AS Chemistry worksheet: measuring and calculating enthalpy changes

How to use this worksheet

This worksheet covers the chemical energetics section of Cambridge International AS Chemistry (9701): definitions, calorimetry, Hess's law, bond energies and enthalpy profiles. There are five sets of questions, numbered continuously, worth 50 marks in total. Work through each set, then check your working against the answer block that follows it. Marks are shown in square brackets. Where a question gives data, use that data, because the examiner marks the method as well as the final figure.

Unless a question says otherwise, take the specific heat capacity of water and of dilute aqueous solutions as 4.18 J g^{-1} K^{-1}, the density of dilute aqueous solutions as 1.00 g cm^{-3}, and standard conditions as 298 K and 101 kPa. Give enthalpy changes to three significant figures with a sign and the unit kJ mol^{-1}.

> **Exam tip.** A sign and a unit are part of every enthalpy answer: exothermic changes have a negative ΔH, endothermic changes a positive ΔH. Writing "55.2 kJ mol^{-1}" for a neutralisation loses the mark because the sign is missing. Keep unrounded values in your calculator until the final line.

Set 1: definitions and standard conditions

1. Define the term *standard enthalpy change of formation*, and write the equation, including state symbols, that corresponds to the standard enthalpy change of formation of ethanol, $C_2H_5OH(l)$. [3]

2. Define the term *standard enthalpy change of combustion*. [2]

3. State what is meant by *standard conditions* in enthalpy measurements. [2]

4. Define the term *standard enthalpy change of neutralisation*. [1]

5. Define the term *bond energy*, and explain why the bond energy quoted for the C-H bond in the data booklet is described as an average value. [2]

> **1.** The standard enthalpy change of formation is the enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions, 298 K and 101 kPa [1 for "one mole of compound from its elements", 1 for "standard states and standard conditions"]. Equation: $2C(s, graphite) + 3H_2(g) + ½O_2(g) \rightarrow C_2H_5OH(l)$ [1]. The equation must make exactly one mole of ethanol, so the fractional coefficient is expected.
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> **2.** The standard enthalpy change of combustion is the enthalpy change when one mole of a substance is completely burned in oxygen [1] under standard conditions, with all substances in their standard states [1]. The word "completely" matters: the carbon must end up as CO_2, not CO.
>
> **3.** A temperature of 298 K (25 °C) and a pressure of 101 kPa (1 atmosphere) [1], with any solutions at a concentration of 1 mol dm^{-3} and every substance in its normal physical state under these conditions [1].
>
> **4.** The enthalpy change when an acid and an alkali react to form one mole of water under

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standard conditions [1]. It is defined per mole of water, not per mole of acid.

5. Bond energy is the energy needed to break one mole of a particular covalent bond, with the species in the gaseous state [1]. The strength of a C-H bond depends slightly on the other atoms attached to the carbon, so the data booklet value is an average taken over many different compounds containing that bond [1].

Set 2: calorimetry calculations

6. A student mixed 50.0 cm^3 of 1.00 mol dm^{-3} hydrochloric acid with 50.0 cm^3 of 1.00 mol dm^{-3} sodium hydroxide solution in a polystyrene cup. Both solutions were at 21.0 °C before mixing. The highest temperature recorded after mixing was 27.6 °C.

(a) Calculate the enthalpy change of neutralisation for this reaction. Show the heat energy released, the amount of water formed and the final value with its sign and unit. [3]

(b) The accepted value for the enthalpy change of neutralisation of a strong acid by a strong alkali is about -57 kJ mol^{-1}. Suggest one reason why the student's value is less exothermic than this. [1]

7. Ethanol was burned in a spirit burner under a copper can containing 200 g of water. The mass of the burner fell by 0.460 g and the temperature of the water rose by 11.0 °C. (M_r of ethanol = 46.0)

(a) Calculate the heat energy transferred to the water, in kJ. [2]

(b) Calculate the enthalpy change of combustion of ethanol from these results. [2]

(c) The data booklet gives the standard enthalpy change of combustion of ethanol as -1367 kJ mol^{-1}. Suggest two reasons why the experimental value differs so much from this. [2]

8. Excess zinc powder was added to 25.0 cm^3 of 0.200 mol dm^{-3} copper(II) sulfate solution in a polystyrene cup. The student recorded the temperature every half minute, before and after adding the zinc, and plotted a graph of temperature against time. The temperature before mixing was 21.0 °C. By extending the cooling part of the graph back to the moment of mixing, the student found an extrapolated maximum temperature of 31.0 °C.

(a) Explain why the student extrapolated the cooling line instead of simply using the highest temperature read from the thermometer. [1]

(b) Calculate the enthalpy change for the reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, stating one assumption you make. [3]

6 (a). Total mass of solution = 50.0 + 50.0 = 100.0 g (density taken as 1.00 g cm^{-3}). Temperature rise ΔT = 27.6 - 21.0 = 6.6 K.

Heat released: $q = m \times c \times \Delta T$ = 100.0 g × 4.18 J g^{-1} K^{-1} × 6.6 K = 2759 J = 2.759 kJ [1].

Amount of HCl = 1.00 mol dm^{-3} × 0.0500 dm^3 = 0.0500 mol; amount of NaOH is the same, so 0.0500 mol of water is formed [1].

$\Delta H_{neut} = -q / n$ = -2.759 kJ / 0.0500 mol = -55.2 kJ mol^{-1} [1 for the correct value with the negative sign and unit].

6 (b). Any one: some heat is lost to the surroundings or absorbed by the cup and thermometer; the temperature was read before the true maximum or after cooling had begun; the specific heat capacity of the solution is slightly lower than that of pure water. [1]

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7 (a). q = m × c × ΔT = 200 g × 4.18 J g^{-1} K^{-1} × 11.0 K = 9196 J [1] = 9.20 kJ (to three significant figures) [1].

7 (b). Amount of ethanol burned = 0.460 g / 46.0 g mol^{-1} = 0.0100 mol [1]. ΔH_c = -9.196 kJ / 0.0100 mol = -920 kJ mol^{-1} [1]. (Accept -919.6 or -920.)

7 (c). Any two of the following, each for one mark: a large share of the heat from the flame escapes to the air around the can rather than entering the water; the copper can itself absorbs heat, which was not included in the calculation; the combustion may be incomplete, giving some carbon monoxide or soot, so less energy is released per mole; some ethanol evaporates from the wick without burning, so the mass loss overstates the amount combusted; the reaction was not carried out under standard conditions. [2]

8 (a). The reaction takes time to finish and the cup is losing heat to the surroundings throughout, so the highest reading on the thermometer is lower than the temperature the mixture would have reached if no heat had been lost. Extrapolating the cooling line back to the time of mixing corrects for that heat loss. [1]

8 (b). ΔT = 31.0 - 21.0 = 10.0 K. Mass of solution = 25.0 g, assuming the solution has the density and specific heat capacity of water, and ignoring the mass of the zinc. q = 25.0 g × 4.18 J g^{-1} K^{-1} × 10.0 K = 1045 J = 1.045 kJ [1 for q with a stated assumption]. Amount of Cu^{2+} = 0.200 mol dm^{-3} × 0.0250 dm^3 = 0.00500 mol; zinc is in excess, so copper(II) ions are the limiting reagent [1]. ΔH = -1.045 kJ / 0.00500 mol = -209 kJ mol^{-1} [1].

Exam tip. In q = mcΔT the mass m is the mass of the material whose temperature changes (the water or the solution), never the mass of the fuel or the solid reactant. The moles in the second step are the moles of the limiting reagent, or of water formed in a neutralisation.

Set 3: Hess's law cycles

9. Use the standard enthalpy changes of formation below to calculate the standard enthalpy change of combustion of propane, $C_3H_8(g)$.

Substance	Standard ΔH_f / kJ mol^{-1}
$C_3H_8(g)$	-104
$CO_2(g)$	-394
$H_2O(l)$	-286

Write the balanced equation for the combustion first. [3]

10. The standard enthalpy change of formation of methane cannot be measured directly. Use the standard enthalpy changes of combustion below to calculate it: C(s, graphite) -394 kJ mol^{-1}; $H_2(g)$ -286 kJ mol^{-1}; $CH_4(g)$ -890 kJ mol^{-1}. Describe in words the Hess's law cycle you use, and explain why direct measurement is not possible. [4]

11. A student wanted to find the enthalpy change for the thermal decomposition of sodium hydrogencarbonate: $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$. The student measured the following enthalpy changes by adding each solid to an excess of dilute hydrochloric acid.

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ΔH_1: $NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$, $\Delta H_1 = +28.5$ kJ mol^{-1}

ΔH_2: $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$, $\Delta H_2 = -26.0$ kJ mol^{-1}

Calculate the enthalpy change for the thermal decomposition of two moles of sodium hydrogencarbonate. [3]

9. Equation: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ [1].

ΔH_r = sum of ΔH_f(products) - sum of ΔH_f(reactants). Oxygen is an element in its standard state, so its ΔH_f is zero.

Sum for products = 3 × (-394) + 4 × (-286) = -1182 + (-1144) = -2326 kJ mol^{-1} [1].

ΔH_c = -2326 - (-104) = -2222 kJ mol^{-1} [1].

10. Why not directly: carbon does not react cleanly with hydrogen; carbon and hydrogen form a mixture of hydrocarbons rather than methane alone, and the reaction is far too slow at standard conditions to measure a temperature change, so the heat for forming one mole of methane cannot be isolated [1].

The cycle: write the formation equation $C(s) + 2H_2(g) \rightarrow CH_4(g)$ across the top. Both the reactants and the product burn in oxygen to give the same combustion products, $CO_2(g) + 2H_2O(l)$, so draw an arrow from each side of the equation down to these products. The route from the elements to the combustion products directly must equal the route via methane [1 for a correct description of the cycle].

Elements to combustion products: $\Delta H_c(C) + 2 \times \Delta H_c(H_2) = -394 + 2 \times (-286) = -966$ kJ mol^{-1}. Methane to combustion products: $\Delta H_c(CH_4) = -890$ kJ mol^{-1} [1 for both totals].

$\Delta H_f(CH_4) = -966 - (-890) = -76$ kJ mol^{-1} [1].

11. Two moles of $NaHCO_3$ react with acid, so the first step must be doubled: $2 \times \Delta H_1 = 2 \times (+28.5) = +57.0$ kJ [1]. The decomposition products, $Na_2CO_3(s) + H_2O(l) + CO_2(g)$, react with acid to give the same final mixture, $2NaCl(aq) + 2H_2O(l) + 2CO_2(g)$, with enthalpy change ΔH_2. By Hess's law, $\Delta H_{decomposition} + \Delta H_2 = 2 \times \Delta H_1$ [1]. So $\Delta H_{decomposition} = +57.0 - (-26.0) = +83.0$ kJ mol^{-1} [1]. The positive sign is expected for a thermal decomposition.

Learn this. Hess's law: the total enthalpy change of a reaction is independent of the route taken, provided the initial and final conditions are the same. Two rearrangements cover almost every exam question. From formation data: $\Delta H_r = \Sigma\Delta H_f$(products) - $\Sigma\Delta H_f$(reactants). From combustion data: $\Delta H_r = \Sigma\Delta H_c$(reactants) - $\Sigma\Delta H_c$(products).

Set 4: bond energy calculations

Use these average bond energies, in kJ mol^{-1}, for questions 12 to 14: C-C 350; C=C 610; C-H 410; H-H 436; O=O 496; C=O (in CO_2) 805; O-H 460; N≡N 944.

12. Calculate the enthalpy change for the hydrogenation of ethene: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$. [3]

13. (a) Calculate the enthalpy change of combustion of methane, $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$, using bond energies. [3]

(b) The data booklet value for the standard enthalpy change of combustion of methane is -890 kJ

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mol^{-1}. Explain why the bond energy answer in (a) is different. [1]

14. The enthalpy change for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is -92 kJ mol^{-1}. Use this value to calculate the average N-H bond energy. [3]

12. ΔH = sum of bond energies broken - sum of bond energies formed. Only the bonds that actually change need to be counted: the four C-H bonds in ethene are still there in ethane.

Bonds broken: one C=C (610) and one H-H (436) = 1046 kJ mol^{-1} [1].

Bonds formed: one C-C (350) and two new C-H (2 × 410 = 820) = 1170 kJ mol^{-1} [1].

ΔH = 1046 - 1170 = -124 kJ mol^{-1} [1]. More energy is released in making bonds than is needed to break them, so the reaction is exothermic.

13 (a). Bonds broken: 4 C-H (4 × 410 = 1640) + 2 O=O (2 × 496 = 992) = 2632 kJ mol^{-1} [1].

Bonds formed: 2 C=O (2 × 805 = 1610) + 4 O-H (4 × 460 = 1840) = 3450 kJ mol^{-1} [1].

ΔH = 2632 - 3450 = -818 kJ mol^{-1} [1].

13 (b). Either of: bond energies are averages over many compounds, so they are not exactly right for the bonds in these particular molecules; or the bond energy calculation refers to water as a gas, whereas the standard enthalpy change of combustion refers to liquid water, and the extra heat released when steam condenses makes the standard value more exothermic. [1]

14. Let the N-H bond energy be E. Bonds broken: one N≡N (944) + 3 H-H (3 × 436 = 1308) = 2252 kJ mol^{-1} [1]. Bonds formed: two NH_3 molecules each have three N-H bonds, so 6E [1].

ΔH = 2252 - 6E = -92, so 6E = 2252 + 92 = 2344 and E = 2344 / 6 = 391 kJ mol^{-1} (390.7) [1]. This agrees closely with the data booklet value for N-H.

Set 5: enthalpy profile diagrams

15. Describe the enthalpy profile diagram for the exothermic reaction between zinc and copper(II) sulfate solution. In your description state what is plotted on each axis, where the reactants and products are placed, and how the enthalpy change and the activation energy are shown. [3]

16. The thermal decomposition of calcium carbonate, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, has ΔH = +178 kJ mol^{-1}.

(a) Describe how the enthalpy profile for this reaction differs from the profile in question 15. [1]

(b) A catalyst is added to a different reaction. State how the enthalpy profile changes and how it stays the same, and explain in terms of the profile why the catalyst speeds up the reaction. [2]

15. The vertical axis is enthalpy (or energy) and the horizontal axis is the progress of the reaction (sometimes labelled reaction pathway or extent of reaction) [1]. The reactants, $Zn(s) + Cu^{2+}(aq)$, are drawn as a horizontal level on the left and the products, $Zn^{2+}(aq) + Cu(s)$, as a horizontal level on the right that is lower than the reactants, because the reaction is exothermic. ΔH is the vertical gap between the two levels, drawn as a downward arrow from reactants to products and labelled with a negative value [1]. The curve rises from the reactant level to a maximum, the transition state, before falling to the product level. The activation energy E_a is the vertical gap from the reactant level up to the top of this hump, drawn as an upward arrow [1].

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16 (a). The product level, CaO(s) + CO_2(g), is drawn above the reactant level, $CaCO_3$(s), and ΔH is an upward arrow from reactants to products labelled +178 kJ mol^{-1}. The hump still rises above the product level, so E_a is larger than ΔH. [1]

16 (b). With a catalyst the hump is lower, because the catalyst provides an alternative route with a lower activation energy; the reactant and product levels, and therefore ΔH, are unchanged [1]. Because E_a is lower, a larger proportion of the colliding particles have at least this energy, so more collisions each second are successful and the rate increases [1].

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