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.

NOW TEST YOURSELF

1 Think of some examples of chemical reactions that transfer:

  a sound

  b light

  c electrical energy

Exothermic and endothermic reactions

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.

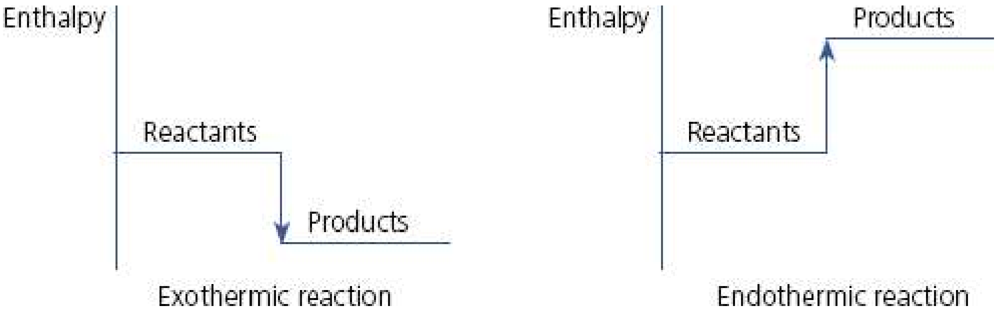

Figure 5.1 Energy changes in an exothermic and an endothermic reaction

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 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).

NOW TEST YOURSELF

2 Sketch a reaction pathway diagram of an **exothermic reaction**.

Label the activation energy for the reaction *A* and the overall energy change *E*.

Enthalpy changes

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.

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).

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.

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	$2Li(s) + ½O_2(g) \rightarrow Li_2O(s)$
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

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 ΔH

- 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).

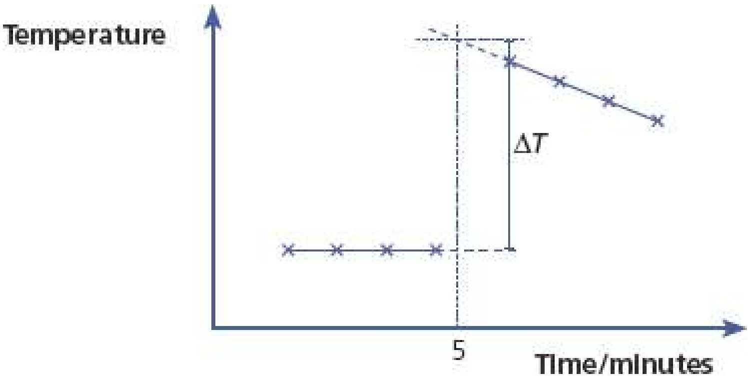

Figure 5.2

- 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 J g^{-1} K^{-1}.

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

mass of propan-1-ol burned = 0.72 g

M_r (C_3H_7OH) = 60

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

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

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

Hess's law

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).

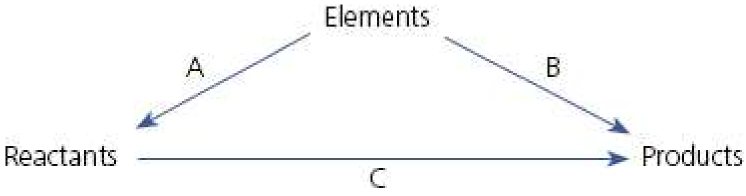

Figure 5.3 The enthalpy change labelled A is (sum of the enthalpies of formation of the reactants), B is (sum of the enthalpies of formation of the products), C is therefore (B − A)

You can see how this works in practice from an example.

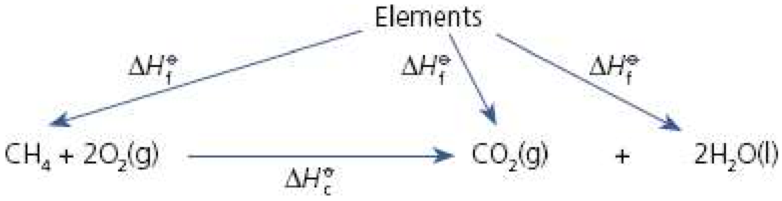

Figure 5.4

Figure 5.4 shows how the enthalpy change for the combustion of methane, CH_4, can be calculated using the enthalpies of formation of methane, carbon dioxide and water.

$$\Delta H^\ominus{}_c(CH_4) = \Delta H^\ominus{}_f(CO_2) + 2\Delta H^\ominus{}_f(H_2O) - \Delta H^\ominus{}_f(CH_4)$$

Inserting the values of $\Delta H^\ominus{}_f$ for the three compounds gives:

$$\begin{aligned}\Delta H^\ominus{}_c(CH_4) &= -393.5 + 2(-285.8) - (-74.8)\\ &= -393.5 - 571.6 + 74.8\\ &= -890.3\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

Reverse calculations to determine the enthalpy of formation of a compound using enthalpy of combustion data can also be done.

NOW TEST YOURSELF

3 Figure 5.5 shows a Hess's law diagram to determine the enthalpy of formation of ethane, C_2H_6.

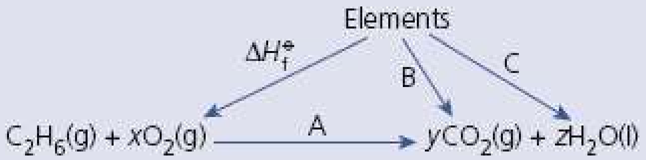

Figure 5.5

a What are the enthalpy changes represented by A, B and C?

b What are the numbers of moles represented by x, y and z?

c Write an expression to calculate the enthalpy of formation of ethane from the other enthalpies you have identified.

Average bond energies

Hess's law can be used to find approximate values for $\Delta H^{\ominus}$ using average bond energies (sometimes referred to as mean bond enthalpies). These average bond energies are determined from bonds in a variety of molecules. There is a list of those you are likely to need in the syllabus.

The Hess's law diagram for use with bond energies is shown in Figure 5.6.

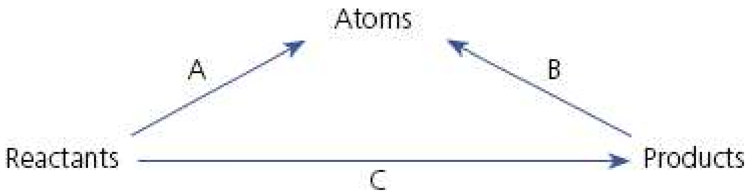

Figure 5.6 The enthalpy change labelled A is the sum of the bond energies of the reactants, B is the sum of the bond energies of the products, C is therefore (A − B)

Note that bond energies are always endothermic, i.e. they are *positive*.

When using bond energies it is useful to remember the following:

- Write the reaction using structural formulae so that you can see all the bonds present.

- Ignore bonds or groups of bonds that are unchanged in the reaction.
- Remember to indicate the sign of the bond energy for any bonds formed.

Why are some bonds stronger than others?

In Chapter 3 we saw that the strengths of covalent bonds depend on the degree of overlap between the atomic orbitals on adjacent atoms. Shorter bonds are always stronger than longer ones, and double bonds are always stronger than single bonds. For similar bonds, such as H–F and H–Cl, the weaker the bond, the more reactive it is. So HCl is a stronger acid (forming H^+ and Cl^-) than HF.

Remember that you need to compare the same type of bonds. C=C is more reactive than C–C because the weaker π-bond breaks first.

Activation energy

Remember, even with strongly exothermic reactions, such as the burning of magnesium, the reaction does not happen immediately when magnesium is exposed to air.

In order to start the reaction the magnesium has to be heated, i.e. it has to be provided with energy. This is called the **activation energy** (see also page **59**).

Reactions can be summarised in diagrammatic form, as shown in Figure 5.7.

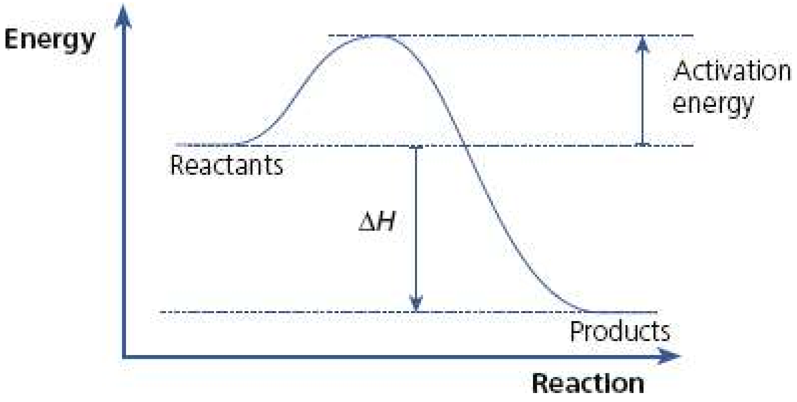

Figure 5.7 Activation energy

NOW TEST YOURSELF

4 The enthalpy of combustion, $\Delta H^{\ominus}_c$ of methane, CH_4, is −890 kJ mol^{-1}.

Sketch a reaction pathway diagram including the starting materials, products, activation energy, E_a, and the enthalpy of combustion, $\Delta H^{\ominus}_c$

REVISION ACTIVITY

a Identify the types of enthalpy changes shown in these equations:

i $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

ii $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

iii $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

b Sketch a Hess's law cycle to show how you could work out the enthalpy of combustion, $\Delta H^{\ominus}_c$ of ethane, C_2H_6.

c Use the following data to calculate the enthalpy of combustion, $\Delta H^{\ominus}_c$ of ethane:

$\Delta H^{\ominus}_f[CO_2] = -393.5\,kJ\,mol^{-1}$; $\Delta H^{\ominus}_f[H_2O] = -241.8\,kJ\,mol^{-1}$;
$\Delta H^{\ominus}_f[C_2H_6] = -84.7\,kJ\,mol^{-1}$.

END OF CHAPTER CHECK

By now you should be able to:

- understand enthalpy changes, Δ*H*, and bond energies
- construct and use reaction pathway diagrams and calculate enthalpy changes
- apply Hess's law and calculate enthalpy changes using energy cycles