Chem Factsheet

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Improve Your Mark: AS Energetics

This Factsheet aims to give you tips to help improve your marks when answering AS Energetics questions. The areas covered are:-
Check your understanding of basic energetics ideas

- Defining energetics terms
- Using signs and units correctly
- Putting it into practice

Answer these questions as best you can:-

1. **Combustion of Methane**
   Methane burns according to the equation:-
   $CH_4(g) + 2O_2(g) \rightarrow 2H_2O(l) + CO_2(g)$ The reaction is exothermic, releasing energy to the surroundings.
   (a) Why is a spark or match needed to start methane burning?
   (b) Where does the energy come from when methane burns?

2. **Reaction of Sodium with Chlorine**
   Sodium and chlorine react to make sodium chloride:-
   $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$ The reaction is exothermic, releasing energy to the surroundings.
   (a) Draw an energy level diagram to show the reaction between sodium and chlorine to make sodium chloride.
   (b) Where was the energy before it was released?

Answers are available at the end of the factsheet.

Explanations

It would be a safe bet that you got one or more of these questions ”wrong”! This does not matter – the point of these questions is to sort out your understanding. Now read the following extended explanations and check your understanding.

Combustion of Methane

1. The spark or match supplies *activation energy*. The vast majority of methane molecules and oxygen gas molecules are energetically “stable” since they do not have enough energy to react. A spark or match puts energy into the reaction system, causing bonds to break between atoms in *some* methane and oxygen molecules. The “free” atoms so formed then react together, forming new bonds as molecules of water and carbon dioxide with lower energy levels than the reactant molecules. Excess energy is released to the surroundings, lighting up carbon particles (making a visible flame) and heating up particles in the area around the reaction (hence a saucepan and its contents get hot when placed on a lit gas burner). Some excess energy breaks bonds in more molecules, creating a “chain” effect that ends only when the supply of a reactant is cut off (such as by turning off the gas), or by cooling the reaction mixture.
2. The energy comes from *bond formation* in the reaction products. The stronger the bond being formed, the more energy is released. Of course, the net energy release is what remains after allowing for the energy to break bonds in the reactant molecules.

Sodium and Chlorine

3. As the reaction is *exothermic*, the *enthalpy level of the products must be lower than that of the reactants*. The difference is energy is released to the surroundings.
4. *Energy cannot be created or destroyed.* We only transfer energy from one form to another. This is the “First Law of Thermodynamics”. The energy must have existed before the reaction occurred, but we couldn’t “see” it. In an exothermic chemical reaction energy is transferred from the reactants to the products *and* surroundings. Conversely, in an endothermic chemical reaction energy is transferred from the reactants *and* surroundings to the products.

These introductory questions covered important ideas. If you don’t understand them, this is likely to affect your ability to answer examination questions, as these often assume you understand these basic ideas behind them.

Defining energetics terms

Energetics questions often begin by asking you to “define a term”. Common terms and their definitions are shown in the following table. The key points that usually score marks are highlighted.

Energetics term	Definition	Symbol and units	Sign
Standard enthalpy change of formation 2 marks are usually available	The enthalpy change occurring when ***1 mole (1 mark)*** of a compound / substance is formed ***from its elements under standard conditions (1 mark)***	$\Delta H^{\ominus}_{f}$ kJmol^{-1}	Can be a +ve or –ve value
Standard enthalpy change of reaction 2 marks are usually available	The enthalpy change occurring when ***the mole quantities written in the balanced reaction equation (1 mark)*** react ***under standard conditions (1 mark)***	$\Delta H^{\ominus}_{R}$ kJmol^{-1}	Can be a +ve or –ve value
Standard enthalpy change of combustion 3 marks are usually available	The enthalpy change occurring when ***1 mole (1 mark)*** of a compound / substance is ***completely burned in oxygen (1 mark) under standard conditions (1 mark)***	$\Delta H^{\ominus}_{c}$ kJmol^{-1}	**Always** a **–ve** value
Average (or mean) bond enthalpy 2 marks are usually available	The energy required to break ***1 mole of specific covalent bonds in the gaseous state (1 mark) averaged over a range of similar compounds (1 mark)***	$\Delta H^{\ominus}_{be}$ kJmol^{-1}	**Always** a **+ve** value
Bond dissociation enthalpy (or standard bond enthalpy) 1 mark is usually available	The energy required to break ***1 mole of specific covalent bonds*** in the gaseous state	$\Delta H^{\ominus}_{D}$ kJmol^{-1}	**Always** a **+ve** value

Remember:
- *Energy is released when chemical bonds form.*
- *Energy is needed to break chemical bonds.*
- *Energy cannot be created or destroyed, but we can transfer energy from one form to another.*

"Under standard conditions" is *vital* to score the final mark available for the first three enthalpy changes in the table. "Standard conditions" means "298K and 100 kPa". You can give the values instead of simply stating "standard conditions".

There is almost no leeway in responses to these questions. Using the phrase "*enthalpy change*" as stated is *strongly recommended.* Phrases such as "*heat evolved*", "*energy evolved*" and "*energy change*" are regarded as "vague", and although not always detrimental to your mark, tend to put examiners in negative frames of mind. "Why 'enthalpy' change?" is discussed later in this Factsheet.

Defining **average (or mean) bond enthalpy** often signals a request later in the question to calculate the average value for *the C-H bond enthalpy in methane. This is +412 kJmol^{-1}.* This value is worth remembering as a way of checking your answer. The value is obtained by calculating the average of the 1st, 2nd, 3rd and 4th bond dissociation enthalpies of the C-H bonds in the methane molecule. When each bond is broken separately, the potential energy of the remaining particle (-CH_3, =CH_2 and =CH) changes, altering the energy required to break any remaining bonds. So, each C-H bond has a different bond enthalpy. The *average* is +412 kJmol^{-1}.

Why "enthalpy change"?
Enthalpy is a measure of how much energy there is in total in the volume of space occupied by chemical reactants / products at a *specific pressure*. Chemists want to know how enthalpy *changes* when a reaction occurs. The Greek symbol "Δ" (called "delta") represents change, hence "ΔH" is the symbol for "enthalpy change". As chemists use moles as their way of counting amounts of substance, a standard reference is the "enthalpy change per mole", with units "kJmol^{-1}". Examiners like accuracy, so "enthalpy change" is correct.

Using signs and units correctly

Signs

The sign refers to the enthalpy change of the system involved in the reaction. "*System*" means the reactants and products. The "surroundings" is everything other than the reactants and products.

*If a reaction **GIVES OUT** energy, this must have come from the system. The system has **LOST ENERGY** so the sign is **NEGATIVE**. We call this an "**EXOTHERMIC**" reaction – literally "**HEAT OUT**".*

*If a reaction **TAKES IN** energy from the surroundings, the enthalpy level of the system has **INCREASED** so the sign is **POSITIVE**. We call this an **ENDOTHERMIC** reaction – literally "**HEAT IN**".*

***Remember: Examiners always expect you to give the sign at the end of a calculation**. This is good practice, as it shows you understand the point about enthalpy change! Don't forget the sign.*

***Remember:** Since your calculator will not show a "+" sign for an endothermic reaction, you must remember to insert the "+" sign.*

Why do bond dissociation enthalpies always have positive values?

We can answer this using *"Why 'enthalpy change'?"* and the explanation for signs, above. The system in this case consists of the molecules of substance, let's say, methane, formula CH_4.

Methane molecules are "stable" – simply, under atmospheric pressure and range of temperatures, they don't break up into atoms spontaneously. To make a reaction happen, energy needs to be put into the system. This means that the enthalpy level of the system has increased, so the sign is positive.

Why do enthalpy changes of combustion always have a negative value?

Combustion reactions are *exothermic* so must always have negative signs. Overall, the system loses energy, mostly as heat, to the surroundings – if you are part of the surroundings then you can feel the heat! The internal energy decreases so the enthalpy level is lower after the reaction.

Why can an enthalpy change of formation or reaction be either positive or negative?

This depends on the enthalpy values relating to the reactants and products. There is no fixed "rule" – a reaction system can take in energy or lose energy overall, resulting in a higher or lower internal energy level. When calculating these, take note of the type of reaction to help decide what the sign may be.

Neutralisation and combustion reactions, for example, are exothermic, while dissolving may be either depending on the solute. In general, if reaction results in an increase in the number of molecules, you should expect the enthalpy change to be positive since there is a net decrease in bonding. Similarly, a decrease in the number of molecules would be associated with a negative enthalpy change.

Units

The units examiners look for are "kJmol^{-1}". This reads as "kiloJoules per mole". The units tie in with the definitions, so must be consistent – if you look back at the table, you will see the reference to "enthalpy change" and "1 mole". Enthalpy is measured in Joules, but as the numbers are usually large "kilo" is used as the prefix. "1 mole" is the amount of substance involved in a standard enthalpy change.

***Remember:** The units are essential. If you get a calculation correct, but forget the units, you can lose a mark. **Don't forget the units**.*

Putting it into practice

You need to be able to do two main types of calculation. The first is from experimental data. The remaining four (2-5 in the list below) are applications of Hess's Law, although it is not always necessary to draw a full cycle to get the answer.

1. Enthalpy change of combustion from quantitative data

Remember that combustion reactions are always EXOTHERMIC. Heat is given out to surroundings. We can measure this using a "calorimeter", literally a "heat measurer". The heat energy transferred to a fixed mass of water (m_{H_2O}) is measured by finding the change in temperature of the water (ΔT_{H_2O}) when a known number of moles (n) of a fuel is burned.

$$\Delta H_c = \frac{-m_{H_2O} \times \Delta T_{H_2O} \times C_{H_2O}}{1000 \times n}$$

(a) C_{H_2O} is the *specific heat capacity of water* i.e. the number of Joules needed to raise the temperature of 1g of water by 1K

(b) The "1000" is included to convert the Joules of "C_{H_2O}" to kJ

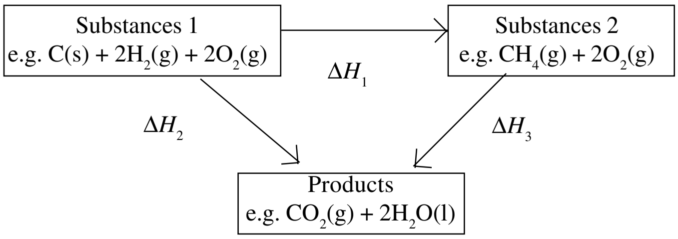
(c) The negative sign is inserted to show the combustion is exothermic.

2. Calculations involving a Hess's Law cycle

Hess's law puts the First Law of Thermodynamics in chemical terms, by saying :

> *The total enthalpy change occurring in a reaction is independent of the route taken.*

In other words, energy is conserved when we get the same product (or products) from the same starting materials regardless of what we do to the starting materials in between. In exam questions, the principle is to react two different substances or sets of substances to make the same product. If you put the two substances / sets of substances in an equation across the top and the product(s) underneath, you get a triangle. You will always be given data for two "sides" of the triangle and have to work out the value for the third "side". This is illustrated as follows :



Any one of the three enthalpy changes can be calculated by substituting two given values into :

$\Delta H_2 = \Delta H_1 + \Delta H_3$ and then calculating the third.

> **Remember:** *When applying Hess's Law to such a cycle, it is often useful to use "sum of clockwise ΔH = sum of anti-clockwise ΔH" to help you get the arithmetic correct.*

In this example you may be given:

$\Delta H^\ominus_f [CO_2(g)] = -393.5$ kJ mol^{-1}, $\Delta H^\ominus_f [H_2O(l)] = -285.8$ kJ mol^{-1} and $\Delta H^\ominus_C [CH_4(g)] = -890.3$ kJ mol^{-1} which means :

$\Delta H_2 = (-393.5) + 2(-285.8) = -965.1$kJ mol^{-1} and $\Delta H_3 = -890.3$ kJ mol^{-1}

Giving $-965.1 = \Delta H_1 + -890.3$ and hence, ΔH_1
$= \Delta H^\ominus_f [CH_4(g)] = +890.3 - 965.1 = -74.8$ kJ mol^{-1}

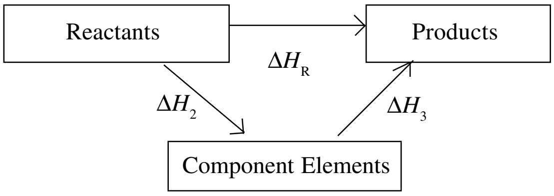
3. Enthalpy change of reaction from enthalpy change of formation values

> ***Remember**: "enthalpy change" measures the loss or gain in internal energy of the system.*

So, the enthalpy change for a reaction will be, very simply:-
The "energy level" of the products – "energy level" of the reactants

In "exam-speak", this is:- $\Delta H_R = \Sigma\Delta H_{f\ (products)} - \Sigma\Delta H_{f\ (reactants)}$

It is useful to remember this equation to allow quick calculation of ΔH_R when ΔH_f values are available. However, remember this is the result of an application of Hess's Law as shown in the following cycle:



$$\begin{aligned} \Delta H_R &= \Delta H_2 + \Delta H_3 \\ &= -\Sigma\Delta H_{f\ (reactants)} + \Sigma\Delta H_{f\ (products)} \\ &= \Sigma\Delta H_{f\ (products)} - \Sigma\Delta H_{f\ (reactants)} \end{aligned}$$

Note the "-" sign before $\Delta H_{f\ (reactants)}$ because the reactants are being converted to elements which is the opposite direction to the definition of ΔH_f.

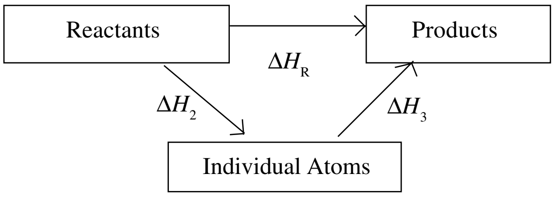
4. Enthalpy change of reaction from bond enthalpy values

Again, remember that "enthalpy change" measures the loss or gain in internal energy of the system. If this is given as bond enthalpy values, we are looking at, very simply:-

> The energy needed to break bonds – the energy released when bonds are formed.

In "exam-speak", this is:- $\Delta H_R = \Sigma\Delta H_{be\ (broken)} - \Sigma\Delta H_{be\ (formed)}$

It is also useful to remember this equation to allow quick calculation of ΔH_R when ΔH_{be} values are available. Again, it is also the result of an application of Hess's Law as shown in the following cycle:



$$\begin{aligned} \Delta H_R &= \Delta H_2 + \Delta H_3 \\ &= \Sigma\Delta H_{be\ (reactants)} - \Sigma\Delta H_{be\ (products)} \end{aligned}$$

Note the "-" sign before $-\Delta H_{be\ (products)}$ because the here bonds are being *formed* which is the opposite direction to the definition of ΔH_{be}.

5. Enthalpy change of reaction from enthalpy of combustion values

This applies when the reactants and products are both combustible. Again, you may care to remember:

$$\Delta H_R = \Delta H_{c\ (reactants)} - \Delta H_{c\ (products)}$$

to allow quick calculation of ΔH_R when ΔH_C values are available but remember it is also the result of an application of Hess's Law as shown in the following cycle:

$$\begin{tikzcd}
\boxed{\text{Reactants} + O_2(g)} \arrow[rr, "\Delta H_R"'] \arrow[dr, "\Delta H_2"'] & & \boxed{\text{Products} + O_2(g)} \\
& \boxed{\text{Oxides of Component Elements}} \arrow[ur, "\Delta H_3"'] &
\end{tikzcd}$$

$$\begin{aligned}\Delta H_R &= \Sigma\Delta H_2 + \Sigma\Delta H_3 \\ &= \Sigma\Delta H_{c\ (reactants)} - \Sigma\Delta H_{c\ (products)}\end{aligned}$$

Finally, here are examples of the different types of calculation with a sample answer, mark scheme and examiner's notes in the same order as above.

Question	**Answer**	**Mark scheme and Examiner's notes**
Enthalpy change of combustion from experimental data 1.45 g propanone were completely burned in oxygen. The energy was used to raise the temperature of 100 g water from 293.1 K to 351.2 K. Calculate the number of moles of propanone. Calculate the heat energy used to raise the temperature of 100 g water from 293.1 K to 351.2K. The specific heat capacity of water is 4.18 J K^{-1} g^{-1}. Calculate a value in kJmol^{-1} for the enthalpy change of combustion of propanone 5 marks available	Moles = mass / relative molecular mass Propanone formula CH_3COCH_3 $M_r = 58$ Moles = 1.45 / 58 = 0.025 Heat energy = 100 × 4.12 × 58.1 = 24300 J Enthalpy change of combustion = -24.3/ 0.025 = - 972 kJmol^{-1} Check:- • Formula of propanone • 100 used as mass of water needed, NOT mass of propanone • 58.1 is the temperature rise • sign negative as this is COMBUSTION	1 mark for relative molecular mass 1 mark for mole calculation 1 mark for this line 1 mark for this line, could be 24.3 kJ, but not 24.3 without units 1 mark for this line Notes:- • If the wrong M_r value is used, all other marks are awarded consequentially • If the mass of propanone is used instead of water, no marks awarded for this part, but if the value is used in the final stage then one consequential mark is given
Enthalpy change of combustion from other enthalpy change of combustion values Calculate the enthalpy change of combustion for gaseous methanol using the following data: $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$ $\Delta H = -91$ kJmol^{-1} ΔH_c/kJmol^{-1} CO(g) -283 H_2 (g) -286 3 marks available	Using a Hess's Law cycle:- $\begin{tikzcd} CO(g) + 2H_2(g) \arrow[rr, "-91"] \arrow[dr, "(-283 + 2x-286)"'] & & CH_3OH(g) \arrow[dl, "x"] \\ & CO_2(g) + 2H_2O(g) & \end{tikzcd}$ x = (-283+2x-286) - -91 = -855 + 91 = -764 kJmol^{-1} Check:- • By Hess's law: the enthalpy change for the direct route from carbon monoxide and hydrogen to carbon dioxide and water must be the same as that for the formation of methanol first, then the combustion of methanol • 2 x -286 as 2 moles of hydrogen are in the equation • sign and units	1 mark for correct cycle 1 mark for this line 1 mark for this line Notes:- • The sign on the " – 91" is vital to get the right answer • +764 scores 1 mark • Units are not essential, but one mark is lost if incorrect units are given

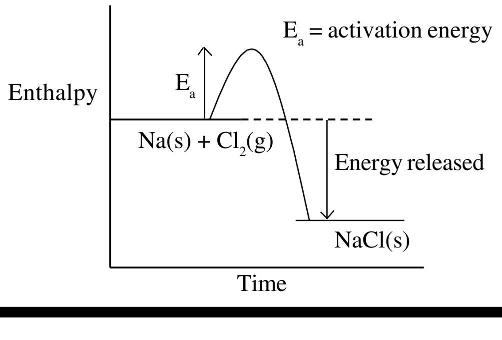
Question	Answer	Mark scheme and Examiner's notes
Enthalpy change of reaction from enthalpy changes of formation values Calculate the enthalpy change of reaction for the reaction:- $CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 4H_2(g)$ Using:- ΔH_f/kJmol^{-1} $CH_4(g)$ -75 $H_2O(l)$ -286 $CO_2(g)$ -394 3 marks available	$\Delta H_R = \Sigma\Delta H_{f\ (products)} - \Sigma\Delta H_{f\ (reactants)}$ $= -394 - (-75 + 2 \times -286)$ $= -394 - -647$ $= +253$ kJmol^{-1} Check:- • Sign and units • Multiply by 2 as 2 moles of water involved • Hydrogen is an element so $\Delta H_f = 0$ • All working shown	1 mark for this line 1 mark for the correct answer 1 mark for correct +/- signs Notes:- • 2 marks awarded for values -33, +103, -253, -891, + 1041 • 1 mark awarded for values +33, -183, -605, +755, -1041
Enthalpy change of reaction from average bond enthalpy values Calculate the enthalpy change of reaction for the reaction:- 2Cl-S-Cl(g) → Cl-S-S-Cl (g) + Cl-Cl(g) Using:- ΔH_{be}/kJmol^{-1} Cl-Cl +242 S-Cl +255 S-S +266 3 marks available	$\Delta H_R = \Sigma\Delta H_{be\ (broken)} - \Sigma\Delta H_{be\ (formed)}$ $= 4 \times 255 - (2 \times 255 + 266 + 242)$ $= 1020 - 1018$ $= +2$ kJmol^{-1} Check:- • Sign and units • Multiply by 4 as 2 moles of SCl_2 involved • Small value sensible as this is an equilibrium reaction	1 mark for the sum of bonds broken 1 mark for the sum of bonds formed 1 mark for the correct answer Notes:- • 2 marks awarded for values -2, +268, +/- 2038, +/- 1018 • 1 mark awarded for value -268 other values may also score
A mean bond dissociation enthalpy value Calculate a value for the C-H bond enthalpy in ethane from the equation:- C=C + H-H → H-C-C-H $\Delta H_r = -136$ kJmol^{-1} Using:- ΔH_{be}/kJmol^{-1} H-H = +436 C-C = +348 C=C = +612 3 marks available	$\Delta H_R = \Sigma\Delta H_{be\ (broken)} - \Sigma\Delta H_{be\ (formed)}$ -136 = 4 × C-H + 612 + 436 – (6 × C-H + 348) -136 = 2 × C-H + 612 + 436 – 348 2 × C-H = + 836 1 × C-H = + 418 kJmol^{-1} Check:- • Value is close to the +412 for C-H in methane • Divide by 2 at the end to get value for 1 bond • Sign and units	1 mark for this line OR 1 mark for this line 1 mark for this line 1 mark for this line Notes:- 1 mark only awarded for -836 or -418

Answers to Introductory Questions

1. The spark or match is needed to initiate the reaction. That is, supply energy which is used to break bonds in methane gas molecules and in oxygen gas molecules and so begin the transformation to products.

2. The energy comes from bond formation. Energy is released when chemical bonds form. New bonds are formed making carbon dioxide gas molecules and water molecules.

3.



4. The energy must have existed (as potential energy) in the chlorine molecules and sodium atoms

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