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Topic 6.7: Bond Enthalpies

Worksheet · AP Chemistry

UNIT 6 · THERMOCHEMISTRY

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How to Use This Worksheet

Work in order. Section A checks the foundations: what a bond enthalpy is, how bonds are counted from Lewis structures, what controls a bond's size, and why the method only estimates. Section B practises the full calculation on six reactions, ending with a back-calculation of an unknown bond enthalpy. Section C is exam style: a full combustion inventory, six claims to judge, and a hydrazine problem built around a structure to price bond by bond.

Reference data. Average bond enthalpies in kJ mol^{-1}, the same table as the revision notes: 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. Every reaction in this worksheet is treated as taking place entirely in the gas phase.

Three habits protect every answer. Build the inventory first: list every bond broken and every bond formed before reaching for a calculator. Keep the formula the right way round: broken minus formed, because breaking is the cost and forming is the payback. Finish by checking the sign against the chemistry: combustions must come out negative, and a positive result there means the sums were almost certainly swapped.

Do not look at the answer key until you have attempted every question.

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Section A: Recall and Concepts

A1. (a) Define bond enthalpy, including the phase it is defined for. (b) State the sign of the energy change when a bond breaks, and when the same bond forms. (c) The H−H bond enthalpy is 436 kJ mol^{-1}. State, in words, the two energy changes this one number describes. (d) Explain why the unit is quoted per mole of bonds rather than per mole of molecules.

A2. Ammonia synthesis: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. (a) List every bond broken, with its count. (b) List every bond formed, with its count. (c) Explain why the nitrogen bond is counted once, at 945 kJ mol^{-1}, and not as three separate bonds. (d) Each NH_3 molecule carries a lone pair on nitrogen. State whether it enters either list, and why.

A3. (a) Arrange C−C, C=C and C≡C in order of increasing bond enthalpy, giving each value. (b) Explain the order in terms of bond order. (c) Arrange H−F, H−Cl, H−Br and H−I in order of decreasing bond enthalpy. (d) Explain that order in terms of atomic size and bond length. (e) A triple bond is the strongest of the three carbon bonds. State whether its enthalpy is three times the single bond's, and support the answer with the numbers.

A4. (a) Write the formula that estimates ΔH from bond enthalpies. (b) Explain why the formed sum is subtracted rather than added. (c) State the sign of ΔH, and whether the reaction is exothermic or endothermic, when the formed total is bigger than the broken total. (d) State ΔH for a reaction in which the two totals happen to be exactly equal, and what that equality means physically.

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A5. (a) Explain why bond enthalpies are average values, using C−H in methane and in ethane as the example. (b) State the phase assumption built into every bond enthalpy calculation. (c) A calculation for burning methane gives about −818 kJ, but the measured ΔH for methane burning to liquid water is −890 kJ. Give two reasons for the gap. (d) State one job for which a bond enthalpy estimate is good enough, and one for which it is not.

Section B: Core Practice

B1. Hydrogen bromide formation: $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$. (a) List the bonds broken and formed, with counts. (b) Calculate each total. (c) Calculate ΔH and state whether the reaction is exothermic or endothermic.

B2. Steam formation: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$. (a) List the bonds broken and formed, with counts. (b) Calculate ΔH for the equation as written. (c) Calculate ΔH per mole of water formed. (d) A student counts only 2 O−H bonds as formed. State the ΔH the student gets and identify the error.

B3. Methanol combustion: $2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$. Each methanol molecule contains 3 C−H bonds, 1 C−O bond and 1 O−H bond. (a) List the bonds broken, with counts for the equation as written. (b) List the bonds formed, with counts. (c) Calculate ΔH for the equation as written. (d) Calculate ΔH per mole of methanol burned.

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B4. Ethyne hydrogenation: $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$. Ethyne contains one C≡C bond and two C−H bonds; ethane contains one C−C bond and six C−H bonds. (a) List every bond broken and every bond formed, counting the full inventories. (b) Calculate ΔH. (c) Repeat the calculation pricing only the bonds that change, and confirm the same answer. (d) State which C−H bonds cancel, and how many.

B5. Chloromethane formation: $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$. (a) Using cancellation, list only the bonds that change. (b) Calculate ΔH. (c) State the three C−H bonds that survive, and explain why omitting them from both lists leaves ΔH unchanged. (d) A student prices the C−Cl bond as a second H−Cl bond. State the student's ΔH and the size of the error.

B6. Finding an unknown bond enthalpy. For $H_2(g) + F_2(g) \rightarrow 2HF(g)$, the measured ΔH is −537 kJ. (a) Write the bond enthalpy equation for this reaction, with F−F as the unknown x. (b) Solve for x. (c) Explain why the F−F value comes out so much smaller than Cl−Cl (242 kJ mol^{-1}) would lead you to expect. (Think about the small fluorine atoms and their lone pairs.) (d) State why the answer is still only an estimate of the true F−F bond enthalpy.

Section C: Exam Style

C1. Ethane combustion: $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$. Each ethane molecule contains one C−C bond and six C−H bonds. (a) List the bonds broken, with counts and the total. (b) List the bonds formed, with counts and the total. (c) Calculate ΔH for the equation as written. (d) Calculate ΔH per mole of ethane burned. (e) Calculate ΔH per mole of CO_2 formed, and explain why it differs from the answer to (d).

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C2. Judge each claim, supporting each verdict with the rule it depends on. (a) "Combustion is exothermic because breaking the bonds in the fuel releases energy." (b) "ΔH is calculated as bonds formed minus bonds broken." (c) "Each C=O bond in CO_2 should be priced as two C−O bonds, 2 × 358 = 716 kJ." (d) "An estimate of −818 kJ against a measured −890 kJ for methane combustion proves the arithmetic was wrong." (e) "The lone pairs on the oxygen atoms in water count toward the formed total." (f) "Because C≡C is a triple bond, its enthalpy is exactly three times that of C−C."

C3. Hydrazine, N_2H_4, burns in oxygen: $N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$. The hydrazine molecule has the structure $H_2N{-}NH_2$: four N−H bonds and one N−N bond. (a) List the bonds broken, with counts and the total. (b) List the bonds formed, with counts and the total. (c) Calculate ΔH, and state the heat released per mole of hydrazine burned. (d) The reaction breaks an N−N single bond yet is strongly exothermic. Explain, using the totals, what pays for the breaking. (e) State two reasons the calculated value will not match a measured ΔH exactly.

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Answer Key

A1. (a) Bond enthalpy is the energy required to break one mole of a particular bond in gaseous molecules, separating the atoms completely; it is defined for the gas phase. (b) Breaking absorbs energy, so its enthalpy change is positive. Forming releases the same amount, so its enthalpy change is negative. (c) Breaking one mole of H−H bonds in gaseous H_2 into separate atoms requires 436 kJ, and forming one mole of H_2 from separated gaseous hydrogen atoms releases 436 kJ. (d) The table prices bonds, not molecules: a mole of CH_4 contains four moles of C−H bonds, and each mole of bonds carries the same price, so counting is done in moles of bonds.

A2. (a) Broken: 1 N≡N and 3 H−H. (b) Formed: 6 N−H, because each of the 2 NH_3 molecules holds 3 N−H bonds. (c) A triple bond is one bond of order three, a single entry in the structure, and the table prices it as one unit at 945 kJ mol^{-1}; it is not three separate single bonds, and three N−N values (3 × 163 = 489) would badly underprice it. (d) It enters neither list. A lone pair is a non-bonding pair of electrons, not a bond, and bond enthalpy tables price only bonds.

A3. (a) C−C 347, then C=C 614, then C≡C 839 kJ mol^{-1}. (b) Higher bond order means more shared electron pairs between the same two atoms, a stronger attraction, and more energy needed to separate them, so the enthalpy rises from single to double to triple. (c) H−F 567, then H−Cl 431, then H−Br 366, then H−I 299 kJ mol^{-1}. (d) Down the group the halogen atom grows, so the shared pair sits further from both nuclei, the bond is longer, and a longer bond is weaker and cheaper to break. (e) No. Three single bonds would cost 3 × 347 = 1,041 kJ mol^{-1}, well above the triple bond's 839 kJ mol^{-1}. Each added shared pair strengthens the bond by less than the one before.

A4. (a) $\Delta H \approx \Sigma$(bond enthalpies of bonds broken) − Σ(bond enthalpies of bonds formed). (b) Forming releases energy, which is a negative contribution to the system's enthalpy change. Subtracting the formed total is how that release enters the sum: cost of breaking, minus energy paid back by forming. (c) ΔH is negative and the reaction is exothermic: the products hold less enthalpy than the reactants, and the difference leaves as heat. (d) $\Delta H = 0$. The energy absorbed in breaking is exactly repaid by the energy released in forming, so there is no net heat exchange with the surroundings.

A5. (a) The environment of a bond changes slightly from molecule to molecule: a C−H bond in methane sits beside three other C−H bonds, while in ethane it sits beside a C−C bond, and the two differ slightly in strength. Tables publish one average gathered over many compounds. (b) All reactants and products are gases. (c) First, the table values are averages, so the methane C−H and water O−H prices are not exact for these molecules. Second, the method prices gaseous water, while the measured value forms liquid water; the condensation of steam releases extra energy that bond enthalpies never include. (d) Good enough: predicting whether a proposed reaction is exothermic and roughly by how much, or comparing two fuels. Not good enough: any purpose needing a precise ΔH, such as engineering design.

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B1. (a) Broken: 1 H−H and 1 Br−Br. Formed: 2 H−Br. (b) Broken total: 436 + 193 = 629 kJ. Formed total: 2 × 366 = 732 kJ. (c) ΔH = 629 − 732 = −103 kJ. Negative, so the reaction is exothermic.

B2. (a) Broken: 2 H−H and 1 O=O. Formed: 4 O−H, because each of the 2 water molecules holds 2 O−H bonds. (b) Broken total: 2 × 436 + 498 = 1,370 kJ. Formed total: 4 × 467 = 1,868 kJ. ΔH = 1,370 − 1,868 = −498 kJ. (c) The equation forms 2 mol of water, so per mole: −498 ÷ 2 = −249 kJ mol^{-1}. (d) The student forms only 2 × 467 = 934 kJ, giving ΔH = 1,370 − 934 = +436 kJ. The error is forgetting the coefficient: the 2 in front of H_2O doubles the O−H count to 4, and missing it even flips the sign of the answer.

B3. (a) Broken: 6 C−H, 2 C−O, 2 O−H and 3 O=O, doubling the methanol inventory for the coefficient 2. (b) Formed: 4 C=O (two in each CO_2) and 8 O−H (two in each of the 4 water molecules). (c) Broken total: 6 × 413 + 2 × 358 + 2 × 467 + 3 × 498 = 2,478 + 716 + 934 + 1,494 = 5,622 kJ. Formed total: 4 × 799 + 8 × 467 = 3,196 + 3,736 = 6,932 kJ. ΔH = 5,622 − 6,932 = −1,310 kJ. (d) The equation burns 2 mol of methanol, so per mole: −1,310 ÷ 2 = −655 kJ mol^{-1}.

B4. (a) Broken: 1 C≡C, 2 C−H and 2 H−H. Formed: 1 C−C and 6 C−H. (b) Broken total: 839 + 2 × 413 + 2 × 436 = 839 + 826 + 872 = 2,537 kJ. Formed total: 347 + 6 × 413 = 347 + 2,478 = 2,825 kJ. ΔH = 2,537 − 2,825 = −288 kJ. (c) Pricing only the changes: broken 1 C≡C + 2 H−H = 839 + 872 = 1,711 kJ; formed 1 C−C + 4 new C−H = 347 + 1,652 = 1,999 kJ; ΔH = 1,711 − 1,999 = −288 kJ, the same answer. (d) Two C−H bonds cancel: ethyne's two C−H bonds are still present in ethane, so they are broken on paper and re-formed at the same price, contributing nothing to the difference.

B5. (a) Only one C−H bond and the Cl−Cl bond break; one C−Cl bond and one H−Cl bond form. The other three C−H bonds are untouched. (b) Broken: 413 + 242 = 655 kJ. Formed: 328 + 431 = 759 kJ. ΔH = 655 − 759 = −104 kJ. (c) The three surviving C−H bonds would add 3 × 413 = 1,239 kJ to both totals if they were listed, and equal additions to both sides of a subtraction cancel, so ΔH is unchanged. (d) The student forms 2 × 431 = 862 kJ in place of 759 kJ, giving ΔH = 655 − 862 = −207 kJ. The error is 103 kJ: the reaction looks far more exothermic than it is because C−Cl (328) was priced at the stronger H−Cl value (431).

B6. (a) Broken: 1 H−H and 1 F−F, total 436 + x. Formed: 2 H−F, total 2 × 567 = 1,134 kJ. ΔH = (436 + x) − 1,134 = −537 kJ. (b) 436 + x = 1,134 − 537 = 597, so x = 597 − 436 = 161 kJ mol^{-1}. (c) Fluorine atoms are so small that the lone pairs on the two bonded atoms sit very close and repel each other, weakening the F−F bond well below the trend set by the other halogens. (d) The measured ΔH is exact for the reaction, but the calculation leans on the H−F table value, which is an average; any averaging error in H−F is transferred into x, so x is an estimate of the F−F bond enthalpy, not a direct measurement.

C1. (a) Broken: 2 C−C, 12 C−H and 7 O=O. Total: 2 × 347 + 12 × 413 + 7 × 498 = 694 + 4,956 + 3,486 = 9,136 kJ. (b) Formed: 8 C=O (two in each of the 4 CO_2 molecules) and 12 O−H (two in each of the 6 water molecules). Total: 8 × 799 + 12 × 467 = 6,392 + 5,604 = 11,996 kJ. (c) ΔH = 9,136 − 11,996 = −2,860 kJ. (d) The equation burns 2 mol of ethane, so per mole: −2,860 ÷ 2 = −1,430 kJ mol^{-1}. (e)

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Per mole of CO_2: −2,860 ÷ 4 = −715 kJ. It differs because the two prices divide the same total by different amounts: the equation names 2 mol of ethane but 4 mol of carbon dioxide, so the per-mole price for CO_2 is half that for ethane.

C2. (a) False. Breaking bonds always absorbs energy. Combustion is exothermic because the bonds formed in CO_2 and H_2O release more energy than the breaking absorbs; the release comes from forming, never from breaking. (b) False. The formula is broken minus formed. Forming is the payback and is subtracted from the cost of breaking; the claim reverses the sums and flips every sign. (c) False. A double bond is one bond priced at its own enthalpy, 799 kJ mol^{-1}. Two C−O prices give 716 kJ mol^{-1}, which is both the wrong structure and the wrong value: a double bond is not two single bonds. (d) False. A gap is expected: the table values are averages, and the estimate prices steam while the measured value forms liquid water, whose condensation releases extra energy. Neither gap implies an arithmetic slip. (e) False. Lone pairs are non-bonding electron pairs, not bonds, and bond enthalpy tables price bonds only. They enter neither the broken nor the formed total. (f) False. C≡C is 839 kJ mol^{-1} and 3 × 347 = 1,041 kJ mol^{-1}. Bond enthalpy rises with bond order, but each extra shared pair adds less than the previous one.

C3. (a) Broken: 4 N−H and 1 N−N, plus 1 O=O. Total: 4 × 391 + 163 + 498 = 1,564 + 163 + 498 = 2,225 kJ. (b) Formed: 1 N≡N and 4 O−H (two in each water molecule). Total: 945 + 4 × 467 = 945 + 1,868 = 2,813 kJ. (c) ΔH = 2,225 − 2,813 = −588 kJ for the equation as written, which burns 1 mol of hydrazine, so the heat released per mole of hydrazine is 588 kJ. (d) The formed total is what pays. Forming the very strong N≡N triple bond (945 kJ) and four O−H bonds releases 2,813 kJ, comfortably more than the 2,225 kJ spent breaking every bond in hydrazine and oxygen; the weak N−N bond is a small part of the cost. (e) The table values are averages, so the N−H price gathered from other molecules is not exact for hydrazine; and the method assumes gases throughout, so any real measurement involving liquid hydrazine or liquid water includes intermolecular effects the table never prices.

Continue Revising

Topic 6.7 Revision Notes

Topic 6.7 Quiz: Bond Enthalpies

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Next Worksheet: Topic 6.8 Enthalpy of Formation

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