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Topic 6.7: Bond Enthalpies

Revision Notes · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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What a Bond Enthalpy Is

Bond enthalpy is the energy required to break one mole of a particular bond in gaseous molecules. It is measured in kJ mol^{-1}.

Breaking a bond always takes energy in. The atoms are held together by attractions, and pulling them apart against those attractions costs energy, so every bond enthalpy is a positive number.

The same value runs in reverse. Forming one mole of that bond releases exactly the same amount of energy. The H−H bond enthalpy of 436 kJ mol^{-1} means both things at once: breaking a mole of H_2 into atoms costs 436 kJ, and forming a mole of H_2 from its atoms releases 436 kJ.

One table therefore prices both halves of a reaction.

Bond Enthalpies Used in These Notes

All values are average bond enthalpies in kJ mol^{-1}: H−H 436, H−F 567, H−Cl 431, H−Br 366, H−I 299, Cl−Cl 242, Br−Br 193, O=O 498, N≡N 945, N−N 163, N−H 391, O−H 467, C−H 413, C−C 347, C=C 614, C≡C 839, C−O 358, C=O 799, C−Cl 328.

One set of values is used throughout these notes and the worksheet.

Count the Bonds From the Structures

A bond enthalpy calculation stands or falls on the inventory. Take each molecule's Lewis structure, count every bond in it, and multiply by its coefficient in the balanced equation.

A double bond is a single entry, priced at its own larger value. The C=O in carbon dioxide counts once, at 799 kJ mol^{-1}, not as two C−O bonds. A triple bond also counts once: N≡N at 945 kJ mol^{-1}.

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Lone pairs are not bonds and are never counted. Neither are the attractions between separate molecules: the table prices only the covalent bonds inside molecules.

Bonds that survive the reaction unchanged can be left out of both lists, because they would be paid for and paid back in full. The four C−H bonds of ethene are still present in the ethane it forms, so a hydrogenation calculation only needs the bonds that actually change.

The Calculation: Broken Minus Formed

Picture the reaction in two imaginary steps. First, every bond in the reactants breaks, leaving separated gaseous atoms: that costs the sum of the broken bond enthalpies. Then the atoms join up into the products: that releases the sum of the formed bond enthalpies.

The net enthalpy change is the cost minus the payback:

$\Delta H = \Sigma(\text{bond enthalpies of bonds broken}) - \Sigma(\text{bond enthalpies of bonds formed})$

The order is fixed by the physics. Breaking is endothermic and enters positively; forming is exothermic and is subtracted. Writing the sums the other way round returns the same number with the wrong sign.

Reading the Sign of the Answer

If the formed total is the larger one, more energy is released forming the products than was spent breaking the reactants. The products sit lower in enthalpy than the reactants, ΔH is negative, and the reaction is exothermic.

If the broken total is larger, the reaction must draw the difference from the surroundings: ΔH is positive and the reaction is endothermic.

This is why burning is exothermic even though it starts by breaking bonds: the new bonds in carbon dioxide and water repay that cost with energy to spare.

What Makes a Bond Enthalpy Large or Small

Higher bond order means a larger bond enthalpy. More shared electron pairs pull the atoms together more strongly: C−C is 347 kJ mol^{-1}, C=C is 614 kJ mol^{-1}, and C≡C is 839 kJ mol^{-1}. Note that the triple bond is stronger than the single, but not three times as strong.

Smaller atoms form shorter bonds, and shorter bonds are stronger. Down the hydrogen halides the values fall steadily: H−F 567, H−Cl 431, H−Br 366, H−I 299 kJ mol^{-1}. The halogen atom grows, the bond lengthens, and the bond weakens.

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Bond length and bond enthalpy run in opposite directions: the longer the bond, the less energy breaks it.

Why the Answer Is Only an Estimate

The table values are averages. A C−H bond in methane is not in exactly the same environment as a C−H bond in ethane, and its true enthalpy differs slightly from molecule to molecule. The table lists one mean value gathered from many compounds, so every calculation built on it inherits that averaging error.

The values are also defined for the gas phase only, so the attractions between molecules in liquids and solids are never priced. Methane burning to liquid water has a measured ΔH of −890 kJ; the estimate of about −818 kJ sits closer to the value for steam, because the extra release when steam condenses is outside the table's reach.

The method therefore gives the right sign and a good size for ΔH, never a precise experimental value.

Worked Examples

Example 1: Hydrogen and chlorine. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$. Broken: 1 H−H (436) + 1 Cl−Cl (242) = 678 kJ. Formed: 2 H−Cl = 2 × 431 = 862 kJ. ΔH = 678 − 862 = −184 kJ. Exothermic: forming the two H−Cl bonds repays the breaking cost and releases 184 kJ more.

Example 2: Burning methane. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$. Broken: 4 C−H (4 × 413 = 1,652) + 2 O=O (2 × 498 = 996) = 2,648 kJ. Formed: 2 C=O (2 × 799 = 1,598) + 4 O−H (4 × 467 = 1,868) = 3,466 kJ. ΔH = 2,648 − 3,466 = −818 kJ, about −800 kJ.

Example 3: Making ammonia. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. Broken: 1 N≡N (945) + 3 H−H (3 × 436 = 1,308) = 2,253 kJ. Formed: 6 N−H (6 × 391 = 2,346) = 2,346 kJ. ΔH = 2,253 − 2,346 = −93 kJ, close to the measured −92 kJ for this all-gas reaction: the averages serve this reaction well.

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Example 4: Hydrogenating ethene. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$. Only the changed bonds are priced. Broken: 1 C=C (614) + 1 H−H (436) = 1,050 kJ. Formed: 1 C−C (347) + 2 new C−H (2 × 413 = 826) = 1,173 kJ. ΔH = 1,050 − 1,173 = −123 kJ. The four original C−H bonds appear in neither list because they survive intact.

Traps That Cost Marks in Topic 6.7

"Formed minus broken." The most expensive error in the topic. The formula is broken minus formed, because breaking is the cost. Reversing the sums flips the sign and turns an exothermic answer into an endothermic one.

"Count C=O as two C−O bonds." A double bond is one entry at its own value, 799 kJ mol^{-1}. Two single C−O values give 716 kJ mol^{-1}, and both the price and the bond are wrong.

"Forget the coefficients." The inventory counts bonds per equation, not per molecule. The 2 in front of H_2O means 4 O−H bonds are formed, not 2. Count the molecule, then multiply by its coefficient.

"Breaking bonds releases energy." It never does. Breaking always absorbs energy; a reaction is exothermic only because its bond forming releases more than its bond breaking absorbs.

"Include the lone pairs." Lone pairs are not bonds. The lone pairs on nitrogen in ammonia and on oxygen in water add nothing to either list.

"Treat the estimate as exact." The arithmetic can be perfect and the answer still approximate, because the inputs are averages and the method assumes gases.

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Key Relationships to Remember

- Bond enthalpy is the energy needed to break one mole of a bond in gaseous molecules; it is always positive, and forming the same bond releases the same amount
- $\Delta H \approx \Sigma$(bond enthalpies broken) $-$ Σ(bond enthalpies formed); breaking enters positively, forming is subtracted
- Count bonds from Lewis structures, multiplied by the coefficients in the balanced equation; lone pairs and intermolecular attractions are never counted
- A double or triple bond counts once, at its own value, never as repeated single bonds
- Higher bond order and shorter bond length both mean a larger bond enthalpy
- ΔH is negative when the formed total exceeds the broken total (exothermic) and positive when the broken total is larger (endothermic)
- Table values are averages over many molecules, so bond enthalpy calculations estimate ΔH rather than measure it
- The method assumes the gas phase throughout; phase changes and intermolecular forces in liquids and solids fall outside it

Continue Revising

Topic 6.7 Quiz: Bond Enthalpies

Topic 6.7 Worksheet

Unit 6: All Topics

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