

Unit 6

AP Chemistry

Thermochemistry

Endothermic and exothermic · Energy diagrams · Heat transfer · Calorimetry · Phase changes · Enthalpy of reaction · Bond enthalpies · Enthalpy of formation · Hess's law

Unit 1
7–9%
Atomic structure

Unit 2
7–9%
Compound structure

Unit 3
18–22%
Substances and mixtures

Unit 4
7–9%
Chemical reactions

Unit 5
7–9%
Kinetics

Unit 6
7–9%
Thermochemistry

Unit 7
7–9%
Equilibrium

Unit 8
11–15%
Acids and bases

Unit 9
7–9%
Thermodynamics, electrochemistry

Unit 6 is 7–9% of the multiple-choice section. In the free-response section it most often appears as a calorimetry experiment, where you turn a temperature change into ΔH , and also as Hess's law, bond-enthalpy and phase-change calculations.

6.1
Endo- and exothermic

6.2
Energy diagrams

6.3
Heat transfer

6.4
Calorimetry

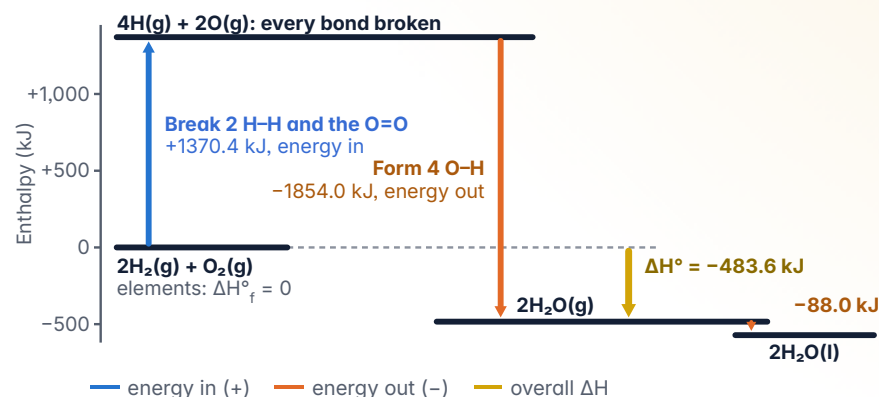
6.5
Phase changes

6.6
Enthalpy of reaction
kJ/mol

6.7
Bond enthalpies

6.8
Enthalpy of formation

6.9
Hess's law



Burning hydrogen at 25 °C, topic by topic

6.7 Bond enthalpies (table averages)
estimate ΔH : $2(436) + 498 - 4(464) = -486 \text{ kJ}$.

6.8 Formation enthalpies give the accepted value, $2(-241.8) - 0 = -483.6 \text{ kJ}$.

6.9 Hess's law: measured values for these molecules, +1370.4 and -1854.0 kJ, add to exactly -483.6 kJ.

6.5 Liquid water: condensing the steam at 25 °C adds $2(-44.0) = -88.0 \text{ kJ}$, so $\Delta H = -571.6 \text{ kJ}$.

6.6 The -483.6 kJ is for 2 mol of H_2 (4.03 g) and 1 mol of O_2 .

6.4 The 483.6 kJ could warm 1.4 kg of water by 80 °C.

What the exam asks most

1 ΔH from a temperature change. Find q for the solution with $q = mc\Delta T$, using the mass of the whole solution. The reaction's q has the opposite sign. Divide it by the moles of reaction (moles of a reactant ÷ its coefficient) to get ΔH in kJ/mol.

6.4 6.6

2 The effect of a lab mistake. Reason from the temperature change you measured. If heat escaped from an exothermic reaction, the rise was too small, so the calculated ΔH comes out less negative than the true value.

6.4

3 Why a process is endothermic or exothermic. Say which way energy flowed: "The water cooled, so it lost energy to the dissolving salt, which means the dissolving is endothermic."

6.1

4 ΔH by Hess's law. Reverse an equation and its ΔH changes sign; double it and ΔH doubles. Add the changed equations and check that only the target equation is left.

6.9

5 ΔH from bond or formation enthalpies. With bond enthalpies, $\Delta H = (\text{bonds broken}) - (\text{bonds formed})$, counting every bond. With ΔH°_f values, $\Delta H = \text{products} - \text{reactants}$, each value times its coefficient.

6.7 6.8

On the equation sheet

$$q = mc\Delta T$$

$$\Delta H^\circ_{\text{reaction}} =$$

$$\sum \Delta H^\circ_f \text{ products} - \sum \Delta H^\circ_f \text{ reactants}$$

q is heat, m mass, c specific heat; ° means standard conditions; ΔH°_f is an enthalpy of formation.

Know by heart

- Energy is conserved:
 $q_{\text{system}} = -q_{\text{surroundings}}$. If the water around a reaction warms, $\Delta H < 0$ (exothermic); if it cools, $\Delta H > 0$.
- $q = n\Delta H$ is the heat for n moles of a phase change or reaction.
- An element in its standard state has $\Delta H^\circ_f = 0$, as for $\text{O}_2(\text{g})$, C(graphite) and $\text{Br}_2(\text{l})$.
- Melting and boiling absorb energy ($\Delta H > 0$); freezing and condensing release the same amounts ($\Delta H < 0$).

Not on the exam

- Defining a "state function", or explaining how enthalpy differs from internal energy.

6.1 Endothermic and exothermic processes

ΔH is the reaction's energy change. When the water around a reaction warms, the water gained energy from the reaction, so ΔH is negative.

Endothermic
 $\Delta H > 0$, surroundings cool

ice melting

sweat evaporating (skin cools)

NH_4NO_3 dissolving: cold pack

splitting water into H_2 and O_2

Exothermic
 $\Delta H < 0$, surroundings warm

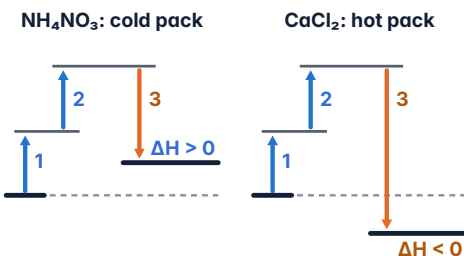
water freezing

steam condensing on skin

CaCl_2 dissolving: hot pack

fuel burning

Why dissolving can go either way



The dashed line is where you start, with the solid and the water apart. The blue steps take energy in: 1 pulling the ions apart and 2 pushing water molecules apart. The orange step gives energy out: 3 ions attracting water. If 1 and 2 cost more than 3 gives back, dissolving is endothermic.

Explaining the sign for dissolving

Pulling the ions apart and pushing the water molecules apart takes more energy than the new ion-water attractions give back, so dissolving NH_4NO_3 is endothermic.

Exam trap

- Saying the salt "released cold" because the beaker got cold. The water cooled because it lost energy to the dissolving salt: if 50.0 g of water cools by 2.0°C , it lost $(50.0)(4.18)(2.0) = 4.2 \times 10^2 \text{ J}$, so q for dissolving is $+4.2 \times 10^2 \text{ J}$, endothermic.

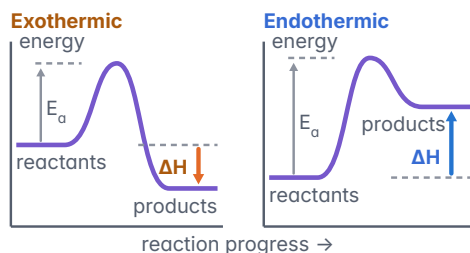
Quick check

As CaCl_2 dissolves, 100.0 g of solution warms from 22.0°C to 26.5°C ($c = 4.18 \text{ J/(g}\cdot^\circ\text{C)}$). Find q for the dissolving.

Answer: the solution gained $(100.0)(4.18)(4.5) = +1.9 \times 10^3 \text{ J}$ (two significant figures, from 4.5°C), so $q_{\text{dissolving}} = -1.9 \text{ kJ}$: exothermic.

6.2 Energy diagrams

On an energy diagram, height means enthalpy. ΔH is the products' height minus the reactants', negative when the products sit lower.

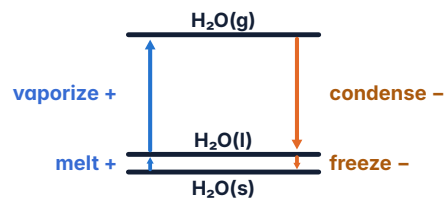


The hump's height above the reactants is the activation energy, E_a , which controls how fast the reaction goes (Unit 5). ΔH depends only on the two end levels.

Drawing an energy diagram that earns the point

- 1 Label the vertical axis **energy (kJ)**, and label each level with formulas and states.
- 2 Put the products **lower** for an exothermic reaction and **higher** for an endothermic one.
- 3 Draw the ΔH arrow **from the reactants to the products** and write its value and sign.
- 4 Add the hump only for a reaction energy profile or a question about E_a , rate or a catalyst.

Phase changes on an energy diagram



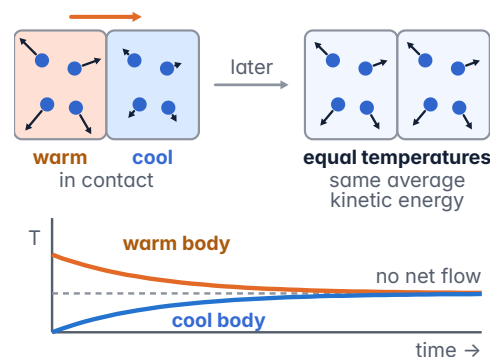
Drawn to scale: boiling water takes 40.7 kJ/mol , almost seven times the 6.01 kJ/mol for melting ice.

Exam trap

- Drawing the ΔH arrow from the products back to the reactants. Start it at the reactants: down for exothermic, up for endothermic. For $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$, $\Delta H = +91.9 \text{ kJ}$: $\text{N}_2 + 3\text{H}_2$ sits 91.9 kJ higher, so the arrow points up.
- Thinking a catalyst changes ΔH . A catalyst lowers the hump, but the reactant and product levels don't move, so ΔH stays the same. $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ has $\Delta H = -198 \text{ kJ}$ with or without its catalyst; only the speed changes.

6.3 Heat transfer and thermal equilibrium

Temperature tracks the **average kinetic energy** of the particles. When a warm object touches a cool one, collisions pass energy to the cooler one until the averages match.



Explaining heat transfer in three sentences

- 1 The warmer body's particles have the greater **average kinetic energy**.
- 2 **Collisions** pass energy from the faster particles of the warmer body to the slower ones of the cooler body. That transfer is heat.
- 3 At **thermal equilibrium** the average kinetic energies, and so the temperatures, are equal.

Drawing particles at a higher temperature

Draw the same number of the same molecules, and make the motion arrows **longer on average** at the higher temperature.

Exam trap

- Thinking equal temperatures mean equal energy. A bathtub and a cup at 40°C have the same average energy per particle, but the bathtub holds far more energy in total.
- Saying the particles stop at thermal equilibrium. They keep colliding and passing energy both ways, equally, so there is no net flow.

	Heat, q	Temperature, T
What it is	energy transferred, in J	a measure of average kinetic energy, in $^\circ\text{C}$ or K
Depends on how much matter?	yes	no

6.4 Heat capacity and calorimetry

From a thermometer reading to ΔH

The example: 100.0 mL of 0.500 M lactic acid is mixed with 100.0 mL of 0.500 M NaOH, and the mixture warms from 20.0 °C to 23.2 °C. Take the density as 1.00 g/mL and $c = 4.2 \text{ J/(g}\cdot^\circ\text{C)}$, as the question gives it.

1 Read ΔT

$$\text{final} - \text{initial} \\ 23.2 - 20.0 = 3.2^\circ\text{C}$$

2 q of the solution

$$mc\Delta T: (200.0)(4.2)(3.2) \\ = +2.7 \times 10^3 \text{ J}$$

3 q of the reaction

$$\text{the opposite sign} \\ = -2.7 \text{ kJ}$$

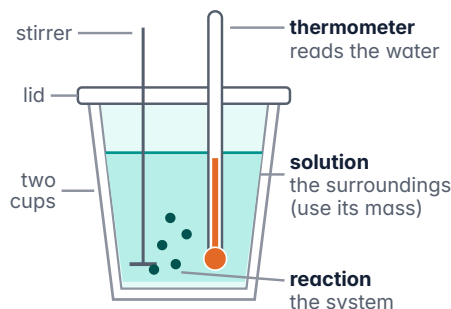
4 Moles of reaction

$$(0.100 \text{ L})(0.500 \text{ M}) \div 1 \\ = 0.0500 \text{ mol}$$

 ΔH

$$q_{\text{rxn}} \div \text{moles of reaction} \\ = -54 \text{ kJ/mol}$$

A calorimeter measures heat through a temperature change. The reaction is the system; the solution is the surroundings.



On the equation sheet

$$q = mc\Delta T$$

q is the heat in J, m the mass in grams of whatever changes temperature, c its specific heat (the question gives it), and $\Delta T = T_{\text{final}} - T_{\text{initial}}$.

Three common set-ups

- A reaction or a solid dissolving in water: $q_{\text{rxn}} = -m_{\text{soln}} c \Delta T$.
- A hot object dropped into cool water: $q_{\text{hot}} + q_{\text{cold}} = 0$.
- A calorimeter that absorbs heat too: $q_{\text{rxn}} = -(mc\Delta T + C_{\text{cal}}\Delta T)$. C_{cal} is the cup's heat capacity in J/°C. With 100.0 g of water ($c = 4.18$) and a 10.0 J/°C cup warming 2.50 °C, $q_{\text{rxn}} = -(1045 + 25) = -1070 \text{ J}$.

A change of 1 °C equals a change of 1 K, so never add 273 to a ΔT .

Water	Ice	Steam	Al	Fe	Cu
4.18	2.09	2.01	0.897	0.449	0.385

Typical values in J/(g·°C). Questions give water's as 4.18, 4.184 or 4.2; use the value the question gives.

Explaining a lab error

In an exothermic trial, heat lost to air makes the measured temperature change smaller, so the calculated q_{soln} is smaller and the magnitude of ΔH is smaller than the true value.

The heat is calculated from the temperature change, so start every error argument from ΔT .

Worked example hot metal into water

A 98.1 g metal cube at 100.0 °C gives 2940 J to the water around it; both end at 38.5 °C. Find the metal's specific heat.

- 1 Use the metal's own numbers. It lost heat, so $q = -2940 \text{ J}$.
- 2 $\Delta T = 38.5 - 100.0 = -61.5^\circ\text{C}$
- 3 $c = \frac{q}{m\Delta T} = \frac{-2940}{(98.1)(-61.5)}$

$c = 0.487 \text{ J/(g}\cdot^\circ\text{C)}$. A specific heat is always positive.

Comparing two metals

If 98.1 g of aluminum ($c = 0.897$) lost the same 2940 J, its temperature would drop only $2940 \div (98.1 \times 0.897) = 33.4^\circ\text{C}$.

Aluminum has the larger specific heat, so the same heat and mass give a smaller temperature change.

Worked example final temperature

50.0 g of copper at 100.0 °C drops into 50.0 g of water at 17.0 °C. What is the final temperature?

- 1 $q_{\text{Cu}} + q_{\text{water}} = 0$
- 2 $50.0(0.385)(T - 100.0) + 50.0(4.184)(T - 17.0) = 0$
- 3 Divide by 50.0 and multiply out: $0.385T - 38.5 + 4.184T - 71.1 = 0$, so $4.569T = 109.6$

$T = 24.0^\circ\text{C}$: water's large specific heat keeps its temperature from changing much

Exam trap

- Using the mass of the acid and base instead of the solution. All 200.0 g of solution warms, so $m = 200.0 \text{ g}$, not the 6.5 g of dissolved acid and base.
- Using the final temperature as ΔT . $\Delta T = 23.2 - 20.0 = 3.2^\circ\text{C}$, not 23.2°C .
- Adding both reactants' moles. One mole of reaction uses one mole of each, so there is 0.0500 mol of reaction, not 0.100.

Worked example significant figures

0.100 g of P_4O_{10} (283.9 g/mol) reacts in 100.0 g of water ($c = 4.18 \text{ J/(g}\cdot^\circ\text{C)}$), warming it from 22.00 to 22.38 °C. Find ΔH per mole of P_4O_{10} .

- 1 Use the solution's 100.1 g, not the 0.100 g of solid
- 2 $\Delta T = 22.38 - 22.00 = 0.38^\circ\text{C}$, which has two significant figures
- 3 The solution gains $(100.1)(4.18)(0.38) = 1.6 \times 10^2 \text{ J}$, so the reaction's $q = -0.16 \text{ kJ}$
- 4 $0.100 \div 283.9 = 3.52 \times 10^{-4} \text{ mol}$, so $\Delta H = -0.16 \text{ kJ} \div 3.52 \times 10^{-4} \text{ mol}$

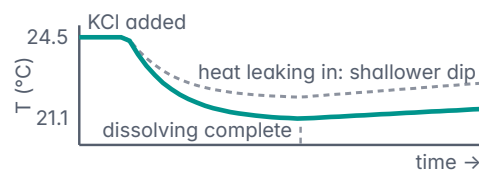
$-4.5 \times 10^2 \text{ kJ/mol}$: the subtraction left two significant figures

Worked example dissolving

6.80 g of KCl (0.0912 mol) dissolves in 97.5 g of water; the solution ($c = 3.95 \text{ J/(g}\cdot^\circ\text{C)}$) cools from 24.5 to 21.1 °C. Find ΔH .

- 1 $q_{\text{soln}} = (104.3)(3.95)(-3.4) = -1.4 \times 10^3 \text{ J}$
- 2 The solution lost that heat to the dissolving, so for the dissolving $q = +1.4 \text{ kJ}$
- 3 $\Delta H = +1.4 \text{ kJ} \div 0.0912 \text{ mol}$

$+15 \text{ kJ/mol}$, endothermic, using the given $c = 3.95$, not 4.18

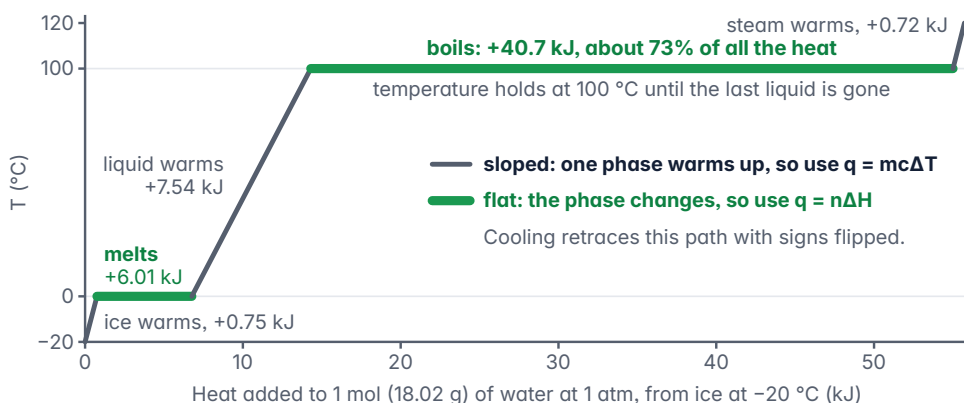


The temperature stops falling once all the solid has dissolved. The more heat leaks in, the smaller the measured drop and ΔH .

What went wrong	Size of ΔT	ΔH you calculate
No lid, so heat leaked out (or in)	smaller	closer to zero
Less solid dissolved than you weighed	smaller	closer to zero
The cup took or gave heat you didn't count	smaller	closer to zero

6.5 Energy of phase changes

At a fixed pressure, a pure substance changes phase at a constant temperature even though energy keeps flowing. The energy pulls the particles apart (or comes out as they lock together) instead of speeding them up.



Not on the equation sheet, so know it by heart

$$q = n \Delta H_{\text{phase change}}$$

Melting and vaporizing absorb energy (+). Freezing releases what melting absorbs, and condensing releases what vaporizing absorbs (-). For water, ΔH_{fus} (fusion means melting) = 6.01 kJ/mol at 0 °C and ΔH_{vap} = 40.7 kJ/mol at 100 °C. ΔH_{vap} is a little larger when colder: 44.0 kJ/mol at 25 °C.

Worked example

How much heat vaporizes 6.85 g of HF? (ΔH_{vap} = 25.2 kJ/mol, molar mass 20.01 g/mol)

- $n = 6.85 \div 20.01 = 0.3423 \text{ mol}$
- $q = 0.3423 \text{ mol} \times 25.2 \text{ kJ/mol}$

+8.63 kJ absorbed; condensing it would release 8.63 kJ

Explaining why the temperature stays flat

The added energy overcomes the attractions between the molecules instead of making them move faster, so their **average kinetic energy**, and the temperature, stay the same.

Quick check

5.00 g of steam at 100 °C condenses, then the water cools to 25.0 °C. Find q for the water.

Answer: condensing gives $(5.00 \div 18.02)(-40.7) = -11.3 \text{ kJ}$ and cooling gives $5.00(4.184)(-75.0) = -1.57 \text{ kJ}$, so $q = -12.9 \text{ kJ}$. Most of it comes from condensing, which is why steam burns worse than boiling water.

Worked example

three steps

How much heat takes 25.0 g of ice at -10.0 °C to liquid water at 20.0 °C? ($c_{\text{ice}} = 2.09$, $c_{\text{water}} = 4.184 \text{ J/(g}\cdot\text{°C)}$)

- Ice warms: $25.0(2.09)(10.0) = 523 \text{ J} = 0.523 \text{ kJ}$
- Melts: $\frac{25.0}{18.02}(6.01) = 8.34 \text{ kJ}$
- Water warms: $25.0(4.184)(20.0) = 2092 \text{ J} = 2.09 \text{ kJ}$

10.95 kJ in all, about three quarters of it for melting

Worked example

How much heat must be removed to condense 8.59 g of CH_3OH ? ($\Delta H_{\text{vap}} = 37.6 \text{ kJ/mol}$)

- $\frac{8.59 \text{ g}}{32.04 \text{ g/mol}} \times \frac{37.6 \text{ kJ}}{1 \text{ mol}}$; the units cancel to leave kJ

10.1 kJ must be removed, so $q = -10.1 \text{ kJ}$

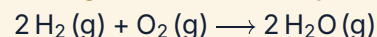
Exam trap

- Using $mc\Delta T$ across a flat part of the curve. ΔT is zero there, but heat still flows. Use $q = n\Delta H$: melting 1.00 mol of ice takes 6.01 kJ while the temperature stays at 0 °C.
- Putting ΔH_{vap} into $mc\Delta T$ as if it were a specific heat. ΔH_{vap} is in kJ/mol, so multiply it by moles, never by grams and a ΔT .
- Saying boiling breaks bonds. Boiling only overcomes the attractions between molecules. The covalent bonds stay, so water vapor is still H_2O .

6.6 Enthalpy of reaction

ΔH is the heat released (-) or absorbed (+) when the amounts in the balanced equation, read as moles, react. That much reaction is **one mole of reaction** (mol_{rxn}).

Reading a thermochemical equation



$$\Delta H = -483.6 \text{ kJ/mol}_{\text{rxn}}$$

2 mol of H_2 reacting with 1 mol of O_2 to make 2 mol of H_2O is one mole of reaction; it releases 483.6 kJ. After an equation, "-483.6 kJ" means the same.

$$q = n_{\text{rxn}} \Delta H$$

moles of reaction, n_{rxn} = moles of a substance $\div$ its coefficient

Worked example

How much heat does burning 0.250 mol of H_2 release?

- $0.250 \text{ mol H}_2 \times \frac{-483.6 \text{ kJ}}{2 \text{ mol H}_2}$

$q = -60.5 \text{ kJ}$, so 60.5 kJ is released. Forgetting the 2 gives -121 kJ

Worked example

limiting reactant

$4 \text{Na}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{Na}_2\text{O}(\text{s})$, $\Delta H^\circ = -828 \text{ kJ/mol}_{\text{rxn}}$. 18.4 g of Na reacts with 12.8 g of O_2 . Find the heat released.

- $18.4 \div 22.99 = 0.800 \text{ mol}$ of Na, and $0.800 \div 4 = 0.200 \text{ mol}_{\text{rxn}}$
- $12.8 \div 32.00 = 0.400 \text{ mol}$ of O_2 , and $0.400 \div 1 = 0.400 \text{ mol}_{\text{rxn}}$
- Na gives fewer moles of reaction, so it runs out first: $0.200 \times (-828) = -166 \text{ kJ}$

166 kJ released, set by the sodium

Where the heat comes from

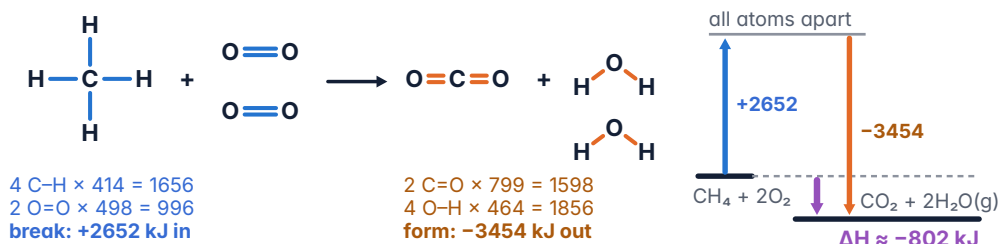
When the products have less chemical potential energy than the reactants, the difference becomes kinetic energy, so the mixture gets hotter.

Exam trap

- Thinking twice the fuel doubles ΔH . Burning twice as much doubles q , the heat you get. ΔH belongs to the equation as written and doubles only if you double its coefficients.
- Giving kJ/mol without naming the substance. -828 kJ per mole of reaction makes 2 mol of Na_2O , so it is -414 kJ per mole of Na_2O .

6.7 Bond enthalpies

Breaking a bond always costs energy, and forming one always releases it. Add the energy for every bond broken in the reactants, subtract the energy for every bond formed in the products, and you have an estimate of ΔH .



Count bonds from drawn structures. A double bond counts once, at the double-bond value. The measured ΔH for this reaction, making water vapor, is -802 kJ , and the estimate matches it.

■ bonds broken: energy in (+) ■ bonds formed: energy out (-) ■ the overall ΔH

Not on the equation sheet, so know it by heart

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

Σ means "add up": add the enthalpies of every bond broken, then subtract those of every bond formed. Bonds broken come first because they are the energy put in. Formation enthalpies (Topic 6.8) use the opposite order, products - reactants.

- 1 Draw every Lewis structure so you can count every bond.
- 2 List bonds broken, multiplying by coefficients.
- 3 List bonds formed the same way.
- 4 Subtract: broken - formed, in $\text{kJ/mol}_{\text{rxn}}$.

Bond	kJ/mol	Bond	kJ/mol
H-H	436	C=O (in CO_2)	799
O=O	498	N-H	390
O-H	464	$\text{N}\equiv\text{N}$	946
C-H	414	Cl-Cl	243
H-Cl	431	Br-Br	193

Typical average values; each question gives its own table. The C=O value is the one for CO_2 ; in other tables C=O averages about 745. Between the same two atoms, a triple bond is stronger than a double, and a double stronger than a single.

Worked example

endothermic

Estimate ΔH :



- 1 Broken: $6 \text{ N-H} = 6(390) = 2340 \text{ kJ}$
- 2 Formed: $\text{N}\equiv\text{N} + 3 \text{ H-H} = 946 + 3(436) = 2254 \text{ kJ}$

$\Delta H \approx +86 \text{ kJ}$, endothermic: forming the new bonds released less energy than breaking the old ones cost

Worked example

working backward

$2 \text{ BrCl}(\text{g}) \rightarrow \text{Br}_2(\text{g}) + \text{Cl}_2(\text{g})$, $\Delta H = +1.6 \text{ kJ/mol}_{\text{rxn}}$. Br-Br = 193 and Cl-Cl = 243 kJ/mol . Find the Br-Cl bond enthalpy, D .

- 1 Two Br-Cl bonds break: $+1.6 = 2D - (193 + 243)$
- 2 $2D = 437.6$

$D = 219 \text{ kJ/mol}$. Don't forget the 2: two Br-Cl bonds break

Explaining the sign of ΔH from bonds

More energy is released forming the bonds in the products than is required to break the bonds in the reactants, so the reaction is exothermic.

Why it is only an estimate

Most table values, such as C-H, are averages over many molecules, and all assume gases. The measured ΔH for breaking down ammonia is $+91.9 \text{ kJ}$, not $+86$.

Exam trap

- Subtracting formed - broken. That flips the sign. For $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{ HCl}$ with H-H 436, Cl-Cl 243 and H-Cl 431 kJ/mol , broken - formed = $(436 + 243) - 2(431) = -183 \text{ kJ}$, not $+183$.
- Miscounting bonds. CH_4 has four C-H bonds, and CO_2 has two C=O double bonds, not four C-O bonds. Then multiply by the coefficients: 2 O_2 means two O=O bonds.
- Saying breaking bonds releases energy. Breaking a bond always takes energy. The heat of a flame comes from bonds forming.

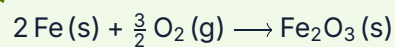
6.8 Enthalpy of formation

ΔH_f° is the ΔH for making one mole of a compound from its elements in their standard states.

On the equation sheet

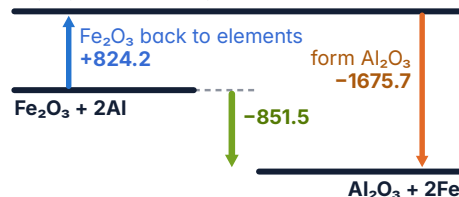
$$\Delta H_{\text{reaction}}^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

What counts as a formation reaction



- It makes exactly 1 mol of the compound, using fractions like $3/2 \text{ O}_2$ if needed.
- Elements in their standard states are zero: $\text{O}_2(\text{g})$, C(graphite), Fe(s), $\text{Br}_2(\text{l})$.
- O(g) and $\text{O}_3(\text{g})$ are not standard states, so their ΔH_f° is not zero.

Fe, Al, O_2 : elements, all zero



Products - reactants works like breaking the reactants into elements, then building the products.

Worked example

$\text{Fe}_2\text{O}_3(\text{s}) + 2 \text{ Al}(\text{s}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 2 \text{ Fe}(\text{s})$; ΔH_f° : Fe_2O_3 -824.2 , Al_2O_3 -1675.7 kJ/mol

$$1 \quad [-1675.7 + 2(0)] - [-824.2 + 2(0)]$$

$\Delta H = -851.5 \text{ kJ/mol}_{\text{rxn}}$, enough heat to melt the iron

Working backward to an unknown ΔH_f°

For $4 \text{ Na}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ Na}_2\text{O}(\text{s})$, $\Delta H^\circ = -828 \text{ kJ/mol}_{\text{rxn}}$. Call ΔH_f° of Na_2O x : $-828 = 2x - 0$, so $x = -414 \text{ kJ/mol}$.

Exam trap

- Subtracting reactants - products. That flips the sign: thermite would come out at $+851.5 \text{ kJ}$.
- Skipping coefficients. Burning propane makes 3 CO_2 and $4 \text{ H}_2\text{O}$, so multiply their ΔH_f° values by 3 and 4.
- Using the wrong phase. Burning C_3H_8 gives -2219 kJ if the water is liquid but -2043 kJ if it is gas. They differ by $4 \times 44.0 = 176 \text{ kJ}$, the energy to vaporize 4 mol of water at 25°C .

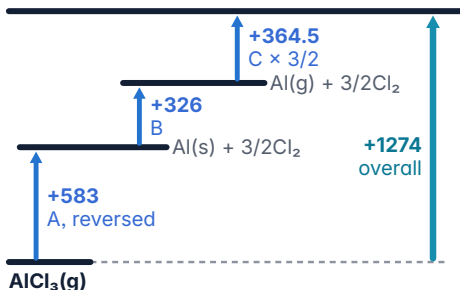
6.9 Hess's law

Energy is conserved, so a reaction's ΔH is the same whether it happens in one step or in many. Split the reaction into steps whose ΔH you know, and add them up.

A reaction and its ΔH change together

Reverse the reaction	same size, opposite sign
Multiply its coefficients by a number	multiply ΔH by the same number
Add reactions	add their ΔH values

- For each substance in the target, pick a given equation that contains it, ideally one where it appears only once.
- Reverse that equation if the substance is on the wrong side.
- Multiply it so the coefficient matches the target.
- Add the equations, cancel anything that appears on both sides in the same phase, and check that exactly the target is left.



- each step: energy in (+)
- the overall ΔH , whichever path you take

Exam trap

- Adding the given ΔH values without changing them. In the AlCl_3 example, $-583 + 326 + 243 = -14$ kJ, which is wrong. Reverse and multiply each equation first, then add.
- Changing an equation but not its ΔH . Reversing A but not multiplying C's ΔH by $3/2$ gives $583 + 326 + 243 = 1152$ kJ instead of 1274.
- Answering a different equation. Give ΔH for the target exactly as written, $\text{AlCl}_3 \rightarrow \text{Al} + 3\text{Cl}$, not for $2\text{AlCl}_3 \rightarrow 2\text{Al} + 6\text{Cl}$.
- Cancelling across phases. $\text{H}_2\text{O(l)}$ does not cancel $\text{H}_2\text{O(g)}$, because they have different enthalpies.

Worked example AlCl_3 into atoms

Find ΔH for $\text{AlCl}_3(\text{g}) \rightarrow \text{Al}(\text{g}) + 3\text{Cl}(\text{g})$ from these three reactions (ΔH in kJ/mol_{rxn}):

- $\text{Al}(\text{s}) + \frac{3}{2}\text{Cl}_2(\text{g}) \rightarrow \text{AlCl}_3(\text{g}) -583$
- $\text{Al}(\text{s}) \rightarrow \text{Al}(\text{g}) +326$
- $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g}) +243$

- Reverse A:
 $\text{AlCl}_3(\text{g}) \rightarrow \text{Al}(\text{s}) + \frac{3}{2}\text{Cl}_2(\text{g}) +583$
- Keep B as written: $\text{Al}(\text{s}) \rightarrow \text{Al}(\text{g}) +326$
- Multiply C by $3/2$:
 $\frac{3}{2}\text{Cl}_2(\text{g}) \rightarrow 3\text{Cl}(\text{g}) +364.5$
- $\text{Al}(\text{s})$ and $\frac{3}{2}\text{Cl}_2$ appear on both sides and cancel. Add the three ΔH values.

$$\Delta H = +1274 \text{ kJ/mol}_{\text{rxn}}$$

Worked example a formation enthalpy

$\text{P}_4(\text{s}) + 6\text{Cl}_2(\text{g}) \rightarrow 4\text{PCl}_3(\text{g})$, -1148 kJ;
 $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{g})$, -88 kJ.
 Find ΔH°_f of $\text{PCl}_5(\text{g})$.

- The target makes 1 mol:
 $\frac{1}{4}\text{P}_4(\text{s}) + \frac{5}{2}\text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{g})$
- Divide the first equation and its ΔH by 4 (-287 kJ), then add the second (-88 kJ). PCl_3 cancels.

$$\Delta H^\circ_f = -375 \text{ kJ/mol}$$

Phase changes count as steps too

$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ has $\Delta H = -198$ kJ. Making $\text{SO}_3(\text{l})$ instead adds a condensing step, which releases more energy, so ΔH is more negative.

Ice turning straight into vapor (sublimation) is melting plus vaporizing. At 0°C , where water's ΔH_{vap} is 45.0 kJ/mol, that is $6.01 + 45.0 = 51.0$ kJ/mol.

Quick check

$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$, $+180.6$ kJ;
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$, -114.2 kJ. Find ΔH for
 $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$.

Answer: add the equations as written. 2NO appears on both sides and cancels, so $\Delta H = 180.6 - 114.2 = +66.4$ kJ.

Quick check

$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ has $\Delta H = -285.8$ kJ. Find ΔH for
 $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$.

Answer: reversing gives $+285.8$ kJ, and doubling gives $+571.6$ kJ.

Finding ΔH°_f of CO, which can't be measured directly

Burning carbon in too little oxygen always makes some CO_2 as well, so ΔH°_f of CO can't be measured directly. It comes from two reactions you can measure:

Burning carbon: $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$, -393.5 kJ

Burning CO, reversed:
 $\text{CO}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$, $+283.0$ kJ

Adding them gives $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$, -110.5 kJ/mol.

Measuring ΔH°_f of MgO with Hess's law

A $\text{Mg}(\text{s}) + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2(\text{g})$

B $\text{MgO}(\text{s}) + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O}(\text{l})$

C $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) -285.8$

HCl and MgCl_2 are in solution (aq). Measure ΔH for A and B in a calorimeter. Then A, plus B reversed, plus C gives
 $\text{Mg}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{MgO}(\text{s})$.

Finding a bond enthalpy with Hess's law

Pulling $\text{AlCl}_3(\text{g})$ apart into $\text{Al}(\text{g}) + 3\text{Cl}(\text{g})$ takes $+1274$ kJ. That breaks three Al–Cl bonds, so the Al–Cl bond enthalpy is $1274 \div 3 = 425$ kJ/mol.

Four ways to find ΔH

	If you are given	find ΔH with
6.4	calorimeter data	$q_{\text{rxn}} \div \text{moles of reaction}$
6.7	bond enthalpies	bonds broken – bonds formed
6.8	ΔH°_f values	products – reactants
6.9	ΔH values of other reactions	reverse, multiply and add

Worked example from combustion data

Find ΔH for $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$ from these burns (kJ/mol_{rxn}):

A. $\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) -1411$

B. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) -285.8$

C. $\text{C}_2\text{H}_6(\text{g}) + \frac{7}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) -1560$

- C_2H_4 and H_2 are reactants, so keep A and B as written.
- C_2H_6 is a product, so reverse C; its ΔH becomes $+1560$.
- O_2 , CO_2 and H_2O cancel, so $\Delta H = -1411 - 285.8 + 1560$

$$\Delta H = -137 \text{ kJ/mol}_{\text{rxn}}$$

Free-response questions on Unit 6

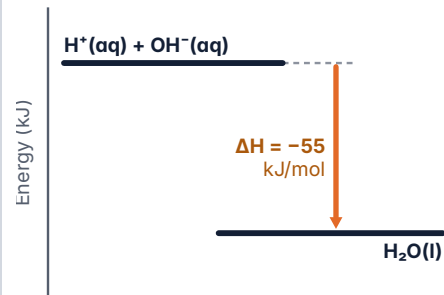
A calculator is allowed, and every number needs its setup and units

⊙ A calorimetry question in the exam's style, worked point by point

A student mixes 50.0 mL of 1.00 M HCl with 50.0 mL of 1.00 M NaOH in a foam-cup calorimeter. The temperature rises from 21.0 °C to 27.6 °C. Take the solution's density as 1.00 g/mL and its specific heat as 4.18 J/(g·°C).

The question asks	An answer that earns the point	What earns it, and what loses it
(a) q for the solution	$q = (100.0 \text{ g})(4.18 \text{ J/(g·°C)})(6.6 \text{ °C}) = 2.8 \times 10^3 \text{ J}$	Use the mass of the whole solution, 100.0 g. $\Delta T = 27.6 - 21.0 = 6.6 \text{ °C}$ has two significant figures, so the answer gets two.
(b) ΔH of neutralization	$q_{\text{rxn}} = -2.7588 \text{ kJ}$, so $\Delta H = \frac{-2.7588 \text{ kJ}}{0.0500 \text{ mol}} = -55 \text{ kJ/mol}$	The reaction's q is the opposite of the solution's. $(0.0500 \text{ L})(1.00 \text{ M}) = 0.0500 \text{ mol}$ of each reactant, which is 0.0500 mol of reaction. Use the unrounded q , in kJ.
(c) justify the sign	The solution's temperature rose, so it gained energy from the reaction. The reaction released energy, so ΔH is negative.	Say which way energy flowed, from what to what. "It got hot" alone does not earn the point.
(d) no lid, so heat escaped	Lost heat makes the measured ΔT too small, so the calculated q is too small and ΔH comes out less negative than the true value.	Start from the measurement, ΔT , then go to q , then to ΔH . Give the direction of the error, not just "it is wrong".
(e) predict ΔT with 100.0 mL of each	The temperature still rises by 6.6 °C.	Twice as much acid and base react and release twice the heat, but twice the mass of solution absorbs it.
(f) draw an energy diagram	Reactants above products, joined by a downward arrow labeled $\Delta H = -55 \text{ kJ/mol}$, as drawn on the right.	The products must be lower, the arrow must start at the reactants, and ΔH needs its sign. Label both levels with formulas and states.
(g) heat from 0.200 mol of NaOH	$q = (0.200 \text{ mol})(-55 \text{ kJ/mol}) = -11 \text{ kJ}$, so 11 kJ is released.	Multiply moles of reaction by ΔH ; give "heat released" as a positive amount.

The energy diagram for part (f)



The net ionic equation is $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$. Writing $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ on the levels is also fine.

🔗 How Unit 6 connects to other units

- Unit 3** Stronger attractions between particles mean a larger ΔH_{vap} and a higher boiling point.
- Unit 5** The energy diagram gains a hump, the activation energy. A catalyst lowers the hump and leaves ΔH unchanged.
- Unit 7** Heating an exothermic reaction at equilibrium shifts it toward the reactants, so the equilibrium constant K gets smaller.
- Unit 9** A reaction is thermodynamically favorable when $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ is negative (ΔS° is the entropy change). A negative ΔH° helps make ΔG° negative.

🔗 Other Unit 6 free-response questions

- To justify endothermic or exothermic**, give the temperature change, the direction energy flowed, and the sign of q for the process.
- To compare two temperature changes**, remember that with the same mass of solution, a larger specific heat or fewer moles reacting gives a smaller ΔT .
- To explain a flat part of a heating curve**, say that the energy overcomes attractions between particles, so their average kinetic energy, and the temperature, stay the same.
- To explain ΔH from bonds**, compare the energy released forming the product bonds with the energy needed to break the reactant bonds.
- For Hess's law**, write out each equation as you changed it, with its new ΔH , before you add.

📖 Units, signs and significant figures

- Convert J to kJ before you divide q by moles, so ΔH comes out in kJ/mol.
- ΔH always carries its sign. When a question asks for the heat released, give a positive amount: "483.6 kJ released" means $\Delta H = -483.6 \text{ kJ}$.
- A subtraction keeps decimal places, not significant figures: $22.38 - 22.00 = 0.38$ has only two.

⚠️ Wording that loses points

- "Bonds release energy when they break." Write: breaking bonds **requires** energy, and forming bonds releases it.
- "Water boils because its bonds break." Write: the **attractions between** water molecules are overcome.
- "Cold flows into the drink." Write: energy flows **from the warmer** object to the cooler one.

📱 Keep every digit until the end

TI-84 Plus CE. Type $100.0 \times 4.18 \times 6.6$ and press **sto→** **alpha** **math** (the letter A) and **enter**. Then type **(-)**, **A** (**alpha** **math** again), **÷** **1000 ÷** **0.0500**. **(-)** is the negative key, not the minus key.

TI-Nspire CX. Type $100.0 \times 4.18 \times 6.6$, press **ctrl** **var** (**sto→**), type q and press **enter**. Then type **(-)** $q \div 1000 \div 0.0500$.

Desmos. Type $q = 100.0 \cdot 4.18 \cdot 6.6$ on one line and $-q/1000/0.0500$ on the next.

Rounding q to 2.8 kJ first gives -56 kJ/mol instead of -55 .

What the question words ask for

- Calculate:** the setup with numbers, then the answer with units and the right significant figures.
- Justify:** the evidence or principle behind your answer.
- Explain:** how or why it happens, in terms of particles and energy.