

5

Thermochemistry

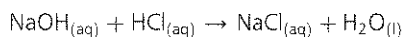
This chapter starts by looking at how you process the results of experiments to measure the amount of heat evolved or absorbed during reactions which are easy to do in the laboratory. The bulk of the chapter then looks at how you can estimate the heat evolved or absorbed for all sorts of changes by working from published data. The level of maths needed for processing experimental results is similar to that needed for basic mole calculations. Most of the rest of the chapter involves little more than addition and subtraction.

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Processing the results from thermochemistry experiments

A neutralisation reaction

This is chosen because it is typical of the sort of reaction that you can easily do with a minimal amount of apparatus, and yet still produce good results. It measures the amount of heat evolved when an acid and an alkali react together to give a salt and water. For example:



The equation shows that the alkali and acid react 1 mole to 1 mole. If their concentrations were the same, you would have to take equal volumes of the two solutions – for example, 25 cm³ of each at 1.0 mol dm⁻³.

The experiment

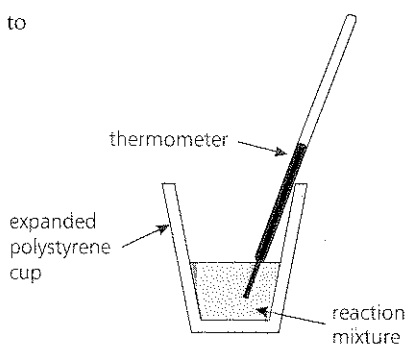
An expanded polystyrene cup is used (see Figure 5.1) because it is a good insulator – helping to prevent heat losses – and because it absorbs hardly any heat itself.

Leave both solutions in the laboratory to reach the same temperature if possible because it makes the calculation very slightly easier! (We will consider what to do if they aren't the same temperature later.) Measure out 25 cm³ of the sodium hydroxide solution and place it in the cup. Record the temperature. Add 25 cm³ of the acid, stir, and record the highest temperature reached.

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Figure 5.1 Apparatus to measure temperature change during a simple reaction



The sum

The heat evolved is worked out using:

$$\text{heat evolved} = \text{mass} \times \text{specific heat} \times \text{temperature rise}$$

This is sometimes written as:

$$\text{heat evolved or absorbed} = m s \Delta T$$

where m is the mass, s is the specific heat and ΔT is the change in temperature. If there is a drop in temperature, then heat has been absorbed during the reaction; an increase shows that heat has been evolved.

The mass in this case is 50 g. This is because you have a total of 50 cm³ of solutions with densities of 1 g cm⁻³. (This is only an approximation, of course. In reality, the density will not be **exactly** the same as water.)

The specific heat can be taken as the same as that of water: 4.18 J g⁻¹ K⁻¹.

The temperature rise is whatever you have just measured. If the temperature rise was, say, 6.7 °C:

$$\begin{aligned} \text{Heat evolved} &= 50 \times 4.18 \times 6.7 \text{ J} \\ &= 1400 \text{ J} \end{aligned}$$

What if the temperatures of the two solutions at the start were different?

Suppose:

Temperature of hydrochloric acid	= 17.9 °C
Temperature of sodium hydroxide solution	= 18.3 °C
Maximum temperature reached	= 24.8 °C

In this case you would split the sum into two parts. 25 g of solution had its temperature raised by 6.9 °C (24.8 – 17.9). The other 25 g had its temperature raised by 6.5 °C (24.8 – 18.3).

$$\begin{aligned} \text{Heat evolved} &= (25 \times 4.18 \times 6.9) + (25 \times 4.18 \times 6.5) \\ &= 1400 \text{ J} \end{aligned}$$

Making the sum more useful

We have worked out the amount of heat in joules evolved when the reaction happened between the arbitrary amounts of chemicals we chose. It is more usual to standardise this by working out the amount of heat which would have been evolved if mole quantities of substances had reacted.

In the case of neutralisation reactions, heat evolved is calculated “per mole of water formed”.

Each mole of sodium hydroxide gives one mole of water (look back at the equation). We started with 25 cm³ of sodium hydroxide solution containing 1 mole in every 1000 cm³. 25 cm³ is 1/40 of 1000 cm³, and so we have 1/40 of a mole of sodium hydroxide that will have produced 1/40 of a mole of water.

To work out how much heat would have been evolved if we had produced 1 mole rather than 1/40 of a mole, we simply multiply our answer for the amount of heat evolved by 40.

is read as “delta T”.
The capital letter, Δ, is
taken to mean “change

Specific heat is the heat
to raise the
temperature of 1 g of a
substance by 1 K (or 1 °C). You
may come across this
value in slightly different
units, for example kJ kg⁻¹ K⁻¹.
In chemistry, we tend to work
in quantities rather than
masses, and so it is more
convenient to use the value in
J g⁻¹ K⁻¹.

In this case, we are assuming
that the densities of all the
solutions are the same as
water (1 g cm⁻³). 25 cm³
of solution is 25 g.

➤ It is important not to quote your answer to too many significant figures. Given the inaccuracies in the information we are starting with, 2 is the maximum acceptable in this case.

Using the figure of 1400 J calculated above, this would give 40×1400 J for each mole of water produced. That is 56 000 J.

To show that heat is evolved during the reaction, the number is given a negative sign (the logic behind this will be explained later in this chapter), and because of the large numbers involved, it is usually expressed in kilojoules – where 1 kJ is 1000 J.

The answer would normally be quoted as -56 kJ mol^{-1} where, in a neutralisation reaction, the “per mole” (mol^{-1}) means “per mole of water formed”.

Improving the experiment – plotting a cooling curve

Although the neutralisation reaction is virtually instantaneous, the temperature recorded on the thermometer does not instantly reach a peak. Time is needed for the thermometer to respond to changes in the temperature of the solution. During that time, heat is being lost to the surroundings. It would be useful to be able to estimate how much heat was being lost, so that we could work out what the maximum temperature should have been. To do this, the temperature is recorded at a series of times during the experiment.

For example, suppose the temperature of the solution in the cup was measured at 1 minute intervals. The second solution was added a few seconds after the 2 minute temperature reading in the table that follows.

Time (mins)	0	1	2	3	4	5	6
Temperature (°C)	18.1	18.1	18.1	24.8	24.7	24.6	24.5

If you look at the figures in the table, you can see that after the temperature reached its peak, it fell at a steady 0.1°C per minute because heat was being lost to the surroundings. It would therefore be reasonable to assume that it fell by a similar amount between the point of mixing (at minute 2) and the maximum temperature recorded (at minute 3). The true maximum temperature should have been 24.9°C if there had been no heat losses. This corrected temperature can be used in the calculations.

These are made-up numbers, of course. In reality, the pattern isn't likely to be so obvious, and so a graph is plotted (see Figure 5.2).

➤ Extrapolating a curve means establishing the trend in the curve and then continuing it either backwards or forwards from the known points.

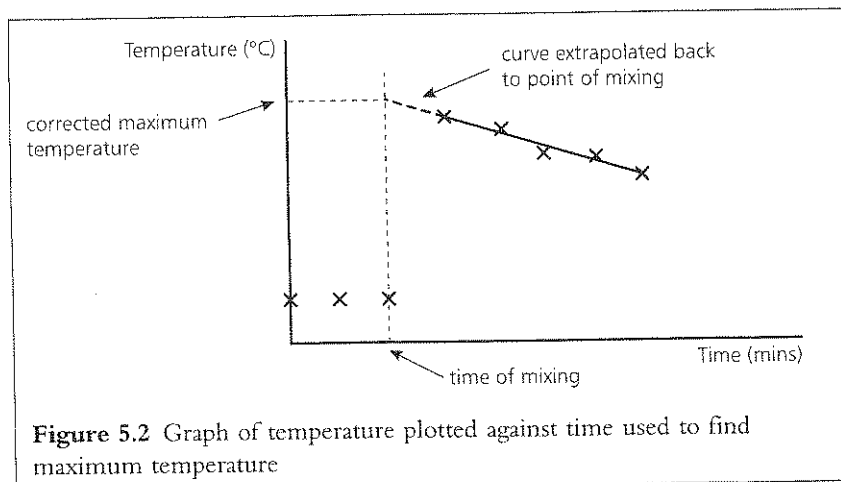


Figure 5.2 Graph of temperature plotted against time used to find maximum temperature

A combustion reaction

Heat is evolved when things burn, and it is quite easy to measure the amount of heat evolved when a liquid like ethanol burns – although the results tend to be very inaccurate using simple apparatus. Ethanol and other alcohols are frequently used because they burn cleanly and completely without producing soot.

The experiment – quick and inaccurate version

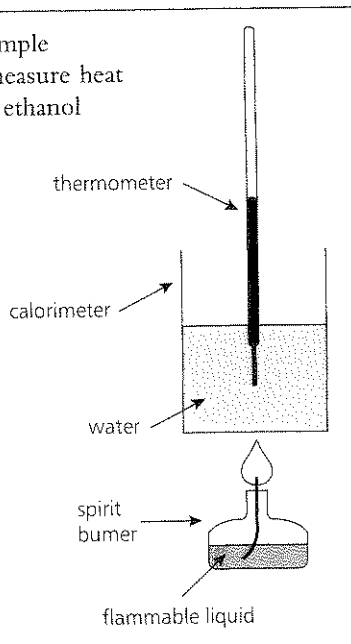
The calorimeter can be made of copper or glass (or can be as simple as an old baked bean tin) and contains a known mass of water (see Figure 5.3). The whole apparatus is surrounded by some sort of shielding to prevent draughts. The water will need to be stirred – either with the thermometer or with an extra stirrer.

The initial temperature of the water is measured. The spirit burner containing the flammable liquid (ethanol, perhaps) is weighed, and then lit and placed under the calorimeter. The temperature is allowed to rise a few degrees, and then the flame is blown out and the maximum temperature recorded. A cap is placed over the wick to prevent loss of liquid vapour, and then the spirit burner is reweighed.

Sample results

Mass of water	= 250 g
Original temperature of water	= 19.5 °C
Final temperature of water	= 23.7 °C
Original mass of burner + ethanol	= 41.36 g
Final mass of burner + ethanol	= 41.18 g

Figure 5.3 Simple apparatus to measure heat evolved when ethanol burns



CHAPTER 5

➤ Temperature rise = $23.7 - 19.5 = 4.2\text{ }^{\circ}\text{C}$ or 4.2 K (the degree size is the same on both scales).

The value of 4389 J is quoted too accurately, but it is not the final answer. Don't round numbers off too soon.

➤ You may be confused about how a number can suddenly become negative. It depends on how you describe it. If you use the statement that the heat **evolved** during a reaction is 1100 kJ, then you don't really need the negative sign. If you talk about the heat change (properly called the **enthalpy change**) during the reaction, then the negative sign shows that heat has been evolved. The logic behind this will be dealt with shortly.

The sum

The specific heat of water is $4.18\text{ J g}^{-1}\text{ K}^{-1}$. For the moment, we are going to ignore the heat absorbed by the calorimeter and the thermometer.

$$\begin{aligned}\text{Heat evolved} &= \text{mass} \times \text{specific heat} \times \text{temperature rise} \\ &= 250 \times 4.18 \times 4.2\text{ J} \\ &= 4389\text{ J (or 4.389 kJ)}\end{aligned}$$

$$\begin{aligned}\text{Mass of ethanol burnt} &= 41.36 - 41.18\text{ g} \\ &= 0.18\text{ g}\end{aligned}$$

1 mole of ethanol ($\text{C}_2\text{H}_5\text{OH}$) weighs 46 g.

$$\begin{aligned}\text{The heat evolved per mole of ethanol burnt} \\ &= 4.389 \times \frac{46}{0.18}\text{ kJ} \\ &= 1100\text{ kJ (to 2 significant figures)}\end{aligned}$$

The answer should properly be recorded as -1100 kJ mol^{-1} . The negative sign shows that heat is evolved; the " mol^{-1} " means "per mole of ethanol".

Comments

The accepted value for the amount of heat evolved when 1 mole of ethanol burns is -1367 kJ mol^{-1} . The answer that these results produce is therefore much too low. We have not allowed for the heat absorbed by the calorimeter and the thermometer (and, perhaps, the stirrer), and we have made no allowance for the heat losses to the atmosphere. Plotting a cooling curve will not work this time, because the heat wasn't all evolved in one instant – there is no obvious time that you could extrapolate a curve back to.

Improving the experiment in a simple way

Suppose you knew the amount of heat given out when 1 mole of methanol (CH_3OH) burns. The value is -726 kJ mol^{-1} . To find a more accurate value for ethanol, you would do the experiment twice, once with methanol and once with ethanol, in each case keeping the amount of water identical and the temperature rise much the same, so that similar heat losses are involved in both cases.

Results with methanol

Mass of water	= 250 g
Original temperature of water	= $19.1\text{ }^{\circ}\text{C}$
Final temperature of water	= $23.8\text{ }^{\circ}\text{C}$
Original mass of burner + methanol	= 42.56 g
Final mass of burner + methanol	= 42.30 g

Results with ethanol

Mass of water	= 250 g
Original temperature of water	= $19.5\text{ }^{\circ}\text{C}$
Final temperature of water	= $24.0\text{ }^{\circ}\text{C}$
Original mass of burner + ethanol	= 40.87 g
Final mass of burner + ethanol	= 40.67 g

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➤ 1 mole of methanol weighs 32 g.

Remember:

$$\text{Number of moles} = \frac{\text{mass (g)}}{\text{mass of 1 mole (g)}}$$

The sum

The methanol results are used to find the **heat capacity** of the apparatus – that is the amount of heat needed to raise the temperature by 1 °C (the same as 1 K).

$$\begin{aligned} \text{Mass of methanol used} &= 0.26 \text{ g} \\ \text{Number of moles of methanol used} &= \frac{0.26}{32} \\ &= 8.125 \times 10^{-3} \end{aligned}$$

Each mole evolves 726 kJ of heat when it burns.

$$\text{Total heat evolved} = 8.125 \times 10^{-3} \times 726 \text{ kJ}$$

This raised the temperature by 4.7 °C. The heat capacity of the apparatus is the amount of heat needed to raise the temperature by 1 °C.

$$\begin{aligned} \text{Heat capacity} &= \frac{8.125 \times 10^{-3} \times 726}{4.7} \text{ kJ } ^\circ\text{C}^{-1} \\ &= 1.26 \text{ kJ } ^\circ\text{C}^{-1} \end{aligned}$$

In the ethanol experiment, the temperature rose by 4.5 °C. The heat capacity of the apparatus is unchanged, provided the amount of water is still the same. Every degree increase in temperature needed 1.26 kJ of heat to be evolved.

$$\begin{aligned} \text{Heat evolved in ethanol case} &= 4.5 \times 1.26 \text{ kJ} \\ &= 5.67 \text{ kJ} \end{aligned}$$

$$\text{Mass of ethanol used} = 0.20 \text{ g}$$

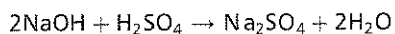
If 46 g of ethanol (1 mole) had been burnt, the heat evolved would have been

$$\frac{46}{0.20} \times 5.67 = 1300 \text{ kJ (to 2 significant figures)}$$

The heat evolved when ethanol burns is therefore $-1300 \text{ kJ mol}^{-1}$. Notice that this answer is closer to the accepted one ($-1376 \text{ kJ mol}^{-1}$), but the experiment is still full of errors. The practical details could be improved further, but there would be no difference in the way the calculation is done.

Problem • 1

A student carried out an experiment to measure the heat evolved when sodium hydroxide solution was neutralised with dilute sulphuric acid:



He placed 50 cm³ of 1.0 mol dm⁻³ sodium hydroxide solution in a plastic cup and recorded its steady temperature. He poured 25 cm³ of 1.0 mol dm⁻³ sulphuric acid into a measuring cylinder and recorded the temperature of that. Then he added the sulphuric acid to the sodium hydroxide and started timing at the point of mixing, recording temperatures at 1 minute intervals for 5 minutes.

Results:

Temperature of sodium hydroxide solution = 20.5 °C

Temperature of dilute sulphuric acid = 20.8 °C

Time (mins)	0	1	2	3	4	5
Temp of mixture (°C)		29.5	29.3	29.1	28.9	28.7

Problem • 2

Assume that the density of all solutions is 1 g cm^{-3} and their specific heats are all $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.

- Estimate the maximum temperature which would have been reached in the absence of any heat losses.
- Calculate the total amount of heat evolved during this reaction.
- Calculate the amount of heat evolved per mole of water formed during the neutralisation.

The apparatus shown in Figure 5.3 was used to measure the amount of heat evolved when 1 mole of hexane, C_6H_{14} , burns completely to give carbon dioxide and water. The heat capacity of the apparatus had been previously found to be $1.15 \text{ kJ } ^\circ\text{C}^{-1}$, and everything was kept the same in this experiment.

Results:

Mass of burner + hexane before experiment	= 45.63 g
Mass of burner + hexane after experiment	= 45.50 g
Original temperature of water	= 19.7°C
Final temperature of water	= 24.9°C

- Calculate the heat evolved during this experiment.
- Calculate the heat evolved when 1 mole of hexane burns.

(H = 1; C = 12)

➤ **Beyond A level:** Strictly speaking, the enthalpy change is a measure of the heat evolved or absorbed if the reaction is done at **constant pressure**. Because almost all reactions in the lab are done open to the atmosphere (and therefore at constant atmospheric pressure), this is a sensible measure to use. When an experiment is done in a closed container of fixed volume, the heat evolved or absorbed in these conditions is called the **internal energy change** and is given the symbol ΔU .

For reactions involving no change in volume (for example, if no gases are evolved), the two measures are identical, but in other cases, there is a slight difference. If you want to find out more, you will need to refer to a reasonably advanced text book.

Hess's Law cycles

Defining some terms

We are going on now to look at how you can estimate the amount of heat evolved or absorbed during reactions from published data. You can't do this until you know what all the words mean.

Enthalpy changes

During almost all chemical reactions there are changes in the energy of the system, and you normally see this as heat either being evolved or absorbed. Energy is needed to break bonds in the original materials, and energy is released when new bonds are made in the products. It is very, very unlikely that these two processes will be exactly in balance, and so some energy will either be released to the surroundings, or absorbed from the surroundings.

The heat evolved or absorbed during a reaction is known as the **enthalpy change** for the reaction and is given the symbol ΔH – read as “delta H”. You can't actually measure the heat content (or **enthalpy**) of a particular substance – just the **change in enthalpy** when it reacts to form something new.

If heat is evolved during a reaction, the reaction is said to be **exothermic**, and the value of ΔH is given a negative sign (for example, -200 kJ).

If heat is absorbed during a reaction, the reaction is **endothermic**, and ΔH is given a positive sign (for example, $+100 \text{ kJ}$). The “+” must always be written – you cannot just assume it.

The reason for these signs is that the reactions are looked at from the point of view of the substances reacting (the reactants). This is more readily seen on an enthalpy diagram (see Figure 5.4).

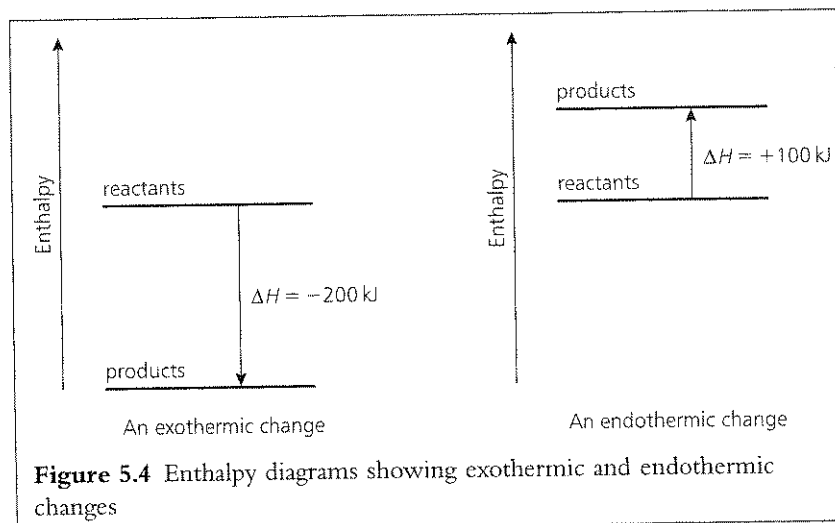


Figure 5.4 Enthalpy diagrams showing exothermic and endothermic changes

In an exothermic change, the reactants lose heat energy to the surroundings; in an endothermic change, they gain it from the surroundings.

In the exothermic case, for example, you could perhaps do an experiment which showed that 200 kJ of heat energy was evolved when particular quantities of substances reacted. You would not know what the actual enthalpy (heat content) of either the reactants or the products was – but you would know that the products had an enthalpy of 200 kJ less than the reactants. All we are interested in is enthalpy **changes**.

Standard conditions

An enthalpy change quoted under standard conditions is given the symbol ΔH^\ominus , which you read as “delta H standard” or as “delta H nought”. Even where the reaction does not take place under standard conditions, the measured value under other conditions is corrected to give a standard one. At A level this doesn’t really concern you – all values quoted will be standard ones.

Standard conditions include:

- 298 K (unless some other temperature is specifically stated);
- a pressure of 1 atmosphere;
- solution concentrations of 1 mol dm^{-3} ;
- substances present in their standard states.

“Standard state” means the physical state that you would expect a substance to be in under these conditions. For example, water as a liquid, $\text{H}_2\text{O}_{(l)}$; sodium as a solid, $\text{Na}_{(s)}$; hydrogen as gaseous molecules, $\text{H}_{2(g)}$.

➤ You may find standard pressure quoted as 100 KPa which is slightly less than 1 atmosphere. Find out which your examiners want.

➤ **Note:** These various **enthalpy changes** are sometimes called by slightly different terms. The correct term is "enthalpy change of . . ." (reaction or combustion or formation or neutralisation). Frequently the word "change" is missed out, so that "enthalpy of . . ." (reaction, etc.) means the same thing.

In older text books, you may find the original term "heat of . . ." (reaction, etc.).

➤ **Dynamic equilibrium:** In the example quoted, the reaction combining nitrogen and hydrogen is happening at exactly the same rate as that splitting up the ammonia. The result is a mixture of nitrogen, hydrogen and ammonia – called an equilibrium mixture.

Standard enthalpy change of reaction, ΔH^\ominus

This is the enthalpy change when substances react under standard conditions in quantities given by the equation for the reaction.

Instead of using the term "enthalpy change", you can also use the phrase "the heat evolved or absorbed when . . .". For example, suppose



This means that if 2 moles of A react with 1 mole of B under standard conditions, 153 kJ of heat is evolved. The use of the unit "mol⁻¹" in this context is a bit odd. It isn't "per mole of A" or "per mole of B". It relates to the whole equation expressed in mole quantities.

If you have a reversible reaction in a state of dynamic equilibrium, the standard enthalpy change of reaction is calculated on the assumption that the reaction goes completely to the right hand side. For example,



This means that if 1 mole of nitrogen and 3 moles of hydrogen reacted **completely** to give 2 moles of ammonia, 92 kJ of heat would be evolved (see Figure 5.5). In reality, only about 15% usually combines under the conditions used industrially, but the standard enthalpy change is still quoted as -92 kJ mol^{-1} .

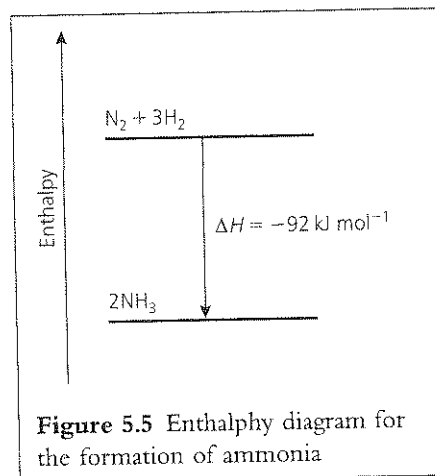
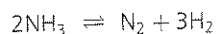


Figure 5.5 Enthalpy diagram for the formation of ammonia

If the reaction is written in the reverse direction:



the sign of the enthalpy change is also reversed, i.e. $\Delta H^\ominus = +92 \text{ kJ mol}^{-1}$. This is important: if you reverse the direction of a reaction, the sign of the enthalpy change reverses as well. This is all fairly obvious if you look at the enthalpy diagram. If 92 kJ is evolved when nitrogen and hydrogen combine to make ammonia, then 92 kJ must be put back in to make ammonia split up again.

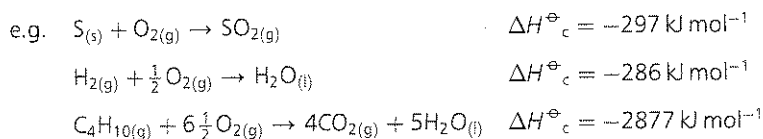
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➤ This is a good example of the case where a standard enthalpy change has to be calculated from a reaction done under non-standard conditions. Hardly anything will actually burn at a temperature of 298 K (25 °C). Don't worry about this at A level – just use the standard value given to you.

Standard enthalpy change of combustion, ΔH_c^\ominus

This is the enthalpy change when 1 mole of a substance is burned completely in oxygen under standard conditions.

Be careful if you use the alternative phraseology for this. You could say “the heat evolved when . . .”. Be careful not to say “heat evolved or absorbed when . . .” – a combustion reaction absorbing heat is a contradiction in terms!

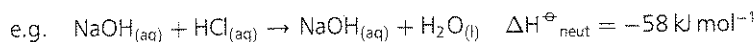


Notice that you will often have to write halves into combustion equations. The definition must have 1 mole of the substance you are burning, and if this means that the rest of the equation needs to contain halves, then so be it.

Standard enthalpy change of neutralisation, $\Delta H_{\text{neut}}^\ominus$

This is the enthalpy change when an acid and an alkali react together under standard conditions to give one mole of water.

Heat is always **evolved** when an acid and an alkali neutralise each other, so the alternative phraseology would be “the heat evolved when . . .”.



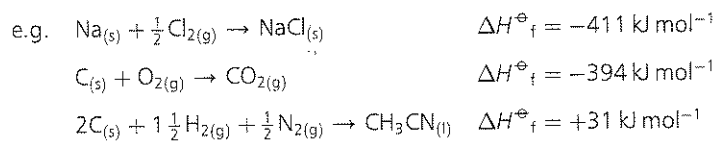
In this case, the “ mol^{-1} ” refers to the 1 mole of water being formed. We looked at how this enthalpy change could be measured earlier in this chapter.

Standard enthalpy change of formation, ΔH_f^\ominus

This is the enthalpy change when 1 mole of a substance is formed from its elements under standard conditions.

In this case, you can replace the term “enthalpy change” in the definition by “heat evolved or absorbed”. Some substances have positive enthalpy changes of formation, others negative.

This is a very important term, and a large proportion of calculations will need you to use it somewhere.



Notes

In some cases, an enthalpy change can be called by different names. For example, the enthalpy change of formation of CO_2 is also the enthalpy change of combustion of carbon.

CHAPTER 5

➤ We have not done any calculations for several pages now, but it is a complete waste of time trying to do the thermochemistry calculations which follow if you do not fully understand the meanings of all the terms we have discussed, and how to write equations for things like enthalpy change of combustion or formation.

If you aren't reasonably happy about writing or balancing the sorts of equations we have been using, now is a good time to go back and do some revision.

Problem • 3

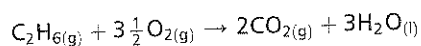
In all cases, the equation must be written so that 1 mole of the substance is formed, even if this means writing fractions into the equation. You must also start from **elements** – the only compound in the equation is the one being formed.

Everything must be present in its standard state, which is the state you would expect it to be in at 298 K and 1 atmosphere pressure. This is not just the physical state, but also implies the fact that hydrogen is H_2 molecules, nitrogen is N_2 molecules, and so on. It is important that you do not write the hydrogens as “ $3\text{H}_{(g)}$ ”. You must show the hydrogens as H_2 molecules – not as individual atoms – because this is how they exist at 298 K.

Enthalpy changes of formation can be quoted for substances which you can't make directly from the elements. For example, in the third equation above, there is no way that you can persuade carbon, hydrogen and nitrogen to combine together to make CH_3CN (ethanenitrile) directly. The value can, however, be calculated in ways that we will look at shortly.

The enthalpy change of formation of any element in its standard state is zero. This is fairly obvious if you think about it. How much heat is going to be evolved or absorbed if you make $\text{O}_{2(g)}$ from $\text{O}_{2(g)}$, for example, or $\text{Na}_{(s)}$ from $\text{Na}_{(s)}$? Not a lot!

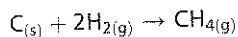
The enthalpy change of combustion of ethane, C_2H_6 , is represented by the equation:



Write equations representing the enthalpy change of combustion of:

- carbon,
- methane, $\text{CH}_4(g)$
- ethanol, $\text{C}_2\text{H}_5\text{OH}(l)$
- octane, $\text{C}_8\text{H}_{18}(l)$

The enthalpy change of formation of methane is represented by the equation:

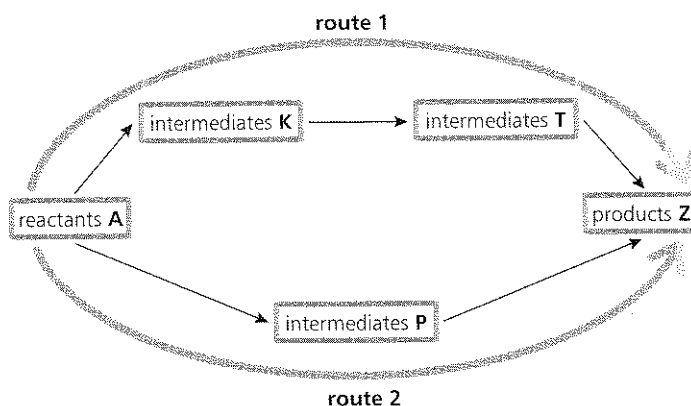


Write equations representing the enthalpy change of formation of:

- sodium iodide, $\text{NaI}_{(s)}$
- water, $\text{H}_2\text{O}_{(l)}$
- ethanol, $\text{C}_2\text{H}_5\text{OH}_{(l)}$
- calcium carbonate, $\text{CaCO}_{3(s)}$
- sodium chlorate(V), $\text{NaClO}_{3(s)}$

Hess's Law

The enthalpy change accompanying a chemical change is independent of the route by which the chemical change occurs.



This means that if you convert reactants **A** into products **Z** in one step or in many steps, the overall enthalpy change is always the same.

The overall enthalpy change is determined by the gap between the reactants and the products on an enthalpy diagram, and that gap is not affected in any way by the route you use to get from one to the other (see Figure 5.6). Whichever route you use, the overall enthalpy change is the same, ΔH .

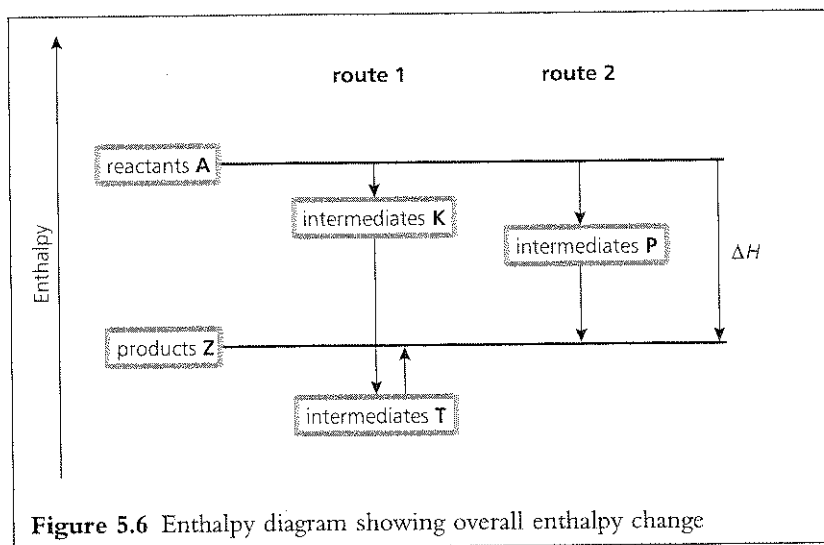


Figure 5.6 Enthalpy diagram showing overall enthalpy change

➤ **Note!** With the exception of Born–Haber cycles (see later) which are usually drawn in a way similar to Figure 5.6, all enthalpy change calculations can be done using the method described in the main body of the text. Provided you don't try to take short cuts, this method is virtually foolproof.

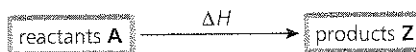
You may come across other ways of doing these calculations which are sometimes slightly quicker, but these other methods need you to learn several different techniques depending on what you are asked to do, and what information you are given. This is potentially confusing. Practice **one** method which will cover **all** sums.

Using Hess's Law to calculate enthalpy changes

A typical question will give you an enthalpy change to find, together with a list of relevant data.

Step 1

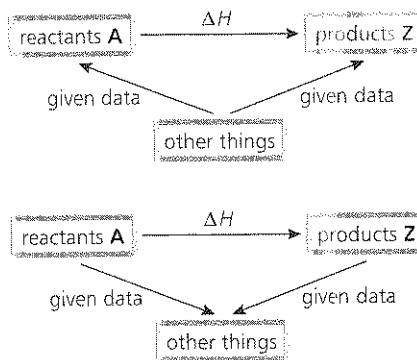
Write down the equation for the enthalpy change you are asked to find. Write ΔH over the top of the arrow. Take care at this stage that you have got the equation properly balanced. If your equation is wrong, your final answer will almost certainly be wrong as well. Get into the habit of putting state symbols in the equation. In some cases, they matter.



Step 2

Now use the information you are given in the question to complete a cycle (often, but not always a triangle) that you can apply Hess's Law to.

Your diagram will often end up looking like one of the following:

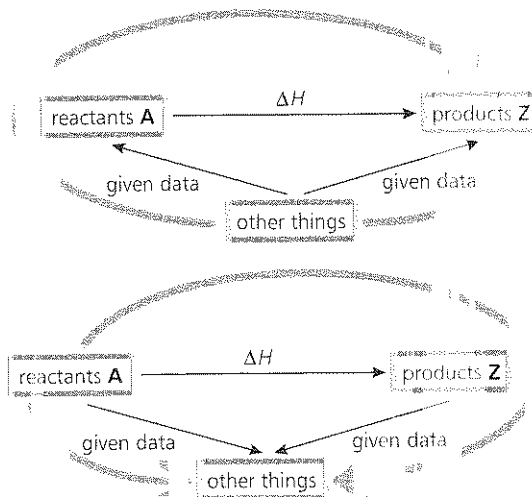


Which way the arrows point in the bottom part of the diagram will depend entirely on what information you are given. Examples coming up shortly will make this clear.

Step 3

Apply Hess's Law. You need to find two routes within the diagram **which do not go against the flow of any arrows**. The starting point for the two routes will be a corner of the diagram that arrows are leaving from. The end point of the two routes is the corner where arrow heads are arriving.

For the two diagrams above, the routes would be:



Notice that the pattern of the two routes is quite different in the two cases. You must not try to learn a particular pattern – it varies too much. Work out what the two routes are in each new situation. It will not take you more than a few seconds anyway!

➤ **Note!** You must be sure that you go with the flow of the arrows. It is possible to reverse the flow of an arrow, but if you do that you must also reverse the sign of the enthalpy change. It is confusing, and you are likely to forget to do it. It also means that you will have to stop and think! Just accept the arrows the way they are, and find two routes which don't involve changing anything.

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Hess's Law says that the total enthalpy change on the two routes will be identical – so add together the enthalpy changes on each route, and equate them. This gives you an equation in which the only unknown is ΔH .

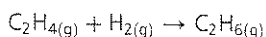
Examples will make this process very obvious.

Example 1

➤ In this and all future examples, we are calculating **standard** enthalpy changes, ΔH^\ominus , because we are working from standard data. In the calculations which follow, however, the standard symbol will be missed out to avoid clutter in the equations.

➤ It doesn't matter whether you draw boxes around the substances or not. Sometimes it's helpful.

Calculate the standard enthalpy change for the reaction:



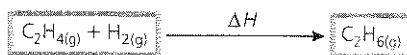
given the following standard enthalpy changes of combustion:

$$\Delta H^\ominus_{\text{c}}(\text{C}_2\text{H}_4(\text{g})) = -1411 \text{ kJ mol}^{-1}$$

$$\Delta H^\ominus_{\text{c}}(\text{H}_2(\text{g})) = -286 \text{ kJ mol}^{-1}$$

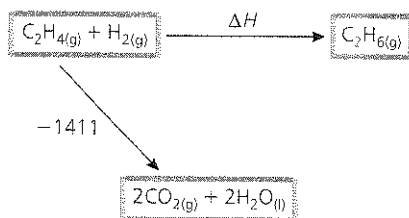
$$\Delta H^\ominus_{\text{c}}(\text{C}_2\text{H}_6(\text{g})) = -1560 \text{ kJ mol}^{-1}$$

You are given the equation, so write it down with ΔH written over the arrow:



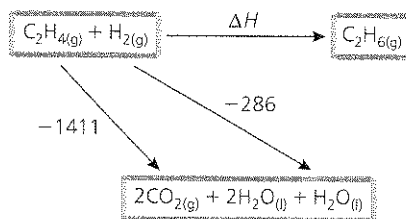
Now slot in the information you have been given. Think carefully about what it means. Enthalpy change of combustion is about burning 1 mole of the substance completely in oxygen – in other words, you start from the substance and turn it into something else. In this case, then, your arrows will start from the ethene, hydrogen and ethane and go towards the bottom corner of the diagram.

Start with the ethene value (because that's the first one you are given):



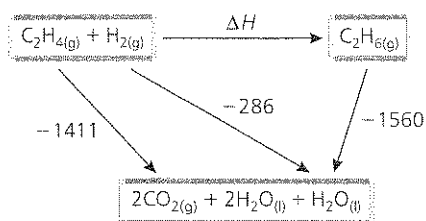
Notice that we have not bothered to write the oxygens into the equation – we simply assume that we can obtain all we need from the air. You must however, be careful to balance the carbons and hydrogens – hence the 2CO_2 and $2\text{H}_2\text{O}$.

Now add in the value for hydrogen:

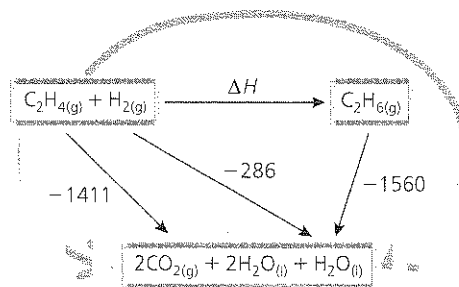


This leaves the value for the ethane. If you burn ethane, you get the same $2\text{CO}_2 + 3\text{H}_2\text{O}$ as before – you are bound to, because you have still got

exactly the same number of carbons and hydrogens. Putting in the ethane value gives:



Now all you need to do is find two routes around the diagram without going against the flow of any arrows. In this case, the routes will start in the top left hand corner, because that is where arrows are leaving from. The routes end in the bottom corner, because that is where all the arrow heads end up.



Now use Hess's Law, which says that the total enthalpy changes on the two routes are equal:

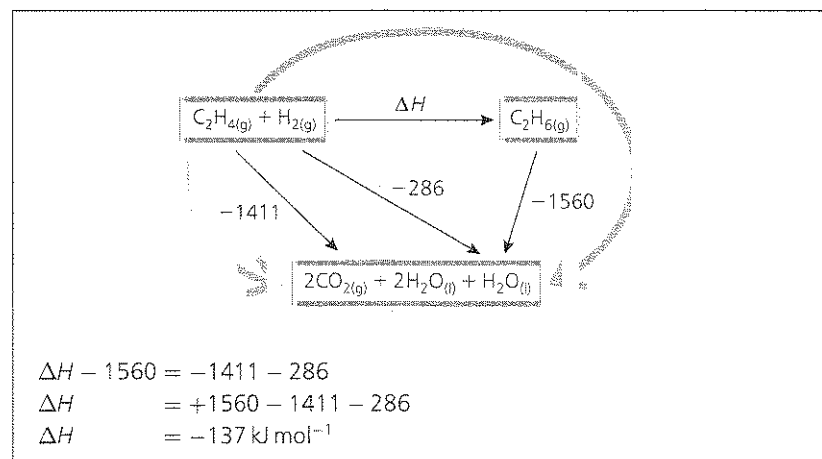
$$\Delta H - 1560 = -1411 - 286$$

Solving for ΔH gives:

$$\Delta H = +1560 - 1411 - 286$$

$$\Delta H = -137 \text{ kJ mol}^{-1}$$

This has taken a lot of paper to describe, but most of it goes on in your mind. The final answer in an exam would look like this:



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Example 2

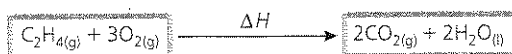
Calculate the enthalpy change of combustion of ethene, C_2H_4 , given the following standard enthalpy changes of formation:

$$\Delta H_f^\ominus(C_2H_4(g)) = +52 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus(CO_2(g)) = -394 \text{ kJ mol}^{-1}$$

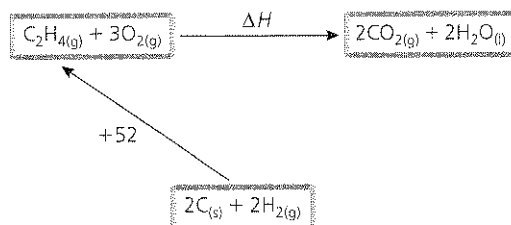
$$\Delta H_f^\ominus(H_2O(l)) = -286 \text{ kJ mol}^{-1}$$

Start by writing the equation with ΔH over the top of the arrow. Be careful to get it balanced properly, otherwise your sum is bound to be wrong.



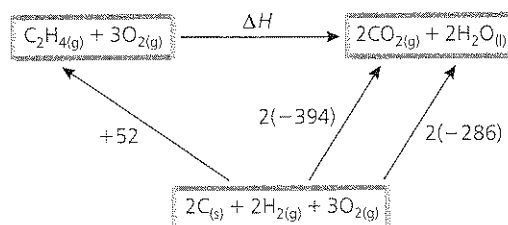
This time you are given enthalpy changes of formation. This is about making 1 mole of substance from the elements – with everything being in its standard state (the state you would expect to find it in under standard conditions).

This time, the arrows will point towards the substances in the equation, and at the bottom corner of the diagram will be the elements. Start with the first bit of information you are given and put it into the diagram:



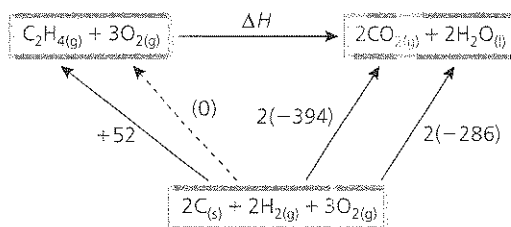
➤ The hydrogen is $2H_2$ – not $4H$. Hydrogen exists as H_2 molecules under standard conditions.

Now add in the values for carbon dioxide and water. **Be very careful at this point!** In both cases you are making **2 moles** of compound. The ΔH_f^\ominus values relate to making **1 mole**. You must remember to multiply both values by 2. Forgetting to do this is one of the commonest mistakes in this type of calculation.

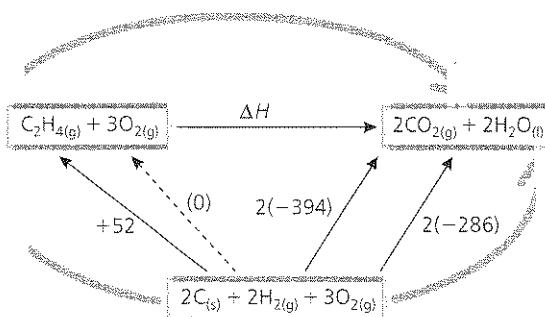


➤ This is a good example of a case where it is useful to draw boxes around substances – especially the collection of elements at the bottom. It is impossible to draw arrows from the correct combination of elements to all the substances. Think of the bottom corner as a box of elements that you can draw on as you need.

What about the oxygen? This is already an element in its standard state. There will be no enthalpy change involved in taking the oxygen from the bottom corner to the top left. You could include it by writing (0) over a dotted arrow if you wished. At least you would be forced to stop and think about it – and not just casually leave it out!



Finally find two routes around the diagram without going against the flow of an arrow, and then apply Hess's Law.



➤ **Hint:** Read your calculator instruction book so that you understand how to do this simple sum as quickly as possible. It could save you a lot of time fiddling around with brackets or memory if you understand the order that your calculator does things in.

$$\begin{aligned} \Delta H + 52 &= 2(-394) + 2(-286) \\ \Delta H &= -52 + 2(-394) + 2(-286) \\ \Delta H &= -1412 \text{ kJ mol}^{-1} \end{aligned}$$

Once again, all you would write down in an exam is the final diagram and the sum.

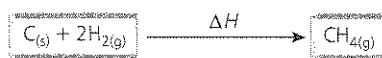
Example 3

➤ This is a simple example of a way of finding an enthalpy change of formation for a compound which can't actually be made directly from its elements. This doesn't matter. You can draw a valid Hess's Law cycle even if one of the steps is an imaginary one. Most compounds, in fact, can't be made directly from their elements, but they can still have a calculated enthalpy change of formation assigned to them – and this can be used to calculate other enthalpy changes involving that compound.

Calculate the standard enthalpy change of formation of methane from the following enthalpy changes of combustion:

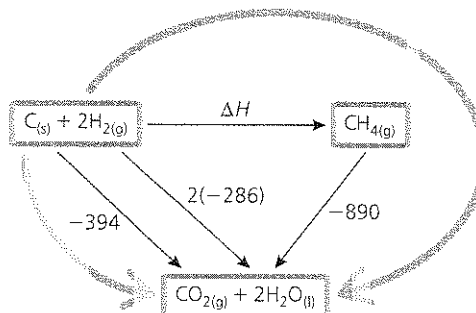
$$\begin{aligned} \Delta H_c^\ominus(\text{CH}_4(\text{g})) &= -890 \text{ kJ mol}^{-1} \\ \Delta H_c^\ominus(\text{H}_2(\text{g})) &= -286 \text{ kJ mol}^{-1} \\ \Delta H_c^\ominus(\text{C}(\text{s})) &= -394 \text{ kJ mol}^{-1} \end{aligned}$$

Start by writing the equation for the enthalpy change you want, with ΔH written over the top of the arrow:



Then slot in all the information you have been given. In this case, we are burning everything, and so arrows will start from the substances in the

equation and go down to combustion products in the bottom corner. The final diagram will look like this:



$$\Delta H - 890 = -394 + 2(-286)$$

$$\Delta H = +890 - 394 + 2(-286)$$

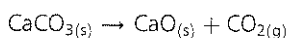
$$\Delta H = -76 \text{ kJ mol}^{-1}$$

➤ **Note!** There are 2 moles of hydrogen being burnt – the value for hydrogen therefore has to be multiplied by 2.

Example 4

➤ This is a simple example of a problem involving an enthalpy change of formation of a compound (the calcium carbonate) that can't be made directly from its elements. The -1207 value will have been worked out using the sort of calculations we've been doing. You can then use this value to work out the enthalpy change in familiar reactions like the example on the right.

Calculate the enthalpy change for the reaction:



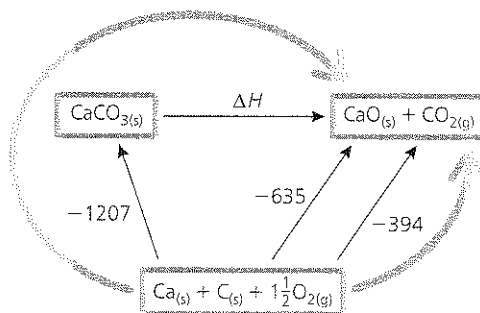
Standard enthalpy changes of formation:

$$\Delta H_f^\ominus(\text{CaCO}_3(\text{s})) = -1207 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus(\text{CaO}(\text{s})) = -635 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\ominus(\text{CO}_2(\text{g})) = -394 \text{ kJ mol}^{-1}$$

This time you are given the equation – so write it down again with ΔH over the top of the arrow and then construct the rest of the cycle using the information you have been given. In this case, the bottom corner of the diagram will consist of the elements because you have been given standard enthalpies of formation.



$$\Delta H - 1207 = -635 - 394$$

$$\Delta H = +1207 - 635 - 394$$

$$\Delta H = +178 \text{ kJ mol}^{-1}$$

➤ **Note!** You must include the + sign in the answer. It isn't enough just to write 178. It has to be +178.

CHAPTER 5

Example 5

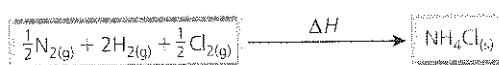
Calculate the standard enthalpy change of formation of solid ammonium chloride, NH_4Cl , using the following data:

$$\Delta H_f^\ominus(\text{NH}_3(\text{g})) = -46.1 \text{ kJ mol}^{-1}$$

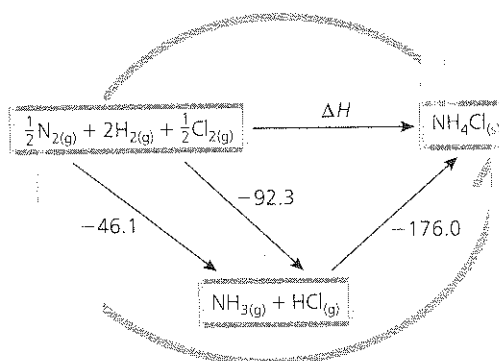
$$\Delta H_f^\ominus(\text{HCl}(\text{g})) = -92.3 \text{ kJ mol}^{-1}$$



As always, write down the equation for the enthalpy change you want, with ΔH written over the top of the arrow:



Now use the information to complete a cycle:



$$\Delta H = -46.1 - 92.3 - 176.0$$

$$\Delta H = -314.4 \text{ kJ mol}^{-1}$$

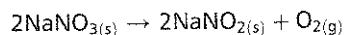
(Strictly speaking this should be written as $\Delta H_f^\ominus = -314.4 \text{ kJ mol}^{-1}$.)

➤ **Remember:** Enthalpy change of formation must start from **elements**. Although ammonium chloride is being made when ammonia and HCl react, this does not fit the definition for enthalpy change of formation.

➤ You have an unusual assortment of information in this example, but just think about what each piece means, and slot it onto the diagram, taking care that the arrows point in the right direction. The two routes this time do not correspond to ones we've come across before. This doesn't matter – you just work them out as you need them. Don't leave this example until you are **sure** that you understand why the cycle is drawn as it is.

Problem • 5

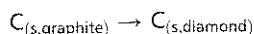
Calculate the enthalpy change for the reaction:



given the following standard enthalpy changes of formation in kJ mol^{-1} : NaNO_3 -468 ; NaNO_2 -359

Problem • 6

The standard enthalpy change of combustion of carbon in the form of graphite is $-393.5 \text{ kJ mol}^{-1}$; for carbon in the form of diamond it is $-395.4 \text{ kJ mol}^{-1}$. Calculate the enthalpy change for the reaction



Problem • 7

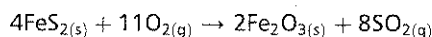
Calculate the standard enthalpy change of formation of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, given the following standard enthalpy changes of combustion: carbon -394 kJ mol^{-1} ; hydrogen -286 kJ mol^{-1} ; sucrose $-5640 \text{ kJ mol}^{-1}$.

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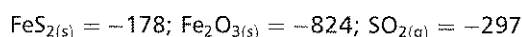
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Problem • 8

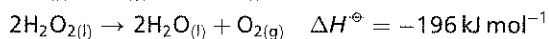
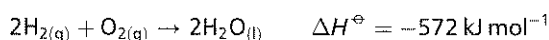
Calculate the standard enthalpy change of the reaction:



Standard enthalpy changes of formation in kJ mol^{-1} :



Calculate the standard enthalpy change of formation of liquid hydrogen peroxide, H_2O_2 , from the following information:



➤ **Note!** Remember that mol^{-1} refers to mole quantities of the whole equation as it is written – not to 1 mole of H_2 or 1 mole of H_2O_2 .

Problem • 9

Defining some more terms

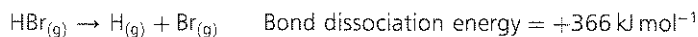
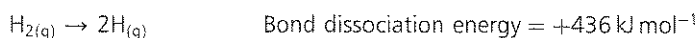
Bond enthalpy or bond energy

To break a bond needs an input of energy – an endothermic process. When a bond is made, energy is evolved – an exothermic change. Bond energy is a measure of the amount of energy needed to **break** a bond.

Unfortunately (for simple understanding) there are two confusingly similar terms used, and one of these can have somewhat different meanings depending on the context! Fortunately this doesn't turn out to be a problem as far as actually doing the sums is concerned.

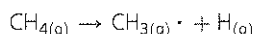
Bond dissociation energy (or enthalpy)

If you have a simple diatomic molecule (one containing only two atoms) like hydrogen, H_2 , or hydrogen bromide, HBr , the energy needed to break one mole of the bond is called the bond dissociation energy (or bond dissociation enthalpy):



You must always start from the original compound in the gas state, and what you end up with must also be in the gas state.

This term becomes more problematic if you start with a compound containing more than 2 atoms – for example, in methane, CH_4 . If you break off one mole of hydrogen atoms, you will end up with methyl **radicals**, $\text{CH}_3\cdot$:



The hydrogen atoms left attached to the carbon are no longer in exactly the same environment as they were in methane, and so the strength of the bond will be different in $\text{CH}_3\cdot$ than in CH_4 . Breaking off a second mole of hydrogen atoms will require a different bond dissociation enthalpy from the first. Taking the third one off will need a different amount of energy again, and so will the fourth.

It is much more convenient to take an average value.

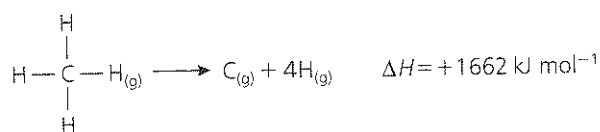
➤ **Radical** is an atom or group of atoms which contains an unpaired electron. The dot in $\text{CH}_3\cdot$ shows this unpaired electron. The hydrogen atom formed is also a radical, of course. With atoms, the dot isn't usually written, unless you are trying to make a particular point – it is not relevant here.

CHAPTER 5

► **Hint:** When you are doing problems involving bond enthalpies, it is usually a good idea to draw the full structural formula of the compounds involved. By doing this, it is easy to count the numbers of bonds being broken. It is surprisingly easy to get the number of bonds wrong if you work from a formula like C_2H_5OH , for example.

Mean (or average) bond enthalpies (or energies)

Suppose +1662 kJ are needed to break all the bonds in a mole of methane to produce gaseous carbon atoms and gaseous hydrogen atoms:



4 moles of C–H bonds are being broken, and so the mean bond enthalpy is

$$\frac{+1662}{4} = +415.5 \text{ kJ mol}^{-1}$$

Mean bond enthalpies are the ones you will almost always use in calculations. Mean bond enthalpies are also known as **bond energy terms**. Throughout the rest of this topic, they will simply be called bond enthalpies.

Important

When you are using bond enthalpies, you must start from the compound in the gas state, and end up with individual atoms of the elements, also in the gas state. If you are given a problem which involves a liquid, you first have to convert it into a gas before you can do any bond enthalpy sums. If you need to do this, the examiners will give you the necessary enthalpy change information.

Standard enthalpy change of vaporisation, ΔH^{\ominus}_v

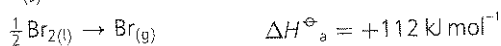
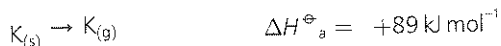
This is the heat needed to convert one mole of substance from liquid to gas. The substance should be at its boiling point and a pressure of 1 atmosphere.

For example, ΔH^{\ominus}_v for water is +41 kJ mol⁻¹. This means that if you have 1 mole of water at 100 °C, it will take 41 kJ to convert it entirely to steam.

Standard enthalpy change of atomisation, ΔH^{\ominus}_a

This is the heat needed to produce 1 mole of gaseous atoms from the element in its standard state.

It is essential to remember that the “per mole” in this case refers to a mole of gaseous atoms – and not a mole of the original element. All the following changes represent enthalpy changes of atomisation:



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Calculations involving bond enthalpies

➤ There is considerable variation in values quoted for **bond enthalpies** depending on what source you use. Often, there is even inconsistency within a single book – a value used on one page being inconsistent with one used a page or two later.

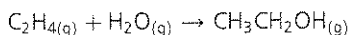
Part of the problem is that there are two different meanings of the word "average" (or "mean"). We have just calculated the average C–H bond enthalpy in methane to be $+415.5 \text{ kJ mol}^{-1}$. But "average" can also be taken to apply to an average value for all C–H bonds – whatever their environment, for example, in ethane or ethene or benzene or ethanal or whatever. Because the hydrogen is bonded slightly differently in all of these (a problem largely beyond A level), the strength will not be exactly the same as the average value in methane. To make life easier, an average value is taken which is approximately right for all C–H bonds (but not exactly right for any of them!). The average value which we shall take in the calculations which follow is $+413 \text{ kJ mol}^{-1}$.

Because of this averaging, calculations using bond enthalpies only ever give an approximate answer. Little of this need really concern you for exam purposes. Just use whatever values you are given, but bear in mind the inaccuracies which are bound to be present in bond enthalpy sums.

There are two different approaches to these calculations. There is a quick, short-cut method for which you will need to learn a different technique, and which will present you with some difficulties if a slightly unusual problem comes up. Or, you can use exactly the same technique that we have used up to now. Each question will take a little longer to do, but you will be able to cope with any problem you may be given, with the minimum amount of thinking in an exam! This is the way we are going to do it.

Example 6

Estimate the enthalpy change for the reaction:

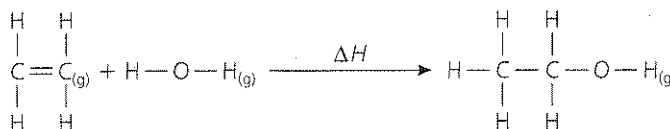


given the following bond enthalpies:

C—C	+ 347 kJ mol ⁻¹
C=C	+ 612 kJ mol ⁻¹
C—H	+ 413 kJ mol ⁻¹
O—H	+ 464 kJ mol ⁻¹
C—O	+ 358 kJ mol ⁻¹

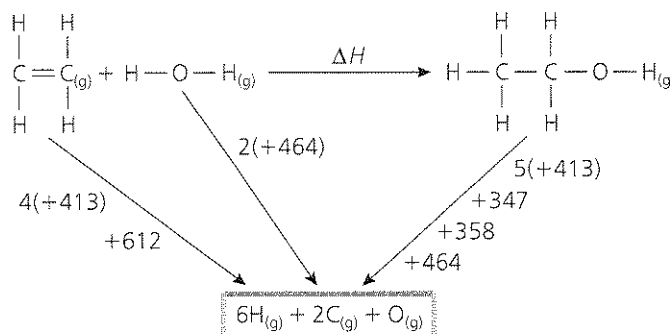
Notice that the water and the ethanol are not in their standard states, which should be liquid. This is partly because, when the reaction is done industrially, they would be gases anyway, but mainly it is to make the sum more straightforward.

Start by writing the equation with ΔH over the arrow exactly as before. Show the structures of **all** the molecules to make counting bonds easier.

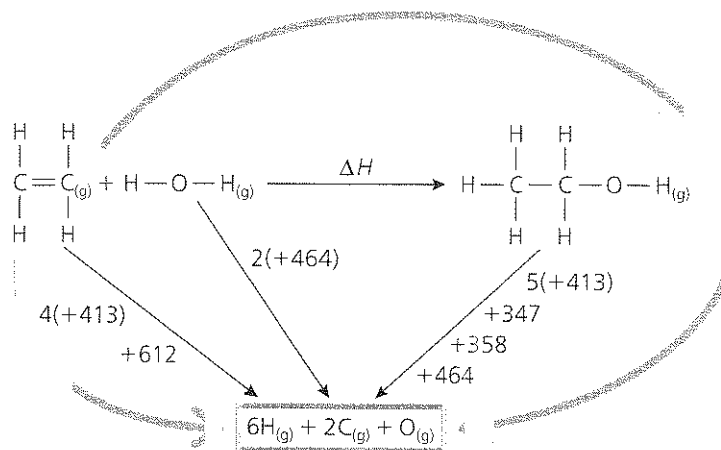


Now stop and think about the information you are given. Mean bond enthalpies measure the energy needed to break 1 mole of a particular bond in a gaseous compound to give gaseous atoms. In this example, all the compounds are gaseous, so this isn't a problem. Your arrows will run from the compounds down to gaseous atoms in the bottom corner.

Make sure that you understand the reason for every single number on the following cycle.



Now find two routes around the diagram without going against the flow of an arrow, and equate them according to Hess's Law.



$$\Delta H + 5(+413) + 347 + 358 + 464 = 4(+413) + 612 + 2(+464)$$

Solving for ΔH gives:

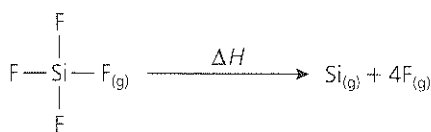
$$\Delta H = -42 \text{ kJ mol}^{-1}$$

Example 7

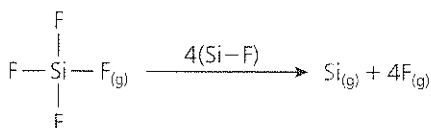
Calculate the mean bond enthalpy of the Si-F bond in $\text{SiF}_4(\text{g})$, given the following enthalpy changes:

Formation of $\text{SiF}_4(\text{g})$:	$-1615 \text{ kJ mol}^{-1}$
Atomisation of silicon:	$+456 \text{ kJ mol}^{-1}$
Atomisation of fluorine:	$+79 \text{ kJ mol}^{-1}$

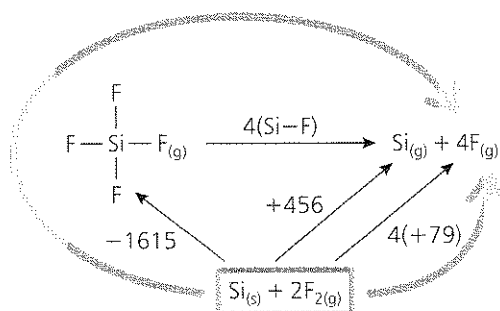
Start by writing an equation for the change you are interested in:



You could work out a value for ΔH exactly as before, but you would have to remember to divide it by 4 at the end of the calculation, because you are breaking 4 bonds. This time, then, it would make life easier to write something different over the arrow – not ΔH , but $4(\text{Si-F})$, where (Si-F) represents the mean bond enthalpy of the Si-F bond, which is what you are trying to find.



To complete the diagram, use the information you are given. The enthalpy change of formation of SiF_4 concerns making the compound from its elements in their standard states – silicon as $\text{Si}(\text{s})$ and fluorine as $\text{F}_2(\text{g})$. The enthalpy changes of atomisation take the elements in their standard states and turn them into gaseous atoms.



Notice that fluorine's atomisation enthalpy has been multiplied by 4. This is because of the 4 moles of fluorine atoms that are being formed. Remember that it is the number of moles of atoms formed that matters – not how many moles of molecules of element you start from.

$$4(\text{Si-F}) - 1615 = +456 + 4(+79)$$

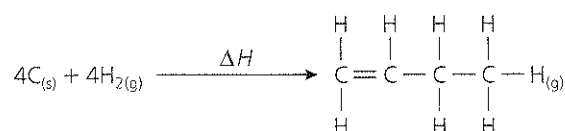
Which solves to give $(\text{Si-F}) = +597 \text{ kJ mol}^{-1}$

Example 8

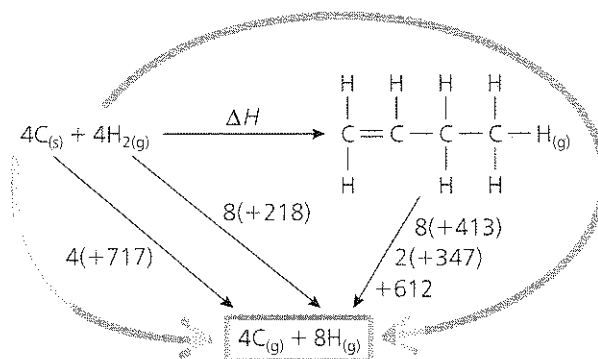
Estimate the enthalpy change of formation of but-1-ene, $\text{CH}_2=\text{CHCH}_2\text{CH}_3(\text{g})$, given the following information:

Enthalpy changes of atomisation:	carbon:	$+717 \text{ kJ mol}^{-1}$
	hydrogen:	$+218 \text{ kJ mol}^{-1}$
Mean bond enthalpies:	C-H:	$+413 \text{ kJ mol}^{-1}$
	C-C:	$+347 \text{ kJ mol}^{-1}$
	C=C:	$+612 \text{ kJ mol}^{-1}$

As always, write the equation for the change you are going to calculate. You must remember to start from the elements in their standard states.



At the bottom corner of the diagram will be the gaseous atoms, formed by atomising the two elements, or taking the compound to pieces.



$$\Delta H + 8(+413) + 2(+347) + 612 = 4(+717) + 8(+218)$$

$$\Delta H = 4(+717) + 8(+218) - 8(+413) - 2(+347) - 612$$

$$\Delta H = +2 \text{ kJ mol}^{-1}$$

► **“Estimate”** In bond enthalpy calculations the word “estimate” is often used rather than “calculate”. This reflects the inaccuracies involved when you use mean bond enthalpies. The answer will only be an approximation to the correct value.

► **Think about this!** Make sure that you understand the reason for every single number on this diagram.

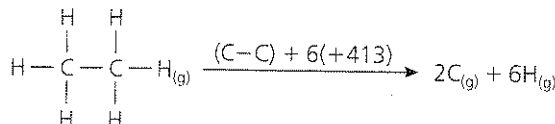
CHAPTER 5

Example 9

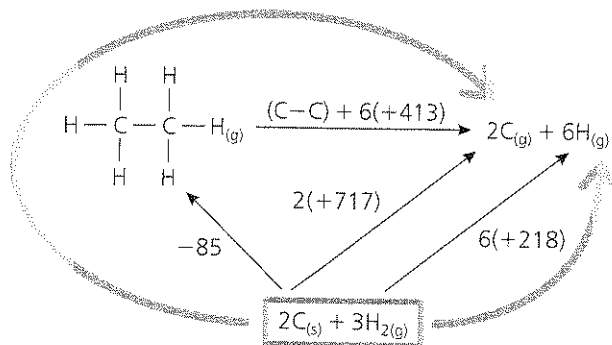
Estimate the bond enthalpy for the C—C bond in ethane, $C_2H_6(g)$, given the following information:

Standard enthalpy of formation of ethane:	-85 kJ mol^{-1}
Mean bond enthalpy of C—H:	$+413 \text{ kJ mol}^{-1}$
Enthalpy changes of atomisation:	
carbon:	$+717 \text{ kJ mol}^{-1}$
hydrogen:	$+218 \text{ kJ mol}^{-1}$

The problem this time is that there isn't an equation you can write which only involves breaking a C—C bond. The C—C bond enthalpy is a **part** of the enthalpy change involved if you break ethane up to produce gaseous atoms – and this is as close as you can get to what you actually want.



Once you are over this hurdle, the problem then becomes like all the others. The bottom corner of the diagram this time will consist of the elements in their standard states:

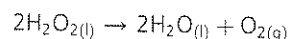


$$\begin{aligned}
 -85 + (\text{C}-\text{C}) + 6(+413) &= 2(+717) + 6(+218) \\
 (\text{C}-\text{C}) &= 2(+717) + 6(+218) + 85 - 6(+413) \\
 (\text{C}-\text{C}) &= +349 \text{ kJ mol}^{-1}
 \end{aligned}$$

Example 10

This final worked example involving bond enthalpies shows you how to cope if liquids are present in your equation. Remember that bond enthalpies can only be used if everything is in the gas state.

Estimate the enthalpy change when hydrogen peroxide decomposes to water and oxygen according to the equation:



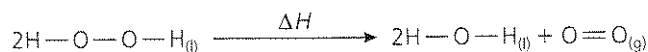
The structural formula of hydrogen peroxide is H—O—O—H.

Bond enthalpies:	H—O	$+464 \text{ kJ mol}^{-1}$
	O—O	$+144 \text{ kJ mol}^{-1}$
	O=O	$+498 \text{ kJ mol}^{-1}$
Enthalpy changes of vaporisation	$\text{H}_2\text{O}_2(l)$	$+43 \text{ kJ mol}^{-1}$
	$\text{H}_2\text{O}(l)$	$+41 \text{ kJ mol}^{-1}$

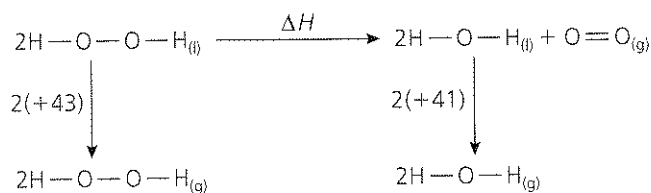
► Careful of bc than Don' draw num of ea coun

Thermochemistry

There aren't any problems at the beginning this time. You are given the equation – just rewrite it showing all the bonds, and with ΔH over the arrow:

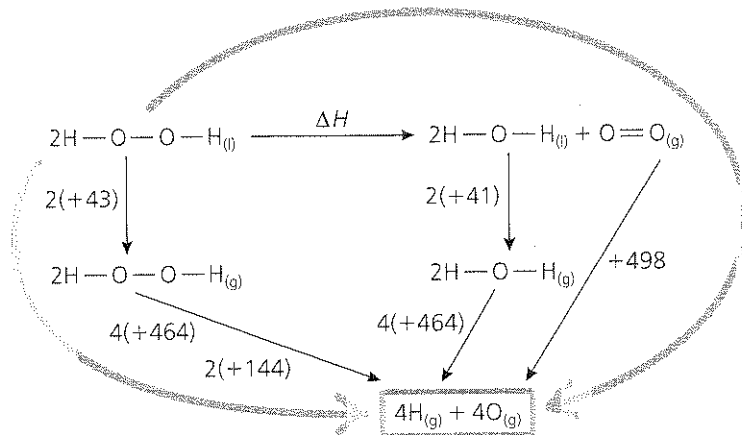


You **cannot** use bond enthalpies on either the hydrogen peroxide or the water if they are liquids, but you do have the information to convert them into gases.



Now you can use the bond enthalpy data. The bottom corner of the diagram will consist of gaseous atoms of hydrogen and oxygen:

➤ **Note!** You need to be very careful counting the number of bonds when you have more than one mole of substances. Don't be afraid actually to draw the molecules the correct number of times (in this case 2 of each), and then physically count the bonds.



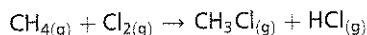
$$\Delta H + 2(+41) + 4(+464) + 498 = 2(+43) + 4(+464) + 2(+144)$$

Solving this for ΔH gives:

$$\Delta H = -206 \text{ kJ mol}^{-1}$$

Problem • 10

Estimate the enthalpy change in the following reaction between methane and chlorine:



Mean bond enthalpies:	C—H	+413 kJ mol ⁻¹
	Cl—Cl	+243 kJ mol ⁻¹
	C—Cl	+346 kJ mol ⁻¹
	H—Cl	+432 kJ mol ⁻¹

Calculate the mean bond enthalpy of the H—S bond in hydrogen sulphide, H₂S(g).

Standard enthalpy change of formation of H₂S(g): -21 kJ mol⁻¹

Enthalpy changes of atomisation:	sulphur:	+279 kJ mol ⁻¹
	hydrogen:	+218 kJ mol ⁻¹

Problem • 11

CHAPTER 5

Problem • 12

Estimate the enthalpy change of combustion of propane, $C_3H_8(g)$.

Mean bond enthalpies:	C—C	+347 kJ mol ⁻¹
	C—H	+413 kJ mol ⁻¹
	O=O	+498 kJ mol ⁻¹
	C=O(in CO ₂)	+805 kJ mol ⁻¹
	H—O	+464 kJ mol ⁻¹

Enthalpy change of vaporisation of water: +41 kJ mol⁻¹

Problem • 13

Estimate the enthalpy change of formation of tetrachloromethane, $CCl_4(l)$.

Mean bond enthalpies:	C—Cl	+346 kJ mol ⁻¹
	Cl—Cl	+243 kJ mol ⁻¹

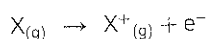
Enthalpy change of vaporisation of $CCl_4(l)$: +30 kJ mol⁻¹

Enthalpy change of atomisation of carbon: +717 kJ mol⁻¹

Defining even more terms

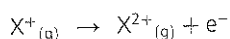
First ionisation energy

The first ionisation energy is the energy required to remove the most loosely held electron from one mole of gaseous atoms to produce 1 mole of gaseous ions each carrying a charge of 1+:



Successive ionisation energies

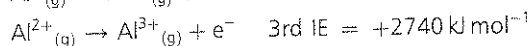
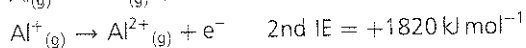
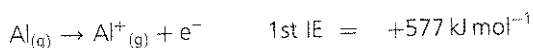
The second ionisation energy is defined by the equation:



It is the energy needed to remove a second electron from each ion in 1 mole of gaseous 1+ ions to give gaseous 2+ ions.

You can then have as many successive ionisation energies as there are electrons in the original atom.

The first three ionisation energies of aluminium, for example, are given by:

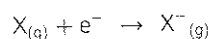


In order to form an $Al^{3+}_{(g)}$ ion from $Al_{(g)}$, you would have to supply:

$$+577 + 1820 + 2740 = +5137 \text{ kJ mol}^{-1}$$

First electron affinity

The first electron affinity is the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous 1- ions:



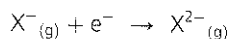
Whereas ionisation energies always have positive values, first electron affinities have negative values. For example, the first electron affinity of chlorine is -364 kJ mol^{-1} .

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Y
Tl
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Second electron affinity

The second electron affinity is defined by the equation:



It is the energy needed to add a second electron to each ion in 1 mole of gaseous 1- ions to give gaseous 2- ions.

Notice that second electron affinities are positive. Energy is needed to force an electron into an already negative ion. For example, the second electron affinity of oxygen is $+844 \text{ kJ mol}^{-1}$.

Lattice enthalpy

Lattice enthalpy is a measure of the enthalpy difference between a solid ionic crystal and its scattered gaseous ions. The enthalpy diagram in Figure 5.7 shows the lattice enthalpy for sodium chloride.

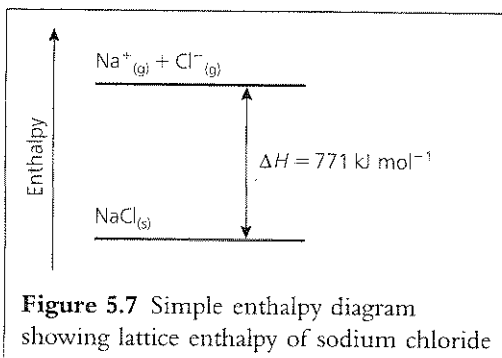


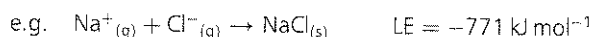
Figure 5.7 Simple enthalpy diagram showing lattice enthalpy of sodium chloride

You could, of course, define lattice enthalpy either as the exothermic change as you go from gaseous ions to solid crystal, or as the endothermic change as the crystal is split into its separated gaseous ions. Unfortunately **both** definitions are in current use.

Before you read on, find out which version of the definition your syllabus uses, and then stick to that in all the examples you do.

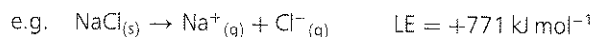
Definition 1

Lattice enthalpy is the heat evolved when 1 mole of solid crystal is formed from its scattered gaseous ions:



Definition 2

Lattice enthalpy is the heat needed to convert 1 mole of solid crystal into its scattered gaseous ions:



If you look at the sign of the lattice enthalpy given to you in a question, it will be obvious which of these definitions is being used. The problem only arises if you are asked to define lattice enthalpy or to calculate a lattice enthalpy – in which case you need to be in tune with your examiners.

➤ The terms "lattice enthalpy" and "lattice energy" are often used as if they mean exactly the same thing. In fact there is a slight difference between them which relates to the conditions under which they are defined. You don't need to worry about this at A level.

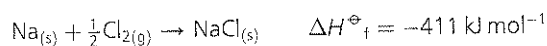
➤ "Scattered gaseous ions" The gaseous ions have to be far enough apart for there to be no residual attractions between them. Lattice enthalpy is a measure of the attractive forces within the crystal.

Born-Haber cycles

A Born-Haber cycle is a particular form of Hess's Law cycle which relates to the formation of ionic crystals. Born-Haber cycles are drawn differently from the cycles we have used up to now, but there is no difference in the way the sums are done. It is easier to explain how a Born-Haber cycle works by using a specific example.

The Born-Haber cycle for sodium chloride

The enthalpy change of formation of sodium chloride is -411 kJ mol^{-1} :

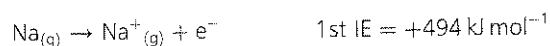


A Born-Haber cycle looks in detail at all the individual changes which contribute to this. For convenience, we will look at the changes affecting the sodium first, and the chlorine afterwards.

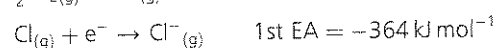
The sodium ends up as sodium ions, Na^+ . To go from sodium atoms to sodium ions involves the first ionisation energy of the sodium. But ionisation energies apply only to gaseous atoms – so first the sodium has to be atomised. You need the enthalpy change of atomisation:



Now you can make the ions. You need the first ionisation energy of sodium:



Repeating the process for the chlorine, you need to atomise the chlorine, and then form the negative ion. This time you need the enthalpy change of atomisation and the electron affinity:



Putting this onto an enthalpy diagram we get Figure 5.8 (which is not to scale)

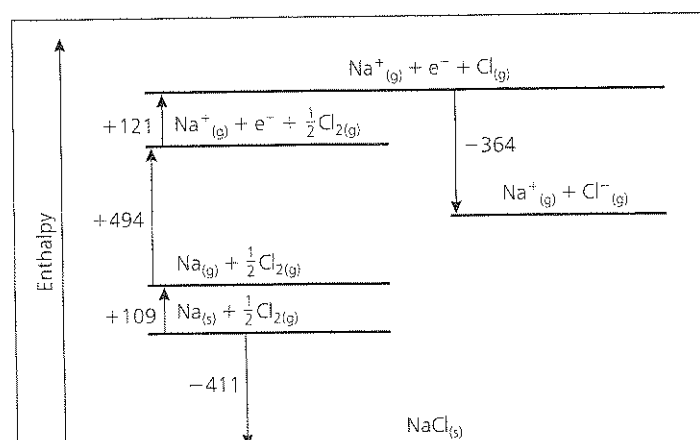


Figure 5.8 Enthalpy diagram showing Born-Haber cycle for formation of sodium chloride

You could now use this cycle to find the lattice enthalpy of sodium chloride. Diagrams are given for both definitions of lattice enthalpy, in Figures 5.9 and 5.10. Refer **only** to the one which corresponds to your syllabus.

Either:

➤ Use this diagram and calculation if your syllabus defines lattice enthalpy as the exothermic change making the crystal from the gaseous ions.

When you have worked out the lattice enthalpy, you will find that it has a negative sign showing that heat has been evolved. As long as you point the arrow in the right direction, the calculation automatically works out the correct sign.

Do not be tempted to write “-LE” into your equation or cycle (because you think that the lattice enthalpy should be negative). The symbol “LE” already includes that negative sign. In this case, $LE = -771$.

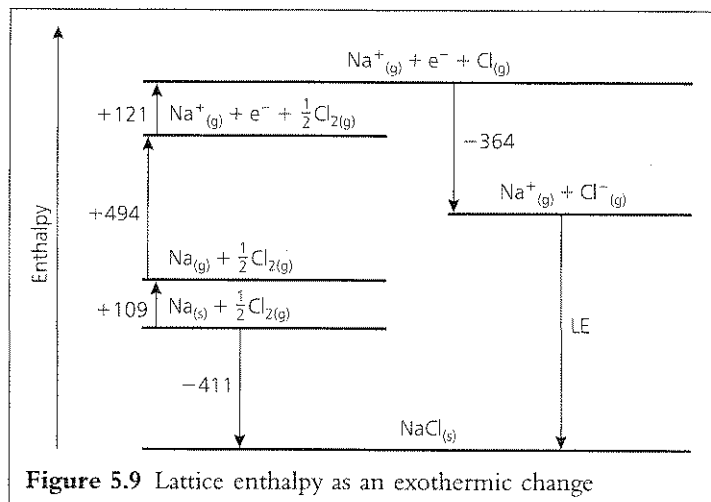


Figure 5.9 Lattice enthalpy as an exothermic change

Finding two routes around the diagram in Figure 5.9 without going against the flow of any arrows gives:

$$+109 + 494 + 121 - 364 + LE = -411$$

Solving this gives

$$LE = -771 \text{ kJ mol}^{-1}$$

Or:

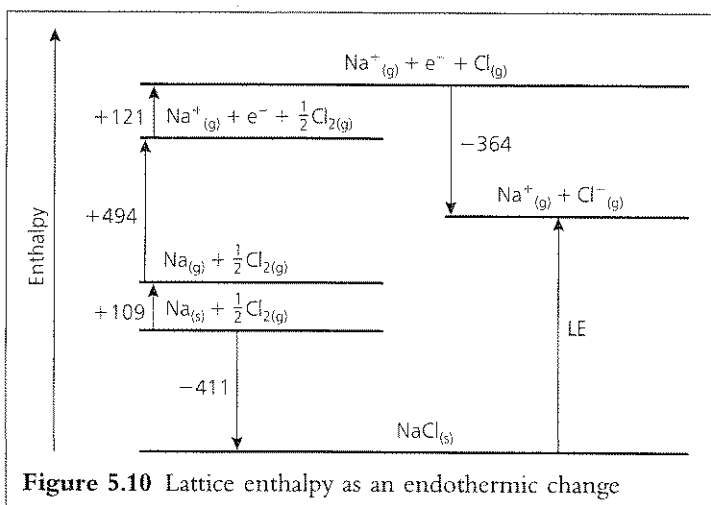


Figure 5.10 Lattice enthalpy as an endothermic change

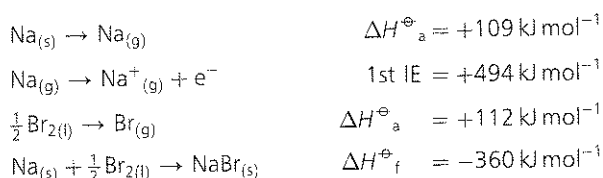
Finding two routes around the diagram in Figure 5.10 without going against the flow of any arrows gives:

$$+109 + 494 + 121 - 364 = -411 + LE$$

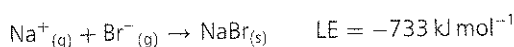
Solving this gives

$$LE = +771 \text{ kJ mol}^{-1}$$

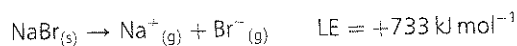
You can perfectly well use a Born–Haber cycle to find any one of the terms which make it up. You might, for example, be asked to draw a Born–Haber cycle and then find the electron affinity of bromine from the following data:



and either



or



The cycle has just the same form as for sodium chloride (see Figure 5.11).

➤ It would be a good idea to redraw this (and other similar diagrams) showing only the arrow corresponding to the definition of lattice enthalpy that your particular syllabus wants.

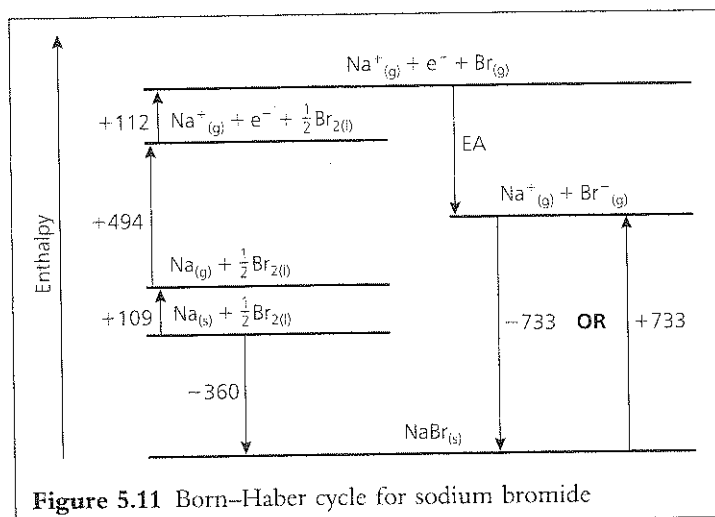


Figure 5.11 Born–Haber cycle for sodium bromide

Depending on which definition of lattice enthalpy you are using, you will use one of the following equations:

either

$$+109 + 494 + 112 + \text{EA} - 733 = -360$$

or

$$+109 + 494 + 112 + \text{EA} = -360 + 733$$

If you look carefully at these, you will see that they are variations on the same expression. Whichever you use, the answer comes out as:

$$\text{EA} = -342 \text{ kJ mol}^{-1}$$

➤ Take some time! Be sure that you understand exactly how the expression which matches your definition of lattice enthalpy arises from the Born–Haber cycle.

Some more complicated Born–Haber cycles

Any compound which consists of 1+ and 1– ions will have a Born–Haber cycle of exactly the same form as the sodium chloride or sodium bromide one. The complication comes if you have ions with charges greater than 1.

The Born–Haber cycle for magnesium oxide

Magnesium oxide contains Mg^{2+} and O^{2-} ions. The cycle will have to include a first plus a second ionisation energy to make the 2+ ion, and a first plus a second electron affinity to make the 2- ion. Remember that second electron affinities are positive, and so the diagram looks more complicated (see Figure 5.12).

➤ **What all the numbers mean:**

+150 is the enthalpy change of atomisation of magnesium.
 +736 and +1450 are the first and second ionisation energies of magnesium.
 +248 is the enthalpy change of atomisation of oxygen.
 -142 is the first electron affinity of oxygen.
 +844 is the second electron affinity of oxygen.
 -602 is the enthalpy change of formation of magnesium oxide.

➤ **Your lattice enthalpy arrow won't be double ended.** Yours will either point up or down according to which definition of lattice enthalpy you are using. It would be a good idea to redraw this diagram to avoid getting confused.

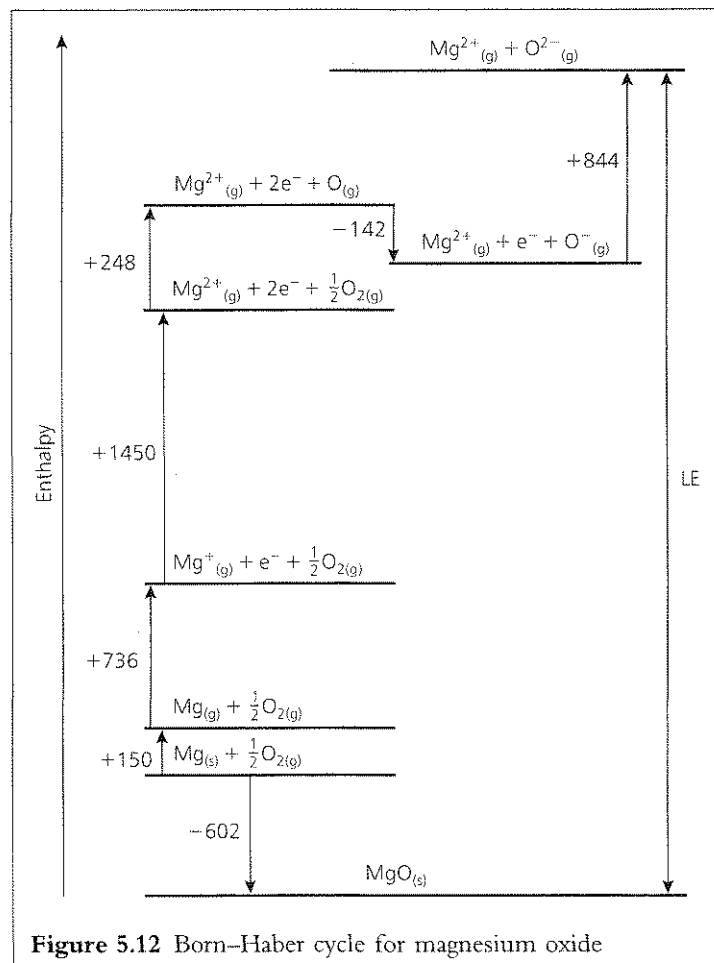


Figure 5.12 Born–Haber cycle for magnesium oxide

Although the cycle looks more complicated, you can simply find two routes around it which don't go against the flow of any arrows.

If your lattice enthalpy arrow points downwards

$$+150 + 736 + 1450 + 248 - 142 + 844 + \text{LE} = -602$$

$$\text{Solving to give: } \text{LE} = -3888 \text{ kJ mol}^{-1}$$

If your lattice enthalpy arrow points upwards

$$+150 + 736 + 1450 + 248 - 142 + 844 = -602 + \text{LE}$$

$$\text{Solving to give: } \text{LE} = +3888 \text{ kJ mol}^{-1}$$

Once again, you could work out **any** of the changes in this cycle, as long as you knew all the other ones.

➤ **What all the numbers mean:**

+150 is the enthalpy change of atomisation of magnesium.

+736 and +1450 are the first and second ionisation energies of magnesium.

+121 is the enthalpy change of atomisation of chlorine. It has to be multiplied by 2 because of the 2 chlorine atoms formed.

–364 is the first electron affinity of chlorine. This also has to be multiplied by 2 because you are adding an electron to each of 2 chlorine atoms.

–642 is the enthalpy change of formation of magnesium chloride.

➤ Once again it would be a good idea to redraw this so that the lattice enthalpy arrow points in the direction required by your syllabus.

The cycle for magnesium chloride

Magnesium chloride is MgCl_2 , containing Mg^{2+} ions and 2Cl^- ions. The changes for the magnesium will be the same as the last cycle – atomisation and then first plus second ionisation energies. This time the two electrons that are released are given one each to two chlorine atoms. Because you are only adding one electron to each chlorine atom, you only need the first electron affinity, but you have to remember to multiply it by 2. The cycle is shown in Figure 5.13.

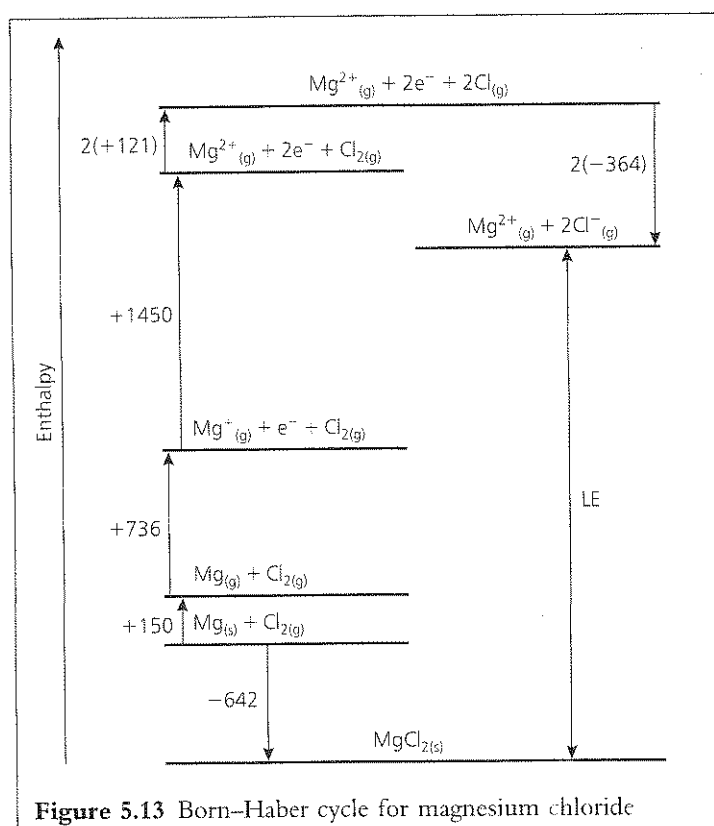


Figure 5.13 Born-Haber cycle for magnesium chloride

In exactly the same way as the previous examples, you could work out the lattice enthalpy of the magnesium chloride. If you do this, you should find it comes to either $-2492 \text{ kJ mol}^{-1}$ or $+2492 \text{ kJ mol}^{-1}$, depending on which definition of lattice enthalpy you are working from.

The cycle for sodium oxide

Sodium oxide is Na_2O , containing 2Na^+ ions and an O^{2-} ion. This time the terms relating to sodium will have to be multiplied by two: 2 times the enthalpy change of atomisation, and 2 times the first ionisation energy (because you are removing 1 electron from each of 2 atoms). In the oxygen case, because 1 atom is accepting both electrons, you will need the first plus second electron affinities.

The cycle is shown in Figure 5.14.

➤ Draw the lattice enthalpy arrow so that it points in the direction required by your syllabus.

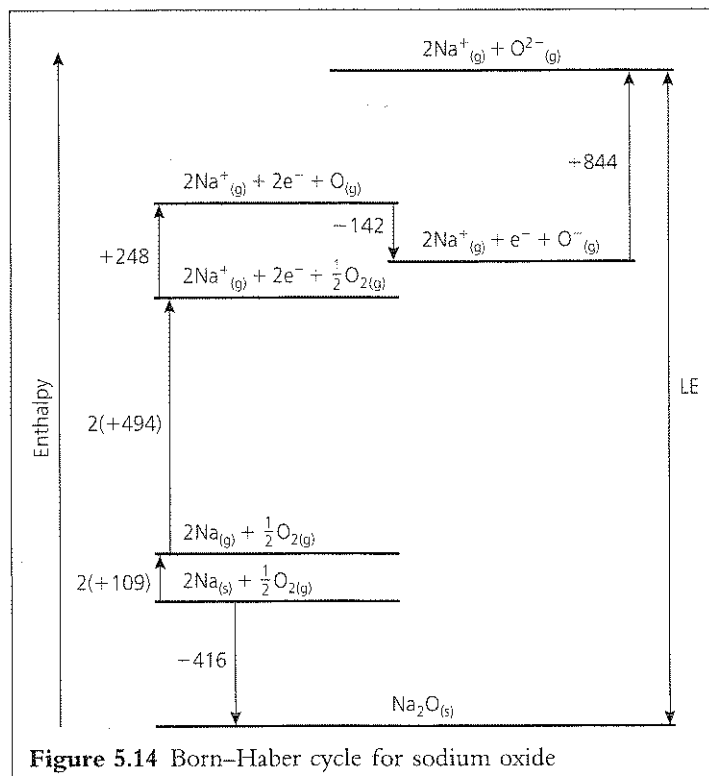


Figure 5.14 Born-Haber cycle for sodium oxide

And again, you can simply find two routes around the diagram which don't go against the flow of any arrows.

If your lattice enthalpy arrow points downwards

$$2(+109) + 2(+494) + 248 - 142 + 844 + \text{LE} = -416$$

$$\text{Solving to give: } \text{LE} = -2572 \text{ kJ mol}^{-1}$$

If your lattice enthalpy arrow points upwards

$$2(+109) + 2(+494) + 248 - 142 + 844 = -416 + \text{LE}$$

$$\text{Solving to give: } \text{LE} = +2572 \text{ kJ mol}^{-1}$$

Problem • 14

Draw a Born-Haber cycle for potassium iodide, KI, and use it to find the lattice enthalpy of KI.

Enthalpy changes of atomisation: potassium $+90 \text{ kJ mol}^{-1}$; iodine $+107 \text{ kJ mol}^{-1}$. First ionisation energy of potassium $+418 \text{ kJ mol}^{-1}$. First electron affinity of iodine -314 kJ mol^{-1} . Enthalpy change of formation of KI(s) -328 kJ mol^{-1} .

Draw a Born-Haber cycle for strontium chloride, SrCl_2 , and use it to find the enthalpy change of formation of $\text{SrCl}_2\text{(s)}$.

Enthalpy changes of atomisation: strontium $+164 \text{ kJ mol}^{-1}$; chlorine $+121 \text{ kJ mol}^{-1}$. Ionisation energies of strontium: first $+548 \text{ kJ mol}^{-1}$; second $+1060 \text{ kJ mol}^{-1}$. First electron affinity of chlorine -364 kJ mol^{-1} . Lattice enthalpy of strontium chloride

(defined in the sense $\text{Sr}^{2+}\text{(g)} + 2\text{Cl}^-\text{(g)} \rightarrow \text{SrCl}_2\text{(s)}$) $-2112 \text{ kJ mol}^{-1}$;

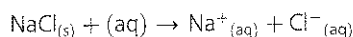
(defined in the sense $\text{SrCl}_2\text{(s)} \rightarrow \text{Sr}^{2+}\text{(g)} + 2\text{Cl}^-\text{(g)}$) $+2112 \text{ kJ mol}^{-1}$.

Problem • 15

Enthalpy changes when ionic compounds dissolve in water

Enthalpy change of solution

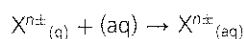
This is the enthalpy change when 1 mole of ionic substance dissolves in water to give a solution of infinite dilution. "Infinitely dilute" is not meant literally! It simply means that you have used enough water so that adding some more doesn't result in any more heat being evolved or absorbed. The equation for the reaction would be written as, for example:



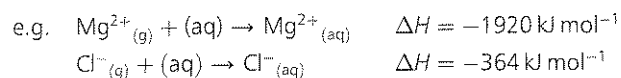
The sodium and chloride ions were already there in the crystal, of course. The process of dissolving in water frees them from the lattice and wraps them in water molecules.

Hydration enthalpy (enthalpy change of hydration)

The hydration enthalpy of an ion refers to the process:

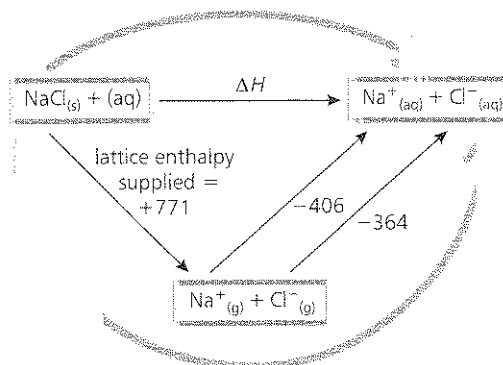


It is the enthalpy change when 1 mole of gaseous ions dissolve in sufficient water to produce an infinitely dilute solution. It applies equally to positive or negative ions, and irrespective of the number of charges – hence the symbol, $\text{X}^{n\pm}$. Hydration enthalpies are always negative. The heat is evolved because of the formation of attractive forces between the ions and water molecules.



Calculating enthalpy changes of solution

You can set up a simple Hess's Law cycle involving lattice enthalpies and hydration enthalpies. For example, for sodium chloride:



This gives

$$\begin{aligned} \Delta H &= +771 - 406 - 364 \\ \Delta H &= +1 \text{ kJ mol}^{-1} \end{aligned}$$

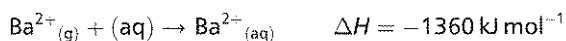
In other words, when 1 mole of sodium chloride dissolves in water to give an infinitely dilute solution, 1 kJ is absorbed from the surroundings – the solution becomes slightly colder.

Notice that whichever definition of lattice enthalpy you are working with, it is usual on these diagrams to draw the arrow from the solid to the gaseous ions – in other words, to consider how much heat you have to supply to split the lattice up, before you recover heat again as the ions become hydrated.

Nobody, of course, is suggesting that when sodium chloride dissolves in water, it first splits into gaseous ions scattered all over the universe, which then become hydrated as they dive back into the water – which is what the enthalpy changes we are using imply. We have calculated the enthalpy change using an imaginary route, but according to Hess's Law, it will produce exactly the same overall enthalpy change as the processes the ions really undergo.

Problem • 16

Calculate the enthalpy change of solution of barium chloride, BaCl_2 , given:



End of chapter checklist

Can you do the following things?

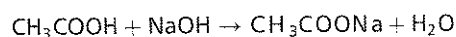
- Calculate enthalpy changes (heat evolved or absorbed) from simple experimental results.
- Relate the sign of an enthalpy change to whether it is exothermic or endothermic.
- Define the term standard as applied to enthalpy changes.
- Define the following standard enthalpy changes: formation, combustion, neutralisation, vaporisation, atomisation, solution, hydration.
- State Hess's Law.
- Define mean bond enthalpy, first (and successive) ionisation energy, first (and successive) electron affinity, lattice enthalpy.
- Use the above terms in simple calculations involving Hess's Law cycles – either as triangular (or occasionally more complicated) diagrams or as Born-Haber cycles as appropriate.

Revision problems

Numerical answers are provided for these problems, but no worked solutions.

Problem • 17

An experiment was carried out to find the enthalpy change of neutralisation of ethanoic acid with sodium hydroxide:



50 cm³ of 2.0 mol dm⁻³ sodium hydroxide solution was placed in a plastic cup and its temperature recorded. 50 cm³ of 2.0 mol dm⁻³ ethanoic acid was placed in a measuring cylinder and its temperature was recorded. The acid was added to the sodium hydroxide solution and the temperature recorded at 1 minute intervals for 5 minutes.

Results:

Temperature of sodium hydroxide solution = 19.4 °C

Temperature of ethanoic acid solution = 18.8 °C

Time (mins)	0	1	2	3	4	5
Temp of mixture (°C)		31.5	31.0	30.5	30.1	29.6

Assume that the density of all solutions is 1 g cm⁻³ and their specific heats are all 4.18 J g⁻¹ K⁻¹.

- Estimate the maximum temperature which would have been reached in the absence of any heat losses.
- Calculate the total amount of heat evolved during this reaction.
- Calculate the amount of heat evolved per mole of water formed during the neutralisation.

Problem • 18

The apparatus in Figure 5.3 was used to determine the enthalpy change of combustion of propanone, CH₃COCH₃. It was first calibrated by burning ethanol, CH₃CH₂OH, which has a known enthalpy change of combustion of -1367 kJ mol⁻¹.

Results with ethanol:

Mass of water	= 250 g
Original temperature of water	= 18.5 °C
Final temperature of water	= 23.3 °C
Original mass of burner + ethanol	= 48.295 g
Final mass of burner + ethanol	= 48.100 g

Results with propanone:

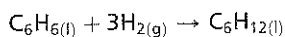
Mass of water	= 250 g
Original temperature of water	= 19.2 °C
Final temperature of water	= 23.5 °C
Original mass of burner + propanone	= 49.623 g
Final mass of burner + propanone	= 49.454 g

- Use the ethanol results to calculate the heat capacity of the apparatus in kJ °C⁻¹.
- Calculate the enthalpy change of combustion of propanone.

(H = 1; C = 12; O = 16)

Problem • 19

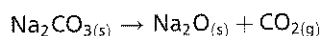
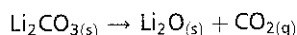
Calculate the enthalpy change of hydrogenation of benzene to cyclohexane:



Standard enthalpy changes of combustion in kJ mol^{-1} : benzene -3267 , hydrogen -286 , cyclohexane -3920 .

Problem • 20

Calculate the enthalpy changes for the thermal decomposition of (a) lithium carbonate, (b) sodium carbonate.



Standard enthalpy changes of formation in kJ mol^{-1} : lithium carbonate -1216 , lithium oxide -598 , sodium carbonate -1131 , sodium oxide -414 , carbon dioxide -394 .

Problem • 21

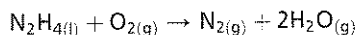
Calculate the standard enthalpy change of formation of ethanol, $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$, from the following standard enthalpy changes of combustion (all in kJ mol^{-1}): carbon -394 , hydrogen -286 , ethanol -1367 .

Problem • 22

Calculate the standard enthalpy change of combustion of ethyne, $\text{C}_2\text{H}_2(\text{g})$, from the following data (all in kJ mol^{-1}): standard enthalpy change of formation of ethyne $+228$; standard enthalpy changes of combustion: hydrogen -286 , carbon -394 .

Problem • 23

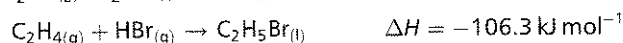
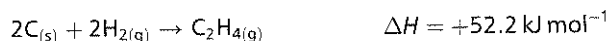
Hydrazine, $\text{N}_2\text{H}_4(\text{l})$, is used as a rocket fuel. It burns in oxygen to produce nitrogen and steam:



- (a) Calculate the enthalpy change when 1 mole of hydrazine burns. Standard enthalpy changes of formation (in kJ mol^{-1}): hydrazine $+50.6$, $\text{H}_2\text{O}(\text{g})$ -242 .
- (b) How much heat is evolved if 1 tonne of hydrazine burns completely in this way? ($\text{H} = 1$; $\text{N} = 14$. 1 tonne = 1000 kg.)

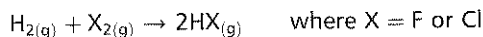
Problem • 24

Calculate the enthalpy change of formation of bromoethane, $\text{C}_2\text{H}_5\text{Br}(\text{l})$, from the following data:



Problem • 25

Estimate the enthalpy change for the reactions between hydrogen and the halogens, fluorine and chlorine:



Bond enthalpies (in kJ mol^{-1}): $\text{H}-\text{H} +436$, $\text{F}-\text{F} +158$, $\text{Cl}-\text{Cl} +243$, $\text{H}-\text{F} +568$, $\text{H}-\text{Cl} +432$