9701 CHEMISTRY · TOPIC 5 · AS LEVEL

Energetics I — Enthalpy

01 · ENTHALPY BASICS

Exothermic — heat released to the surroundings, ΔH **negative**, products lower in energy, temperature of surroundings rises. **Endothermic** — heat absorbed, ΔH **positive**.

Bond breaking is endothermic, bond making exothermic. A reaction is exothermic when the bonds formed are stronger than the bonds broken.

Standard conditions (°): 100 kPa, 298 K, solutions 1 mol dm^{-3}, all substances in their standard states. Always give state symbols and units of kJ mol^{-1}.

02 · DEFINITIONS TO QUOTE

$\Delta H_f°$ — enthalpy change when one mole of a compound forms from its elements in their standard states. Zero for an element.

$\Delta H_c°$ — enthalpy change on complete combustion of one mole of a substance in excess oxygen.

$\Delta H_{neut}°$ — enthalpy change when one mole of water forms from acid and base. About −57 kJ mol^{-1} for strong acid + strong base.

Bond enthalpy — energy to break one mole of a bond in the **gaseous** state; the value quoted is a mean over many compounds.

03 · CALORIMETRY

$$q = mc\Delta T \cdot \Delta H = -q \div n$$

m = mass of **water or solution** in g (never the fuel or the solid), c = 4.18 J g^{-1} K^{-1}, ΔT in K or °C (same size). q comes out in J — divide by 1000 for kJ.

n = moles of the **limiting** reactant. The minus sign converts "heat gained by water" into "enthalpy change of the reaction". Assume the solution has the density and specific heat capacity of water.

04 · WORKED EXAMPLE — CALORIMETRY

0.850 g of propan-1-ol (M = 60.1) burns and raises 150.0 g of water by 22.5 K. Find ΔH_c.

q = 150.0 × 4.18 × 22.5 = **14 108 J** = 14.1 kJ
n = 0.850 ÷ 60.1 = **0.01414 mol**
ΔH_c = −14.1 ÷ 0.01414 = **−999 kJ mol^{-1}**

The data-booklet value is −2021 kJ mol^{-1}; the shortfall is heat lost to the air and apparatus and incomplete combustion.

05 · HESS'S LAW

The enthalpy change of a reaction is independent of the route taken, because enthalpy is a state function. Add the steps of any complete path.

$C(s) + O_2(g)$ → **$CO_2(g)$**

ΔH_1 = DIRECT ROUTE

↘ **$CO(g) + ½O_2(g)$** ↗

ΔH_2 THEN ΔH_3 = INDIRECT ROUTE

$\Delta H_1 = \Delta H_2 + \Delta H_3$

Reverse a step and the sign flips; multiply a step and the value multiplies. Arrows pointing the same way around a cycle add; one pointing against the cycle is subtracted.

06 · WORKED EXAMPLE — HESS CYCLE

Find ΔH for $C(s) + ½O_2(g) \rightarrow CO(g)$, given $\Delta H_c[C(s)]$ = −394 and $\Delta H_c[CO(g)]$ = −283 kJ mol^{-1}.

Both routes end at $CO_2(g)$, so using the cycle above:
$\Delta H_1 = \Delta H_2 + \Delta H_3 \rightarrow -394 = \Delta H_2 + (-283)$
ΔH_2 = −394 + 283 = **−111 kJ mol^{-1}**

07 · EXAM-STYLE QUESTION — DRAW THE CYCLE

Q. Use the enthalpies of formation below to find ΔH for
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$.
ΔH_f: $CaCO_3$ −1207, CaO −635, CO_2 −394 kJ mol^{-1}.

$CaCO_3(s)$ → **$CaO(s) + CO_2(g)$**

ΔH = WHAT WE WANT

↖ **$Ca(s) + C(s) + 1½O_2(g)$** ↗

ΔH_F −1207 **ΔH_F −635 AND −394**

A. Both formation arrows start at the elements, so go **up the left arrow (sign flips)** and down the right:

$\Delta H = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$
$\Delta H = (-635 - 394) - (-1207)$ = **+178 kJ mol^{-1}**

Endothermic — which is why limestone needs a kiln.

08 · THE TWO STANDARD ROUTES

From ΔH_f:

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

From bond enthalpies:

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

Multiply every term by its coefficient. Bond enthalpies only apply to gases, so a reaction involving liquids or solids gives an approximate answer — say so if asked to compare.

09 · WORKED EXAMPLE — BOND ENTHALPIES

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
C–H 414, O=O 498, C=O 804, O–H 463 kJ mol^{-1}

Broken: 4(414) + 2(498) = 1656 + 996 = **2652**
Formed: 2(804) + 4(463) = 1608 + 1852 = **3460**
ΔH = 2652 − 3460 = **−808 kJ mol^{-1}**

Note H_2O is taken as a gas — using $H_2O(l)$ would need the enthalpy of vaporisation as well.

MARKS LOST HERE

— Using the mass of the fuel or solid in q = mcΔT instead of the mass of water or solution.

— Forgetting the minus sign, or leaving the answer in J when the question asks for kJ mol^{-1}.

— Dividing by the total moles rather than the moles of the limiting reactant.

— Reversing a Hess step without flipping the sign.

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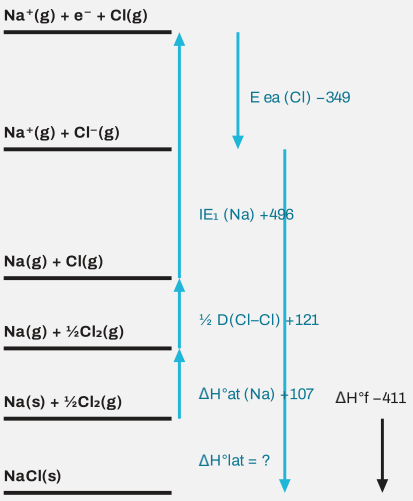
Energetics II — Born–Haber, Entropy, Gibbs

10 · BORN–HABER TERMS

Step	Sign
Atomisation / sublimation	+
Bond dissociation (½ per Cl)	+
Ionisation energy	+
Electron affinity	– (1st)
Lattice enthalpy (formation)	–
Enthalpy of formation	usually –

Lattice enthalpy of formation — enthalpy change when one mole of an ionic solid forms from its gaseous ions. Quoted as **dissociation** in the data booklet, so watch which direction the question wants: the two differ only in sign.

11 · BORN–HABER CYCLE — NACL



Vertical axis is enthalpy; the diagram is schematic, not to scale.

12 · WORKED EXAMPLE — BORN–HABER

Both routes from Na(s) + ½Cl₂(g) reach NaCl(s):

$\Delta H_f = \Delta H_{at} + IE_1 + \tfrac{1}{2}D + E_{ea} + \Delta H_{lat}$
$-411 = 107 + 496 + 121 + (-349) + \Delta H_{lat}$
$-411 = 375 + \Delta H_{lat}$
$\Delta H_{lat} = -411 - 375 =$ **-786 kJ mol^{-1}**

For $MgCl_2$ double the ½D term, add IE_1 *and* IE_2, and take $2 \times E_{ea}$.

13 · LATTICE ENTHALPY TRENDS

Magnitude ↑ with **larger ionic charge** and **smaller ionic radius**: MgO ≫ NaCl ≫ KI. Charge matters more than radius.

The **theoretical** value assumes a perfectly ionic lattice of point charges. Where the experimental (Born–Haber) value is much larger, the bonding has **covalent character** from polarisation of the anion — e.g. AgI.

14 · ENTHALPY OF SOLUTION CYCLE

NaCl(s) → **Na⁺(aq) + Cl⁻(aq)**

ΔH°SOL = DIRECT ROUTE

↗ **Na⁺(g) + Cl⁻(g)** ↘

−ΔH°LAT THEN ΣΔH°HYD

ΔH°sol = −ΔH°lat + ΣΔH°hyd

NaCl: $\Delta H_{lat} = -786$, $\Delta H_{hyd}(Na^+) = -424$, $\Delta H_{hyd}(Cl^-) = -359$
$\Delta H_{sol} = +786 + (-424 - 359) =$ **$+3$ kJ mol^{-1}**
Very small, so dissolving NaCl barely changes the temperature; it is driven by entropy.

15 · ENTROPY

ΔS° = ΣS°(products) − ΣS°(reactants)

Units **J K^{-1} mol^{-1}** — note the J, not kJ. Entropy measures the dispersal of energy among available states; S° of a perfect crystal at 0 K is zero, and S° values are positive for everything, elements included.

ΔS positive when: solid → liquid → gas, moles of gas increase, a solid dissolves, or one particle becomes many. **Negative** when gas moles fall, as in $2NO + O_2 \rightarrow 2NO_2$.

16 · GIBBS FREE ENERGY

ΔG° = ΔH° − TΔS°

T in **kelvin**; divide ΔS by 1000 to convert J to kJ before subtracting. **ΔG negative → spontaneous.**

ΔH	ΔS	Spontaneous?
–	+	always
–	–	low T only
+	+	high T only
+	–	never

At the crossover ΔG = 0, so **T = ΔH ÷ ΔS** — this is the melting or boiling point when the change is a phase change.

17 · WORKED EXAMPLE — GIBBS

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
$\Delta H° = +178$ kJ mol^{-1}, $\Delta S° = +161$ J K^{-1} mol^{-1}

At 298 K: $\Delta G = 178 - (298 \times 0.161) = 178 - 48.0$ = **$+130$ kJ mol^{-1}** → not spontaneous.

Crossover: $T = 178 \div 0.161 =$ **1106 K**. Above this temperature ΔG turns negative and the carbonate decomposes.

DATA BOOKLET & MARKS LOST

Look up: ΔH_f, ΔH_c and S° values, bond enthalpies, ionisation energies, electron affinities, lattice and hydration enthalpies, c = 4.18 J g^{-1} K^{-1}.

— Mixing J and kJ in ΔG = ΔH − TΔS. This is the single most common slip.

— Using the data booklet's lattice *dissociation* value without flipping the sign.

— Forgetting ½ for the bond dissociation of Cl_2, or omitting the second ionisation energy for a 2+ ion.

— Calling a spontaneous reaction fast: ΔG says nothing about rate.