

Unit 6: Thermodynamics

Unit 6 is about energy flow. It covers how to tell whether a process absorbs or releases energy, how to measure heat with calorimetry, how phase changes fit the picture, and three ways to calculate the enthalpy change of a reaction: bond enthalpies, enthalpies of formation, and Hess's law.

AP Chemistry

Thermodynamics

About 14 minutes to read

How to use this guide

Read it in order the first time because the topics build on each other. The sign convention in 6.1 is the foundation for everything after it. Energy diagrams in 6.2 and calorimetry in 6.4 give you the two ways energy shows up in experiments. The three calculation methods in 6.7 through 6.9 all answer the same question, so compare them as you go rather than memorizing each in isolation.

After the first read, use the trap boxes and the sign-convention table to review the distinctions that exam questions test most often. Finish with the practice questions, then complete the recall check on the last page out loud and note any items you cannot explain yet.

What this unit is worth. Thermodynamics is roughly 7 to 9 percent of the AP Chemistry exam, but it connects forward to equilibrium in Unit 7, where the sign of ΔH decides how temperature shifts an equilibrium. Getting the sign convention automatic now pays off there.

6.1 Endothermic and Exothermic Processes

Every energy question starts by drawing a boundary. The **system** is whatever you are studying, and the **surroundings** are everything else. Energy is conserved across that boundary: whatever the system loses, the surroundings gain, and vice versa. This is the **first law of thermodynamics**, and it means an energy change is always a trade, never a disappearance.

An **endothermic process** is one in which the system gains energy from the surroundings. Ice melting and water evaporating are the classic examples. Because the surroundings lose energy, they cool down. An **exothermic process** is the reverse: the system loses energy to the surroundings. Water condensing and freezing are exothermic, and the surroundings warm up as a result.

Dissolving a salt is a good test of whether you really have this. The **heat of solution** can go either way. Ammonium nitrate dissolving in water absorbs energy, which is why it is used in instant cold packs. Calcium chloride dissolving releases energy, which is why it is used in hot packs. Whether dissolving is endothermic or exothermic depends on the balance between the energy needed to pull the solute and solvent particles apart and the energy released when the new solute-solvent interactions form.

Trap. "Endothermic" and "exothermic" describe the system, not the surroundings. When a cold pack gets cold, the surroundings are cooling, but the dissolving process is endothermic because the system is gaining energy. Always anchor the word to the system.

6.2 Energy Diagrams

An **energy diagram** plots the energy of the system against the progress of a process, with reactants on the left and products on the right. Reading it is simple. If the products sit higher than the reactants, the system gained energy and the process is endothermic. If the products sit lower, the system lost energy and the process is exothermic. The vertical difference between the two levels is the enthalpy change.

The same diagram shape works for a reaction and for a phase change. Ice melting has products (liquid water) above the reactants (ice), so it is endothermic. Steam condensing has products (liquid water) below the reactants (steam), so it is exothermic.

Trap. The direction of the arrow on an energy diagram is not the direction of energy flow. Upward means the products have more energy than the reactants, which is endothermic. Students sometimes read an upward arrow as energy leaving the system. It is the opposite: the system had to take energy in to get there.

6.3 Heat Transfer

Heat transfer is energy moving between objects through molecular collisions. Note the careful wording: heat is the process of transfer, not a substance that flows. A hot object does not contain heat the way it contains mass. It has thermal energy, and heat is what you call the energy while it is moving from the hotter object to the cooler one.

Two objects in contact reach **thermal equilibrium** when they stop exchanging net energy. At that point they have the same temperature, which is another way of saying their particles have the same average kinetic energy. A metal spoon left in hot soup eventually reaches the temperature of the soup because collisions keep transferring energy from the faster-moving soup particles to the slower-moving metal particles until the averages match.

Trap. Temperature and thermal energy are not the same thing. Temperature measures average kinetic energy per particle. A bathtub of lukewarm water has a lower temperature than a cup of boiling water but far more total thermal energy, because thermal energy scales with the number of particles. Exam questions exploit this confusion regularly.

6.4 Calorimetry

Calorimetry is the experimental measurement of heat transferred in a process, usually with a calorimeter. The workhorse equation is $q = mc\Delta T$, where q is the heat absorbed or released, m is the mass in grams, c is the **specific heat capacity**, and ΔT is the temperature change. The specific heat capacity of liquid water is $4.184 \text{ J/g}^\circ\text{C}$, the highest of any common liquid, which is why water resists temperature change so stubbornly.

Run the numbers on a simple case. Heating 50.0 g of water from 20.0°C to 35.0°C requires $q = (50.0 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(15.0^\circ\text{C}) = 3.14 \times 10^3 \text{ J}$, or 3.14 kJ . The positive sign means the water gained energy, which matches the fact that its temperature rose. If the temperature had fallen, ΔT would be negative and q would be negative, meaning the water lost energy.

The **molar heat capacity** is the same idea per mole instead of per gram: the energy needed to raise one mole of a substance by 1°C . Convert between the two with the molar mass. And calorimetry only works because of the first law: in an insulated calorimeter, the heat lost by the hot object equals the heat gained by the cold one, so $q_{\text{lost}} = -q_{\text{gained}}$.

Trap. The sign of q follows ΔT , and ΔT is always final minus initial. If you compute initial minus final by mistake, the sign flips and an exothermic process looks endothermic. Write $T_{\text{final}} - T_{\text{initial}}$ explicitly every time until it is habit.

6.5 Enthalpy of Fusion and Vaporization

Phase changes absorb or release energy without changing temperature. The **molar enthalpy of fusion**, ΔH_{fus} , is the energy needed to melt one mole of a substance at constant temperature. For water it is +6.01 kJ/mol. The **molar enthalpy of vaporization**, ΔH_{vap} , is the energy needed to vaporize one mole; for water it is +40.7 kJ/mol. Both are positive because melting and vaporization are endothermic: they break intermolecular attractions, and that takes energy.

The reverse changes release exactly as much as the forward ones absorb. Freezing releases the same energy melting requires, and condensation releases the same energy vaporization requires. That is why steam burns are worse than boiling-water burns: condensing steam deposits its ΔH_{vap} into your skin on top of the cooling that follows.

Notice what stays flat during all of this. Melting, freezing, vaporization, and condensation each happen at **constant temperature** while energy flows in or out. On a heating curve, the temperature rises while you warm a single phase, then holds steady while the phase changes, then rises again. The flat segments are where ΔH_{fus} and ΔH_{vap} are doing their work.

Trap. Temperature does not change during a phase change, so $q = mc\Delta T$ does not apply there. Heating ice from -10°C to 0°C uses $mc\Delta T$. Melting it at 0°C uses $n \times \Delta H_{\text{fus}}$. A heating-curve calculation that mixes the two formulas up is one of the most common arithmetic errors in this unit.

6.6 Enthalpy Change (ΔH)

The **enthalpy change**, ΔH , is the heat absorbed or released by a process at constant pressure. Almost all of the reactions you will meet happen at constant pressure (open to the atmosphere), so ΔH is the quantity the exam cares about. The sign convention is the single most important thing in this unit: a negative ΔH means heat was released, so the process is exothermic; a positive ΔH means heat was absorbed, so the process is endothermic.

SIGN OF ΔH	WHAT HAPPENED	EXAMPLE
$\Delta H < 0$ (negative)	Heat released. Exothermic.	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$, $\Delta H = -890 \text{ kJ}$
$\Delta H > 0$ (positive)	Heat absorbed. Endothermic.	$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$, $\Delta H = +44 \text{ kJ}$

One more detail that matters for calculations: ΔH scales with the amount of reaction. The value -890 kJ above is for the reaction exactly as written, burning one mole of methane. Burn two moles and the enthalpy change is -1780 kJ . Always check the coefficients before using a ΔH value in a calculation.

Trap. A negative ΔH does not mean the reaction absorbs energy. The minus sign means the system's enthalpy went down, which means energy left the system as heat. Exothermic reactions have negative ΔH values. If this still feels backwards, say it out loud: "negative ΔH , heat out."

6.7 Bond Enthalpies

A **bond enthalpy** is the average energy needed to break one mole of a particular bond in the gas phase. The key word is average: the O–H bond in water and the O–H bond in an alcohol are not identical, so tables report averages. Reaction enthalpy can be estimated from bond enthalpies with one equation: $\Delta H = \Sigma(\text{bond enthalpies of bonds broken}) - \Sigma(\text{bond enthalpies of bonds formed})$.

The subtraction order is not arbitrary. **Breaking bonds always requires energy**, so it is endothermic and contributes a positive term. **Forming bonds always releases energy**, so it is exothermic and contributes a negative term. That is the whole logic of the formula: add up what breaking costs, subtract what forming pays back.

Work it for $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$. Break one H–H bond (436 kJ/mol) and one Cl–Cl bond (242 kJ/mol), costing 678 kJ. Form two H–Cl bonds (431 kJ/mol each), releasing 862 kJ. $\Delta H = 678 - 862 = -184$ kJ. Negative, so the reaction is exothermic, which matches the vigorous reaction of hydrogen and chlorine.

Trap. The most common bond-enthalpy error is subtracting in the wrong order: formed minus broken instead of broken minus formed. That flips the sign and turns an exothermic reaction endothermic. Also, bond enthalpies only apply to gases. Using them for a reaction involving liquids or solids gives a wrong answer; that is what enthalpies of formation are for.

6.8 Standard Enthalpy 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. The standard state is the most stable form at 1 atm and (usually) 25°C: $\text{O}_2(\text{g})$ for oxygen, $\text{C}(\text{s, graphite})$ for carbon, and so on. A direct consequence is that $\Delta H_f^\circ = 0$ for every element in its standard state, since forming an element from itself involves no change.

Reaction enthalpy follows from formation enthalpies with a formula that mirrors the bond-enthalpy one but with the subtraction reversed: $\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants})$, with each value multiplied by its coefficient. Take the combustion of methane, $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$. Using ΔH_f° values of -74.8 for CH_4 , 0 for O_2 , -393.5 for CO_2 , and -285.8 kJ/mol for $\text{H}_2\text{O}(\text{l})$: $\Delta H^\circ_{\text{rxn}} = [-393.5 + 2(-285.8)] - [-74.8 + 2(0)] = -890.3$ kJ. Exothermic, as expected for combustion.

Trap. The two estimation formulas subtract in opposite orders, and the exam loves that. Bond enthalpies: broken minus formed. Formation enthalpies: products minus reactants. Write the formula before plugging in numbers, and check the order every time. Also remember to multiply each ΔH_f° by its coefficient; the 2 in front of H_2O is easy to drop.

6.9 Hess's Law

Hess's law says the enthalpy change of an overall reaction equals the sum of the enthalpy changes of the steps that make it up. Enthalpy is a state function: it depends only on where you start and where you end, not on the path. That is what makes the law true, and it is why you can combine reactions like algebra.

Three moves cover every Hess's law problem. **Reversing** a reaction flips the sign of its ΔH . **Scaling** a reaction by a factor scales its ΔH by the same factor. **Adding** reactions adds their ΔH values. Manipulate the given steps until they add up to the target reaction, applying the same operations to the ΔH values, then sum.

Find ΔH for $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ from these steps: (1) $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$, $\Delta H = -110.5 \text{ kJ}$; (2) $\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$, $\Delta H = -283.0 \text{ kJ}$. The steps already add to the target with no reversing or scaling needed: $\text{C} + \frac{1}{2}\text{O}_2 + \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + \text{CO}_2$, and the CO cancels on both sides, leaving $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$. Add the ΔH values: $-110.5 + (-283.0) = -393.5 \text{ kJ}$.

Trap. The usual Hess's law mistake is forgetting to apply an operation to ΔH . If you multiply a reaction by 2 to match coefficients, multiply its ΔH by 2 as well. If you reverse a reaction, flip the sign. Students who get the algebra of the species right and skip the ΔH bookkeeping lose the whole problem.

Three Ways to Find ΔH

METHOD	WHEN TO USE IT	FORMULA
Bond enthalpies	All species are gases; you are given a bond-enthalpy table.	$\Delta H = \Sigma(\text{broken}) - \Sigma(\text{formed})$
Enthalpies of formation	You are given a ΔH_f° table. Works for any phases.	$\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants})$
Hess's law	You are given other reactions with known ΔH values.	Reverse, scale, and add steps; do the same to ΔH .

Practice Questions

Original questions written for this guide in the style of the AP exam. Answers and explanations are on the next page, so complete the questions before checking them.

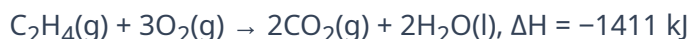
1. A 25.0 g sample of an unknown metal at 95.0°C is placed in 50.0 g of water at 20.0°C in an insulated calorimeter. The final temperature is 24.5°C. What is the specific heat capacity of the metal?

- A. 0.13 J/g°C
- B. 0.53 J/g°C
- C. 0.90 J/g°C
- D. 4.18 J/g°C

2. Which of the following processes is exothermic?

- A. Ice melting at 0°C
- B. Water evaporating at 100°C
- C. Steam condensing at 100°C
- D. Ammonium nitrate dissolving in water

3. Given the following reactions:



What is ΔH for the reaction $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$?

- A. -137 kJ
- B. -149 kJ
- C. +137 kJ
- D. -3120 kJ

4. Using average bond enthalpies, estimate ΔH for the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$. Bond enthalpies: $\text{N}\equiv\text{N}$ 945 kJ/mol, $\text{H}-\text{H}$ 436 kJ/mol, $\text{N}-\text{H}$ 391 kJ/mol.

- A. -93 kJ
- B. +93 kJ
- C. -2253 kJ
- D. +2253 kJ

5. Use standard enthalpies of formation to calculate ΔH for $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$. ΔH_f° values: $\text{CH}_4(\text{g}) = -74.8 \text{ kJ/mol}$, $\text{CO}_2(\text{g}) = -393.5 \text{ kJ/mol}$, $\text{H}_2\text{O}(\text{l}) = -285.8 \text{ kJ/mol}$.

- A. -890 kJ
- B. -605 kJ
- C. +890 kJ
- D. -965 kJ

6. How much heat is required to melt 36.0 g of ice at 0°C? ΔH_{fus} for water = 6.02 kJ/mol.

- A. 12.0 kJ
- B. 217 kJ
- C. 6.02 kJ
- D. 0.332 kJ

Answer Key

1. B. The water gained $q = (50.0 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(24.5 - 20.0^\circ\text{C}) = 941 \text{ J}$. The metal lost the same 941 J, so $941 = (25.0 \text{ g})(c)(95.0 - 24.5^\circ\text{C}) = (25.0)(c)(70.5)$, giving $c = 941 / 1762.5 = 0.53 \text{ J/g}^\circ\text{C}$. A is far too low for a metal and would imply almost no temperature change in the metal. C is close to the value for aluminum but does not match this data. D is the specific heat of water, not the metal.

2. C. Condensation forms intermolecular attractions, releasing energy, so it is exothermic. A and B break attractions and are endothermic. D absorbs energy (cold packs), so it is endothermic.

3. A. Add the first and third reactions and subtract the second: $(\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}) + (\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}) - (\text{C}_2\text{H}_6 + 7/2\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O})$ gives $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$ after canceling. $\Delta H = -1411 + (-286) - (-1560) = -137 \text{ kJ}$. C flips a sign somewhere in the bookkeeping. B and D come from adding reactions without canceling properly.

4. A. Broken: one $\text{N}\equiv\text{N}$ (945) + three $\text{H}-\text{H}$ ($3 \times 436 = 1308$), total 2253 kJ. Formed: six $\text{N}-\text{H}$ bonds ($6 \times 391 = 2346 \text{ kJ}$). $\Delta H = 2253 - 2346 = -93 \text{ kJ}$. B flips the subtraction order. C and D report only one side of the calculation instead of the difference.

5. A. $\Delta H = [\Delta H_f^\circ(\text{CO}_2) + 2\Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{CH}_4)] = [-393.5 + 2(-285.8)] - [-74.8] = -965.1 + 74.8 = -890 \text{ kJ}$. B forgets the coefficient 2 on H_2O , giving $-393.5 - 285.8 + 74.8 = -605 \text{ kJ}$. C flips the subtraction order (reactants minus products). D subtracts nothing for the reactants.

6. A. Convert grams to moles first: $36.0 \text{ g} / 18.02 \text{ g/mol} = 2.00 \text{ mol}$. Then $q = n\Delta H_{\text{fus}} = (2.00 \text{ mol})(6.02 \text{ kJ/mol}) = 12.0 \text{ kJ}$. B multiplies the grams directly by ΔH_{fus} without converting to moles. C is the per-mole value, ignoring the amount present. D divides by ΔH_{fus} instead of multiplying.

7. B. Freezing is the reverse of melting, so $\Delta H_{\text{freezing}} = -\Delta H_{\text{fus}} = -6.02 \text{ kJ/mol}$; the negative sign matches an exothermic process. A is wrong because combustion releases energy, so its ΔH is negative. C is wrong because vaporization absorbs energy, so its ΔH is positive. D is wrong because ammonium nitrate dissolving absorbs energy (cold packs feel cold), so its ΔH is positive.

8. A. The solution gained $q = (105.0 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(27.3 - 22.0^\circ\text{C}) = (105.0)(4.184)(5.3) = 2329 \text{ J} = 2.33 \text{ kJ}$. Moles of $\text{NaOH} = 5.00 \text{ g} / 40.00 \text{ g/mol} = 0.125 \text{ mol}$. Heat of solution = $-2.33 \text{ kJ} / 0.125 \text{ mol} = -18.6 \text{ kJ/mol}$; the sign is negative because the temperature rose, meaning the process released heat. B gets the sign backwards. C reports the total heat without dividing by moles. D slips a decimal place.

One-Page Recall Check

- Define the system and the surroundings, and state the first law of thermodynamics in your own words.
- Give two examples each of endothermic and exothermic processes, and explain what happens to the surroundings in each case.
- Explain why dissolving ammonium nitrate feels cold and dissolving calcium chloride feels hot.
- Sketch an energy diagram for an exothermic reaction and label reactants, products, and ΔH .
- Explain the difference between temperature and thermal energy.
- Write $q = mc\Delta T$ and use it to find the heat when 100 g of water cools from 80°C to 30°C.
- Explain why a phase change happens at constant temperature.
- State the sign convention for ΔH and give one example of each sign.
- State the bond-enthalpy formula and explain why the subtraction goes in that order.
- State the formation-enthalpy formula and explain why $\Delta H_f^\circ = 0$ for elements in standard states.
- List the three Hess's law moves and what each does to ΔH .
- Explain when to use bond enthalpies versus enthalpies of formation versus Hess's law.

Study this unit in Rycal. Turn every missed item above into flashcards and drill them spaced out over several days rather than in one sitting. In Rycal, open the Thermodynamics deck under AP Chemistry at rycal.web.app/apchem. The deck covers the terms in this guide, and its practice questions target the same traps named here. If you have a test date, add it in the Test Planner. You can also start your next review with a Brain Dump, then check what you missed against this guide.

Key terms for this unit

Endothermic process, Exothermic process, System and surroundings, Heat of solution, Energy diagram, Heat transfer, Thermal equilibrium, Specific heat capacity (c), Molar heat capacity, Calorimetry, First law of thermodynamics, Molar enthalpy of fusion and vaporization, Phase changes at constant temperature, Enthalpy change (ΔH), Bond enthalpy (bond energy), Bond breaking vs. bond forming, Standard enthalpy of formation (ΔH_f°), Hess's law.

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