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Topic 6.9: Hess's Law

Revision Notes · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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What Hess's Law States

Hess's law states that the enthalpy change for a reaction is the same whichever route is taken from reactants to products, provided the starting and finishing states are the same.

In practice this means one thing: if a reaction can be written as a sum of step reactions, then its ΔH is the sum of the step ΔH values.

ΔH(target) = ΔH(step 1) + ΔH(step 2) + ΔH(step 3) + ...

The steps need only add up, on paper, to the target equation exactly.

Why It Works: Enthalpy Is a State Function

Enthalpy is a state function. Its value depends only on the state the system is in now, not on how it got there.

Pressure, volume and temperature behave the same way. Heat and work do not: they are path functions, and their values do depend on the route.

Because enthalpy is a state function, the difference in enthalpy between reactants and products is fixed. Every route between the same two states crosses the same enthalpy gap, so the step values along any route must add to the same total.

That is why Hess's law is exact, not approximate. It also explains its main use: a reaction too slow, too dangerous or too tangled with side reactions to measure directly can still be priced, by adding up steps that can be measured.

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The Three Manipulations

Reverse. Turning an equation round swaps reactants and products, so ΔH changes sign and keeps its size. If A → B has ΔH = +50 kJ, then B → A has ΔH = −50 kJ.

Scale. Multiplying every coefficient in an equation by a factor multiplies ΔH by the same factor, because enthalpy is extensive: twice the reaction involves twice the material and twice the heat. Halving an equation halves ΔH, and fractions such as ½ are used freely.

Add. Adding equations together adds their ΔH values. Any species that appears on both sides of the summed equation cancels, exactly as in algebra.

The three moves combine. Reversing and then tripling an equation flips the sign and triples the size: a step with ΔH = −40 kJ becomes +120 kJ. Changing the temperature is not a fourth move; ΔH values belong to the conditions they were measured at.

Building the Target Equation

Start from the target, not from the steps. Write the target equation out in full, with states, and keep it in view while you work.

Find a species that appears in only one step. That step usually decides first: if the species sits on the wrong side of its step, reverse the step; if its coefficient is wrong, scale the step so the coefficient matches the target.

Work species by species until every reactant and product of the target is accounted for. Species that appear in no step and not in the target must cancel between steps; if one is left over at the end, a manipulation is wrong.

Finish with a full check. Add the manipulated steps on paper and confirm the sum reproduces the target exactly: same species, same coefficients, same states. Only then add the manipulated ΔH values, each with its new sign and scale applied.

States Must Match Before Anything Cancels

Cancellation is exact matching. A species cancels only when the same formula, in the same state, with the same total coefficient, appears on both sides.

$H_2O(l)$ and $H_2O(g)$ are different species for this purpose. A step that produces liquid water cannot cancel a step that consumes water vapour: the two waters differ in enthalpy by 44.0 kJ mol^{-1}, the enthalpy of vaporization.

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The same discipline applies to allotropes. C(s, graphite) and C(s, diamond) are both carbon, but they are not the same species, and neither cancels the other.

When states do not match, a step for the state change itself, such as

$H_2O(l) \rightarrow H_2O(g)$ with $\Delta H = +44.0$ kJ,

can be added to convert one into the other before cancelling.

Solving for an Unknown Step

The same addition runs backwards. If the overall ΔH and every step but one are known, the unknown step is whatever makes the sum balance.

Write the sum with the unknown as x, then rearrange:

x = ΔH(overall) − sum of the known steps,

each known step already reversed or scaled as the cycle requires.

This is how many tabulated values are actually obtained. A formation enthalpy that cannot be measured by reacting the elements directly is recovered from a combustion that can be measured, by solving the cycle for the missing step. The formation method of Topic 6.8 is exactly this idea carried out through the elements.

Worked Examples

Example 1: Forming carbon monoxide. Given $C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -393.5$ kJ, and $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$, $\Delta H = -283.0$ kJ. Target: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$. Reverse the second step: $CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$, $\Delta H = +283.0$ kJ. Add: the CO_2 cancels, and $\frac{1}{2}O_2$ of the O_2 cancels, leaving the target. $\Delta H = -393.5 + 283.0 = -110.5$ kJ.

Example 2: Forming nitrogen dioxide. Given $N_2(g) + O_2(g) \rightarrow 2NO(g)$, $\Delta H = +180.6$ kJ, and $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, $\Delta H = -114.2$ kJ. Target: $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$. Neither step needs changing: add them and the 2NO cancels. $\Delta H = +180.6 + (-114.2) = +66.4$ kJ. Endothermic overall, because the first step costs more than the second returns.

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Example 3: Graphite to diamond. Given C(s, graphite) + $O_2(g)$ → $CO_2(g)$, ΔH = −393.5 kJ, and C(s, diamond) + $O_2(g)$ → $CO_2(g)$, ΔH = −395.4 kJ. Target: C(s, graphite) → C(s, diamond). Keep the first step, reverse the second: $CO_2(g)$ → C(s, diamond) + $O_2(g)$, ΔH = +395.4 kJ. Adding cancels both CO_2 and O_2. ΔH = −393.5 + 395.4 = +1.9 kJ. The direct conversion is far too slow to measure, so the two combustions price it instead.

Example 4: Hydrogenating ethene. Given $C_2H_4(g)$ + $3O_2(g)$ → $2CO_2(g)$ + $2H_2O(l)$, ΔH = −1411 kJ; $H_2(g)$ + $½O_2(g)$ → $H_2O(l)$, ΔH = −285.8 kJ; $C_2H_6(g)$ + $7/2O_2(g)$ → $2CO_2(g)$ + $3H_2O(l)$, ΔH = −1560 kJ. Target: $C_2H_4(g)$ + $H_2(g)$ → $C_2H_6(g)$. Take the first step as written, add the second, and reverse the third. The $2CO_2$ cancels, all $3H_2O$ cancels, and the O_2 cancels. ΔH = −1411 + (−285.8) + 1560 = −136.8 kJ.

Traps That Cost Marks in Topic 6.9

"Flip the equation, keep the ΔH." Reversing a step without flipping its sign is the commonest error in the topic. The reversed step carries the negative of its original ΔH, every time.

"Scale the equation, keep the ΔH." ΔH is priced for the equation as written. Double the coefficients and the ΔH doubles; halve them and it halves. A scaled step with an unscaled ΔH breaks the sum.

"Cancel anything with the same formula." States and allotropes are part of the species. $H_2O(l)$ does not cancel $H_2O(g)$, and graphite does not cancel diamond.

"Average the step values." ΔH values add. They are never averaged, and the answer is neither the largest step nor the smallest step.

"Apply the manipulation to ΔH only." Reversing or scaling acts on the whole step, equation and ΔH together. Changing one without the other produces a sum that matches nothing.

"Add first, check later." A leftover species at the end means the manipulations are wrong, however tidy the arithmetic looks. The summed equation must reproduce the target exactly before its ΔH is trusted.

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Key Relationships to Remember

- Hess's law: ΔH for a reaction is independent of the route taken, because enthalpy is a state function
- ΔH(target) = sum of the ΔH values of the steps that add to the target, after each step is manipulated
- Reversing an equation changes the sign of its ΔH and keeps its size
- Multiplying every coefficient by a factor multiplies ΔH by the same factor; halving an equation halves ΔH
- A species cancels only when formula, state and coefficient all match on both sides of the summed equation
- An unknown step follows from x = ΔH(overall) − sum of the known manipulated steps
- $H_2O(l)$ and $H_2O(g)$ differ by 44.0 kJ mol^{-1} and never cancel each other
- A catalyst changes the route and the rate but not ΔH, which is itself a demonstration of path independence

Continue Revising

Topic 6.9 Quiz: Hess's Law

Topic 6.9 Worksheet

Unit 6: All Topics

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