

THERMOCHEMISTRY

Enthalpy

What enthalpy measures, exothermic vs endothermic, Hess's law, bond energies, calorimetry, and a 10-question practice set with full solutions.

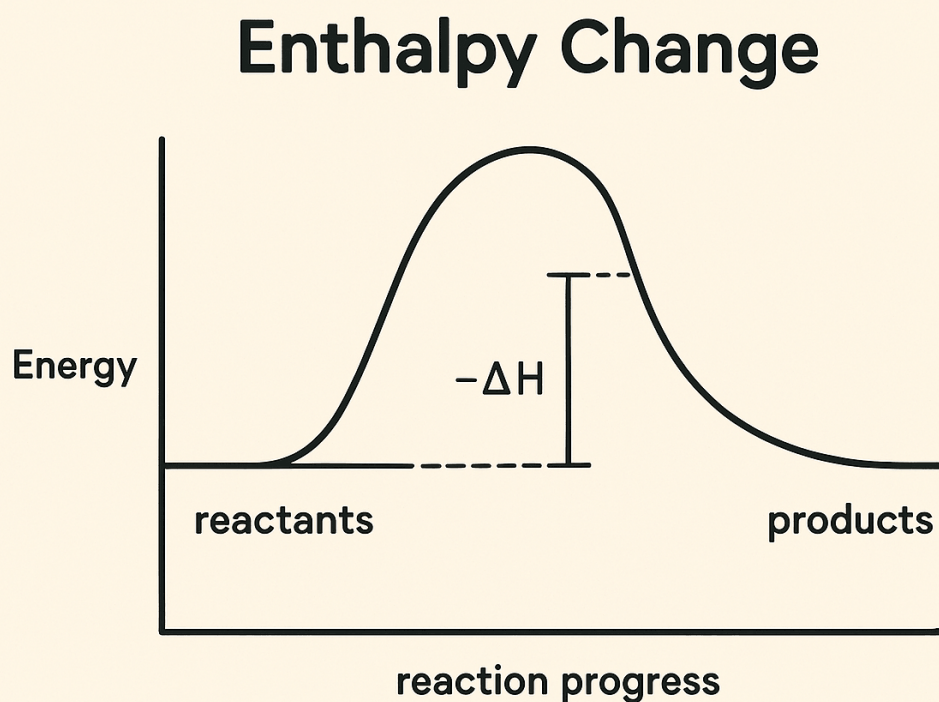
SUBJECT Chemistry	LEVEL High school and early college	INCLUDES Practice set, answer key, revision sheet
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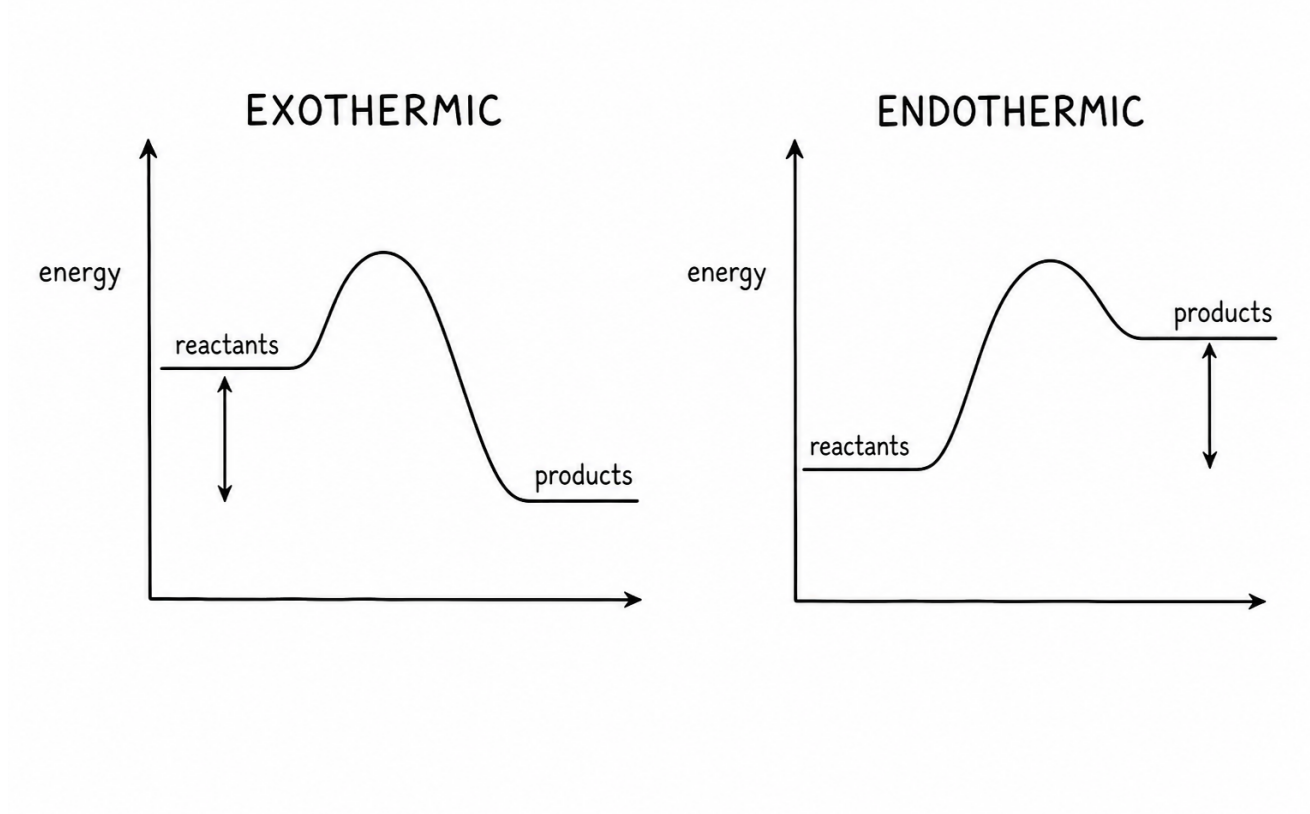
Enthalpy is a thermodynamic quantity that measures the total heat content of a system at constant pressure. The change in enthalpy (ΔH) tells you how much heat a chemical reaction releases or absorbs. Exothermic reactions have $\Delta H < 0$ (release heat to the surroundings). Endothermic reactions have $\Delta H > 0$ (absorb heat). Combustion, neutralization, condensation are exothermic; melting, vaporization, photosynthesis are endothermic. Enthalpy is the central thermodynamic property tracked by almost every chemistry textbook because reactions at constant atmospheric pressure (which is most lab and industrial chemistry) make ΔH directly equal to heat flow.



Enthalpy change ΔH for an exothermic reaction, energy is released from reactants to products.

Definition

Enthalpy H is defined as:



Energy profiles: exothermic reactions end below their starting level ($\Delta H < 0$), endothermic ones end above it ($\Delta H > 0$).

$$H = U + PV$$

where U is internal energy, P is pressure, and V is volume. The product PV is the 'work' contribution from the system pushing against its surroundings at constant pressure.

For a process at constant pressure, the change in enthalpy equals the heat exchanged:

$$\Delta H = q_p$$

This is why enthalpy is so practical, laboratory and industrial chemistry mostly happens at constant atmospheric pressure, so measuring heat flow directly tells you ΔH .

Sign Convention

- $\Delta H < 0$: exothermic. Energy flows OUT of the system as heat. Products have lower energy than reactants. Examples: combustion, neutralization, freezing, condensation.

- $\Delta H > 0$: endothermic. Energy flows INTO the system as heat. Products have higher energy than reactants. Examples: melting, boiling, photosynthesis, dissolving ammonium nitrate in water.

Hess's Law

Hess's law: the total enthalpy change for a reaction is independent of the pathway taken. If a reaction can be broken into intermediate steps, ΔH for the overall reaction equals the sum of ΔH for each step. This is a direct consequence of enthalpy being a state function (it depends only on the initial and final states, not on the path).

Example. To find ΔH for $\text{C(s)} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO(g)}$ (hard to measure directly), use known data for $\text{C(s)} + \text{O}_2 \rightarrow \text{CO}_2$ ($\Delta H = -393.5 \text{ kJ}$) and $\text{CO(g)} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ ($\Delta H = -283.0 \text{ kJ}$). The target reaction's $\Delta H = -393.5 - (-283.0) = -110.5 \text{ kJ}$. Hess's law lets you compute enthalpies of reactions that can't be measured directly.

Standard Enthalpies of Formation

The standard enthalpy of formation ΔH_f° is the enthalpy change when 1 mole of a compound forms from its constituent elements in their standard states (1 atm, 298 K). By convention, ΔH_f° of an element in its standard state is zero.

Tabulated values let you compute ΔH for any reaction:

$$\Delta H_{rxn} = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})$$

where n_p and n_r are the stoichiometric coefficients. A table of ΔH_f° values is the chemistry student's most useful single resource for enthalpy calculations.

Bond Enthalpies

Each chemical bond has a characteristic enthalpy required to break it (in the gas phase). Average bond enthalpies:

BOND	AVERAGE ENTHALPY (KJ/-MOL)	BOND	AVERAGE ENTHALPY (KJ/-MOL)
H-H	436	C-C	346
O=O	498	C=C	614
N≡N	945	C-O	358
O-H	463	C-H	414

Reaction enthalpy can be estimated as: $\Delta H \approx \sum(\text{bonds broken}) - \sum(\text{bonds formed})$. Bonds broken require energy input (positive contribution); bonds formed release energy (negative contribution). Less precise than tabulated formation enthalpies but useful for rough estimates and intuition.

Why Exothermic Doesn't Mean Spontaneous

A common student misconception: that exothermic ($\Delta H < 0$) reactions are always spontaneous. They aren't. Spontaneity depends on the Gibbs free energy change $\Delta G = \Delta H - T\Delta S$, which combines enthalpy and entropy. Even an endothermic reaction can be spontaneous if it produces enough entropy increase (e.g., dissolving ammonium nitrate cools the solution because $\Delta H > 0$ but the entropy gain makes $\Delta G < 0$).

This is why you need both enthalpy and entropy to predict reaction direction. Enthalpy alone is incomplete.

Related study notes: Laws of Thermodynamics, Chemical Equilibrium, Le Chatelier's Principle, Stoichiometry.

Practice Questions

Work each question before reading its solution. The set runs from direct recall and substitution to the applied questions that exams actually use to separate grades.

Q1. Define ΔH and state what its sign tells you about a reaction.

SOLUTION

ΔH is the heat absorbed or released by a reaction at constant pressure. Negative ΔH : exothermic, heat flows out, products sit lower in energy than reactants. Positive ΔH : endothermic, heat flows in. The sign is defined from the system's point of view, not yours.

Q2. How much heat is needed to warm 200 g of water from 25°C to 75°C? ($c = 4.18 \text{ J/g}^\circ\text{C}$)

SOLUTION

$q = mc\Delta T = 200 \times 4.18 \times 50 = 41,800 \text{ J} = 41.8 \text{ kJ}$. Mass in grams, specific heat in $\text{J/g}^\circ\text{C}$, temperature change in $^\circ\text{C}$: the units cancel to joules.

Q3. Given $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$, $\Delta H = -393.5 \text{ kJ/mol}$, and $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$, $\Delta H = -283.0 \text{ kJ/mol}$, find ΔH for $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}$.

SOLUTION

Subtract the second equation from the first: the CO_2 cancels and CO flips to the product side. $\Delta H = -393.5 - (-283.0) = -110.5 \text{ kJ/mol}$. Hess's law: enthalpy changes add like the equations themselves, because enthalpy is a state function.

Q4. Using formation enthalpies (CH_4 : -74.8 , CO_2 : -393.5 , $\text{H}_2\text{O(l)}$: -285.8 , all kJ/mol), find ΔH for $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O(l)}$.

SOLUTION

$\Delta H = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}) = [-393.5 + 2(-285.8)] - [-74.8 + 0] = -965.1 + 74.8 = -890.3 \text{ kJ/mol}$. Elements in their standard states, like O_2 , contribute zero by definition.

Q5. Estimate ΔH for $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ using bond enthalpies: H-H 436, Cl-Cl 242, H-Cl 431 kJ/mol .

SOLUTION

Bonds broken: $436 + 242 = 678$ kJ in. Bonds formed: $2 \times 431 = 862$ kJ out. $\Delta H \approx 678 - 862 = -184$ kJ/mol, exothermic. Break minus form: energy in to break, energy out on forming.

Q6. Why is the enthalpy of vaporization of water (40.7 kJ/mol) so much larger than its enthalpy of fusion (6.0 kJ/mol)?

SOLUTION

Melting only loosens the hydrogen-bond network enough for molecules to slide; most attractions survive into the liquid. Vaporization must separate every molecule from all its neighbors completely, breaking essentially the full set of intermolecular attractions. Nearly 7 times the energy for the full separation is the price.

Q7. Burning 0.5 mol of a fuel releases 445 kJ. Find its molar enthalpy of combustion.

SOLUTION

$\Delta H = -445/0.5 = -890$ kJ/mol, negative because combustion releases heat. Scaling to 1 mole is the whole calculation; forgetting the sign is the common slip.

Q8. Sketch in words the energy profile of an endothermic reaction, distinguishing ΔH from activation energy.

SOLUTION

The curve starts at the reactant level, climbs over a hump, and ends higher than it started. The height from reactants to products is $\Delta H > 0$. The height from reactants to the top of the hump is the activation energy, which exists for exothermic reactions too. ΔH says where you end; activation energy says what the journey costs.

Q9. Why does ΔH for a reaction change when H_2O is produced as gas instead of liquid?

SOLUTION

Standard enthalpies are tied to specific physical states. Producing $\text{H}_2\text{O}(\text{g})$ instead of $\text{H}_2\text{O}(\text{l})$ leaves the vaporization energy, 44 kJ/mol, unreleased, so the reaction gives off 44 kJ less per mole of water. This is exactly why methane's combustion enthalpy is quoted as -890 (liquid water) or -802 kJ/mol (steam).

Q10. A coffee-cup calorimeter measurement of a reaction's heat usually underestimates the true magnitude. Why?

SOLUTION

Some heat leaks to the surroundings: the cup, the thermometer, the air. The water temperature rise then reports less heat than the reaction actually produced. Better insulation and a calibrated calorimeter constant shrink the gap; ignoring it biases every result low.

Answer Key

QUICK ANSWERS

Q1 heat at constant pressure; negative = exothermic **Q2** 41.8 kJ **Q3** -110.5 kJ/mol **Q4** -890.3 kJ/mol **Q5** about -184 kJ/mol
Q6 vaporization breaks all intermolecular attractions **Q7** -890 kJ/mol **Q8** ends higher; ΔH = level difference, E_a = hump **Q9** the 44 kJ/mol of vaporization stays unreleased **Q10** heat loss to the surroundings

Revision Sheet

Signs

$\Delta H < 0$: exothermic, heat out. $\Delta H > 0$: endothermic, heat in.

Calorimetry

$q = mc\Delta T$. Water: $c = 4.18 \text{ J/g}^\circ\text{C}$.

Hess's law

Enthalpy is a state function: add, reverse, and scale equations, and their ΔH values follow the same algebra.

From formation values

$\Delta H_{rxn} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$; elements in standard state count 0.

From bond enthalpies

$\Delta H \approx \sum(\text{bonds broken}) - \sum(\text{bonds formed})$. An estimate: bond values are averages.

States matter

$\text{H}_2\text{O}(\text{l})$ vs $\text{H}_2\text{O}(\text{g})$ differ by 44 kJ/mol. Always write the state symbols.

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