

Hess's Law and Enthalpies of Formation

How do you use Hess's law and enthalpies of formation to calculate ΔH ?

●●○ Intermediate

Thermochemistry & Thermodynamics

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Before you start: it helps to understand [Enthalpy and Calorimetry](#) and [Balancing Chemical Equations](#).

What is it?

Hess's law: the enthalpy change of a reaction is the **same whatever route** is taken from the reactants to the products. Enthalpy is a **state function**: it depends only on the start and end, not on the path.

This means you can find ΔH for a reaction that is hard to measure directly by **adding up** the ΔH values of other reactions that combine to give it.

🔑 KEY IDEA

If equations add up to the target equation, their ΔH values add up to the target ΔH .
Reverse an equation: change the sign of ΔH . Multiply an equation: multiply ΔH by the same number.

Why does it matter?

- **Impossible measurements.** The formation of CO from carbon can't be measured cleanly, because some CO₂ always forms. Hess's law gets it from two easy combustions.
- **Tables instead of experiments.** With a table of **enthalpies of formation**, you can calculate ΔH for thousands of reactions without doing any of them.
- **Energy planning.** Fuel values, metabolic energy and industrial heat balances all rely on these calculations.

How does it work?

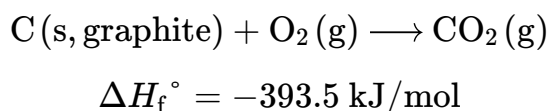
1. Combining equations

To reach a target equation:

1. Write the given equations so that each **target reactant** is on the left and each **target product** is on the right; **reverse** an equation if needed (and change the sign of its ΔH).
2. **Multiply** equations so the amounts match the target (and multiply their ΔH).
3. **Add** the equations; substances that appear on both sides cancel. Add the ΔH values.

2. Standard enthalpy of formation

The **standard enthalpy of formation**, ΔH_f° , is the enthalpy change when **1 mol** of a compound forms from its **elements in their standard states** (the most stable form at 1 bar and 25 °C):



For an element in its standard state, such as $\text{O}_2(\text{g})$, $\text{H}_2(\text{g})$ or $\text{C}(\text{graphite})$, $\Delta H_f^\circ = 0$.

Substance	ΔH_f° (kJ/mol)
$\text{CO}_2(\text{g})$	-393.5
$\text{CO}(\text{g})$	-110.5
$\text{H}_2\text{O}(\text{l})$	-285.8
$\text{H}_2\text{O}(\text{g})$	-241.8
$\text{CH}_4(\text{g})$	-74.6
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.6
$\text{O}_2(\text{g})$, $\text{H}_2(\text{g})$, $\text{C}(\text{graphite})$	0

3. ΔH from enthalpies of formation

$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants})$$

where n is each coefficient (in mol) in the balanced equation. “Products minus reactants.”

THINK OF IT LIKE THIS

Climbing a mountain: your change in height between the car park and the summit is the same whether you take the steep direct path or the long zig-zag trail. Enthalpy works the same way: only the start and the end matter.

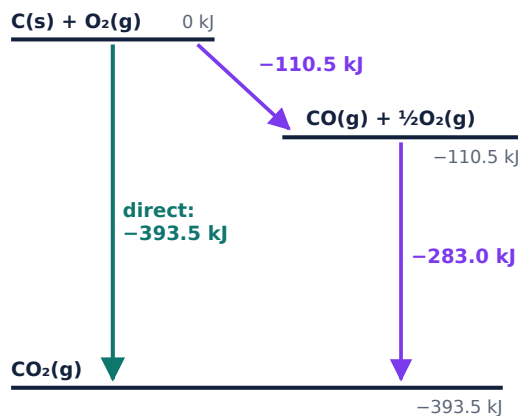
MORE PRECISELY

Hess's law follows from the first law of thermodynamics (energy is conserved). The formation-enthalpy formula is Hess's law applied to a two-step route: break the reactants down into their elements (the reverse of formation), then build the products from those elements. Average **bond enthalpies** give another estimate of ΔH , but because they are averages, the result is only approximate.

Visualise it

Hess's law: two routes, one total

Enthalpy levels drawn to scale (kJ per mole of C).



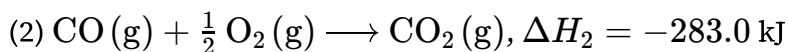
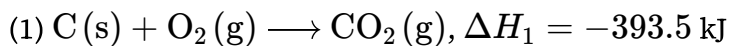
$-110.5 \text{ kJ} + (-283.0 \text{ kJ}) = -393.5 \text{ kJ}$: the total enthalpy change is the same whichever route is taken.

Both routes from $\text{C} + \text{O}_2$ to CO_2 give the same total enthalpy change.

Worked example

WORKED EXAMPLE: Combining equations

Question: Find ΔH for $\text{C}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g})$ from:



Step 1 Keep (1): it has C on the left, as in the target.

Step 2 Reverse (2), so that CO is on the right: $\text{CO}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}), \Delta H = +283.0 \text{ kJ}$

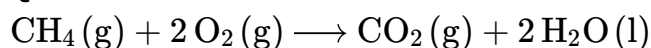
Step 3 Add: CO_2 cancels, and O_2 on the left becomes $1 - \frac{1}{2} = \frac{1}{2} \text{ mol}$:

$$\begin{aligned}\Delta H &= -393.5 \text{ kJ} + 283.0 \text{ kJ} \\ &= -110.5 \text{ kJ}\end{aligned}$$

This matches ΔH_f° of CO in the table.

 WORKED EXAMPLE: Using enthalpies of formation

Question: Calculate ΔH° for the combustion of methane:



Step 1 Products: $(1 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-285.8 \text{ kJ/mol}) = -965.1 \text{ kJ}$

Step 2 Reactants: $(1 \text{ mol})(-74.6 \text{ kJ/mol}) + (2 \text{ mol})(0 \text{ kJ/mol}) = -74.6 \text{ kJ}$

Step 3 Subtract:

$$\begin{aligned}\Delta H^\circ &= -965.1 \text{ kJ} \\ &\quad - (-74.6 \text{ kJ}) \\ &= -890.5 \text{ kJ}\end{aligned}$$

Step 4 The mol units cancel in each product, leaving kJ for the reaction as written (-890.5 kJ per mole of CH_4).

Common mistake

 COMMON MISTAKE: Forgetting to change the sign

When you reverse an equation, ΔH changes sign: if $\text{A} \rightarrow \text{B}$ has $\Delta H = -100 \text{ kJ}$, then $\text{B} \rightarrow \text{A}$ has $\Delta H = +100 \text{ kJ}$.

 COMMON MISTAKE: Forgetting the coefficients

Multiply each ΔH_f° by its coefficient. In methane combustion there are **2 mol** of water: $2 \times (-285.8 \text{ kJ/mol}) = -571.6 \text{ kJ}$.

 COMMON MISTAKE: Reactants minus products

The formula is **products minus reactants**. Reversing the order gives the right size with the wrong sign.

 COMMON MISTAKE: Mixing up the states of water

ΔH_f° of $\text{H}_2\text{O}(\text{l})$ (-285.8 kJ/mol) and of $\text{H}_2\text{O}(\text{g})$ (-241.8 kJ/mol) differ by 44.0 kJ/mol , the enthalpy of vaporization. Use the state in the equation.

NOTATION NOTE

- ΔH_f° is read “standard enthalpy of formation”; the $^\circ$ means standard conditions (1 bar, usually 25 $^\circ\text{C}$).
- Σ (“sigma”) means “the sum of”.
- Equations may contain fractional coefficients (such as $\frac{1}{2} \text{O}_2$) when the target is “per mole” of one substance.

Remember this

REMEMBER THIS

- Hess’s law: ΔH is the same by any route (enthalpy is a state function).
- Reverse an equation: change the sign of ΔH . Multiply it: multiply ΔH .
- $\Delta H_f^\circ = 1$ mol of compound from elements in standard states; elements have $\Delta H_f^\circ = 0$.
- $\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$.

References

1. Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E.; Murphy, C. J.; Woodward, P. M.; Stoltzfus, M. W. Chemistry: The Central Science, 15th ed.; Pearson, 2022.

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