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Topic 6.4: Heat Capacity and Calorimetry

Worksheet · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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How to Use This Worksheet

Work in order. Section A checks the vocabulary and the two instruments: heat capacity in its three sizes, the calorimeter constant, the energy ledger and its signs, and the assumptions that limit accuracy. Section B practises the calculations: a bomb run, a dissolving salt, a hot metal in a calorimeter, a calibration, and an endothermic dissolving with the hardware counted. Section C is exam style: a full experiment with error analysis, five claims to judge, and a combustion in a bomb calorimeter.

Reference facts. Specific heat capacity of water and of dilute aqueous solutions: 4.18 J g^{-1} $°C^{-1}$. Take the density of a dilute solution as 1.00 g mL^{-1}, so a volume in millilitres gives the same number as a mass in grams. $q = mc\Delta T$ for a mass of solution warming or cooling; $q = C\Delta T$ for a whole object or a calorimeter; $q_{reaction} = -(q_{water} + q_{calorimeter})$. Signs are taken from the system's point of view: a reaction that warms its surroundings is exothermic, with $q_{reaction}$ and ΔH negative.

Three habits protect every answer. Work out ΔT first, as final minus initial, and keep the sign it gives you. Count every place the heat went: the water and the hardware both. Finish by dividing by the moles of the limiting reactant, and check whether the instrument you used reports ΔH or ΔE.

Do not look at the answer key until you have attempted every question.

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Section A: Recall and Concepts

A1. (a) State what a coffee-cup calorimeter holds constant, and the quantity its heat measurement gives directly. (b) State what a bomb calorimeter holds constant, and the quantity it gives. (c) Explain why the coffee cup is open to the air. (d) State two reasons a bomb calorimeter, rather than a coffee cup, is used for combustions.

A2. (a) Define the heat capacity of an object, and state its units and its equation. (b) Define specific heat capacity, and state its units. (c) Define molar heat capacity, and state its units. (d) Calculate the heat capacity of 250 g of water. (e) State how the heat capacity of a pure sample is obtained from its specific heat capacity.

A3. (a) State what the calorimeter constant, C_{cal}, accounts for. (b) State its units, and write the equation for the heat the hardware absorbs. (c) Describe how C_{cal} is determined experimentally. (d) State which temperature change is used in the hardware equation, and why it is that one.

A4. (a) Write $q_{reaction}$ in terms of q_{water} and $q_{calorimeter}$, and state the assumption the equation rests on. (b) A reaction in a coffee-cup calorimeter makes the solution temperature rise. State the signs of q_{water}, $q_{reaction}$ and ΔH. (c) Repeat part (b) for a reaction that makes the temperature fall. (d) A hot metal is placed in a calorimeter of water. Write the energy balance connecting the metal, the water and the hardware.

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A5. (a) State the main source of error in coffee-cup calorimetry. (b) State the direction in which that error pushes the calculated ΔH. (c) A student leaves the calorimeter constant out of the calculation. State what happens to the magnitude of the calculated ΔH, and what happens to its sign. (d) State what would happen to temperature changes, and to the precision of the measurements, if the specific heat capacity of water were much lower. (e) State two further assumptions made when a coffee-cup result is calculated.

Section B: Core Practice

B1. A sample burns in a bomb calorimeter with C_cal = 7.50 kJ °C^{-1}, raising the temperature by 2.80 °C. (a) Calculate the heat absorbed by the calorimeter. (b) State the heat released by the combustion, with its sign from the reaction's point of view. (c) The sample mass was 0.600 g and its molar mass is 60.0 g mol^{-1}. Calculate the moles burned. (d) Calculate ΔE for the combustion, in kJ mol^{-1}. (e) State why the answer is ΔE and not ΔH.

B2. 5.55 g of $CaCl_2$ (molar mass 111 g mol^{-1}) dissolves in water in a coffee-cup calorimeter: $CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$. The total solution mass is 100 g, and the temperature rises from 24.0 °C to 33.7 °C. (a) Calculate ΔT. (b) Calculate q for the solution, showing the substitution. (c) State q_reaction, and whether the dissolving is exothermic or endothermic. (d) Calculate the moles of $CaCl_2$ dissolved. (e) Calculate the enthalpy of solution, ΔH, in kJ mol^{-1}.

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B3. A 50.0 g block of metal at 100.0 °C is placed in a calorimeter holding 100 g of water at 25.0 °C. The calorimeter constant is 30.0 J $°C^{-1}$, and everything settles at 28.0 °C. (a) Calculate the heat gained by the water. (b) Calculate the heat gained by the calorimeter hardware. (c) State the heat lost by the metal. (d) Calculate the specific heat capacity of the metal. (e) State the assumption that lets part (c) follow from parts (a) and (b).

B4. A student calibrates a calorimeter by pouring 60.0 g of water at 55.0 °C into 60.0 g of water at 25.0 °C already inside it. The mixture settles at 38.5 °C. (a) Calculate the heat lost by the hot water. (b) Calculate the heat gained by the cold water. (c) Calculate the heat absorbed by the calorimeter hardware. (d) Calculate C_cal. (e) State the temperature change you used for the hardware in part (d), and why it is that value.

B5. 10.7 g of NH_4Cl (molar mass 53.5 g mol^{-1}) dissolves in water in a coffee-cup calorimeter with C_cal = 50 J $°C^{-1}$: $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$. The total solution mass is 200 g, and the temperature falls from 22.0 °C to 18.2 °C. (a) Calculate ΔT, with its sign. (b) Calculate q for the solution. (c) Calculate q for the calorimeter hardware. (d) Calculate q_reaction, and state whether the dissolving is exothermic or endothermic. (e) Calculate ΔH of solution, in kJ mol^{-1}.

B6. (a) Calculate the heat capacity of 400 g of water. (b) A calorimeter assembly with C_cal = 85 J $°C^{-1}$ warms by 4.0 °C during a run. Calculate the heat it absorbed. (c) Using the molar mass of water, 18.0 g mol^{-1}, calculate the molar heat capacity of water. (d) A student doubles the mass of water in a coffee-cup calorimeter and repeats exactly the same reaction. State what happens to ΔT and to the calculated ΔH, and explain both answers.

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Section C: Exam Style

C1. A student reacts 0.243 g of magnesium ribbon (molar mass 24.3 g mol^{-1}) with excess hydrochloric acid in a coffee-cup calorimeter: Mg + 2HCl → $MgCl_2$ + H_2. The solution has mass 50.0 g, the calorimeter constant is 20 J $°C^{-1}$, and the temperature rises from 20.0 °C to 40.4 °C. (a) Calculate the heat absorbed by the solution. (b) Calculate the heat absorbed by the calorimeter hardware. (c) Calculate q_reaction, and hence ΔH for the reaction in kJ per mole of magnesium, stating the sign evidence as you go. (d) A second student ignores the calorimeter constant. Calculate the ΔH she obtains, and state how it compares with the part (c) value. (e) The accepted ΔH is more negative than even the part (c) value. Give the reason, naming the assumption that fails.

C2. Judge each claim, supporting each verdict with the rule it depends on. (a) "A bomb calorimeter measures ΔH, because the combustion heat ends up in the water around the bomb." (b) "The temperature in a coffee-cup calorimeter fell during a reaction, so ΔH for the reaction is negative." (c) "Doubling the mass of solution in the cup doubles the temperature rise produced by the same reaction heat." (d) "Neglecting the calorimeter constant makes the calculated ΔH too large in magnitude." (e) "Adding a catalyst changes the ΔH that a calorimeter measures for a reaction."

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C3. 0.920 g of ethanol (molar mass 46.0 g mol^{-1}) burns completely in a bomb calorimeter with C_cal = 10.5 kJ $°C^{-1}$: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$. The temperature rises by 2.60 °C. (a) Calculate the heat absorbed by the calorimeter. (b) Calculate the moles of ethanol burned. (c) Calculate ΔE for the combustion of ethanol, in kJ mol^{-1}. (d) State what the water bath around the bomb vessel does in this measurement. (e) State two reasons the same combustion is never run in an open coffee cup instead.

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Answer Key

A1. (a) Pressure: the open cup stays at atmospheric pressure, so the measured heat is q_p, which gives ΔH directly. (b) Volume: the rigid, sealed vessel cannot change volume, so the measured heat gives ΔE. (c) Open to the air, the contents stay at atmospheric pressure even as the temperature changes and gases form; that constant pressure is what makes the heat equal to ΔH. (d) Any two: the sealed steel vessel contains the hot, pressurised gases of a combustion safely; the fixed volume means no gas escapes carrying heat away; the vessel withstands the pressure a combustion generates.

A2. (a) The heat needed to raise the temperature of the whole object by one degree Celsius; units J $°C^{-1}$; q = CΔT. (b) The heat needed to raise one gram of a substance by one degree Celsius; units J g^{-1} $°C^{-1}$. (c) The heat needed to raise one mole of a substance by one degree Celsius; units J mol^{-1} $°C^{-1}$. (d) C = mc = 250 × 4.18 = 1,045 J $°C^{-1}$. (e) Multiply the specific heat capacity by the mass of the sample: C = mc.

A3. (a) The heat absorbed by the calorimeter hardware itself: the cup, lid, stirrer and thermometer, rather than by the water. (b) J $°C^{-1}$; $q_{cal} = C_{cal} \times \Delta T$. (c) Mix known masses of hot and cold water inside the calorimeter, record the temperatures, and take the difference between the heat lost by the hot water and the heat gained by the cold water as the heat the hardware absorbed; divide by the hardware's temperature change. (d) The same temperature change as the water: hardware and contents start at one temperature and settle at the same final temperature, so they share ΔT.

A4. (a) $q_{reaction} = -(q_{water} + q_{calorimeter})$. It rests on the calorimeter being perfectly insulated, so no heat crosses between the apparatus and the room. (b) q_{water} is positive, because the solution warmed; $q_{reaction}$ is negative; ΔH is negative: the reaction is exothermic. (c) q_{water} is negative, because the solution cooled; $q_{reaction}$ is positive; ΔH is positive: the reaction is endothermic. (d) Heat lost by the metal = heat gained by the water + heat gained by the calorimeter hardware.

A5. (a) Heat exchange with the surroundings: the foam cup is not a perfect insulator, so heat leaks to or from the room air. (b) It makes the measured temperature change smaller than the reaction alone would produce, so the calculated ΔH is too small in magnitude. (c) The magnitude comes out too small, because real heat absorbed by the hardware goes uncounted; the sign is unchanged. (d) The same heat would produce larger temperature changes, and larger changes are read with less relative error, so the measurements would be more precise. (e) Any two: the solution has the density and specific heat capacity of pure water; the reaction goes to completion; all of the limiting reactant reacts; the final temperature is read at its true extreme before cooling or warming towards room temperature sets in.

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B1. (a) q = C_cal × ΔT = 7.50 × 2.80 = 21.0 kJ absorbed by the calorimeter. (b) The combustion released that heat, so from the reaction's point of view q_reaction = −21.0 kJ. (c) n = 0.600 ÷ 60.0 = 0.0100 mol. (d) ΔE = q_reaction ÷ n = −21.0 ÷ 0.0100 = −2,100 kJ mol^{-1}. (e) The bomb's rigid walls hold the volume constant, and heat measured at constant volume is ΔE; ΔH is the heat at constant pressure.

B2. (a) ΔT = 33.7 − 24.0 = +9.7 °C. (b) q = mcΔT = 100 × 4.18 × 9.7 = +4,054.6 J, about +4.05 kJ. (c) q_reaction = −4,054.6 J. The solution gained heat, so the dissolving released it: exothermic. (d) n = 5.55 ÷ 111 = 0.0500 mol. (e) ΔH = −4,054.6 ÷ 0.0500 = −81,092 J mol^{-1} = −81.1 kJ mol^{-1}.

B3. (a) The water warmed by 28.0 − 25.0 = 3.0 °C: q_water = 100 × 4.18 × 3.0 = +1,254 J. (b) The hardware shared that same 3.0 °C rise: q_cal = 30.0 × 3.0 = +90 J. (c) Heat lost by the metal = 1,254 + 90 = 1,344 J. (d) The metal cooled by 100.0 − 28.0 = 72.0 °C, so c = 1,344 ÷ (50.0 × 72.0) = 1,344 ÷ 3,600 = 0.373 J g^{-1} $°C^{-1}$. (e) That the calorimeter is insulated from the room: every joule the metal lost stayed inside, split between the water and the hardware.

B4. (a) The hot water cooled by 55.0 − 38.5 = 16.5 °C: heat lost = 60.0 × 4.18 × 16.5 = 4,138.2 J. (b) The cold water warmed by 38.5 − 25.0 = 13.5 °C: heat gained = 60.0 × 4.18 × 13.5 = 3,385.8 J. (c) Heat absorbed by the hardware = 4,138.2 − 3,385.8 = 752.4 J. (d) C_cal = 752.4 ÷ 13.5 = 55.7 J $°C^{-1}$. (e) 13.5 °C: the hardware held the cold water, so it started at 25.0 °C and finished at the mixture's 38.5 °C, the same rise as the cold water's.

B5. (a) ΔT = 18.2 − 22.0 = −3.8 °C. (b) q_solution = mcΔT = 200 × 4.18 × (−3.8) = −3,176.8 J. (c) q_cal = C_cal × ΔT = 50 × (−3.8) = −190 J. (d) q_reaction = −(−3,176.8 + (−190)) = +3,366.8 J. Positive: the dissolving absorbed heat from the solution and the hardware, so it is endothermic. (e) n = 10.7 ÷ 53.5 = 0.200 mol, so ΔH = 3,366.8 ÷ 0.200 = 16,834 J mol^{-1} = +16.8 kJ mol^{-1}.

B6. (a) C = mc = 400 × 4.18 = 1,672 J $°C^{-1}$. (b) q = CΔT = 85 × 4.0 = 340 J. (c) Molar heat capacity = 4.18 × 18.0 = 75.24, about 75.2 J mol^{-1} $°C^{-1}$. (d) ΔT halves: the reaction releases the same heat, but q = mcΔT now spreads it over twice the mc product. The calculated ΔH does not change: q_reaction is the same heat and it is still divided by the same moles of limiting reactant; the temperature rise is only the measuring device, not the quantity reported.

C1. (a) ΔT = 40.4 − 20.0 = +20.4 °C, so q_solution = 50.0 × 4.18 × 20.4 = +4,263.6 J. (b) q_calorimeter = 20 × 20.4 = +408 J. (c) q_reaction = −(4,263.6 + 408) = −4,671.6 J. The temperature rose, so the surroundings gained heat and the reaction released it: negative q_reaction, exothermic. n(Mg) = 0.243 ÷ 24.3 = 0.0100 mol, the limiting reactant since the acid is in excess. ΔH = −4,671.6 ÷ 0.0100 = −467,160 J mol^{-1}, about −467 kJ mol^{-1}. (d) Ignoring the hardware: q_reaction = −4,263.6 J, so ΔH = −4,263.6 ÷ 0.0100 = −426 kJ mol^{-1}. It is too small in magnitude, less negative by about 41 kJ mol^{-1}, because 408 J of real reaction heat went uncounted. (e) Heat exchange with the surroundings: during the run the warm solution leaks heat to the room through and above the foam cup, so the measured rise is smaller than the reaction's heat warrants. The assumption of perfect insulation fails.

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C2. (a) False. The bomb's rigid walls fix the volume, so its heat is ΔE whatever the heat ends up warming; ending up in water is only how the change is read, and ΔH belongs to constant pressure. (b) False. A falling temperature means the solution lost heat to the reaction: the reaction absorbed heat, so it is endothermic and ΔH is positive. (c) False, and backwards. Doubling the mass doubles mc in q = mcΔT, so the same heat is spread over twice the heat capacity and ΔT halves. (d) False. The hardware absorbs part of the reaction's heat; leaving it out undercounts the total heat, so the calculated ΔH is too small in magnitude. (e) False. A catalyst changes the pathway and so the rate, but ΔH depends only on the reactants and the products, which a catalyst leaves unchanged; the calorimeter measures the same ΔH, just reached sooner.

C3. (a) q = C_cal × ΔT = 10.5 × 2.60 = 27.3 kJ absorbed by the calorimeter. (b) n = 0.920 ÷ 46.0 = 0.0200 mol. (c) ΔE = −27.3 ÷ 0.0200 = −1,365 kJ mol^{-1}. The sign is negative because the combustion released the heat that the calorimeter absorbed, and the per-mole quantity is ΔE because the bomb holds the volume constant. (d) It absorbs the heat the combustion releases and shows it as a temperature rise; together with the vessel it forms the surroundings whose total heat capacity is the C_cal used in part (a). (e) Any two: the open cup cannot contain the hot pressurised gases a combustion produces, so they would escape carrying heat away and the ledger could never close; the foam cup could not withstand a combustion safely; combustion in open air may be incomplete, so the heat per mole would not match complete burning in oxygen.

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