Energy cycles in reactions

Reactivity 1.2 · SL

Where does a flame's energy come from?

Product bond formation releases more energy in total than reactant bond breaking requires.

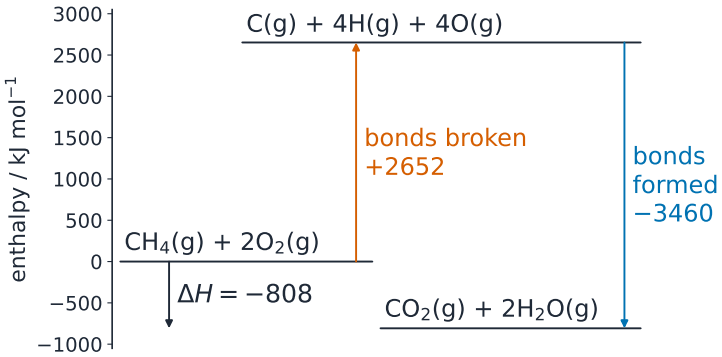
- Burning one mole of methane releases about 800 kJ.
- No atoms are made or destroyed, so the energy comes from bonds.
- This unit: bond enthalpies $\rightarrow$ matched Hess routes.

Breaking needs energy, making releases it

- Bond breaking is endothermic; bond making is exothermic.
- Data booklet values are averages over many compounds.

Bond enthalpy the energy needed to break one mole of a covalent bond, with all substances gaseous

Bonds broken minus bonds formed



$\mathrm{CH_4} + 2\mathrm{O_2}$: $\Delta H = 2652 - 3460 = -808$ kJ mol^{-1}

Check: hydrogen and chlorine

Your turn

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$. Use H–H 436, Cl–Cl 242 and H–Cl 431 kJ/mol. What is ΔH?

A. $+247$ kJ mol^{-1}

B. -184 kJ mol^{-1}

C. -431 kJ mol^{-1}

D. $+184$ kJ mol^{-1}

Why bond enthalpy answers are approximate

Averages

Values are means over many compounds.

Not the exact bonds in these molecules.

Gases only

Bond enthalpies apply to the gas state.

Changes of state are left out.

Hess's law

- Enthalpy is a state function, like height on a mountain.
- Build a cycle with the target reaction on one route.

> **Hess's law** the enthalpy change of a reaction is independent of the route, if the initial and final conditions are the same

Combining equations

1. **Keep.** $\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2}$, -394
2. **Reverse.** $\mathrm{CO_2} \rightarrow \mathrm{CO} + \frac{1}{2}\mathrm{O_2}$, $+283$
3. **Add.** $\mathrm{CO_2}$ cancels, $\frac{1}{2}\mathrm{O_2}$ is left on the left.

Decision

$\mathrm{C} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO}$, $\Delta H = -111$ kJ mol^{-1}

Worked example: ethyne

1. **Double (1).** Target: $2C(s) + H_2(g) \rightarrow C_2H_2(g)$. Double $C + O_2 \rightarrow CO_2$: $2(-394)$ kJ.
2. **Keep (2).** $H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$, -286 kJ.
3. **Reverse (3).** $2CO_2(g) + H_2O(l) \rightarrow C_2H_2(g) + {}^{5}/_{2}O_2(g)$, $+1301$ kJ.

Decision

$\Delta H = -788 - 286 + 1301 = +227 \text{ kJ mol}^{-1}$

Count every bond before cancelling

1. **Inventory.** $CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$. Break C=C + 4C–H + H–H; form C–C + 6C–H.
2. **Data.** C=C 614; C–H 414; H–H 436; C–C 346 kJ/mol.
3. **Subtract.** $(614 + 4{\times}414 + 436) - (346 + 6{\times}414) = -124$ kJ/mol.

Decision

Cancelling four average C–H terms is a model shortcut, not a mechanism.

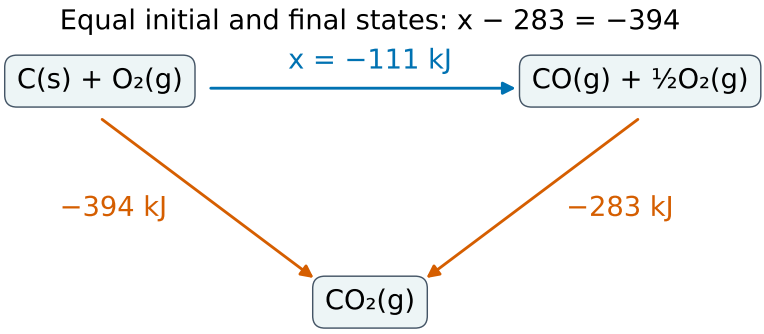
Add the missing condensation step

1. **Gas products.** Supplied bond estimate for $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g)$: -808 kJ/mol.
2. **Condense.** $2H_2O(g) \rightarrow 2H_2O(l)$; supplied change $2(-44) = -88$ kJ.
3. **Add.** Liquid-product estimate: $-808 - 88 = -896$ kJ/mol.

Decision

The estimate need not equal the measured -890 value.

Read a balanced Hess cycle



The two routes start and finish with identical amounts and states.

Solve an unknown average bond enthalpy

1. **Reaction and data.** $CH_3Cl + H_2 \rightarrow CH_4 + HCl$, all gases; illustrative $\Delta H = -70$ kJ/mol.
2. **Known terms.** C–H 414; H–H 436; H–Cl 431 kJ/mol. Cancel three average C–H terms.
3. **Solve.** $-70 = D(C\text{–}Cl) + 436 - 414 - 431$; $D(C\text{–}Cl) = 339$ kJ/mol.

Decision

An inferred average is not an exact molecule-specific bond measurement.

Link calorimetry to a Hess arrow

1. **Given.** Invented neutralization: 100.0 g solution, $c = 4.18\ \mathrm{J\,g^{-1}\,K^{-1}}$, corrected rise 5.00 K; 0.0500 mol water forms.
2. **Heat.** $q_{\mathrm{solution}} = mc\Delta T = 100.0 \times 4.18 \times 5.00 = 2090\ \mathrm{J}$.
3. **Sign and units.** $\Delta H = -q/(1000n) = -2090/(1000 \times 0.0500) = -41.8\ \mathrm{kJ\,mol^{-1}}$.

> The solution gains heat; the reaction loses it. Match states and conditions in the cycle.

Scale the equation and the heat together

1. **Given.** $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$, $\Delta H = -572$ kJ.
2. **Reverse and double.** $4H_2O(l) \rightarrow 4H_2(g) + 2O_2(g)$, $\Delta H = +1144$ kJ.
3. **Sample.** Forming 0.250 mol water: $0.250 \times (-572/2) = -71.5$ kJ.

Decision

A sample heat and a molar enthalpy are different quantities.

Choose the route from the actual starting state

1. **Given.** Same conditions: A→B +35 kJ; A→C −80 kJ.
2. **B→A→C.** Reverse the first arrow: $-35 - 80 = -115$ kJ.
3. **C→B.** Reverse the result: +115 kJ.

Decision

A catalyst changes a pathway, not the specified endpoint difference.

Scaling an enthalpy change

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H = -572$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad -286$ kJ $\qquad \div 2$

$4H_2O(l) \rightarrow 4H_2(g) + 2O_2(g) \qquad +1144$ kJ $\qquad$ reverse, $\times 2$

0.250 mol water formed: $0.250 \times (-286) = -71.5$ kJ $\qquad$ states must match: $H_2O(l) \neq H_2O(g)$

0.250 mol of water: -71.5 kJ

Exam tips

> When you reverse an equation, change the sign of ΔH.

- Write "broken minus formed" before substituting.
- Bond enthalpies are for gases.

Check yourself

Try these

Use H–H 436, Cl–Cl 242 and H–Cl 431 kJ/mol to calculate $H_2 + Cl_2 \rightarrow 2HCl$.

For A$\rightarrow$B $+35$ kJ and A$\rightarrow$C -80 kJ, find B$\rightarrow$C. Explain the signs.

Explain why $H_2O(l)$ cannot cancel $H_2O(g)$ without a phase-change step.