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AS LEVEL

5 Chemical energetics

Almost all chemical reactions are accompanied by energy changes as bonds are broken and formed. Usually the energy changes involve heat, but they can also involve sound, light or even electrical energy.

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1 Think of some examples of chemical reactions that transfer:
 a sound **b** light **c** electrical energy

Exothermic and endothermic reactions

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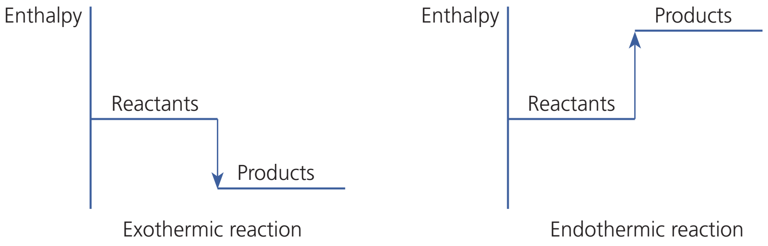
We are most familiar with reactions that give out heat – a test tube gets warmer or a fuel is burned. These are called **exothermic** reactions. A smaller number of reactions take in energy overall and these are known as **endothermic** reactions. The overall energy changes in these two types of reaction are shown in the reaction pathway diagrams in Figure 5.1.



▲ **Figure 5.1 Energy changes in an exothermic and an endothermic reaction**

The vertical (*y*) axes in Figure 5.1 represent the enthalpy (see below) of the compounds. From the figure:

- You can see that in an exothermic reaction the enthalpy change is in the negative direction. This is worth remembering because exothermic reactions always show a negative enthalpy change.
- You can see that it follows that endothermic reactions always show a positive enthalpy change. Enthalpy changes are measured in $\mathrm{kJ\,mol^{-1}}$.

In order to make sense of what happens in a chemical reaction, consider **standard conditions**. Using such conditions means that the results of measurements are reproducible.

Standard conditions are:

- All the reactants and products are in their most stable state.
- The pressure is 1 atmosphere.
- The temperature is specified (usually 298 K, 25°C).

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2 Sketch a reaction pathway diagram of an **exothermic reaction**.
 Label the activation energy for the reaction *A* and the overall energy change *E*.

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Enthalpy changes

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In textbooks you will see references made both to *energy changes* and to *enthalpy changes* – it is important to understand the difference in the way these are used in questions and in the syllabus. **Enthalpy changes** always refer to particular sets of conditions.

The examples that follow outline the specific enthalpy changes you need to know about.

The sorts of reactions for which you may need to measure or calculate the enthalpy change are as shown in Table 5.1.

KEY TERM

A standard enthalpy change refers to the energy transferred at 298 K and standard pressure (usually 1 atmosphere or 100 kPa, although some textbooks refer to 1 atmosphere as 101 kPa).

▼ Table 5.1

Enthalpy change	Definition	Example
Reaction, $\Delta H^\ominus_r$	The enthalpy change when moles of the reactants as shown in the equation are completely converted into products under standard conditions	$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
Formation, $\Delta H^\ominus_f$	The enthalpy change when 1 mole of a substance is formed from its elements under standard conditions	$2Li(s) + \frac{1}{2}O_2(g) \rightarrow Li_2O(s)$
Combustion, $\Delta H^\ominus_c$	The enthalpy change when 1 mole of a substance is completely burnt in oxygen under standard conditions	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
Neutralisation, $\Delta H^\ominus_{neut}$	The enthalpy change when an acid is neutralised by an alkali to produce 1 mole of water under standard conditions	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Another enthalpy change you need to understand is **bond energy**, which was described in Chapter 3. This was expressed as the energy needed to *break* a bond, so it was energy supplied. This means that ΔH is positive.

We generally use **average bond energy** (the energy change, E(X–Y), when one mole of bonds between atoms X and Y are broken in the gas phase. We use this because if a molecule contains more than two atoms the bonds can have slightly different energies depending on their environment in the molecule.

Practical work

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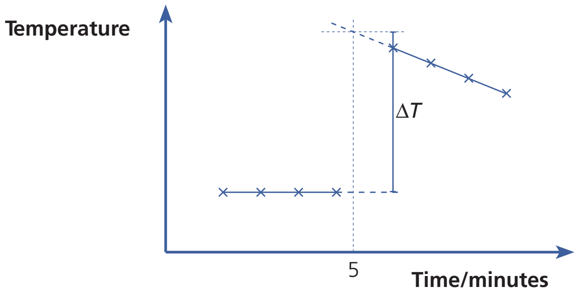
Some of the enthalpy changes described here can be measured practically, but others have to be determined indirectly using other measurements.

SAMPLE PRACTICAL TO MEASURE Δ*H*

- A known volume of an acid of known concentration is poured into an insulated cup.
- The temperature of the acid is measured every minute for 4 minutes.
- At the fifth minute a known volume of alkali of similar concentration is poured into the cup.
- The temperature is then measured every 30 seconds for the next 3 minutes.
- A graph of temperature against time is plotted (like that in Figure 5.2).



▲ Figure 5.2

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- The higher temperature line is extrapolated back to minute 5 to correct for any heat loss from the apparatus.
- The enthalpy change, ΔH, is calculated from $mc\Delta T$, where m is the mass of solution (for dilute solutions this is the same as its volume), c is the specific heat capacity of the solution (usually taken to be that of water) and ΔT is the temperature change based on the extrapolated value.
- The enthalpy change per mole of water formed is then calculated in kilojoules.

This basic method can be used for determining different enthalpy changes.

WORKED EXAMPLE

In an experiment to determine the heat of combustion, $\Delta H^{\ominus}_{c}$, of propan-1-ol, C_3H_7OH, the following readings were obtained. Calculate $\Delta H^{\ominus}_{c}$ for propan-1-ol.

mass of water in the calorimeter = 200 g

mass of propan-1-ol plus burner at start = 512.65 g

mass of propan-1-ol plus burner at end = 511.93 g

temperature of water at start = 19.6°C

temperature of water at end = 33.3°C

Answer

We will ignore the heat taken in by the calorimeter.

temperature rise of water = 13.7°C

$q = mc\Delta T$

The symbol c denotes the amount of energy needed to raise the temperature of water by one degree. This is called the **specific heat capacity** and has a value of $4.18\,\mathrm{J\,g^{-1}\,K^{-1}}$.

$q = 200 \times 4.18 \times 13.7 = 11\,453\,\mathrm{J}$

mass of propan-1-ol burned = 0.72 g

$M_r\,(C_3H_7OH) = 60$

The amount of propan-1-ol burned = $\frac{0.72}{60} = 0.012\,\mathrm{mol}$

Heat is evolved so the reaction is exothermic and $\Delta H^{\ominus}_{c}$ is negative.

$$\Delta H^{\ominus}_{c} = \frac{11\,453}{0.012} = -954\,\mathrm{kJ\,mol^{-1}}$$

Hess's law

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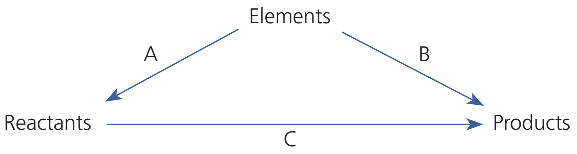
Hess's law states:

- The enthalpy change for a chemical process X → Y is the same whichever route is taken from X to Y, provided that the states of X and Y are the same in all routes.
- Using standard enthalpy changes avoids this problem because the states of X and Y are defined.

Hess's law can be used when it is difficult to measure an enthalpy change experimentally. Other data can be used to calculate this.

For example, the enthalpy of reaction can be calculated using enthalpies of formation (Figure 5.3).



▲ **Figure 5.3 The enthalpy change labelled A is (sum of the enthalpies of formation of the reactants), B is (sum of the enthalpies of formation of the products), C is therefore (B – A)**

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Exam-style questions and answers

In this section is a sample examination paper – similar to the Cambridge International Examinations AS Chemistry Paper 2. All the questions are based on the topic areas described in the previous parts of the book. You have 1 hour and 15 minutes to complete the AS paper. There is a total of 60 marks, so you can spend just over 1 minute per mark.

Some of the questions require you to recall information you have learned. Be guided by the number of marks awarded to suggest how much detail to give in each answer. The more marks there are, the more information you need to give. Some questions require you to use your knowledge and understanding in new situations.

You might find something *completely* new in a question – something you have not seen before. Just think about it carefully and recall something that you do know that will help you to answer it. Make sure that you look carefully at the information provided in the question – it will have been included for a reason!

The best answers are short and relevant – if you target your answer well, you can score a lot of marks for a small amount of writing. Do not say the same thing several times over or wander off into answers that have nothing to do with the question. As a general rule, there will be twice as many answer lines as marks. Try to answer a 3-mark question in no more than six lines of writing. If you are writing much more than that, you almost certainly haven't focused your answer tightly enough.

Look carefully at exactly what each question wants you to do. For example, if it asks you to 'Explain' then you need to say *how* or *why* something happens – not just *describe* what happens. Many students lose many marks because they do not read questions carefully.

Following each question in this part, there is an Answer A which might achieve a C or D grade, and an Answer B which might achieve an A or B grade. The answers are followed by typical examiner comments.

AS exemplar paper

QUESTION 1

The first six ionisation energies of an element, X, are given in the table.

Ionisation energy/kJ mol^{-1}					
First	**Second**	**Third**	**Fourth**	**Fifth**	**Sixth**
550	1064	4210	5500	6908	8761

a Define the term 'first ionisation energy'. (3 marks)

b Write an equation, with state symbols, for the third ionisation energy of element X. (2 marks)

c Use the data provided to deduce in which group of the Periodic Table element X is placed. Explain your answer. (3 marks)

The first ionisation energies of the Group 14 elements are given below.

Element	C	Si	Ge	Sn	Pb
1st IE/kJ mol^{-1}	1086	789	762	709	716

d Use your knowledge of the atomic structure of these elements to explain the trend in ionisation energies. (3 marks)

Total: 11 marks

ANSWER A

a It is the energy required to convert one mole of atoms ✗ of an element into one mole of cations, ✗ with each atom losing one electron. ✓

e There are two errors in this definition. The student fails to refer to the gaseous state of both the atoms and cations.

b $X(g) - 3e^- \rightarrow X^{3+}(g)$ ✗✓

e The student has confused the third ionisation energy with the loss of three electrons. The state symbols are correct, for 1 mark.

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c X is in Group 2 of the Periodic Table. ✓

This correctly states that X is in Group 2. However, the student has not explained the evidence and so loses 2 of the 3 available marks.

d The atoms are getting bigger, so the electrons are further from the nucleus making them easier to remove ✓. The outer electrons are screened from the nuclear charge. ✓

This is a fairly good answer. However, there is no mention of the increasing nuclear charge.

ANSWER B

a This is the energy needed to remove one electron from each ✓ of 1 mole of gaseous atoms ✓ of an element to form 1 mole of gaseous cations. ✓

This good answer gives all three points in the mark scheme.

b $X^{2+}(g) - e^- \rightarrow X^{3+}(g)$ ✓✓

The equation is correct, as are the state symbols.

c X is in Group 2 of the Periodic Table ✓. There is a large jump in energy to remove the third electron, ✓ which is from a full shell. ✓

This very good answer uses the data in the table and the student's own knowledge of the arrangement of electrons in atoms.

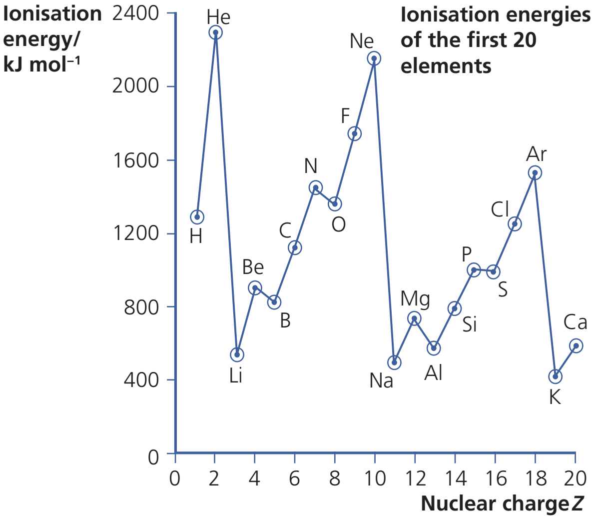
d There are two effects here. First, the atoms are getting bigger, so the electrons are further from the nucleus making them easier to remove. ✓ Second, the outer electrons are screened from the nuclear charge, reducing its pull on them. ✓

This is a good answer. However, the student has not mentioned that these two effects outweigh the increasing nuclear charge and so fails to score the third mark.

QUESTION 2

The modern Periodic Table is based on one proposed by Mendeleev following his observations of patterns in the chemical properties of the elements.

The diagram shows the first ionisation energies of the first 20 elements in the Periodic Table.



a Look at the section of the diagram from Li to Ne. Explain why there is a general increase in first ionisation energy. (3 marks)

b Explain why the first ionisation energy of the third element in each period (B and Al) is lower than that of the second elements (Be and Mg). (2 marks)

c Explain why the first ionisation energy of oxygen is lower than that of nitrogen. (2 marks)

d **i** Explain why the first ionisation energy of potassium is lower than that of sodium. (1 mark)

ii Describe a chemical reaction that illustrates the effect this has on the reactivity of the two elements. (2 marks)

e When Mendeleev produced his table, he did not include the noble gas (Group 18) elements. Suggest why. (1 mark)

Total: 11 marks