Topic 6.4: Heat Capacity and Calorimetry

Revision Notes · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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Two Instruments, Two Different Quantities

A calorimeter lets a reaction warm or cool a known surroundings and reads the temperature change. Two designs dominate, and they do not measure the same quantity.

A coffee-cup calorimeter is two nested foam cups open to the air, so the pressure inside stays atmospheric and the heat it measures is the heat at constant pressure: q_p, the enthalpy change, ΔH.

A bomb calorimeter seals the sample inside a rigid steel vessel surrounded by water. The rigid walls fix the volume, so no expansion work can be done and the heat released is the change in internal energy, ΔE. The sealed bomb is also the safe instrument for combustion.

Heat Capacity: Per Object, Per Gram, Per Mole

Heat capacity, C, is the heat needed to raise a whole object or sample by one degree Celsius, in J $°C^{-1}$, with

$q = C\Delta T$

It belongs to that object: double the material and C doubles.

Specific heat capacity, c, strips the amount away: the heat needed to raise one gram by one degree, in J g^{-1} $°C^{-1}$, with

$q = mc\Delta T$

Water's value is 4.18 J g^{-1} $°C^{-1}$, so a water sample's heat capacity is

C = mc:

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100 g of water has C = 100 × 4.18 = 418 J °C^{-1}.

Molar heat capacity is the same idea per mole, in J mol^{-1} °C^{-1}; for water, 4.18 × 18.0 = 75.2 J mol^{-1} °C^{-1}.

The Calorimeter Constant

The water is not the only thing that warms. The cup, lid, stirrer and thermometer absorb heat too; their combined heat capacity is the calorimeter constant, C_cal, in J °C^{-1}. Their heat is

q_cal = C_cal × ΔT,

with the water's ΔT, because hardware and water start and finish together.

C_cal is found by calibration: mix known masses of hot and cold water in the calorimeter and compare the ledger: the hot water's loss exceeds the cold water's gain, and the shortfall is what the hardware absorbed.

The Energy Ledger of a Calorimetry Run

Treat the calorimeter as insulated and the ledger must balance: every joule the reaction releases is gained by the water and the hardware, and every joule it absorbs is lost by them. So

q_reaction = −(q_water + q_calorimeter)

Signs follow the rule from Topic 6.1, from the system's point of view. An exothermic reaction releases heat: the solution warms, ΔT and q_water are positive, and the minus sign makes q_reaction, and so ΔH, negative. An endothermic reaction absorbs heat: the solution cools, ΔT and q_water are negative, and q_reaction and ΔH come out positive.

The same ledger serves a hot metal dropped into the calorimeter: heat lost by the metal equals heat gained by the water plus heat gained by the hardware.

From Measured Heat to Enthalpy Per Mole

The ledger gives q for the amounts used, not per mole. To report ΔH, divide q_reaction by the moles of limiting reactant that reacted and convert to kilojoules:

ΔH = q_reaction ÷ n, in kJ mol^{-1}

Only the coffee-cup result converts straight into ΔH, because only it runs at constant pressure; a bomb result divided by moles gives ΔE per mole. The divisor is the limiting reactant: excess reactant never reacted, so its moles never entered.

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Where the Measurement Leaks

The calculation assumes no heat crosses to the room, the solution has the density and specific heat capacity of pure water, and the reaction completes. Heat exchange with the surroundings breaks first: the foam cup insulates well but not perfectly, so part of the heat leaks away.

Both big errors shrink the answer rather than flip it: neglecting C_cal leaves part of the absorbed heat uncounted, so ΔH is too small in magnitude, its sign unchanged.

Precision also hides in ΔT, the one quantity actually read: the same heat would move a low-specific-heat liquid through a far larger swing, while water's high c keeps school temperature changes small.

Worked Examples

Example 1: An exothermic neutralisation. 50.0 mL of 1.00 mol L^{-1} HCl mixes with 50.0 mL of 1.00 mol L^{-1} NaOH in a coffee-cup calorimeter: HCl + NaOH → NaCl + H_2O. The 100 g of solution warms from 24.0 °C to 30.7 °C, so ΔT = +6.7 °C. The solution gained q = mcΔT = 100 × 4.18 × 6.7 = +2,800.6 J, so q_reaction = −2,800.6 J: negative, as an exothermic reaction requires. The limiting reactant is 0.0500 mol, so ΔH = −2,800.6 ÷ 0.0500 = −56.0 kJ mol^{-1}.

Example 2: An endothermic dissolving, with the hardware counted. 5.35 g of NH_4Cl (molar mass 53.5 g mol^{-1}, so 0.100 mol) dissolves in water in a calorimeter with C_cal = 40 J $°C^{-1}$; the solution, mass 100 g, cools from 20.0 °C to 16.0 °C: $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$. Here ΔT = −4.0 °C, so q_water = 100 × 4.18 × (−4.0) = −1,672 J and q_calorimeter = 40 × (−4.0) = −160 J. The ledger gives q_reaction = −(−1,672 + (−160)) = +1,832 J: positive, as an endothermic process requires. ΔH = 1,832 ÷ 0.100 = +18.3 kJ mol^{-1}.

Example 3: A bomb calorimeter run. A fuel sample burns in a bomb calorimeter with C_cal = 9.60 kJ $°C^{-1}$, and the temperature rises by 2.50 °C. The calorimeter absorbed q = C_cal × ΔT = 9.60 × 2.50 = 24.0 kJ, so the combustion released 24.0 kJ. The 1.50 g sample (molar mass 100 g mol^{-1}) is 0.0150 mol, so ΔE = −24.0 ÷ 0.0150 = -1.60×10^3 kJ mol^{-1}: ΔE, not ΔH, because the volume never changed.

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Example 4: Calibrating with hot and cold water. 50.0 g of water at 60.0 °C is poured into a calorimeter holding 50.0 g of water at 20.0 °C, and the mixture settles at 38.0 °C, not the 40.0 °C of a simple average. The hot water lost 50 × 4.18 × 22 = 4,598 J; the cold water gained 50 × 4.18 × 18 = 3,762 J. The missing 836 J warmed the hardware through the same 18 °C rise, so C_{cal} = 836 ÷ 18 = 46.4 J $°C^{-1}$.

Traps That Cost Marks in Topic 6.4

"$q_{reaction} = q_{water}$." That drops the sign and the hardware. The reaction's heat is the negative of everything the surroundings gained: $q_{reaction} = -(q_{water} + q_{calorimeter})$.

"The bomb calorimeter measures ΔH." The bomb is rigid: volume constant, heat equal to ΔE. Only constant-pressure calorimetry, the open coffee cup, yields ΔH directly.

"The temperature fell, so ΔH is negative." A falling temperature means the solution gave heat to the reaction: the process absorbed heat, so it is endothermic and ΔH is positive.

"Ignoring C_{cal} makes ΔH too large." It does the opposite. Heat the hardware absorbs is real reaction heat; leaving it out undercounts the total, so ΔH is too small in magnitude.

"Heat capacity and specific heat capacity are the same thing." Heat capacity belongs to a sample and grows with its size; specific heat capacity is per gram, a fixed property of the substance.

"Divide q by the moles of whichever reactant is easiest." ΔH per mole uses the limiting reactant, the one fully consumed; dividing by an excess reactant's moles understates ΔH.

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Key Relationships to Remember

- Coffee-cup calorimeter: open cup, constant pressure, measures $q_p = \Delta H$
- Bomb calorimeter: sealed rigid vessel, constant volume, measures ΔE; the safe choice for combustions
- Heat capacity C of a sample: $q = C\Delta T$, in J $°C^{-1}$; for a pure substance, $C = mc$
- Specific heat capacity c is per gram (J g^{-1} $°C^{-1}$) and molar heat capacity is per mole (J mol^{-1} $°C^{-1}$); water: c = 4.18, molar value 75.2
- Calorimeter constant C_{cal} covers cup, lid, stirrer and thermometer: $q_{cal} = C_{cal} \times \Delta T$, found by mixing hot and cold water
- Energy ledger: $q_{reaction} = -(q_{water} + q_{calorimeter})$; a hot metal obeys the same balance, its lost heat split between water and hardware
- Exothermic: solution warms, $q_{reaction}$ and ΔH negative; endothermic: solution cools, both positive
- $\Delta H = q_{reaction} \div$ moles of limiting reactant, converted to kJ mol^{-1}
- Heat exchange with the surroundings is the main error in coffee-cup work, and neglecting C_{cal} also shrinks the result: both leave ΔH too small in magnitude

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