Topic 6.8: Enthalpy of Formation

Revision Notes · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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What a Standard Enthalpy of Formation Is

The standard enthalpy of formation, $\Delta H°f$, of a compound is the enthalpy change when one mole of that compound forms from its elements in their standard states. It is measured in kJ mol^{-1}.

Every part of the definition carries weight. The amount is exactly one mole of product. The starting materials are the elements themselves. Each element is in its standard state: its most stable form at 298 K and 1 atm (1 bar).

Forming water, for example, is

$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$,

and $\Delta H°f$ is -285.8 kJ mol^{-1}. The half in front of O_2 is not a mistake: the equation must make one mole of water, so the elements are scaled to fit.

Standard Enthalpies of Formation Used in These Notes

All values are $\Delta H°f$ in kJ mol^{-1} at 298 K: $CO_2(g)$ -393.5, $H_2O(l)$ -285.8, $H_2O(g)$ -241.8, $CH_4(g)$ -74.8, $CO(g)$ -110.5, $NH_3(g)$ -46.1, $NO(g)$ $+90.3$, $NO_2(g)$ $+33.2$, $O_3(g)$ $+142.7$, $SO_2(g)$ -296.8, $SO_3(g)$ -395.7, $CaCO_3(s)$ -1206.9, $CaO(s)$ -635.1, $NaCl(s)$ -411.2, $HCl(g)$ -92.3, $C_2H_5OH(l)$ -277.7, $C_6H_{12}O_6(s)$ -1273.3.

One set of values is used throughout these notes and the worksheet. The state in brackets is part of the value: a different state is a different number.

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The Zero Rule for Elements

An element in its standard state has $\Delta H°f = 0$, by definition. Forming oxygen from oxygen changes nothing, so the reference point is set at zero: $O_2(g)$, $H_2(g)$, $N_2(g)$, Fe(s) and C(s, graphite) all carry the value 0.

The standard state must be the most stable form. Carbon's standard state is graphite, so diamond is not zero: $\Delta H°f$ of diamond is about +1.9 kJ mol^{-1}. Oxygen's standard state is $O_2(g)$, so ozone, $O_3(g)$, is not zero either: its value is +142.7 kJ mol^{-1}.

A positive $\Delta H°f$ means the compound sits higher in enthalpy than its elements: energy had to be put in to form it, so it is less stable than its elements. A large negative value means the compound sits far below its elements and is stable relative to them.

Writing a Formation Equation

A formation equation has three features. The product side holds exactly one mole of the compound, with its state shown. The reactant side holds only elements, each in its standard state. Fractional coefficients are normal, because one mole of product rarely needs whole moles of every element.

For ammonia:

$\frac{1}{2}N_2(g) + 3/2H_2(g) \rightarrow NH_3(g)$, $\Delta H°f = -46.1$ kJ mol^{-1}

For calcium carbonate:

$Ca(s) + C(s, \text{graphite}) + 3/2O_2(g) \rightarrow CaCO_3(s)$, $\Delta H°f = -1206.9$ kJ mol^{-1}

An equation such as

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

is not a formation equation, even though it uses the same elements: it makes two moles. Its enthalpy change, −571.6 kJ, is twice $\Delta H°f$.

The Calculation: Products Minus Reactants

$$\Delta H°rxn = \Sigma\, n\Delta H°f(\text{products}) - \Sigma\, n\Delta H°f(\text{reactants})$$

Each $\Delta H°f$ is multiplied by its coefficient in the equation before summing, because the table prices one mole and the equation rarely uses one mole. Element terms contribute zero and can be written in or left out; the sum is the same.

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Note the order and hold it apart from Topic 6.7. Bond enthalpies are worked as broken minus formed, because that method prices reactants first. Formation enthalpies are worked as products minus reactants. The two formulas run in opposite directions, and using the bond enthalpy order here flips every sign.

Behind the formula sits one idea: any reaction can be pictured as reactants unforming back to their elements, then forming the products. The formation method is Hess's law applied through the elements, which is why the elements' zero values anchor every calculation.

Reading the Sign of the Answer

The sign of ΔH°rxn comes from the difference between the two sums, never from the signs of the individual values. A lower products total gives a negative ΔH and an exothermic reaction; a higher one gives a positive ΔH.

A table full of negative values can still produce an endothermic reaction. In

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$,

every ΔH°f is negative, yet the products' total (−1028.6) is higher than the reactant's (−1206.9), so ΔH is positive. What matters is which side sits lower, not whether the numbers carry minus signs.

States Decide Which Value Applies

ΔH°f belongs to one specified state. Water is the sharpest case: $H_2O(l)$ is −285.8 kJ mol^{-1} and $H_2O(g)$ is −241.8 kJ mol^{-1}. The 44.0 kJ mol^{-1} gap between them is the enthalpy of vaporization of water at 298 K: the energy needed to turn the liquid into gas.

Picking the wrong state's value is not a rounding error. Using the gas value where the equation produces liquid water shifts ΔH by 44.0 kJ for every mole of water in the equation.

Worked Examples

> **Example 1: Burning methane. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$. Products sum: −393.5 + 2(−285.8) = −965.1 kJ. Reactants sum: −74.8 + 2(0) = −74.8 kJ. ΔH°rxn = −965.1 − (−74.8) = −890.3 kJ. Forming the products from elements releases far more than forming methane did, so the difference leaves as heat.**

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Example 2: Decomposing limestone. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Products sum: −635.1 + (−393.5) = −1028.6 kJ. Reactants sum: −1206.9 kJ. ΔH°rxn = −1028.6 − (−1206.9) = +178.3 kJ. Endothermic: the very stable carbonate sits lower than its products, and the gap must be supplied as heat, which is why lime kilns are fired.

Example 3: Oxidising sulfur dioxide. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$. Products sum: 2(−395.7) = −791.4 kJ. Reactants sum: 2(−296.8) + 0 = −593.6 kJ. ΔH°rxn = −791.4 − (−593.6) = −197.8 kJ. The coefficient 2 multiplies both values; leaving it off would halve the answer.

Example 4: Forming nitric oxide. $N_2(g) + O_2(g) \rightarrow 2NO(g)$. Products sum: 2(+90.3) = +180.6 kJ. Reactants sum: 0 + 0 = 0 kJ. ΔH°rxn = +180.6 kJ, or +90.3 kJ per mole of NO, which is ΔH°f itself. Both reactants are elements, so this is the one case where the reaction sum and the formation value tell the same story directly.

Traps That Cost Marks in Topic 6.8

"Reactants minus products." That is the bond enthalpy order from Topic 6.7, and it is backwards here. Formation enthalpies are subtracted as products minus reactants; reversing the order flips the sign of every answer.

"Ignore the coefficients." ΔH°f prices one mole. The 2 in front of H_2O in a combustion equation means −285.8 enters twice. Forgetting a coefficient is the commonest arithmetic error in the topic.

"Use whichever water value is handy." $H_2O(l)$ and $H_2O(g)$ differ by 44.0 kJ mol^{-1} per mole. Read the state in the equation, then take the value for that state.

"Every element is zero." Only the standard form is zero. Diamond is not graphite, and O_3 is not O_2; both carry positive ΔH°f values because neither is the reference form of its element.

"Negative values mean exothermic." Individual signs mean nothing for the reaction. ΔH°rxn is a difference: a reaction between compounds with all-negative values can still be endothermic, as the limestone example shows.

"A formation equation can make two moles." It cannot. One mole of product is built into the definition; an equation making two moles carries twice ΔH°f, and halving it is part of the working, not a shortcut to skip.

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Key Relationships to Remember

- $\Delta H°f$ is the enthalpy change when one mole of a compound forms from its elements in their standard states, at 298 K and 1 atm (1 bar)
- An element in its standard state has $\Delta H°f = 0$; the standard state is the most stable form, graphite for carbon and O_2 for oxygen
- $\Delta H°rxn = \Sigma\, n\Delta H°f(\text{products}) - \Sigma\, n\Delta H°f(\text{reactants})$, with every value multiplied by its coefficient in the balanced equation
- The formation order, products minus reactants, is the reverse of the bond enthalpy order, broken minus formed
- A large negative $\Delta H°f$ marks a compound stable relative to its elements; a positive value marks one less stable than its elements
- $\Delta H°f$ belongs to a stated physical state: $H_2O(l)$ -285.8 and $H_2O(g)$ -241.8 kJ mol^{-1} differ by the 44.0 kJ mol^{-1} enthalpy of vaporization
- A formation equation forms exactly one mole of product from elements only, so fractional coefficients such as $\frac{1}{2}O_2$ are expected
- The sign of $\Delta H°rxn$ depends only on which sum is lower, never on the signs of the individual formation values

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