma \Delta H^\circ_f(\text{react})$	given ΔH°_f of all species
Combustion data	$\Delta H^\circ_r = \Sigma \Delta H^\circ_c(\text{react}) - \Sigma \Delta H^\circ_c(\text{prod})$	given ΔH°_c of all species
Bond enthalpies	$\Delta H^\circ \approx \Sigma(\text{broken}) - \Sigma(\text{made})$	all species gaseous; estimate only
Born–Haber (HL)	$\Delta H^\circ_f = \Delta H^\circ_{at} + \text{IE} + \Delta H^\circ_{at} + \text{EA} + \Delta H^\circ_{lat}$	ionic solid; find lattice / EA / IE
Solution cycle (HL)	$\Delta H^\circ_{sol} = -\Delta H^\circ_{lat} + \Sigma \Delta H^\circ_{hyd}$	dissolving an ionic solid in water
Golden rules	reverse → flip sign; scale → × the ΔH°	every Hess calculation

10. Test yourself

Attempt all ten without notes, then check against the full worked answers. All data is in kJ mol^{-1}.

Q1 (formation). Find ΔH°_r for $2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l)$. ΔH°_f: H_2S −21, SO_2 −297, $H_2O(l)$ −286.

Q2 (formation). Find ΔH°_r for $C_2H_4(g) + H_2O(l) \rightarrow C_2H_5OH(l)$. ΔH°_f: C_2H_4 +52, $H_2O(l)$ −286, C_2H_5OH −278.

Q3 (combustion). Find ΔH°_f for $2C(s) + H_2(g) \rightarrow C_2H_2(g)$. ΔH°_c: C −394, H_2 −286, C_2H_2 −1300.

Q4 (combustion). Find ΔH°_f for $C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$. ΔH°_c: C −394, H_2 −286, CH_3OH −726.

Q5 (Hess). Find ΔH°_f for $2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$ from (1) $C + O_2 \rightarrow CO_2$, −394; (2) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, −286; (3) $C_2H_6 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$, −1560.

Q6 (Hess). Find ΔH°_r for $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$. ΔH°_f: Fe_2O_3 −824, CO −111, CO_2 −394.

Q7 (bond enthalpy). Estimate ΔH° for $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$. Bonds: H–H 436, Cl–Cl 242, H–Cl 431.

Q8 (bond enthalpy). Estimate ΔH° for $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. Bonds: N≡N 945, H–H 436, N–H 391.

Q9 (Born–Haber, HL). Find the lattice enthalpy (formation) ΔH°_{lat} for KCl. ΔH°_f −437; ΔH°_{at}[K] +90; IE_1[K] +419; ΔH°_{at}[Cl] +121; EA_1[Cl] −349.

Q10 (solution, HL). Find ΔH°_{sol}[KCl] given lattice dissociation +718, $\Delta H^\circ_{hyd}[K^+]$ −322, $\Delta H^\circ_{hyd}[Cl^-]$ −378.

Worked answers

A1. $\Delta H^\circ_r = [2(-297) + 2(-286)] - [2(-21) + 0] = [-594 - 572] - (-42) = -1166 + 42 = \mathbf{-1124\ kJ\ mol^{-1}}$.

A2. $\Delta H^\circ_r = [-278] - [(+52) + (-286)] = -278 - (-234) = -278 + 234 = \mathbf{-44\ kJ\ mol^{-1}}$.

A3. Using $\Sigma\Delta H^\circ_c$(react) − $\Sigma\Delta H^\circ_c$(prod): $\Delta H^\circ_f = [2(-394) + (-286)] - [(-1300)] = [-788 - 286] + 1300 = -1074 + 1300 =$ **+226 kJ mol^{-1}** (endothermic — ethyne is energetically unstable relative to its elements).

A4. $\Delta H^\circ_f = [(-394) + 2(-286)] - [(-726)] = [-394 - 572] + 726 = -966 + 726 =$ **−240 kJ mol^{-1}**. (O_2 is an element: no ΔH°_c term.)

A5. Target = 2×(1) + 3×(2) − (3): $\Delta H^\circ_f = 2(-394) + 3(-286) - (-1560) = -788 - 858 + 1560 =$ **−86 kJ mol^{-1}**.

A6. $\Delta H^\circ_r = [2(0) + 3(-394)] - [(-824) + 3(-111)] = -1182 - (-1157) = -1182 + 1157 =$ **−25 kJ mol^{-1}**.

A7. Broken 436 + 242 = 678; made 2(431) = 862. $\Delta H^\circ = 678 - 862 =$ **−184 kJ mol^{-1}**.

A8. Broken 945 + 3(436) = 945 + 1308 = 2253; made 6(391) = 2346. $\Delta H^\circ = 2253 - 2346 =$ **−93 kJ mol^{-1}** (per 2 mol NH_3; experimental −92).

A9. $\Delta H^\circ_{lat} = \Delta H^\circ_f - [\Delta H^\circ_{at}(K) + IE + \Delta H^\circ_{at}(Cl) + EA] = (-437) - [90 + 419 + 121 + (-349)] = (-437) - (+281) =$ **−718 kJ mol^{-1}** (dissociation +718).

A10. $\Delta H^\circ_{sol} = +718 + (-322) + (-378) = +718 - 700 =$ **+18 kJ mol^{-1}** (endothermic; KCl dissolving cools the solution).