

## Energetics I - Hess's Law

To succeed with this topic, you need to:

- understand how to produce balanced chemical equations
- be able to do arithmetic involving negative numbers on a calculator

After working through this Factsheet, you will be able to:

- recall and understand the definitions of standard enthalpy changes needed at AS level
- understand and use bond enthalpies
- use Hess's Law to calculate enthalpy changes for reactions

### Exam Hint:

1. In examination questions there are always marks for correctly giving the definitions of enthalpy changes and quoting Hess's Law. These marks are lost by lack of thorough learning.
2. Calculations on Hess's Law have marks for drawing the correct cycle and then for using the data to produce a correct answer. If the cycle is not correct you cannot get full marks. Do not underestimate the need to draw full and detailed cycles before doing the mathematical calculation.

### Introduction - Energy

Energy may take various forms, such as heat, light or electrical energy, and these types may be converted from one to the other (a light bulb converts electrical energy into light, for example). However, all energy conversions are governed by the **First Law of Thermodynamics** (or the **Law of Conservation of Energy**), which states:

**Energy can be neither created nor destroyed, but can be converted from one form to another**

The **total energy content** of a system is known as the **enthalpy** or **heat content** of the system and has the symbol  $H$ . The **higher** the energy content of a system, the more **unstable** it is.

### Enthalpy Changes

It is impossible to measure the total enthalpy of a system; the chemist is interested in **changes** in enthalpy accompanying a physical or chemical process.

When chemical reactions take place there are **always** energy changes taking place because;

- energy needs to be put in to **break** bonds.
- energy is given out when bonds are **made**.

These two amounts of energy are rarely equal in value and the difference between the energy absorbed or given out is the **enthalpy change** for the reaction. Enthalpy changes have the symbol  $\Delta H$  (read as "delta H")

There are two types of enthalpy changes:-



#### Exothermic reactions:

- **Give out heat** to the surroundings (so there is a **rise** in temperature).
- The **internal** energy of the system **decreases** so  $\Delta H$  is **negative**.

#### Endothermic reactions:

- Take in heat from the surroundings (so there is a **fall** in temperature).
- The **internal** energy of the system **increases** so  $\Delta H$  is **positive**.

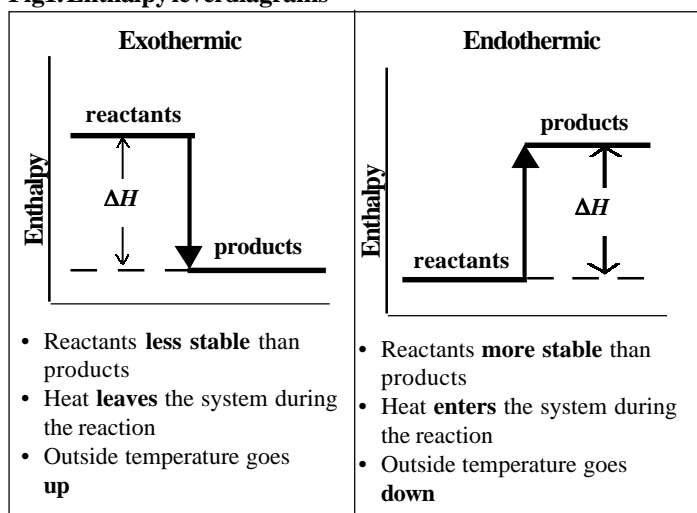
**Exam Hint:** Do not assume that a reaction is endothermic just because heat must be applied to make it happen; many highly exothermic reactions (such as the combustion of magnesium) require heat to start the reaction.

**Exam Hint:** You must always show the + or - signs for  $\Delta H$  values

### Enthalpy Level Diagrams

Enthalpy changes can be represented on an enthalpy level diagram. This measures the energy of **the system**, **not** the temperature of the surroundings.

Fig1. Enthalpy level diagrams



### Standard conditions

Since the amount of energy taken in or given out will vary depending on the pressure and temperature, **standard enthalpy changes** are defined, which are measured under **standard conditions**.

These are:

- 1 atmosphere pressure
- temperature 298K (= 25° C)
- substances present in their standard states at 298K (e.g.  $H_2O(l)$  not  $H_2O(g)$  or  $H_2O(s)$ )
- all solutions having a concentration of 1 mol dm<sup>-3</sup> (= 1M)

The symbol used to show 'standard conditions' is  $\ominus$ .

The enthalpy change symbol now becomes  $\Delta H^\ominus$  - read it as "delta H nought" or "delta H standard".

The units of  $\Delta H^\ominus$  are kJ mol<sup>-1</sup> - that is, kilojoules per mole. The "per mole" is in there because the actual amount of energy given out or taken in during a reaction will depend on how much of the chemicals there are - two tons of magnesium burning will give out more energy than two grammes! So we consider the energy given out per mole.

**Enthalpy change definitions**

The following definitions need to be learnt.


**Table 1: Standard Enthalpies**

Name and Symbol of Enthalpy Change	Definition	Example	Key Points
$\Delta H_f^\ominus$ Standard Enthalpy of Formation	The enthalpy change when <b>one mole</b> of a compound in its standard state is formed from its <b>elements</b> in standard state, under standard conditions	$\Delta H_f^\ominus$ (C <sub>2</sub> H <sub>6</sub> (g)): 2C(s) + 3H <sub>2</sub> (g) → C <sub>2</sub> H <sub>6</sub> (g)	<ul style="list-style-type: none"> <li>For <b>elements</b>, this is zero by definition</li> <li>It must be one mole of the <b>compound</b></li> <li>For compounds, it may be exothermic (most commonly) or endothermic.</li> </ul>
$\Delta H_c^\ominus$ Standard Enthalpy of Combustion	The enthalpy change when <b>one mole</b> of an element or compound is <b>completely</b> burned in <b>excess oxygen</b> under standard conditions.	$\Delta H_c^\ominus$ (CH <sub>3</sub> OH(l)): CH <sub>3</sub> OH(l) + 1½O <sub>2</sub> (g) → CO <sub>2</sub> (g) + 2H <sub>2</sub> O(l)	<ul style="list-style-type: none"> <li>This is <b>always</b> exothermic.</li> </ul>
$\Delta H_a^\ominus$ Standard Enthalpy of Atomisation	The enthalpy change when <b>one mole</b> of <b>gaseous</b> atoms is formed from an element under standard conditions	$\Delta H_a^\ominus$ (Cl <sub>2</sub> (g)): ½Cl <sub>2</sub> (g) → Cl(g)	<ul style="list-style-type: none"> <li>This is <b>always endothermic</b></li> <li>This term may also be used to describe the shattering of <b>one mole</b> of a <b>gaseous molecule</b> into its <b>constituent atoms</b></li> </ul>
$\Delta H_r^\ominus$ Standard Enthalpy of Reaction	The enthalpy change for <b>the reaction as written in the equation</b> under standard conditions	$\Delta H_r^\ominus$ : NH <sub>3</sub> (g) + HCl(g) → NH <sub>4</sub> Cl(s)	<ul style="list-style-type: none"> <li>Values are always quoted for the reaction as written - the enthalpy of reaction for H<sub>2</sub>(g) + Cl<sub>2</sub>(g) → 2HCl(g) will be twice that for ½H<sub>2</sub>(g) + ½Cl<sub>2</sub>(g) → HCl(g)</li> </ul>
$\Delta H_D^\ominus$ Standard Bond Enthalpy	The enthalpy change when <b>one mole</b> of a particular chemical bond is broken <b>in the gaseous state</b> to give <b>gaseous atoms</b> under standard conditions	$\Delta H_D^\ominus$ (H-Cl(g)) : HCl(g) → H(g) + Cl(g)	<ul style="list-style-type: none"> <li>This is <b>always endothermic</b></li> <li>The <b>weaker</b> the bond, the <b>easier</b> it is to break, and so the <b>lower</b> the bond enthalpy</li> <li><b>Making</b> bonds is the <b>reverse</b>, and is <b>always exothermic</b></li> </ul>
$\Delta H_{be}^\ominus$ Average Bond Enthalpy	The <b>average enthalpy required per bond</b> to break all the bonds of a particular type in one mole of a <b>gaseous</b> molecule to give <b>gaseous atoms</b> , under standard conditions	H <sub>2</sub> O(g) → 2H(g) + O(g) $\Delta H_r^\ominus = +926 \text{ kJ mol}^{-1}$ So $\Delta H_{be}^\ominus$ (H-O(g)) = 926÷2 = + 463kJ mol <sup>-1</sup>	<ul style="list-style-type: none"> <li>In a molecule with several identical bonds (eg water), the different bonds may require different energies to break - this is why an average is needed.</li> <li>Calculations using average bond enthalpies can only give approximate values</li> </ul>

You will notice that fractions e.g. ½ have appeared in some of the equations in the table - particularly in those for combustion and formation. This is because we need to have 1 mole of the substance being burned or formed (as the definition says), so we have to balance the rest of the equation around this. To do this, you balance the equation as normal, then divide everything by the number in front of the substance being burned/formed - eg for  $\Delta H_c^\ominus$ (CH<sub>3</sub>OH(l)): the "normal" equation is 2CH<sub>3</sub>OH(l) + 3O<sub>2</sub>(g) → 2CO<sub>2</sub>(g) + 4H<sub>2</sub>O(l), but we need 1 mole of CH<sub>3</sub>OH, so divide by 2 to give CH<sub>3</sub>OH(l) + 1½ O<sub>2</sub>(g) → CO<sub>2</sub>(g) + 2H<sub>2</sub>O(l)

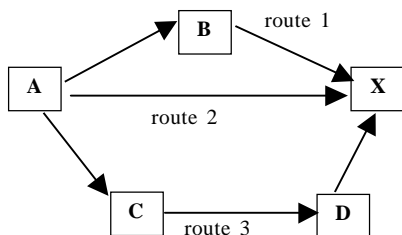
**Hess's Law**

This law says:-

 The enthalpy change for a reaction is independent of the route taken to achieve the overall change.

This makes it possible to find enthalpy changes that cannot be measured directly by using data such as bond enthalpies, enthalpies of formation or enthalpies of combustion (see Table 1 overleaf).

The diagram shows how Hess's Law works for changing substance A into substance X.



There are three ways of converting A into X. Hess's Law says that,  $\Delta H$  (Route 1) =  $\Delta H$  (Route 2) =  $\Delta H$  (Route 3)

This is the basis of all calculation work using Hess's Law.

Hess's law calculations involve drawing a "cycle". These look like upside-down triangles. The reaction of interest is written on the top side, with an arrow from reactants to products, as normal.

The third "point" of the triangle depends on what data is given - it will be one of:

- enthalpies of formation
- enthalpies of combustion
- bond enthalpies

The direction of the other arrows in the cycle is again determined by the information given; if formation enthalpies are given, for example, these refer to a reaction **starting** with the elements, so the arrows start at the elements and point **away** from them. With enthalpies of combustion, on the other hand, the reaction concerned **ends** with the combustion products, so the arrows point **towards** the combustion products.

Once the triangle is constructed, the known enthalpies are written on the appropriate sides. The enthalpy of reaction is found by getting from reactants to products "the long way round". If this involves going in the direction of an arrow, the appropriate enthalpy values are added; if it involves going against the direction of an arrow, the enthalpy values are subtracted.

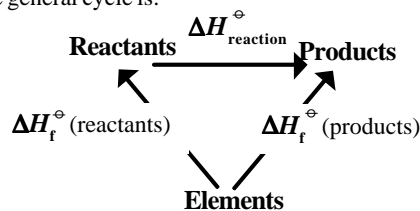
The examples following show the three types of cycles required for AS level.

**Exam Hint:** Many candidates lose marks by carelessness with addition and subtraction of negative enthalpies. You should write the calculation out in full, rather than trying to simplify too much in your head or just putting it straight into the calculator.

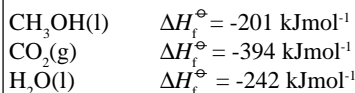
**Exam Hint:** You must always check carefully what data you have before drawing your cycle. Note in particular that if you are given  $\Delta H_f^\ominus$  [oxide], this is the **same as**  $\Delta H_c^\ominus$  [element] - in other words, it is combustion data

**Enthalpy of Formation**

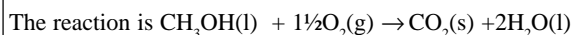
The general cycle is:



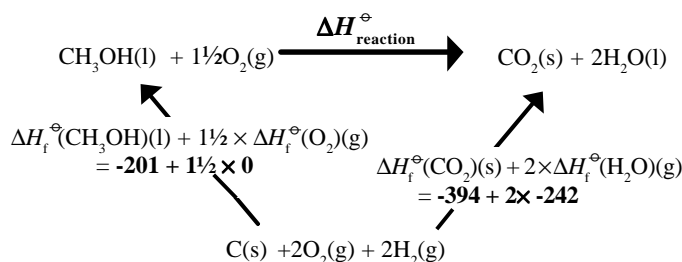
e.g. Calculate the standard enthalpy of combustion of methanol, given the following enthalpy of formation data:



First construct the triangle:



We are given enthalpies of formation, so the third "point" is the elements in their standard states.



To get from reactants to products we go **against** the first arrow, so **subtract** that enthalpy value. We then go **with** the second arrow, so **add** those enthalpy values.

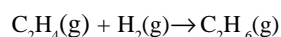
$$\text{So } \Delta H_{\text{reaction}}^\ominus = -(-201) + (-394 + 2 \times -242) = -677 \text{ kJ mol}^{-1}$$

**Exam Hint:** Remember:

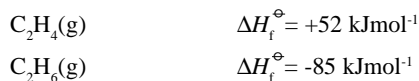
- The enthalpy of formation is zero for an element
- If there is more than one molecule involved (eg  $2\text{H}_2\text{O}$  in the above example), then the enthalpies must be multiplied by the appropriate number.

**Now try this question:**

Calculate the standard enthalpy change for the following reaction:



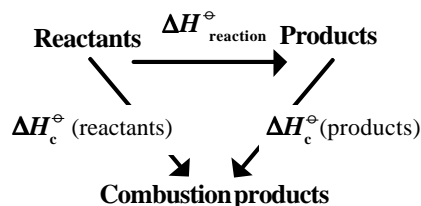
given the following data:



Answer:  $-137 \text{ kJmol}^{-1}$

**Enthalpy of Combustion**

The general cycle is:



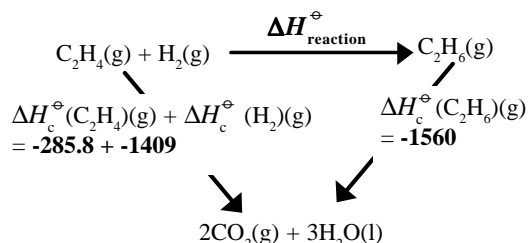
e.g. Calculate the enthalpy of reaction for the hydrogenation of ethene under standard conditions, using the following enthalpy of combustion data:

$$\text{H}_2(\text{g}) \quad \Delta H_c^\ominus = -285.8 \text{ kJmol}^{-1}$$

$$\text{C}_2\text{H}_4(\text{g}) \quad \Delta H_c^\ominus = -1409 \text{ kJmol}^{-1}$$

$$\text{C}_2\text{H}_6(\text{g}) \quad \Delta H_c^\ominus = -1560 \text{ kJmol}^{-1}$$

First construct the triangle: The reaction is  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$ . We are given enthalpies of combustion, so the third "point" is the combustion products -  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

To get from reactants to products we go **with** the first arrow, and **against** the second:

$$\text{So } \Delta H_{\text{reaction}}^\ominus = (-285.8 + -1409) - (-1560) = \mathbf{-134.8 \text{ kJ mol}^{-1}}$$

**Now try this question:**Calculate the standard enthalpy of formation of ethyne ( $\text{C}_2\text{H}_2(\text{g})$ ), given the following combustion data:

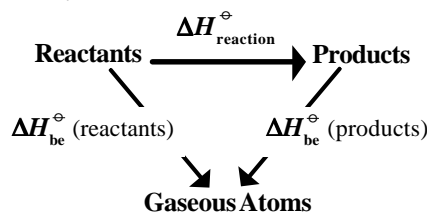
$$\text{C}(\text{s}) \quad \Delta H_c^\ominus = -394 \text{ kJmol}^{-1}$$

$$\text{H}_2(\text{g}) \quad \Delta H_c^\ominus = -286 \text{ kJmol}^{-1}$$

$$\text{C}_2\text{H}_2(\text{g}) \quad \Delta H_c^\ominus = -1300 \text{ kJmol}^{-1}$$

Answer: +226 kJ mol<sup>-1</sup>**Bond Enthalpies**

The general cycle is:



e.g. Calculate the enthalpy of reaction for the hydrogenation of ethene under standard conditions, given the following average bond enthalpy data

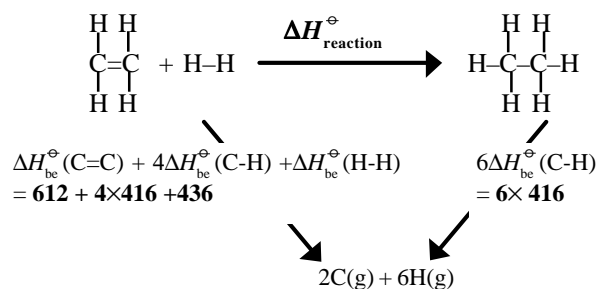
$$\text{C-C} \quad \Delta H_{\text{be}}^\ominus = 348 \text{ kJmol}^{-1}$$

$$\text{C=C} \quad \Delta H_{\text{be}}^\ominus = 612 \text{ kJmol}^{-1}$$

$$\text{C-H} \quad \Delta H_{\text{be}}^\ominus = 416 \text{ kJmol}^{-1}$$

$$\text{H-H} \quad \Delta H_{\text{be}}^\ominus = 436 \text{ kJmol}^{-1}$$

Since bond enthalpies are given, the triangle will be completed with gaseous atoms. **When using bond enthalpies, it is vital to draw out the structural formulae so all the bonds involved can be seen clearly.**



Following the arrows as before, we obtain:

$$\Delta H_{\text{reaction}}^\ominus = 612 + 4 \times 416 + 436 - (6 \times 416) = \mathbf{-130 \text{ kJ mol}^{-1}}$$

**Now try this question:**Calculate the standard enthalpy of formation of methane ( $\text{CH}_4(\text{g})$ ) given the following data:

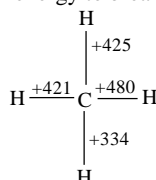
$$\text{C-H} \quad \Delta H_{\text{be}}^\ominus = 416 \text{ kJmol}^{-1}$$

$$\text{H-H} \quad \Delta H_{\text{be}}^\ominus = 436 \text{ kJmol}^{-1}$$

$$\Delta H_{\text{at}}^\ominus(\text{C}(\text{s})) = +718 \text{ kJmol}^{-1}$$

Answer: -74 kJmol<sup>-1</sup>**The difference between bond dissociation enthalpies and mean bond enthalpies**Bond dissociation enthalpy refers to the energy required to break a **specific** bond in a **specific** molecule.Mean bond enthalpy refers to the **average** energy required to break a specific bond.

To see the difference, consider methane ( $\text{CH}_4$ ). This contains 4 C-H bonds. If we break them one at a time, they will not all require the same energy. That is because taking a hydrogen away from  $\text{CH}_4$  is not the same as taking a hydrogen away from  $\text{CH}_3$ . In fact, we will require a different amount of energy to break each bond, as shown in the diagram below:



The **mean bond enthalpy** for the C-H bond in methane is therefore  $(425 + 421 + 480 + 334) \div 4 = +415 \text{ kJmol}^{-1}$

## Practice Questions

1. The following are standard enthalpy of combustion values in  $\text{kJ mol}^{-1}$

C(s):	-394	$\text{C}_3\text{H}_8(\text{g})$	-2220
$\text{H}_2(\text{g})$ :	-286	$\text{CH}_3\text{OH}(\text{l})$	-715
$\text{CH}_4(\text{g})$ :	-891	$\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$	-2246
$\text{C}_4\text{H}_6(\text{g})$ :	-2542		

Use these values to calculate the standard enthalpies of formation of:

- $\text{CH}_4(\text{g})$
- $\text{C}_4\text{H}_6(\text{g})$
- $\text{C}_3\text{H}_8(\text{g})$
- $\text{CH}_3\text{OH}(\text{l})$
- $\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$

2. The following are standard enthalpy of formation values in  $\text{kJ mol}^{-1}$

$\text{CO}_2(\text{g})$ :	-394	$\text{CH}_4(\text{g})$	-76
$\text{H}_2\text{O}(\text{l})$ :	-286	$\text{PbO}(\text{s})$	-219
$\text{C}_2\text{H}_4(\text{g})$ :	+52	$\text{CO}(\text{g})$	-111
$\text{CaO}(\text{s})$ :	-635	$\text{Al}_2\text{O}_3(\text{s})$	-1700
$\text{CaCO}_3(\text{s})$ :	-1207	$\text{MgO}(\text{s})$	-602
$\text{C}_4\text{H}_6(\text{g})$ :	-2542		

Use these values to calculate the following

- the standard enthalpy of combustion of ethene ( $\text{C}_2\text{H}_4(\text{g})$ )
- the standard enthalpy change for the reaction:  
 $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- the standard enthalpy of combustion of methane ( $\text{CH}_4(\text{g})$ )
- the standard enthalpy change for the reaction:  
 $\text{PbO}(\text{s}) + \text{CO}(\text{g}) \rightarrow \text{Pb}(\text{s}) + \text{CO}_2(\text{g})$
- the standard enthalpy change for the reaction:  
 $3\text{Mg}(\text{s}) + \text{Al}_2\text{O}_3(\text{s}) \rightarrow 2\text{Al}(\text{s}) + 3\text{MgO}(\text{s})$

3. The following are mean bond enthalpies and standard enthalpies of atomisation in  $\text{kJ mol}^{-1}$ :

C – C	+348	$\Delta H_{\text{At}}^\ominus(\text{C}(\text{s}))$	+718
C = C	+612	$\Delta H_{\text{At}}^\ominus(\frac{1}{2}\text{H}_2(\text{g}))$	+218
C – H	+412		
C – O	+360		
O – H	+464		

Use these values to calculate the standard enthalpy change for the following reactions:

- $2\text{C}(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}_3(\text{g})$
- $2\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_2=\text{CH}_2(\text{g})$
- $\text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}$

Use the data to calculate the standard enthalpy of formation of:

- $\text{CH}_3\text{OCH}_3(\text{g})$
- $\text{CH}_2=\text{CHCH}=\text{CH}_2(\text{g})$

## Answers

All answers are in  $\text{kJ mol}^{-1}$

- 75
  - +108
  - 106
  - 251
  - 471
- 1412
  - +178
  - 890
  - 64
  - 106
- 76
  - +48
  - 42
  - 200
  - +136

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