Chem Factsheet

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How To Answer Questions On Enthalpy Changes

A good way to begin serious revision for this topic would be to study FactSheet 08.

If you are revising the Born Haber Cycle at A2 level, then study FactSheets 28 and 29.

The topic always deals with *energy changes* rather than with the total energy of a system.

Enthalpy (H) is also concerned with the Law of Conservation of Energy (otherwise known as the First Law of Thermodynamics) - energy cannot be created or destroyed, only converted from one form to another.

In the questions you will meet the only form of energy will be heat and the two terms enthalpy and heat will both mean the same. Strictly speaking, enthalpy is *the heat content measured at constant pressure*.

Hess's Law is vital here. This may be stated as "the total energy change when a system changes from one state to another is independent of the route taken in bringing about the change".

Hess's Law is a direct consequence of the First Law of Thermodynamics as, if the energy change *were* dependent on the route, it would be possible to construct a heat engine or cycle such that heat energy could be extracted from the system indefinitely.

Enthalpy changes (ΔH) are *always* dependent on the temperature and pressure of the initial and final states, so when asked for a *definition* be sure to include '*measured under standard conditions of temperature and pressure (10^5 Pa and 298K)*' and LEARN THE DEFINITIONS!

Extracts from Recent Examiner's Reports:
'*only 20% of the candidates stated that enthalpy change is the heat change at constant pressure*'

'The range of answers.........indicated the variation in the ability of the candidates to learn basic information'.

'15% of candidates failed to score any marks' (the question was 'define the term standard enthalpy of formation' – worth 3 marks!)

Many candidates incorrectly stated the "enthalpy required" rather than the "enthalpy change" and some omitted the one mole from the definition'

Make sure that you always use the correct sign:
If the products contain less energy than the reactants, heat energy is given out to the surroundings (i.e. the reaction is exothermic) and *ΔH is negative*.

Conversely, if the products contain more energy than the reactants, heat energy is taken in from the surroundings (i.e. the reaction is endothermic) and *ΔH is positive*.

The more energy a compound needs to break its bonds, the more stable it will be and the greater the positive value of ΔH. Bond breaking is endothermic so ΔH is always positive. (This applies to Standard Enthalpy Change of Atomisation, Standard Bond Enthalpy and Average Bond Enthalpy).

Considering physical changes, processes such as melting and boiling of simple molecular substances will involve relatively small positive ΔH values as the intermolecular bonds broken are relatively weak. Liquids such as water which form hydrogen bonds will have somewhat higher ΔH values for changes of state. However, melting and boiling giant ionic or covalent structures will have very large positive ΔH values because covalent and ionic bonds are very strong.

Extract from Recent Examiner's Report:-*'the majority of candidates did not realise that the chlorine-chlorine bond enthalpy is twice the enthalpy of atomisation'*

Standard Enthalpy of Atomization, $\Delta H^{\ominus}_{at,298}$

This refers to the enthalpy change in forming one mole of free gaseous atoms from an element in its normal physical state under standard conditions.

For diatomic molecules in the gaseous state, this is equal to *half* the standard bond enthalpy.

For example, for hydrogen,

$\frac{1}{2}H_2(g) \rightarrow H(g)$ corresponds to the standard enthalpy of atomisation whereas $H_2(g) \rightarrow 2H(g)$ corresponds to the standard bond enthalpy.

[For elements whose standard states are solid or liquid, other enthalpy changes, for example the enthalpy of sublimation and the enthalpy of vaporisation will need to be used in the calculation.]

Bond enthalpy is a topic which has been highlighted as demanding in many examiners' reports.

Extract from Recent Examiner's Report:-*'the calculation of a value for the H-H bond enthalpy proved very demanding and half the candidates scored* ***no*** *marks'*

Worked Example No 1 (Bond Enthalpy)

Part One. Hydrogen and oxygen form hydrogen peroxide as per the following equation:

$$H_2(g) + O_2(g) \rightarrow H_2O_2(l) \qquad \Delta H = -188 \text{ kJ mol}^{-1}$$

Use the equation above together with the following data to calculate the bond enthalpy of the O-O bond.

Bond Type	H-H	O=O	H-O
Mean Bond Enthalpy kJmol^{-1}	436	498	460

(3 marks)

Part Two. The calculated bond enthalpy does not agree with the average bond enthalpy given in standard data tables. Suggest a reason for this and explain the difference observed. (Considering the following equation and data may help you with your answer: $H_2O(l) \rightarrow H_2O(g)$; ÄH = +44.0 kJ mol^{-1}) (2 marks)

Part One Answer

Bonds broken	H-H	+436 kJ mol^{-1}
	O=O	+498 kJ mol^{-1}
Bonds formed	H-O **× 2**	-460 × 2 = -920 kJmol^{-1}
	O-O	?

Energy change (ΔH) of reaction is -188 kJ mol^{-1}

Bonds broken - Bonds formed = Energy change of reaction, ΔH.

436 + 498 - 920 + ? = -188

Hence, the energy given out by formation of the O-O in hydrogen peroxide is 202 kJ mol^{-1}

The bond enthalpy is +202 kJmol^{-1}

Note: bond enthalpies are always positive.

Part Two Answer.
The hydrogen peroxide is formed in the *liquid* state rather than the *gaseous* state under which bond enthalpy data apply.(1 mark)

In the liquid state the hydrogen peroxide molecules produced would undergo *hydrogen bonding* (1 mark) with each other, thus the energy released when these form would have to be included in the calculation.

Worked Example No 2 (Using Bond Enthalpies to Determine Enthalpy Change of a Reaction)

Part One. The combustion of methanol can be represented by the following equation:

$$CH_3OH(g) + 1\tfrac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Use this equation plus the following average bond enthalpy data to calculate the enthalpy of combustion of methanol.

Bond	C-H	C-O	O-H	O=O	C=O
Average Bond Enthalpy kJmol^{-1}	+412	+335	+465	+500	+805

(3 marks)

Part Two. Give two reasons why the value obtained differs from the standard enthalpy change of combustion for methanol. (2 marks)

Part Three. Calculate the energy given out per gram of methanol burned. (1 mark)

Part one answer

Bonds broken	**3** C-H	3 × +412 = +1236 kJ
	C-O	+335 kJ
	O-H	+465 kJ
	1½ O=O	1½ × +500 = +750 kJ
Bonds formed	**2** C=O	2 × -805 = -1610 kJ
	4 H-O	4 × -465 = -1860 kJ

Enthalpy change due to bond breaking:
= 1236 + 335 + 465 + 750 = +2786 kJ (1 mark)

Enthalpy change due to bond formation:
= -1610 – 1860 = -3470 kJ (1 mark)

Net Enthalpy Change = Enthalpy of combustion of methanol
= - 3470 + 2786
= - 684 kJmol^{-1} (1 mark)

Part Two Answer

1. Methanol and water are liquids, not gases, under standard conditions. (1 mark)
2. The actual bond enthalpies in the molecules in the equation may differ from those quoted as ‘average bond enthalpies’.(1 mark)

Part Three Answer
M_r of methanol is 32. Energy given out per gram of methanol burned is 684 ÷ 32 = 21.4 kJ

> ***Extract from Examiner’s Report***
> *‘calculating the energy per gram for the fuel proved to be a difficult concept for most candidates and only 25% used the* M_r *effectively’*

Worked Example No 3 (Using Standard Enthalpy of Formation Values to Determine the Standard Enthalpy Change for a Reaction)

Part One. Given the following equation and the data in the table calculate the standard enthalpy of combustion for ethanol. (2 marks)

Compound	C_2H_5OH (l)	O_2 (g)	CO_2 (g)	H_2O (l)
$\Delta H^{\ominus}_{\text{Formation}}$ kJ mol^{-1}	-279	0	-395	-285

Part Two. Ethanol is often used as a fuel. Calculate the energy given out per gram of ethanol burned. (1 mark)

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Part One Answer
Converting C_2H_5OH and O_2 back to elements would *take in* (+ve) 279 + 0 kJ

Converting these elements to the oxides would *release* (-ve) 2 × 395 = 790kJ for $2CO_2$ and 3 ×285 = 855kJ for $3H_2O$

Hence, net energy change = +279 + 0 - 790 - 855 kJ

Standard Enthalpy of combustion for ethanol is -1366 kJmol^{-1}.(2 marks)

This may be better seen as an energy cycle

$$\begin{tikzcd}
C_2H_5OH + 3O_2 \arrow[rr, "\Delta H_c"] \arrow[dr, "+279"'] & & 2CO_2 + 3H_2O \\
& 2C + 3H_2 + 3\tfrac{1}{2}O_2 \arrow[ur, "2(-395) + 3(-285)"'] &
\end{tikzcd}$$

Part Two Answer
The M_r of ethanol is 46, and so 46 grams of ethanol are calculated to give 1366 kJ of energy.

Energy given out per gram is 1366 ÷ 46 = 29.7 kJ (or 30kJ to 2sf) (1 mark)

Using Experimental Results

Experimental results often give rise to calculations with two (or more) stages.

For example: burning a mass of fuel and calculating the heat produced by measuring a temperature change in water by using the equation:

$$\boxed{\text{Energy transferred to water}} = \boxed{\text{mass}} \times \boxed{\text{specific heat capacity}} \times \boxed{\text{temperature change.}}$$

i.e. $q = mC\Delta T$

The quantities (m, C and ΔT) will be for the substance which is being heated (i.e. water in most cases) - not for the substance supplying the heat!.

Then you can use the heat energy transferred to do the calculation of the enthalpy of the substance whose chemical change produced the heat.

Worked Example No 4 (Using Experimental Results)

Part 1 In an experiment to determine the enthalpy of combustion of glucose, a student burns 0.953g of glucose. The heat energy released is supplied to 100 cm^3 of water. The temperature of the water increases from 20.6 °C to 40.6 °C.

Part 2 Having adjusted his results for heat losses, the student found the value obtained was less exothermic than that given by a book of standard data, suggest a reason for this. (1 mark)

Answer to Part 1

The equation for the combustion of glucose is

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

Specific Heat Capacity of Water = 4.18 J g^{-1} K^{-1}

Density of Water = 1.00 g cm^{-3}

Calculate the enthalpy of combustion of glucose. (6 marks)

A good idea is to split up your answer into 3 parts (there will be 2 marks for each part).

(a) Calculate the number of moles of glucose burnt

$M_r = 156$ Moles of glucose = $0.953 \div 156 = \mathbf{6.11 \times 10^{-3}}$ moles

(b) Calculate the heat supplied to the water

$$\begin{aligned}\text{Heat supplied} &= mC\Delta T \\ &= (\text{volume} \times \text{density}) \times C \times \Delta T \\ &= (100 \times 1.0) \times 4.18 \times (40.6 - 20.6) \\ &= 8360\text{ J}\end{aligned}$$

If you need any help with units look at the units of specific heat capacity and density given in the question and also remember that *differences* in temperature are the same in K as in °C.

The units for enthalpy of combustion are kJ mol^{-1} so you will need to convert your joules to kilojoules 8360J ÷ 1000 = **8.360kJ**

(c) Now divide the measured energy change by the number of moles

$8.360 \div 6.11 \times 10^{-3} = 1.37 \times 10^3$ kJ mol^{-1} and for combustion heat energy is given out to the surroundings so the enthalpy of combustion is always negative.

The enthalpy of combustion of glucose is **-1370 kJ$\mathbf{mol^{-1}}$** with the answer to three significant figures (as that was the degree of accuracy of the data you were given).

Answer to Part 2

Incomplete combustion of glucose.

Extract from Examiner's Report

'frequent errors in relating signs of temperature changes and enthalpy changes – if the ΔT = T(final) – T(initial) is positive then ΔH is negative and vice versa'

Worked Example No 5 (Hess's Law)

Consider the following series of reactions and use them to find the standard enthalpy change for combustion of methane.

Reaction 1: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H_1 = -803\text{ kJ mol}^{-1}$

Reaction 2: $2H_2O(g) \rightarrow 2H_2O(l) \quad \Delta H_2 = -89\text{ kJ mol}^{-1}$

(3 marks)

First write down the equation which gives the reaction which you want:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

[Note that all the compounds are in their standard states – liquid for water!](1 mark)

Then draw an energy cycle to add the two reactions you know so that the reaction you want is made.

$$\begin{tikzcd}
CH_4(g) + 2O_2(g) \arrow[rr, "\Delta H_c"] \arrow[dr, "\text{Reaction 1: } \Delta H = -803"'] & & CO_2(g) + 2H_2O(l) \\
& CO_2(g) + 2H_2O(g) \arrow[ur, "\text{Reaction 2: } \Delta H = -89"'] &
\end{tikzcd}$$

(1 mark)

Then it is easy to see that, by Hess's Law, adding reaction 1 + reaction 2 will give you the required reaction:

$$-803\text{ kJmol}^{-1} + -89\text{ kJmol}^{-1} = -892\text{ kJmol}^{-1}$$

Hence, the standard enthalpy change of combustion of methane is - 890 kJmol^{-1} (1 mark)

Note: You do not have to use an energy cycle in order to achieve full marks, but it often is very helpful, especially for more complicated reactions

Worked Example No 6 (Hess's Law using Standard Enthalpies of Combustion)

Write down the equation for the enthalpy of *formation* of liquid methanol. (1 mark)

Use your equation together with the following data to calculate the enthalpy of formation of methanol. (3 marks)

Standard enthalpies of combustion:

$C(s) = -394\text{ kJmol}^{-1}$ $H_2(g) = -287\text{ kJmol}^{-1}$ $CH_3OH(l) = -717\text{ kJ mol}^{-1}$

Answer

"Formation" → the equation must show *one mole* of methanol being formed from its constituent elements in their standard states.

Hence, $C(s) + 2H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow CH_3OH(l)$ (1 mark)

Construct a Hess's Law cycle, beginning with the equation for the *required* enthalpy of formation of methanol. You are given enthalpies of combustion. The cycle is completed by realising that the combustion products of carbon and hydrogen are the same as those of methanol. i.e. carbon dioxide and water.

$$\begin{tikzcd}
C(s) + 2H_2(g) + \tfrac{1}{2}O_2(g) \arrow[rr, "\Delta H_f"] \arrow[dr, "+1\tfrac{1}{2}O_2\ \Delta H_1"'] & & CH_3O(l) \arrow[dl, "+1\tfrac{1}{2}O_2\ \Delta H_2"] \\
& CO_2(g) + 2H_2O(g) &
\end{tikzcd}$$

Combustion products shown : $CO_2(g) + 2H_2O(l)$ - NB in their standard states (1 mark)

Applying Hess's Law to the energy cycle gives you:

$$\Delta H_f = \Delta H_1 + (-\Delta H_2)$$

- note the *reversal* of ΔH_2 to complete the alternative reaction route from elements to methanol.

$$\Delta H_1 = \Delta H_c[C(s)] + \mathbf{2}\Delta H_c[H_2(g)] = -394 + 2(-287)\ \text{kJ mol}^{-1}$$
and $$-\Delta H_2 = -\Delta H_c[CH_3OH(l)] = -(-717) = +717\ \text{kJ mol}^{-1}$$

Hence, $\Delta H_f[CH_3OH(l)] = -394 + 2(-287) + 717$ (1 mark)
$= -251$ kJ mol^{-1} (1 mark)

Free Radical Chain Mechanism Reactions

These have an initiating step under the action of UV light.

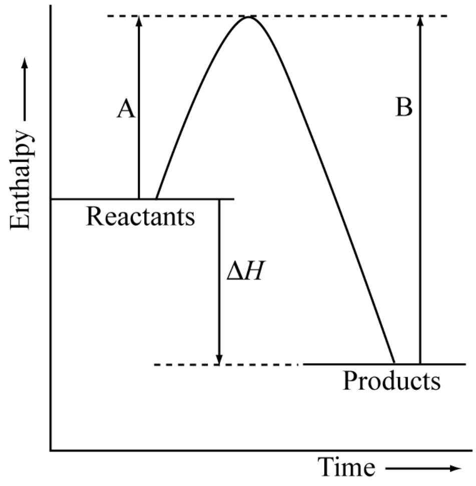
$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ and other similar reactions are *initiated* by the step $Cl_2 \rightarrow 2Cl^{\cdot}$

and so the light involved must be of a wavelength which will have enough energy (enthalpy) to break the Cl-Cl bond.

This can be done by comparing enthalpy values for each light with those for the Cl-Cl bond.

The *enthalpies* for the various colours or wavelengths / frequencies *cannot be added together* to give an energy sufficient to break a bond since light energy is quantised.

Reaction Profiles



The enthalpy change (ΔH) is given by A – B and is negative for this exothermic reaction.

The sum of the bond enthalpies of the reactants is less than the sum of the bond enthalpies of the products.

Practice Questions

1. Hydrogen can react with fluorine to produce hydrogen fluoride
   $H_2(g) + F_2(g) \rightarrow 2HF(g)$ $\Delta H = -540$ kJ mol^{-1}
   Bond enthalpies are: 435 kJmol^{-1} for H-H
   155 kJmol^{-1} for F-F
   Calculate the bond enthalpy of the H-F bond. (3 marks)
2. Methane and chlorine react according to the following equation:
   $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$ $\Delta H = -105$ kJ mol^{-1}
   Use this equation together with the following data to calculate the bond enthalpy of the H-Cl bond.

	C-H	Cl-Cl	C-Cl	H-Cl
Mean Bond Enthalpy kJmol^{-1}	414	243	331	?

(3 marks)

3. Why do bond enthalpies always have positive values? (1 mark)
4. Define the term 'bond enthalpy' (2 marks)
5. Define the term 'standard enthalpy of formation' (3 marks)
6. Give the meaning of the term 'standard enthalpy of combustion' (3 marks)
7. Use the data given to calculate the standard enthalpy change of atomisation for oxygen.
   Bond energy for O=O is 496 kJ mol^{-1} (1 mark)
8. Calculate the enthalpy change of formation of bromoethane from ethene and hydrogen bromide. $C_2H_4\,(g) + HBr\,(g) \rightarrow C_2H_5Br\,(l)$ using the following enthalpies of formation:
   $C_2H_4\,(g) = +52$ kJ mol^{-1} $HBr\,(g) = -37$ kJ mol^{-1}
   and $C_2H_5Br\,(l) = -86$ kJ mol^{-1} (3 marks)

Answers

1. +565 kJmol^{-1}
2. +431 kJmol^{-1}
3. Bond breaking is always endothermic because energy is required to overcome the force of attraction created between the atoms by the covalent bond. Hence, energy must be supplied and ΔH is positive.
4. The energy needed to break one mole of bonds (1 mark) in the substance in the gaseous state (1 mark)
   – note that *mean* bond energies are often quoted, these being derived from bond enthalpy values for the bond in a variety of similar compounds.
5. The enthalpy / heat change at constant pressure when 1 mole of a substance (1 mark) is formed from its elements (1 mark) with all reactants and products in normal states under standard conditions (1 mark).
   Instead of 'standard conditions' you can specify '100kPa and 298K'.
6. The enthalpy/heat change at constant pressure when 1 mol of a substance (1 mark) is burned completely in oxygen/burned in excess oxygen (1 mark) with all reactants and products in normal states under standard conditions (1 mark).
   [Note the similarity between the answers to 5) and 6), only the second mark needs a different statement – in general this applies to all of the enthalpy definitions.]
7. +248 kJmol^{-1} (1 mark)
8. – 101 kJmol^{-1} (3 marks)

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