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Topic 6.9: Hess's Law

Worksheet · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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How to Use This Worksheet

Work in order. Section A checks the foundations: the law, the three manipulations, cancellation and states. Section B practises building target equations on six cycles, including one unknown step and one cycle that needs a state change step. Section C is exam style: a graphite and diamond problem, six claims to judge, and a propane problem that recovers a formation enthalpy.

Every step value is given inside its question. States are printed in every equation because states decide what may cancel.

Three habits protect every answer. Write the target first and keep it in view. Apply each manipulation to the equation and its ΔH together, never to one without the other. Before adding ΔH values, add the manipulated equations and check the sum reproduces the target exactly.

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 Hess's law. (b) Define a state function, and name two other state functions besides enthalpy. (c) Explain why Hess's law follows from enthalpy being a state function. (d) State the main practical use of the law.

A2. A step P → Q has ΔH = −120 kJ. State the equation and ΔH after each manipulation: (a) the step is reversed; (b) the step is multiplied by 2; (c) the step is halved; (d) the step is reversed and then multiplied by 3.

A3. (a) State the three conditions a species must meet before it cancels when equations are added. (b) One step produces $H_2O(l)$ and another step consumes $H_2O(g)$. State whether they cancel, and explain why, giving the enthalpy difference between the two states. (c) A summed equation has $3H_2O(l)$ on the product side and $2H_2O(l)$ on the reactant side. State what remains after cancellation. (d) State whether C(s, graphite) can cancel C(s, diamond) in a summed equation, and explain why.

A4. (a) Describe what a Hess cycle diagram shows. (b) A cycle has a direct route with ΔH(direct) and an indirect route through two steps with ΔH values ΔH(1) and ΔH(2). Write the equation connecting them. (c) Explain why the enthalpy change for C(s, graphite) → C(s, diamond) is found from a cycle rather than measured directly. (d) A catalyst is added to the direct route of a cycle. State whether ΔH(direct) changes, and explain your answer.

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A5. (a) State the first thing to write down when tackling a Hess calculation. (b) Explain which given step is usually manipulated first, and what decides whether it is reversed or scaled. (c) A species needed on the product side of the target appears only on the reactant side of its step. State the manipulation required. (d) State the check that must pass before the ΔH values are added, and what a failed check means.

Section B: Core Practice

B1. Given (1) $N_2(g) + O_2(g) \rightarrow 2NO(g)$, $\Delta H = +180.6$ kJ; (2) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, $\Delta H = -114.2$ kJ. Target: $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$. (a) State which species cancels when the steps are added, and whether either step needs reversing or scaling. (b) Calculate ΔH for the target. (c) Calculate ΔH per mole of NO_2 formed. (d) The target is endothermic even though one step is exothermic. Explain why.

B2. Given (1) $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -393.5$ kJ; (2) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$, $\Delta H = -283.0$ kJ. Target: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$. (a) State which step must be reversed, and write the reversed step with its new ΔH. (b) Show which species cancel fully and which cancels only in part. (c) Calculate ΔH for the target. (d) The target is a formation equation. State which tabulated quantity the answer equals.

B3. Given $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$, $\Delta H = -571.6$ kJ. (a) Calculate ΔH for $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$. (b) State the manipulation, or pair of manipulations, that converts the given step into $3H_2O(l) \rightarrow 3H_2(g) + 3/2O_2(g)$, and calculate its ΔH. (c) Calculate ΔH for $4H_2(g) + 2O_2(g) \rightarrow 4H_2O(l)$. (d) Explain why halving an equation in the middle of a cycle is legitimate, even though half a molecule cannot react.

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B4. Given (1) $S(s) + O_2(g) \rightarrow SO_2(g)$, $\Delta H = -296.8$ kJ; (2) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$, $\Delta H = -197.8$ kJ. Target: $S(s) + 3/2O_2(g) \rightarrow SO_3(g)$. (a) Write the halved second step, with its ΔH. (b) State which species cancels when the steps are added. (c) Calculate ΔH for the target. (d) State which tabulated quantity the answer equals, and justify the claim from the target equation.

B5. Finding an unknown step. The overall reaction $2NO_2(g) \rightarrow N_2(g) + 2O_2(g)$ has $\Delta H = -66.4$ kJ. It is the sum of step 1, $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ with $\Delta H = +114.2$ kJ, and step 2, $2NO(g) \rightarrow N_2(g) + O_2(g)$, whose ΔH is unknown. (a) Write the Hess sum as an equation with the unknown as x. (b) Solve for x. (c) State which forward reaction step 2 is the reverse of, using the steps in B1. (d) State what the sign of x says about step 2.

B6. The state conversion. Given (1) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$, $\Delta H = -890.3$ kJ; (2) $H_2O(l) \rightarrow H_2O(g)$, $\Delta H = +44.0$ kJ. Target: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$. (a) State the factor by which step 2 must be multiplied, and why that factor is forced by the target. (b) Calculate ΔH for the target. (c) Calculate how much less heat the target reaction releases than step 1. (d) Explain why burning methane to water vapour releases less heat than burning it to liquid water.

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Section C: Exam Style

C1. Carbon has two solid forms. Given C(s, graphite) + $O_2(g)$ → $CO_2(g)$, $\Delta H = -393.5$ kJ, and C(s, diamond) + $O_2(g)$ → $CO_2(g)$, $\Delta H = -395.4$ kJ. (a) State the manipulations that build the target C(s, graphite) → C(s, diamond) from these steps. (b) Calculate ΔH for the target. (c) Calculate the heat absorbed when 24.02 g of graphite is converted to diamond. Take the molar mass of carbon as 12.01 g mol^{-1}. (d) Explain why this ΔH cannot be measured by a direct experiment. (e) A student argues: "Diamond burns more exothermically, so diamond must be the more stable form." Judge the argument.

C2. Judge each claim, supporting each verdict with the rule it depends on. (a) "Reversing an equation doubles its ΔH." (b) "The ΔH of the target is the average of the step ΔH values." (c) "$H_2O(l)$ produced in one step cancels $H_2O(g)$ consumed in another, because both are water." (d) "Doubling an equation leaves ΔH unchanged, because the ratio of products to reactants is the same." (e) "A catalyst lowers ΔH, so a catalysed reaction has a different ΔH from the same reaction uncatalysed." (f) "If the steps add to the target, their ΔH values may be added as given, whatever manipulations were applied to the equations."

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C3. Propane's formation enthalpy cannot be measured directly, but its combustion can. Given (1) $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -393.5$ kJ; (2) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$, $\Delta H = -285.8$ kJ; (3) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$, $\Delta H = -2219.9$ kJ. (a) Write the target formation equation for propane, $C_3H_8(g)$, with states. (b) State the manipulation each of the three given steps needs: the factor for steps 1 and 2, and what must happen to step 3. (c) Calculate ΔH for the target, showing each manipulated value. (d) Calculate the heat released when 0.50 mol of propane burns completely to liquid water. (e) Explain why reacting carbon and hydrogen together gives no clean measurement of the target in (a).

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Answer Key

A1. (a) The enthalpy change for a reaction is the same whichever route is taken from reactants to products, provided the initial and final states are the same; equivalently, ΔH for a target reaction equals the sum of the ΔH values of steps that add to it. (b) A state function is a property whose value depends only on the current state of the system, not on the path taken to reach it. Pressure, volume and temperature are state functions, as are internal energy and enthalpy itself. (c) Because enthalpy is fixed by the state alone, the enthalpy gap between given reactants and products is fixed, so the step values along every route must sum to that same gap. (d) To find ΔH for reactions that cannot be measured directly: too slow, too dangerous, or spoiled by side reactions.

A2. (a) Q → P, ΔH = +120 kJ: reversing flips the sign and keeps the size. (b) 2P → 2Q, ΔH = −240 kJ: scaling by 2 doubles ΔH. (c) ½P → ½Q, ΔH = −60 kJ: halving halves ΔH. (d) 3Q → 3P, ΔH = +360 kJ: the reversal flips −120 to +120, and multiplying by 3 gives +360 kJ.

A3. (a) The same chemical formula, in the same physical state, with the same total coefficient, appearing on opposite sides of the summed equation. (b) No. $H_2O(l)$ and $H_2O(g)$ hold different enthalpies, differing by 44.0 kJ mol^{-1}, the enthalpy of vaporization, so they are different species for cancellation. They connect only through $H_2O(l) \rightarrow H_2O(g)$, ΔH = +44.0 kJ. (c) $1H_2O(l)$ remains on the product side: 3 mol produced minus 2 mol consumed leaves a net 1 mol. Partial cancellation of this kind is normal. (d) No. Graphite and diamond are different allotropes with different enthalpies, differing by 1.9 kJ mol^{-1}, so neither cancels the other; converting one into the other is itself a reaction with its own ΔH.

A4. (a) A diagram with the reactants and products at two corners and at least two routes drawn between them: a direct route, and an indirect route passing through intermediate states, each route labelled with its ΔH. (b) ΔH(direct) = ΔH(1) + ΔH(2): going round the cycle and returning to the start gives a net enthalpy change of zero, so the two routes carry equal totals. (c) Graphite converts to diamond immeasurably slowly under ordinary conditions, so no calorimeter can capture the change directly. Both forms burn readily, so the cycle through their common combustion product, CO_2, prices the conversion from two measurable steps. (d) No. A catalyst changes the route and the rate, but the reactants and products are unchanged, so the enthalpy gap between them is unchanged; only the path and the activation energy along it differ.

A5. (a) The target equation, written in full with states. Every later decision is a comparison against it. (b) The step containing a species that appears in only one step, because it has no partner to share the species with. Match it to the target: reverse it if the species sits on the wrong side, scale it if the coefficient is wrong, or both. (c) Reverse the step, which moves the species to the product side and flips the sign of its ΔH. (d) Adding the manipulated equations must reproduce the target exactly: same species, same coefficients, same states, nothing left over. A failed check means a manipulation is wrong, and the ΔH sum built on it cannot be trusted.

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B1. (a) 2NO cancels: step 1 produces it and step 2 consumes it, with the same coefficient and state. Neither step needs reversing or scaling; both are used as written. (b) ΔH = +180.6 + (−114.2) = +66.4 kJ. The summed equation is $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$, exactly the target. (c) The target forms 2 mol of NO_2, so per mole: +66.4 ÷ 2 = +33.2 kJ mol^{-1}. (d) Forming NO costs +180.6 kJ, and oxidising it returns only 114.2 kJ, so the products sit 66.4 kJ higher in enthalpy than the reactants, which is what a positive ΔH records.

B2. (a) Step 2 must be reversed, because CO_2 is a product in both given steps but appears nowhere in the target. Reversed: $CO_2(g) \rightarrow CO(g) + ½O_2(g)$, ΔH = +283.0 kJ. (b) CO_2 cancels fully: 1 mol produced by step 1, 1 mol consumed by the reversed step 2. O_2 cancels in part: step 1 consumes 1 mol, the reversed step 2 produces ½ mol, leaving ½ mol consumed, as the target requires. (c) ΔH = −393.5 + 283.0 = −110.5 kJ. (d) It equals the standard enthalpy of formation of CO(g), ΔH°f = −110.5 kJ mol^{-1}, because the target forms one mole of CO from its elements in their standard states.

B3. (a) Halving the equation halves ΔH: −571.6 ÷ 2 = −285.8 kJ. (b) Reverse the step and multiply by 3/2, in either order. Reversing alone gives $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$, ΔH = +571.6 kJ; scaling by 3/2 gives $3H_2O(l) \rightarrow 3H_2(g) + 3/2O_2(g)$, ΔH = +571.6 × 3/2 = +857.4 kJ. (c) Doubling the given step doubles ΔH: 2 × (−571.6) = −1143.2 kJ. (d) A cycle step is a bookkeeping entry, not a claim about a single molecular event. Scaling scales every amount together, so the ratios and the chemistry are unchanged; only the batch size changes, and ΔH, being extensive, scales with it.

B4. (a) $SO_2(g) + ½O_2(g) \rightarrow SO_3(g)$, ΔH = −197.8 ÷ 2 = −98.9 kJ. (b) SO_2 cancels: step 1 produces 1 mol and the halved step 2 consumes 1 mol, same state. The O_2 adds: 1 + ½ = 3/2 mol consumed, as the target requires. (c) ΔH = −296.8 + (−98.9) = −395.7 kJ. (d) It equals ΔH°f of $SO_3(g)$, −395.7 kJ mol^{-1}, because the target forms exactly one mole of SO_3 from its elements in their standard states.

B5. (a) −66.4 = +114.2 + x. (b) x = −66.4 − 114.2 = −180.6 kJ. Check: +114.2 + (−180.6) = −66.4 kJ, the overall value. (c) Step 2, $2NO(g) \rightarrow N_2(g) + O_2(g)$, is the reverse of step 1 in question B1, $N_2(g) + O_2(g) \rightarrow 2NO(g)$, and its ΔH is the negative of that step's value: −(+180.6) = −180.6 kJ, agreeing with the solved x by a different route. (d) The negative sign means step 2 is exothermic: breaking 2NO down to its elements releases 180.6 kJ.

B6. (a) By 2. The target makes 2 mol of $H_2O(g)$, and each use of step 2 converts only 1 mol, so step 2 is taken twice: $2H_2O(l) \rightarrow 2H_2O(g)$, ΔH = 2 × (+44.0) = +88.0 kJ. (b) Add step 1 and the doubled step 2: the $2H_2O(l)$ produced by step 1 is consumed by the doubled step 2 and cancels, leaving $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$. ΔH = −890.3 + 88.0 = −802.3 kJ. (c) −802.3 releases 88.0 kJ less than −890.3: exactly the cost of vaporising the 2 mol of water. (d) Liquid water's molecules sit in a hydrogen bonded network at lower enthalpy. Making the vapour pulls that network apart, so 44.0 kJ per mole stays held in the products.

C1. (a) Keep the graphite combustion as written. Reverse the diamond combustion, giving $CO_2(g) \rightarrow$ C(s, diamond) + $O_2(g)$, ΔH = +395.4 kJ, then add. (b) The CO_2 and the O_2 both cancel, leaving C(s,

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graphite) → C(s, diamond). ΔH = −393.5 + 395.4 = +1.9 kJ. (c) Moles of carbon: 24.02 ÷ 12.01 = 2.00 mol. Heat absorbed: 2.00 × 1.9 = 3.8 kJ. (d) The conversion is immeasurably slow at ordinary conditions, so a calorimeter sees nothing happen. The cycle works because both forms burn quickly and completely to the same product, CO_2. (e) The argument reads the cycle backwards. Burning diamond releases more heat precisely because diamond starts higher in enthalpy: it has further to fall to reach CO_2. The ΔH of +1.9 kJ confirms graphite sits lower and is the more stable form.

C2. (a) False. Reversing changes the sign of ΔH and keeps its size: a step of −40 kJ becomes +40 kJ, not −80 kJ. Doubling happens only when the equation is multiplied by 2. (b) False. ΔH values add, after manipulation. An average would shrink as more steps describe the same reaction, while the true ΔH is fixed by the reactants and products. (c) False. Cancellation needs the same formula, state and coefficient. $H_2O(l)$ and $H_2O(g)$ differ by 44.0 kJ mol^{-1}, so treating them as identical drops a real enthalpy change from the sum. (d) False. ΔH is extensive, priced for the equation as written, so doubling every amount doubles the heat absorbed or released. (e) False. A catalyst changes the route and lowers the activation energy, but reactants and products are the same states, so ΔH is unchanged. The claim would make Hess's law fail on a change of path, the opposite of what the law says. (f) False. Each ΔH must carry the manipulation applied to its equation: reversed steps enter with flipped signs, scaled steps with scaled values. Adding the original values prices different equations, not the ones that sum to the target.

C3. (a) $3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$. (b) Step 1 multiplied by 3: $3C(s) + 3O_2(g) \rightarrow 3CO_2(g)$, ΔH = 3 × (−393.5) = −1180.5 kJ. Step 2 multiplied by 4: $4H_2(g) + 2O_2(g) \rightarrow 4H_2O(l)$, ΔH = 4 × (−285.8) = −1143.2 kJ. Step 3 reversed, so propane becomes a product and CO_2 and H_2O become reactants that cancel: $3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g)$, ΔH = +2219.9 kJ. (c) Adding the manipulated steps cancels $3CO_2$, $4H_2O(l)$ and all $5O_2$, leaving the target. ΔH = −1180.5 + (−1143.2) + 2219.9 = −103.8 kJ, which is $\Delta H°f$ of $C_3H_8(g)$, −103.8 kJ mol^{-1}. (d) Burning releases 2219.9 kJ per mole, from step 3 as written, so 0.50 mol releases 0.50 × 2219.9 = 1109.95 kJ, about 1110 kJ. (e) Carbon and hydrogen heated together do not react cleanly to propane alone: the mixture gives a spread of hydrocarbons and unreacted material, too slow and tangled to price in a calorimeter. Because the direct route cannot be isolated, its ΔH is recovered from steps that can be.

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Topic 6.9 Quiz: Hess's Law

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Next Quiz: Topic 7.1 Introduction to Equilibrium

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