Using the [M + 1] peak

There will always be a very small peak just beyond the molecular ion peak at a mass of [M + 1]. This is caused by molecules in which one of the carbon atoms is the ^{13}C isotope. This is shown in the mass spectrum of ethanol in Figure 3.10.
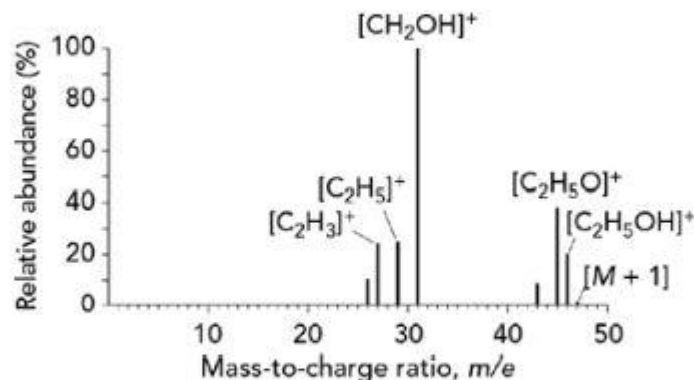

Figure 3.10: The mass spectrum of ethanol, showing the [M + 1] peak.

In any organic compound there will be 1.10% carbon-13. We can use this fact to work out the number of carbon atoms (n) in a molecule. We apply the equation:

$$n = \frac{100}{1.1} \times \frac{\text{abundance of } [M+1]^+ \text{ ion}}{\text{abundance of } M^+ \text{ ion}}$$

1 An unknown compound has a molecular ion peak, M^+, with a relative abundance of 54.5% and has an $[M + 1]^+$ peak with a relative abundance of 3.6%. How many carbon atoms does the unknown compound contain?

Solution

Substituting the values of relative abundance into the equation:

$$n = \frac{100}{1.1} \times \frac{\text{abundance of } [M+1]^+ \text{ ion}}{\text{abundance of } M^+ \text{ ion}}$$

we get:

$$n = \frac{100}{1.1} \times \frac{3.6}{54.5} = 6.0$$

There are 6 carbon atoms in each molecule.

Question

4 A hydrocarbon has a molecular ion peak at a mass-to-charge ratio of 84 (relative abundance of 62.0%) and an $[M + 1]$ peak with a relative abundance of 4.1%.

How many carbon atoms are in the hydrocarbon?

Using [M + 2] and [M + 4] peaks

Note: Material relating to [M + 4] peaks is extension content. It is not part of the syllabus.

We can tell whether there is chlorine or bromine in an organic compound by comparing the relative heights of the M and [M + 2] peaks. If the peak heights are equal, there is one atom of bromine per molecule. If the peak heights are in the ratio 3 [M] to 1 [M + 2], there is one atom of chlorine per molecule.

If the sample compound contains chlorine or bromine atoms, we also get peaks beyond the molecular ion peak because of isotopes of chlorine and bromine. Chlorine has two isotopes, ^{35}Cl and ^{37}Cl, as does bromine, ^{79}Br and ^{81}Br. Table 3.4 shows the approximate percentage of each isotope in naturally occurring samples.

Ionic or covalent?

The most commonly used scale of electronegativity values is called the Pauling electronegativity scale, N_P. Table 4.3 shows some Pauling electronegativity values.

Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0

Table 4.3: Some Pauling electronegativity values.

Note:

- carbon ($N_P = 2.5$) and hydrogen ($N_P = 2.1$) have electronegativities that are lower than those of many other non-metallic elements
- Pauling electronegativity has no units.

Differences in electronegativity values can be used to predict whether a simple compound has ionic or covalent bonds.

- If the electronegativity difference is high, e.g. 2.0 or more, the compound is likely to be ionic. E.g. sodium chloride: Na = 0.9, Cl = 3.0. Difference = 2.1.
- If the electronegativity difference is lower, e.g. below 1.0, the compound is likely to be covalent. E.g. methane: C = 2.5, H = 2.1. Difference = 0.4.
- A zero value shows that there is no ionic character in the bond, e.g. Cl–Cl.
- Some compounds are not entirely covalent and have some ionic character in them. These have intermediate electronegativity differences, e.g. 1.0.

Polarity in molecules

When the electronegativity values of the two atoms forming a covalent bond are the same, the pair of electrons is equally shared. We say that the covalent bond is *non-polar*. For example, hydrogen (H_2), chlorine (Cl_2) and bromine (Br_2) are non-polar molecules.

When a covalent bond is formed between two atoms having different electronegativity values, the more electronegative atom attracts the pair of electrons in the bond towards it.

As a result:

- the centre of positive charge does not coincide with the centre of negative charge
- we say that the electron distribution is asymmetric
- the two atoms are partially charged
- we show:

  - the less electronegative atom with the partial charge δ+ ('delta positive')
  - the more electronegative atom with the partial charge δ– ('delta negative')

- we say that the bond is *polar* (or that it has a dipole).

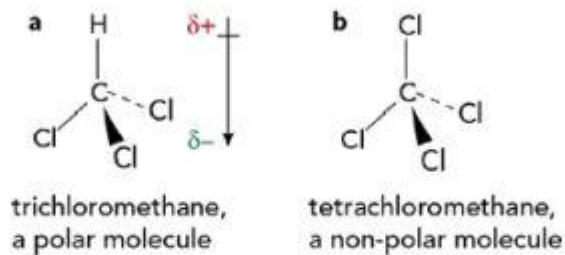Figure 4.32 shows the polar bond in a hydrogen chloride molecule.

a
H

$\delta+$

$\overset{|}{\underset{\overset{|}{C}{}}{C}}$

Cl⋯C⋯Cl

Cl

Cl

$\delta-$

trichloromethane,
a polar molecule

b
Cl

C⋯Cl

Cl

Cl

tetrachloromethane,
a non-polar molecule

Figure 4.33: The polarity of **a** trichloromethane and **b** tetrachloromethane.

IMPORTANT

Remember that not all molecules with polar bonds are polar molecules. Sometimes the polar bonds cancel each other out because the same types of bonds have dipoles 'pulling' in opposite directions.

4.8 Hydrogen bonding

> **Note:** Learners are only expected to describe hydrogen bonding in relation to molecules containing N–H and O–H. The material in this section relating to the F–H group is extension material, and is not on the syllabus.

Hydrogen bonding is the strongest form of intermolecular bonding. It is a type of permanent dipole–permanent dipole bonding.

For hydrogen bonding to occur between two molecules we need:

- one molecule to have a hydrogen atom covalently bonded to F, O or N (the three most electronegative atoms)
- a second molecule to have an F, O or N atom with an available lone pair of electrons.

For hydrogen bonding to happen the molecules must have:

- a H atom covalently bonded to a highly electronegative atom, e.g. N, O or F
- another highly electronegative atom with a lone pair of electrons.

When a hydrogen atom is covalently bonded to a very electronegative atom, the bond is very highly polarised. The δ+ charge on the hydrogen atom is high enough for a bond to be formed with a lone pair of electrons on the F, O or N atom of a neighbouring molecule (Figure 4.41).

Figure 4.41: Hydrogen bonding between two ammonia molecules. A hydrogen bond is represented by a line of dots.

The state of a substance at room temperature and pressure depends on its structure and bonding. Four types of structure are found in elements and compounds:

- simple molecular or simple atomic, e.g. carbon dioxide, argon

- giant ionic, e.g. sodium chloride

- giant metallic, e.g. iron, copper

- giant molecular, e.g. silicon(IV) oxide.

The general gas equation

For an ideal gas, we can combine the laws about how the volume of a gas depends on temperature and pressure. We also know from Section 3.8 that the volume of a gas is proportional to the number of moles present. Putting all these together, gives us the ideal gas equation:

$pV = nRT$

p is the pressure in pascals, Pa

V is the volume of gas in cubic metres, m^3 ($1\ m^3 = 1000\ dm^3$)

n is the number of moles of gas $\left(n = \dfrac{m}{M_t} \right)$

R is the gas constant, which has a value of 8.31 J K^{-1} mol^{-1}

T is the temperature in kelvin, K.

Calculations using the general gas equation

If we know any four of the five physical quantities in the general gas equation, we can calculate the fifth.
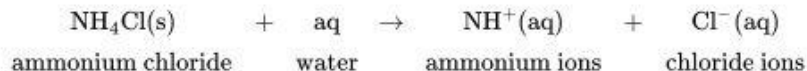
We describe chemical reactions that absorb heat energy from the surroundings as endothermic. In an **endothermic reaction**, the temperature of the surroundings decreases (Figure 6.2). For example, when sodium hydrogencarbonate reacts with an aqueous solution of citric acid in a test-tube, the temperature of the reaction mixture in the tube decreases because the citric acid and sodium hydrogencarbonate are absorbing the heat energy from the solvent, the test-tube and the air.

Figure 6.2: Using a cooling pack to treat a sports injury. When you rub or press the pack, water and ammonium chloride crystals mix. As the crystals dissolve, energy is transferred from the surroundings, cooling the injury.

Other examples of endothermic reactions include:

- the decomposition of limestone by heating (all thermal decomposition reactions are endothermic)
- photosynthesis (in which the energy is supplied by sunlight)
- dissolving certain ammonium salts in water

$$NH_4Cl(s) \quad + \quad aq \quad \rightarrow \quad NH^+(aq) \quad + \quad Cl^-(aq)$$

ammonium chloride   water   ammonium ions   chloride ions

For an exothermic reaction, energy is released to the surroundings. So the enthalpy of the reactants must be greater than the enthalpy of the products. We can see from the reaction pathway diagram for the combustion of methane (Figure 6.3) that $H_{products} - H_{reactants}$ is negative.
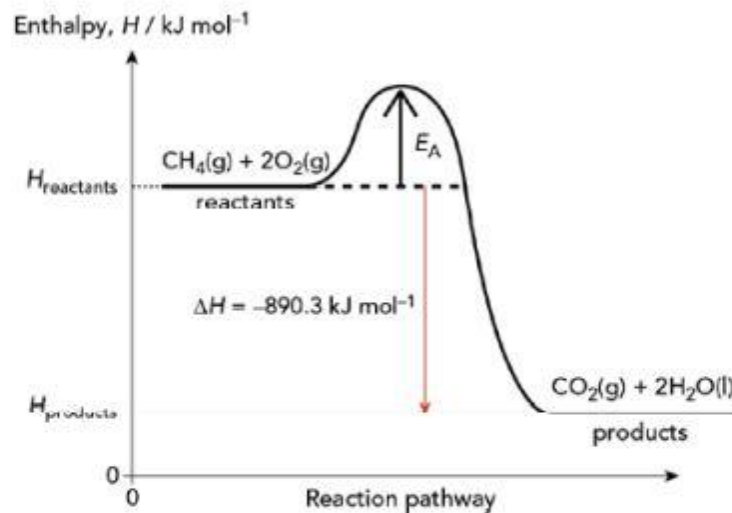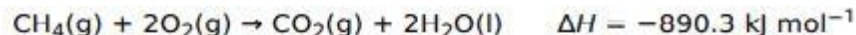

Figure 6.3: Reaction pathway diagram for the combustion of methane.

We can include this information in the equation for the reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.3 \text{ kJ mol}^{-1}$$

The negative sign shows that the reaction is *exothermic*.

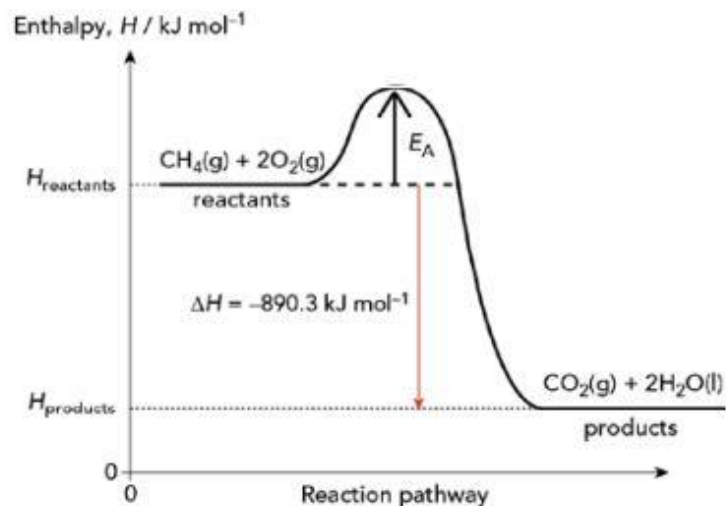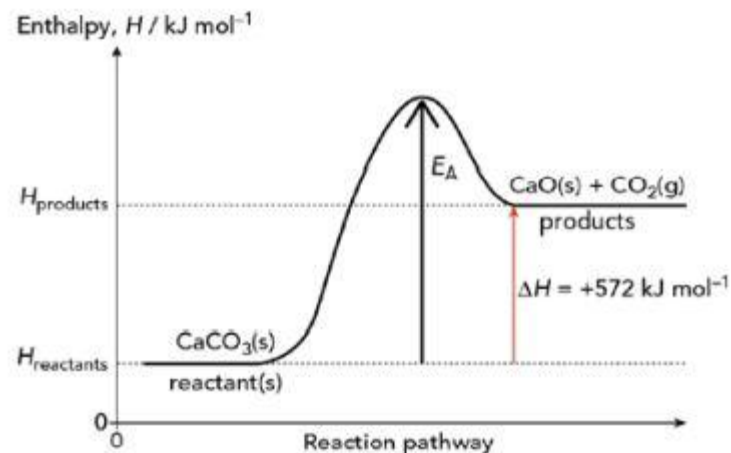For an endothermic reaction, energy is absorbed from the surroundings by the substances in the reaction.

For an exothermic reaction, heat is lost from the reactants. The value of ΔH is negative.

For an endothermic reaction, heat is gained by the reactants. The value of ΔH is positive.

1　When drawing reaction pathway diagrams, remember that the activation energy arrow should start at the level of the reactants and end at the highest point on the energy hump.

2　When drawing the arrow for ΔH make sure that the arrow points downwards for an exothermic reaction and upwards for an endothermic reaction.

Enthalpy, H / kJ mol^{-1}

E_A

$H_{products}$ .... $CaO(s) + CO_2(g)$
products

$\Delta H = +572$ kJ mol^{-1}

$CaCO_3(s)$
reactant(s)

$H_{reactants}$ ....

0
0
Reaction pathway

Enthalpy, H / kJ mol^{-1}

$CH_4(g) + 2O_2(g)$
reactants

E_A

$H_{reactants}$ ....

$\Delta H = -890.3$ kJ mol^{-1}

$H_{products}$ .... $CO_2(g) + 2H_2O(l)$
products

0
0
Reaction pathway

6.2 Standard enthalpy changes

Standard conditions

To make any comparison of enthalpy changes a fair comparison, we must use the same conditions, called standard conditions. These are:

- a pressure of 101 kPa (1.01×10^5 Pa, approximately normal atmospheric pressure)
- a temperature of 298 K (25 °C) (add 273 to the Celsius temperature to convert a temperature into kelvin)
- each substance involved in the reaction is in its normal physical state (solid, liquid or gas) at 101 kPa and 298 K.

The symbol $\ominus$ is used to indicate that the enthalpy change refers to a reaction carried out under standard conditions.

The information in the equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\ominus = -890.3 \text{ kJ mol}^{-1}$$
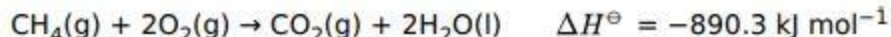
A variety of enthalpy changes

We can describe enthalpy changes according to the type of chemical reaction taking place. For example:

- enthalpy change of formation
- enthalpy change of combustion
- enthalpy change of neutralisation.

In more general cases we can use the term:

- enthalpy change of reaction.

Standard enthalpy change of reaction, $\Delta H_r^{\ominus}$

The **standard enthalpy change of reaction, $\Delta H_r^{\ominus}$** is the enthalpy change when the amounts of reactants shown in the stoichiometric equation react to give products under standard conditions. The reactants and products must be in their standard states.

The symbol for standard enthalpy change of reaction is $\Delta H_r^{\ominus}$. Enthalpy changes of reaction can be exothermic or endothermic.

The equation that describes the reaction must be given. For example, the equation:

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta H_r^{\ominus} = -286 \text{ kJ mol}^{-1}$$
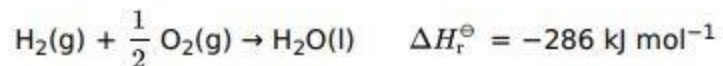
shows us the enthalpy change when one mole of water is formed from hydrogen and oxygen. In this case, 286 kJ of energy is released.
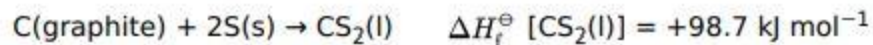
However, if we write the equation as:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H_r^{\ominus} = -572 \text{ kJ}$$

two moles of water are formed from hydrogen and oxygen. In this case, 572 kJ of energy is released.

Standard enthalpy change of formation, $\Delta H_f^{\ominus}$

The **standard enthalpy change of formation,** $\Delta H_f^{\ominus}$ is the enthalpy change when one mole of a compound is formed from its elements under standard conditions. The reactants and products must be in their standard states.

The symbol for standard enthalpy change of formation is $\Delta H_f^{\ominus}$. Enthalpy changes of formation can be exothermic or endothermic. We write the formula of the compound in square brackets after $\Delta H_f^{\ominus}$ to help us when we do calculations involving enthalpy changes. Examples are:

$$2Fe(s) + 1\frac{1}{2}\,O_2(g) \rightarrow Fe_2O_3(s) \qquad \Delta H_f^{\ominus}\,[Fe_2O_3(s)] = -824.2 \text{ kJ mol}^{-1}$$

$$C(graphite) + 2S(s) \rightarrow CS_2(l) \qquad \Delta H_f^{\ominus}\,[CS_2(l)] = +98.7 \text{ kJ mol}^{-1}$$
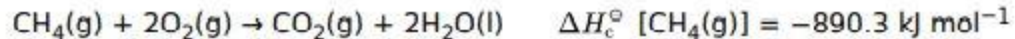
Note that the state symbol for carbon is shown as 'graphite'. This is because there are several forms of carbon but the most stable is graphite. We choose the most stable form when writing equations where enthalpy changes are shown.

By definition, the standard enthalpy change of formation of any element in its standard state is zero.

Standard enthalpy change of combustion, $\Delta H_c^{\ominus}$

The **standard enthalpy change of combustion, $\Delta H_c^{\ominus}$** is the enthalpy change when one mole of a substance is burnt in excess oxygen under standard conditions. The reactants and products must be in their standard states.

The symbol for standard enthalpy change of combustion is $\Delta H_c^{\ominus}$. Enthalpy changes of combustion are always exothermic. The substances combusted can be either elements or compounds.

$$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H_c^{\ominus} \text{ [S(s)]} = -296.8 \text{ kJ mol}^{-1}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c^{\ominus} \text{ [CH}_4(g)] = -890.3 \text{ kJ mol}^{-1}$$

Note that the first equation can be considered as either the enthalpy change of combustion of sulfur or the enthalpy change of formation of sulfur dioxide.
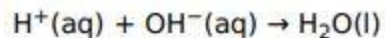
Standard enthalpy change of neutralisation, $\Delta H^{\ominus}_{\text{neut}}$

The **standard enthalpy change of neutralisation,** $\Delta H^{\ominus}_{\text{neut}}$ is the enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions.

For example:

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\Delta H^{\ominus}_{\text{neut}} = -57.1 \text{ kJ mol}^{-1}$
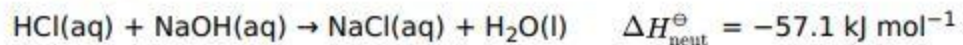
For any acid–alkali reaction the ionic equation is:

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

6.3 Measuring enthalpy changes

We can measure the enthalpy change of some reactions by different techniques.

We can measure the enthalpy change of some reactions by a technique called *calorimetry*. The apparatus used is called a *calorimeter*. A simple calorimeter can be a polystyrene drinking cup (Figure 6.5), a vacuum flask or a metal can.
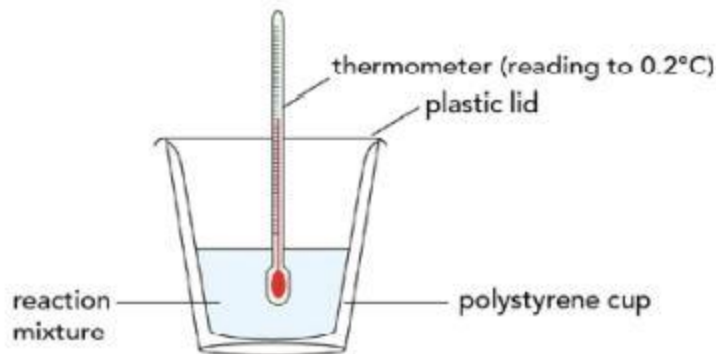

Figure 6.5: A polystyrene cup can act as a calorimeter for finding some enthalpy changes.

Calorimetry relies on the fact that it takes 4.18 J of energy to increase the temperature of 1 g of water by 1 °C. The energy required to raise the temperature of 1 g of a substance by 1 °C (1 K) is called the **specific heat capacity, c,** of the liquid. So, the specific heat capacity of water is $4.18\ \mathrm{J\,g^{-1}\,{}^{\circ}C^{-1}}$.

The energy transferred as heat is given by the relationship:

$$q = mc\Delta T$$

where:

q is the heat transferred, in J

m is the mass of water, in g

c is the specific heat capacity, in $\mathrm{J\,g^{-1}\,{}^{\circ}C^{-1}}$

ΔT is the temperature change, in °C

As 1 cm^3 of water weighs 1 g, we can substitute volume of water in cm^3 of water for mass of water in g in the equation. Aqueous solutions of acids, alkalis and salts are assumed to be largely water.

With solutions we make the assumptions that:

- 1 cm^3 of solution has a mass of 1 g
- the solution has the same specific heat capacity as water.

The heat transferred for a known number of moles of reactants in the calorimeter is given by

$$q = mc\Delta T$$

We can scale this up to get the enthalpy change per mole of defined reactant or product. The relationship we then use is

$$\Delta H = -mc\Delta T$$

Note: A rise in temperature is given a positive sign. So the value of ΔH is negative for an exothermic reaction. A fall in temperature is given a negative sign. So the value of ΔH is positive for an endothermic reaction.

The energy released in calorimetry experiments for a known number of moles of a specified reactant is given by $q = mc\Delta T$.

When we multiply this up to 1 mole of a stated product or reactant, the equation we use is

$$\Delta H = -mc\Delta T$$

The negative sign shows that the reaction is exothermic.

Questions

4   a   Calculate the energy transferred when the temperature of 75 cm^3 of water rises from 23 °C to 54 °C.

   b   When 8 g of sodium chloride is dissolved in 40 cm^3 of water, the temperature falls from 22 °C to 20.5 °C. Calculate the energy absorbed by the solution when sodium chloride dissolves.

   c   A student added 50 cm^3 of sodium hydroxide to 50 cm^3 of hydrochloric acid. Both solutions were at 18 °C to start with. When the solutions were mixed a reaction occurred. The temperature rose to 33 °C. How much energy is released in this reaction?

5   Explain why the enthalpy change of neutralisation of one mole of sulfuric acid, H_2SO_4, is not the standard enthalpy change of neutralisation in kJ mol^{-1}.

6   A student added 10 g (0.25 mol) of sodium hydroxide to 40 cm^3 of water to make a concentrated solution. All the sodium hydroxide dissolved. The student measured the maximum temperature rise. The student suggested that these results would give an accurate value for the standard enthalpy change of solution. Give two reasons why the student is incorrect.

7   A student calculated the standard enthalpy change of combustion of ethanol $\Delta H_c^\ominus$ [C_2H_5OH] by calorimetry as −870 kJ mol^{-1}. The data book value is −1367 kJ mol^{-1}. Explain why there is a difference between these values.

Questions

4 **a** Calculate the energy transferred when the temperature of 75 cm^3 of water rises from 23 °C to 54 °C.

   b When 8 g of sodium chloride is dissolved in 40 cm^3 of water, the temperature falls from 22 °C to 20.5 °C. Calculate the energy absorbed by the solution when sodium chloride dissolves.

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6.4 Hess's law

Conserving energy

The law of conservation of energy states that 'energy cannot be created or destroyed'. This is also called the *first law of thermodynamics*.

The first law of thermodynamics also applies to chemical reactions: the total energy of the chemicals and their surroundings must remain constant. In 1840, Germain Hess applied the law of conservation of energy to enthalpy changes.

Hess's law states that 'the total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same'. The states of the reactants and products must also be the same whichever route is followed.

Enthalpy cycles (Energy cycles)
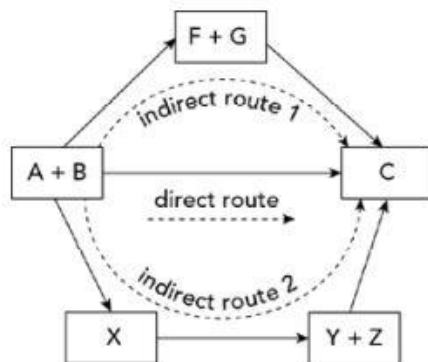
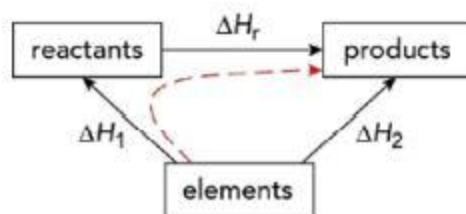**Figure 6.7:** The enthalpy change is the same no matter which route is followed.

Figure 6.8: An enthalpy cycle (energy cycle) for calculating an enthalpy change of reaction. The dashed line shows the indirect (two-step) route.

1 Calculate the standard enthalpy change for the reaction:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

Solution

The relevant enthalpy changes of formation are:

$\Delta H_f^{\ominus}$ [$NaHCO_3(s)$] = −950.8 kJ mol^{-1}

$\Delta H_f^{\ominus}$ [$Na_2CO_3(s)$] = −1130.7 kJ mol^{-1}

$\Delta H_f^{\ominus}$ [$CO_2(g)$] = −393.5 kJ mol^{-1}

$\Delta H_f^{\ominus}$ [$H_2O(l)$] = −285.8 kJ mol^{-1}

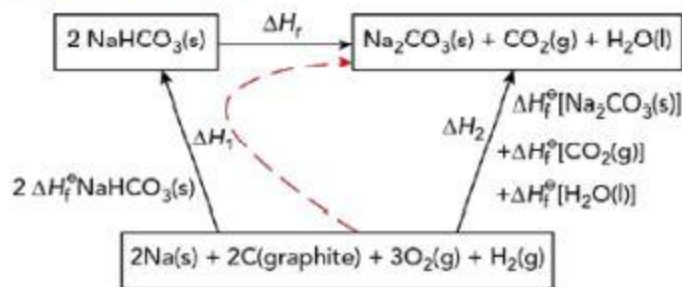The enthalpy cycle is shown in Figure 6.9.

Figure 6.9: The enthalpy cycle for the decomposition of sodium hydrogencarbonate. The dashed line shows the two-step route.
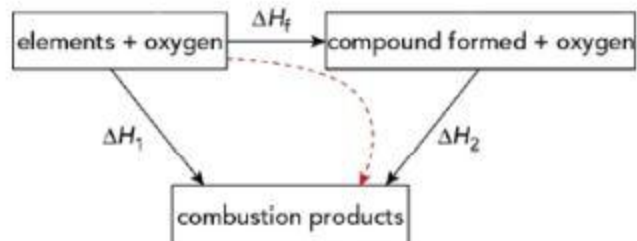
Figure 6.10: An enthalpy cycle for calculating an enthalpy change of formation from enthalpy changes of combustion.

When doing enthalpy cycle (energy cycle) calculations remember that:

1   the enthalpy change of an element in its normal state is zero

2   you must take into account the number of moles of reactants and products in each part of the energy cycle.

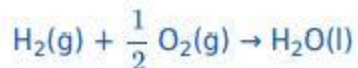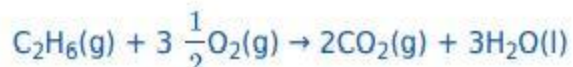**2** Calculate the standard enthalpy change of formation of ethane, C_2H_6.

Solution

The relevant enthalpy changes of combustion are:

$C(graphite) + O_2(g) \rightarrow CO_2(g)$

$\Delta H_c^{\ominus} [C(graphite)] = -393.5 \text{ kJ mol}^{-1}$

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

$\Delta H_c^{\ominus} [H_2(g)] - -285.8 \text{ kJ mol}^{-1}$

$C_2H_6(g) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
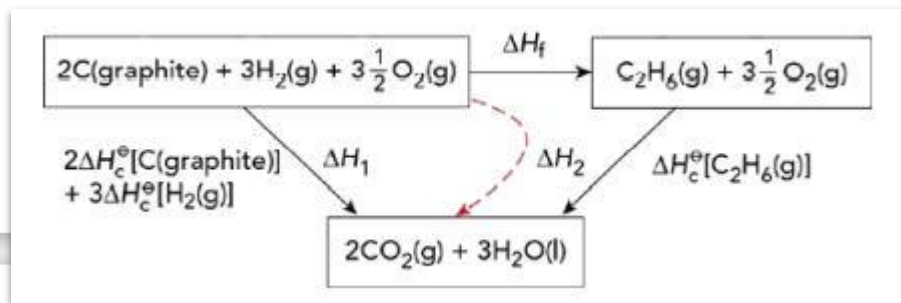
$\Delta H_c^{\ominus} [C_2H_6(g)] = -1559.7 \text{ kJ mol}^{-1}$

Step 1: Write the enthalpy change of formation at the top and then draw the energy cycle with the combustion products at the bottom. Make sure the arrows are in the correct direction.

The enthalpy cycle is shown in Figure 6.11.

Step 2: Apply Hess's law.

$$\Delta H_1 = \Delta H_f + \Delta H_2$$

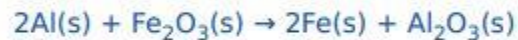**Step 3:** Insert the values of ΔH taking care to multiply by the correct number of moles.

ΔH_1	$= \Delta H_f + \Delta H_2$
$2(-393.5) + 3(-285.8)$	$= \Delta H_f + (-1559.7)$
-1644.4	$= \Delta H_f + (-1559.7)$

Step 4: Rearrange the figures to make ΔH_f the subject.

$$\Delta H_f = -1644.4 - (-1559.7) = -84.7 \text{ kJ mol}^{-1}$$

Question

8 **a** Draw an enthalpy cycle to calculate $\Delta H_r^{\ominus}$ for the reaction

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

   b Calculate ΔH_r using the following information:

$$\Delta H_f^{\ominus} [Fe_2O_3(s)] = -824.2 \text{ kJ mol}^{-1}$$

$$\Delta H_f^{\ominus} [Al_2O_3(s)] = -1675.7 \text{ kJ mol}^{-1}$$

$$\Delta H_1 \quad = \quad \Delta H_f + \Delta H_2$$

direct route   indirect route

So $\Delta H_f = \Delta H_1 - \Delta H_2$

To calculate the enthalpy change of formation using this type of cycle:

- write the equation for enthalpy change of formation at the top; add oxygen on both sides of the equation to balance the combustion reactions
- draw the cycle with the combustion products at the bottom
- draw in all arrows, making sure they go in the correct directions
- apply Hess's law, taking into account the number of moles of each reactant and product.

Questions

9   a   Draw an enthalpy cycle to calculate the enthalpy change of formation of ethanol, C_2H_5OH, using enthalpy changes of combustion.

   b   Calculate a value for ΔH_f [$C_2H_5OH(l)$] using the following data:

$\Delta H_c^{\ominus}$ [C(graphite)] = −393.5 kJ mol^{-1}

$\Delta H_c^{\ominus}$ [$H_2(g)$] = −285.8 kJ mol^{-1}

$\Delta H_c^{\ominus}$ [$C_2H_5OH(l)$] = −1367.3 kJ mol^{-1}

10 Look at this equation.

$$3Mg(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + 3MgO(s)$$

Which one of the following gives the correct value for the enthalpy change of this reaction?

A $\Delta H_r = \Delta H_f [Fe_2O_3(s)] - 3\Delta H_f [MgO(s)]$

B $\Delta H_r = \Delta H_f [MgO(s)] - \Delta H_f [Fe_2O_3(s)]$

C $\Delta H_r = 2\Delta H_f [Fe(g)] + 3\Delta H_f [MgO(g)]$
$- 3\Delta H_f [Mg(g)] + \Delta H_f [Fe_2O_3(g)]$

D $\Delta H_r = 3\Delta H_f [MgO(s)] - \Delta H_f [Fe_2O_3(s)]$

We cannot usually find the value of bond energies directly, so we have to use an enthalpy cycle. The **average bond energy** of the C–H bond in methane can be found using the enthalpy changes of atomisation of carbon and hydrogen and the enthalpy change of combustion or formation of methane.

> ## IMPORTANT
>
> The standard enthalpy change of atomisation, $\Delta H_{at}^{\ominus}$, is the enthalpy change when one mole of gaseous atoms is formed from its element under standard conditions. So, $\Delta H_{at}^{\ominus}$ [H$_2$] relates to the equation $\frac{1}{2}H_2(g) \rightarrow H(g)$
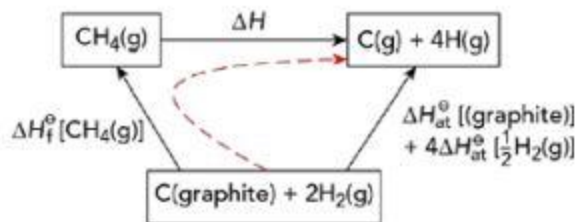

Figure 6.13: An enthalpy cycle to find the average bond energy of the C–H bond. The dashed line shows the two-step route.
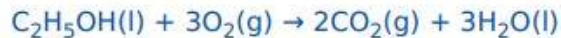
Question

11 Use the information in Figure 6.13 and the information below to demonstrate that the average bond energy of the C–H bond is 415.9 kJ mol^{-1}.

$$\Delta H_f^\ominus \, [CH_4] = -74.8 \text{ kJ mol}$$

$$\Delta H_{at}^\ominus \, [\tfrac{1}{2}H] = +218 \text{ kJ mol}^{-1}$$

$$\Delta H_{at}^\ominus \, [C(graphite)] = +716.7 \text{ kJ mol}^{-1}$$

12 The equation for the combustion of ethanol is:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

a Rewrite this equation to show all the bonds in the reactants and products.

b Use the following bond energies (in kJ mol^{-1}) to calculate a value for the standard enthalpy change of this reaction:

i E(C–C) = +347

ii E(C–H) = +410

iii E(C–O) = +336

iv E(O=O) = +496

v E(C=O) = +805

vi E(O–H) = +465

c The standard enthalpy change of combustion of ethanol is -1367.3 kJ mol^{-1}. Suggest why this value differs from the value obtained using bond energies.

The standard enthalpy change of atomisation, $\Delta H_{at}^{\ominus}$, is the enthalpy change when one mole of gaseous atoms is formed from its element under standard conditions. So, $\Delta H_{at}^{\ominus}$ [H_2] relates to the equation $\frac{1}{2}H_2(g) \rightarrow H(g)$

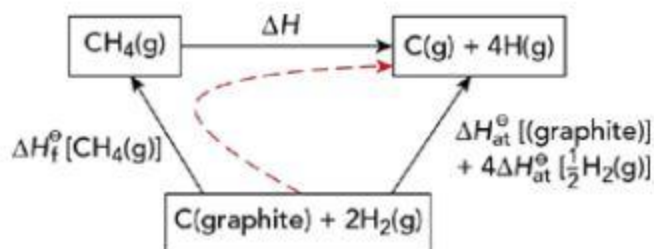**Figure 6.13:** An enthalpy cycle to find the average bond energy of the C–H bond. The dashed line shows the two-step route.

The enthalpy cycle for calculating the average C–H bond energy is shown in Figure 6.13. Using the enthalpy cycle shown in Figure 6.13, the average C–H bond energy can be found by dividing the value of ΔH on the diagram by four (because there are four C–H bonds in a molecule of methane).

2   The elements in Group 17, the halogens, and their compounds, show many similarities and trends in their properties. Some data are given for the elements fluorine to iodine.

element	bond energy /kJ mol^{-1}	standard enthalpy change of atomisation, $\Delta H_{at}^{\ominus}$/kJ mol^{-1}	boiling point of element /K	boiling point of **hydrogen halide** /K
fluorine, F–F	158	79	85	293
chlorine, Cl–Cl	242	121	238	188
bromine, Br–Br	193	112	332	206
iodine, I–I	151	107	457	238

The standard enthalpy of formation of iodine monochloride, ICl, is –24.0 kJ mol^{-1}.

Use this information and the bond energies of iodine and chlorine to calculate the I–Cl bond energy.

I–Cl bond energy = ... kJ mol^{-1} [2]

(b) Boron occurs naturally as a mixture of two stable isotopes, ^{10}B and ^{11}B. The relative isotopic masses and percentage abundances are shown.

isotope	relative isotopic mass	abundance/%
^{10}B	10.0129	19.78
^{11}B	to be calculated	80.22

(i) Define the term *relative isotopic mass*.

....

.... [2]

(ii) Calculate the relative isotopic mass of ^{11}B.

Give your answer to **six** significant figures. Show your working.

[2]

3 The hydrogen halides, HCl, HBr and HI, can undergo thermal decomposition.
In a sealed container an equilibrium is established according to the equation shown.

$$2HX(g) \rightleftharpoons H_2(g) + X_2(g) \qquad \text{(where X = C}l\text{, Br or I)}$$

$$N \equiv N(g) \quad + \quad 3H—H(g) \quad \xrightarrow{\Delta H_r^\circ} \quad 2H—N—H(g)$$

ΔH_1 ΔH_2

$E(N \equiv N)$
$+ 3 \times E(H—H)$ $2 \times 3 \times -E(N—H)$

$2N(g) + 6H(g)$
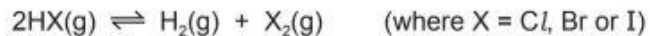
(a) Some bond energies are shown in the table.

	bond energy/kJ mol^{-1}
H–Br	366
H–H	436
Br–Br	193

Use these data to calculate a value for the enthalpy change, ΔH, for the thermal decomposition of hydrogen bromide, HBr, according to the equation shown.
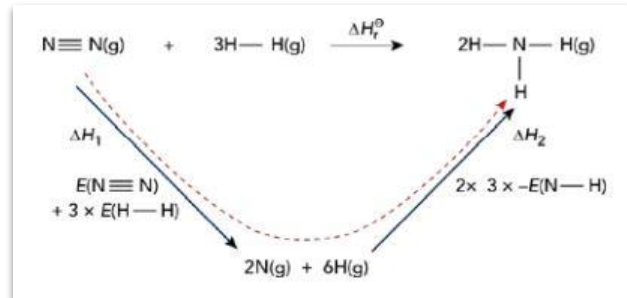
$\Delta H = $ .... kJ mol^{-1} [1]

3   Trihalomethanes are organic molecules in which three of the hydrogen atoms of methane are replaced by halogen atoms, for example CHF_3.

(a) The equation shows a reaction to produce CHF_3.

$$CHI_3(s) + 3AgF(s) \rightarrow CHF_3(g) + 3AgI(s)$$

Use the data to calculate the enthalpy change of reaction, ΔH_r, for this formation of CHF_3.

compound	enthalpy change of formation, ΔH_f/kJ mol^{-1}
$CHI_3(s)$	−182.1
$CHF_3(g)$	−692.9
$AgF(s)$	−204.6
$AgI(s)$	−61.8

enthalpy change of reaction, ΔH_r = ... kJ mol^{-1} [3]