5 Chemical energetics

Enthalpy changes and entropy changes accompany chemical reactions. This topic demonstrates why some reactions and processes are spontaneous and others are not.

5.1 Enthalpy change, Δ*H* ☐

5.2 Hess' Law, including Born-Haber cycles ☐

ENERGETICS

5 Chemical energetics

Enthalpy changes and entropy changes accompany chemical reactions. This topic demonstrates why some reactions and processes are spontaneous and others are not.

	Learning outcomes Candidates should be able to:
5.1 Enthalpy change, ΔH	a) explain that chemical reactions are accompanied by energy changes, principally in the form of heat energy; the energy changes can be exothermic (ΔH is negative) or endothermic (ΔH is positive) b) explain and use the terms: (i) *enthalpy change of reaction* and *standard condition*s, with particular reference to: formation, combustion, hydration, solution, neutralisation, atomisation (ii) *bond energy* (ΔH positive, i.e. bond breaking) **(iii) *lattice energy* (ΔH negative, i.e. gaseous ions to solid lattice)** c) calculate enthalpy changes from appropriate experimental results, including the use of the relationship enthalpy change, $\Delta H = -mc\Delta T$ **d) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy**
5.2 Hess' Law, including Born-Haber cycles	a) apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to: (i) determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion (ii) average bond energies **(iii) the formation of a simple ionic solid and of its aqueous solution** **(iv) Born-Haber cycles (including ionisation energy and electron affinity)** b) construct and interpret a reaction pathway diagram, in terms of the enthalpy change of the reaction and of the activation energy

ENTHALPY CHANGES

Every chemical reaction involves the exchange of energy between (what we call) **the system** and **its surroundings.** For example, when magnesium and sulphuric acid react in a test-tube:

1. **The system** consists of the chemical bonds and other forces of attraction and repulsion between the atoms of reactants and of the products formed.

2. **The surroundings** include:

   a. The test tube.

   b. The air around the test tube.

   c. The thermometer dipped into the reacting mixture etc…

ENTHALPY CHANGES

The **total heat (energy) content** of any substance at constant pressure is called its **enthalpy**. Because of how difficult it is to observe things at the atomic and sub-atomic level, it is not possible to measure the **total enthalpy** of a substance.

A good analogy for this is trying to measure the volume of the Pacific Ocean. The structure of the seabed is so diverse it is practically impossible to measure just how much volume the Pacific Ocean has. **However, you can easily measure changes in the volume of the Ocean.**

Similarly, we can easily measure the **enthalpy change** that accompanies reactions. This is written as **ΔH** and pronounced 'delta H.' ΔH can either have a positive or a negative value, depending on the nature of energy exchange in the reaction.

ENTHALPY CHANGES

When energy flows from **the system** to **the surroundings**, the temperature of the surroundings **increases.** This indicates that heat was **given out** as a result of the reaction, and so the products of the reaction are at a lower energy level than the reactants were. These types of reactions are called **exothermic reactions.**

The value for ΔH is *negative* for exothermic reactions.

When energy flows from **the surroundings** to **the system**, the temperature of the surroundings **decreases.** This indicates that heat was **taken in** as a result of the reaction, and so the products of the reaction are at a higher energy level than the reactants were. These types of reactions are called **endothermic reactions.**

The value for ΔH is *positive* for endothermic reactions.

SKILL CHECK

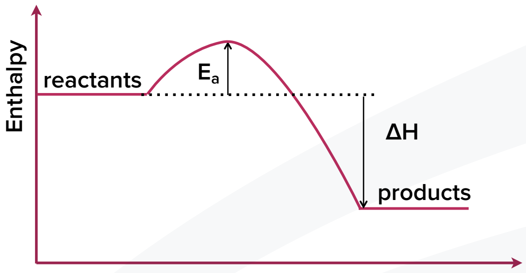
Classify the following reactions as exothermic or endothermic:

1. Burning magnesium in excess oxygen.
2. Crystallisation of copper (II) sulphate from a saturated solution.
3. The thermal decomposition of magnesium nitrate.
4. Fermentation of glucose by yeast.
5. Evaporation of sea water.

ENTHALPY CHANGES

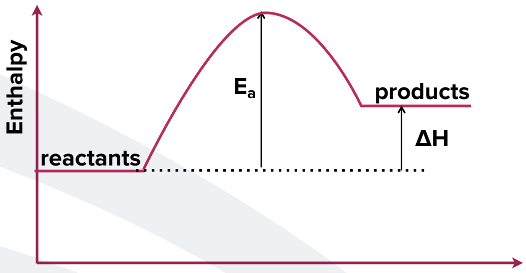
To summarise:

Enthalpy change (ΔH) = Enthalpy of products – Enthalpy of reactants



Enthalpy of reactants > products,ΔH = —ve

EXOTHERMIC: Heat given out



Enthalpy of reactants < products, ΔH = +ve

ENDOTHERMIC: Heat absorbed

ENTHALPY CHANGES

We can draw **enthalpy profile diagrams** (also known as **reaction pathway diagrams**) to show enthalpy changes, as shown on the previous slide.

1. The enthalpy of the reactants and products is shown on the y-axis.

2. The x-axis shows the reaction pathway, with reactants on the left and products on the right.

SKILL CHECK

Draw enthalpy profile diagrams for:

a. Combustion of sulphur to form sulphur dioxide.

b. The neutralisation of potassium hydroxide by nitric acid.

STANDARD ENTHALPY CHANGES

The energy change that accompanies a reaction depends on:

1. The amount of reactants.
2. The physical state of the reactants and products.
3. The temperature of the reactants and products.

As reactants can exist at a variety of energy levels at different physical states, temperatures and pressures, there was a need to standardise conditions under which these values were measured. These are now known as **standard conditions.** They are a *pressure* of 10^5 Pa (100 KPa), *temperature* of 298K (25 °C) and each substance involved in the reaction is in its normal state at these values of temperature and pressure.

STANDARD ENTHALPY CHANGES

Enthalpy change measured under standard conditions is known as **standard enthalpy change.** The ⊖ symbol indicates that the enthalpy change refers to a reaction carried out under standard conditions. The unit of measurement for standard enthalpy change is the kilojoule per mole, written as **kJmol-1.**

The equation below shows us that when one mole of methane gas reacts with two moles of oxygen gas to form one mole of carbon dioxide gas and two moles of water in the liquid state the **standard enthalpy change** is –890.3 kJmol-1.

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

STANDARD ENTHALPY CHANGES

Enthalpy changes are described depending on what type of reaction is taking place. The following are some of the most commonly used enthalpy changes:

1. Standard enthalpy change of formation.
2. Standard enthalpy change of neutralisation.
3. Standard enthalpy change of combustion.
4. Standard enthalpy change of atomisation.

STANDARD ENTHALPY CHANGE OF FORMATION

Definition The enthalpy change when **one mole** of a compound is formed **in its standard state** from its **elements in their standard states** under **standard conditions.**

Symbol $\Delta H^{\ominus}_{f}$

Values Usually, but not exclusively, exothermic.

Examples

$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$

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

$2C_{(graphite)} + \frac{1}{2}O_2(g) + 3H_2(g) \longrightarrow C_2H_5OH(l)$

Notes There should be only **one mole** of product on the right side of the equation.

Elements in their standard states have zero enthalpy of formation

Carbon is usually taken as the graphite allotrope

STANDARD ENTHALPY CHANGE OF COMBUSTION

Definition The enthalpy change when **one mole** of a substance undergoes **complete** combustion **under standard conditions**. All reactants and products are in their **standard states**.

Symbol $\Delta H^{\ominus}_{c}$

Values Always exothermic

Examples

$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$

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

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

Notes There should only **one mole** of what is being combusted on the left side of the equation.

To aid balancing the equation, remember that you get **one carbon dioxide** molecule for **every carbon atom** in the original and **one water molecule** for every **two hydrogen atoms**. When you have done this, go back and balance the oxygen.

STANDARD ENTHALPY CHANGE OF NEUTRALISATION

Definition	The enthalpy change when an **acid** and a **base** react to form **one mole** of water under **standard conditions**.
Symbol	$\Delta H^{\ominus}_{neutralisation}$
Values	Exothermic
Example	$H^+ (aq) + OH^- (aq) \longrightarrow H_2O(l)$
Notes	A value of -57kJmol^{-1} is obtained when strong acids react with strong alkalis.

SKILL CHECK

Classify the following reactions as standard enthalpy changes of formation, combustion or neutralisation:

1. $MgCO_3 (s) \longrightarrow MgO (s) + CO_2 (g)$

2. $C_{(graphite)} + O_2 (g) \longrightarrow CO_2 (g)$

3. $HCl (g) + NH_3 (g) \longrightarrow NH_4Cl (s)$

4. $H_2 (g) + ½O_2 (g) \longrightarrow H_2O (l)$

MEASURING ENTHALPY CHANGES

Calorimetry is used to measure enthalpy changes.

It usually involves heating (or cooling) known amounts of water.

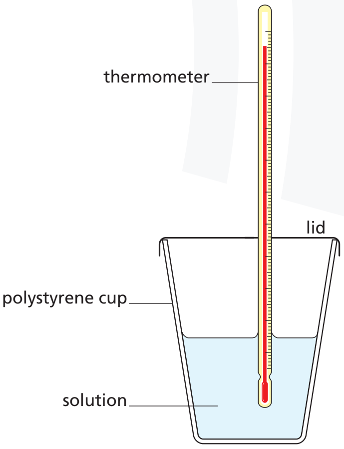
Many reactions take place in aqueous solution – reactants and/or products dissolved in water - so water is the natural choice to measure a variety of enthalpy changes.

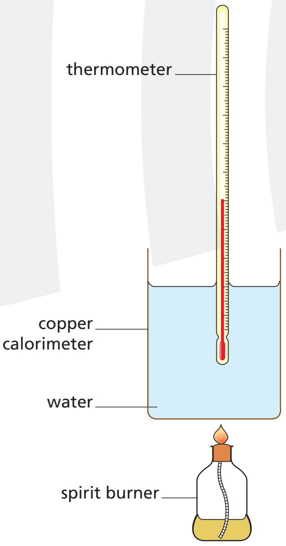
The enthalpy change of reaction causes the temperature of the water to change:

Endothermic reactions take in energy, temperature of water **falls**.

Exothermic reactions give energy out, temperature of water **rises**.

SIMPLE CALORIMETERS





MEASURING ENTHALPY CHANGES

The energy required to change the temperature of a substance can be calculated using:

$$q = m \times c \times \Delta T$$

where **q** = heat energy, measured in Joules (J)

m = mass, measured in grams (g)

ΔT = change in temperature, measured in Kelvin (K) or degree Celsius (°C)

c = Specific Heat Capacity, measured in $JK^{-1}g^{-1}$ or $J°C^{-1}g^{-1}$

MEASURING ENTHALPY CHANGES

We can measure the temperature change using a thermometer marked in degrees Celsius, because a change in temperature is the same on either the Celsius or the Kelvin scale. The value for the specific heat capacity of water is 4.18 $JK^{-1}g^{-1}$ (or $J°C^{-1}g^{-1}$).

If we are dealing with aqueous solutions rather than pure water, it is the mass of water in the solution that should be included as the 'm' in this equation. Since the solutions are often quite dilute, and since the volume and heat capacity of a dilute solution are about the same as those of the water it contains, we normally use the volume of the solution rather than its mass to give this equation:

$$q = \text{volume} \times c \times \Delta T$$

CALCULATING ENTHALPY CHANGES

Step 1: work out the enthalpy change during the reaction → **Step 2**: work out how many moles of water are made from the reaction → **Step 3**: work out how much energy is evolved per mole of water

CALCULATING ENTHALPY CHANGES

25cm^3 of 1 moldm^{-3} HCl (aq) was neutralized by 25 cm^3 of 1 moldm^{-3} NaOH (aq). The temperature was increased by 5°C. Calculate the enthalpy change of neutralisation.

Enthalpy change $q = mc\Delta T$ *where* $m = 50$ g, $c = 4.2$ J°C^{-1}g^{-1}, $\Delta T = 5.0$°C

So, enthalpy change = 50 x 4.2 x 5.0 = 1050 J

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

1 mole *1 mole*

Number of moles of H_2O = number of moles of HCl = 0.025 x 1.0 = 0.025.

So, 0.025 moles of water are made.

CALCULATING ENTHALPY CHANGES

Number of moles of H_2O = number of moles of HCl = 0.025 x 1.0 = 0.025. So, 0.025 moles of water are made.

Enthalpy change when 0.025 moles of water made = 1050J

Enthalpy change when 1 mole of water made = 1050/0.025 = 42000 J

Enthalpy change of neutralisation = — 42 $kJmol^{-1}$

Heat energy gained by the water is lost by the reaction so change the sign!

CALCULATING ENTHALPY CHANGES

0.16g of methanol was burned in a spirit burner. 50g of water was heated from 19°C to 23°C.

(a) Calculate the enthalpy change of combustion of methane.

$q = mc\Delta T$ $m = 50g$, $c = 4.2\ JK^{-1}g^{-1}$, $\Delta T = 4.0°C$

So, enthalpy change of water = 50 x 4.2 x 4.0 = 840 J

moles of methanol burned = mass/mass of 1 mole = 0.16/32 = 0.005 moles

CALCULATING ENTHALPY CHANGES

Enthalpy change of water for 1 mole of methane= 840/0.005 = 168000J = 168kJ

Enthalpy change of combustion = —168 kJ mol^{-1}

(b) Comment on why this experimental value is lower than the data booklet value.

Energy is lost to the surroundings, so that the temperature increase of the water is lower than that under ideal conditions.

CALCULATING ENTHALPY CHANGES

On complete combustion, 0.18g of hexane raised the temperature of 100g water from 22°C to 47°C. Calculate its enthalpy of combustion.

Heat absorbed by the water (q) = 100 x 4.18 x 25 = 10450 J = 10.45 kJ

Moles of hexane burned = mass/Mr = 0.18/86 = 0.00209

Enthalpy change = heat energy/moles = 10.45/0.00209 = 5000 kJ mol^{-1}

CALCULATING ENTHALPY CHANGES

25cm^3 of 2.0M HCl was added to 25cm^3 of 2.0M NaOH in an insulated beaker. The initial temperature of both solutions was 20°C. The highest temperature reached by the solution was 33°C. Calculate the Molar Enthalpy of Neutralisation.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Temperature rise (ΔT) = 306K — 293K = 13K

Volume of resting solution = 25 + 25 = 50cm^3 = 0.05dm^3

Equivalent mass of water = 50g (density is 1 gcm^{-3})

CALCULATING ENTHALPY CHANGES

Heat absorbed by the water (q) = m x c x ΔT = 500 x 4.18 x 13 = 2717 J = 2.717 kJ

Moles of HCl reacting = 2 x 25/1000 = 0.05 mol

Moles of NaOH reacting = 2 x 25/1000 = 0.05 mol

Moles of water produced = 0.05 mol

Enthalpy change per mole (ΔH) = heat energy/moles of water = 2.717/0.05 = 54.34 kJmol^{-1}

CALCULATING ENTHALPY CHANGES

25cm^3 of 2.0M HCl was added to 25cm^3 of 2.0M NaOH in an insulated beaker. The initial temperature of both solutions was 20°C. The highest temperature reached by the solution was 33°C. Calculate the Molar Enthalpy of Neutralisation.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Temperature rise (ΔT) = 306K — 293K = 13K

Volume of resting solution = 25 + 25 = 50cm^3 = 0.05dm^3

Equivalent mass of water = 50g (density is 1 gcm^{-3})

CALCULATING ENTHALPY CHANGES

Heat absorbed by the water (q) = m x c x ΔT = 500 x 4.18 x 13 = 2717 J = 2.717 kJ

Moles of HCl reacting = 2 x 25/1000 = 0.05 mol

Moles of NaOH reacting = 2 x 25/1000 = 0.05 mol

Moles of water produced = 0.05 mol

Enthalpy change per mole (ΔH) = heat energy/moles of water = 2.717/0.05 = 54.34 kJmol^{-1}

SKILL CHECK

75cm^3 of 2.0 moldm^{-3} ethanoic acid, CH_3CO_2H, were placed in a plastic cup. The temperature was 18.2°C. To this were added 75cm^3 of 2.0 moldm^{-3} ammonium hydroxide, NH_4OH, whose temperature was 18.6 °C. After mixing, the highest temperature was 31.0 °C.

Calculate ΔH for the neutralisation.

SKILL CHECK

A burner containing hexanol, $C_6H_{13}OH$, had a mass of 325.68g. It was lit and placed under a copper calorimeter containing 250 cm^3 of water. The temperature of the water rose from 19.2°C to 31.6°C. Afterwards the burner's mass was 324.37 g.

Calculate:

A. The heat evolved.

B. ΔH_c for hexanol.

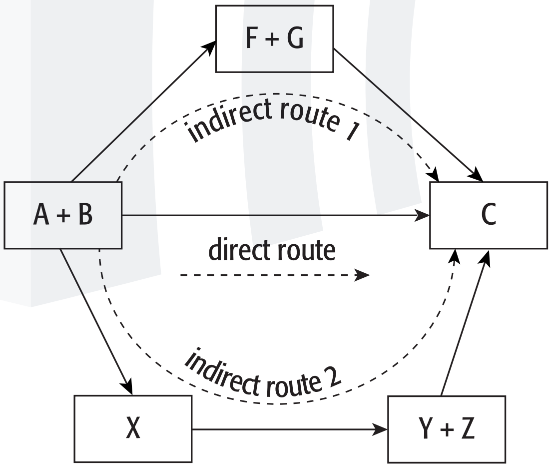
HESS’ LAW

There are very few reactions whose enthalpy change can be measured directly by measuring the change in temperature in a calorimeter. We can find enthalpy changes for other reactions indirectly. To do this we make use of **Hess’ Law**.

Hess’ law is an application of the first law of thermodynamics, which in its simplest form is the law of conservation of energy. Since energy cannot be destroyed or created the energy change in a chemical process should be the same as long as the initial and final states are the same.

HESS’ LAW

Hess’ 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’.



ΔH(direct) = ΔH(indirect 1) = ΔH(indirect 2)

HESS’ LAW

Some enthalpy changes are easy to measure experimentally, e.g.:

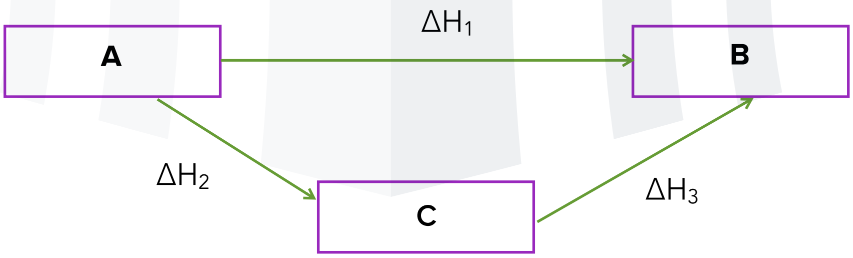
- ΔH°_c, enthalpy change of combustion.
- Some values for ΔH°_f, enthalpy change of formation.

These can be used to calculate some enthalpy changes that are difficult to measure experimentally e.g. :

- Some values for ΔH°_f, enthalpy change of formation.
- Some values for ΔH°_r, enthalpy change of reaction.

HESS’ LAW

This can be shown by making a Hess cycle as shown below:



$$A \rightarrow B \;=\; A \rightarrow C \;+\; C \rightarrow B$$

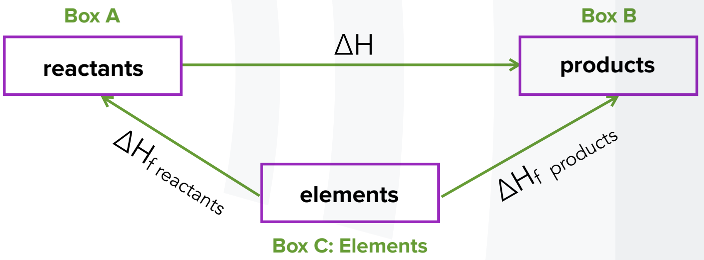
$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

HESS’ LAW

1. Write out balanced equations for **all energy changes** mentioned in question.
2. Choose the most complicated (or populated) equation.
3. Fill the first two boxes with it.
4. Put everything else in the third box.
5. Balance each box to ensure the number of atoms in each box is the same.
6. The box with which your cycle begins is the start box and the one where the cycle ends is the stop box.
7. Construct an equation and solve.

Note: The enthalpies given are per mole therefore as the number of moles change, the energies have to be multiplied by the same number.

SUMMARY CYCLES



FOR FORMATION REACTIONS

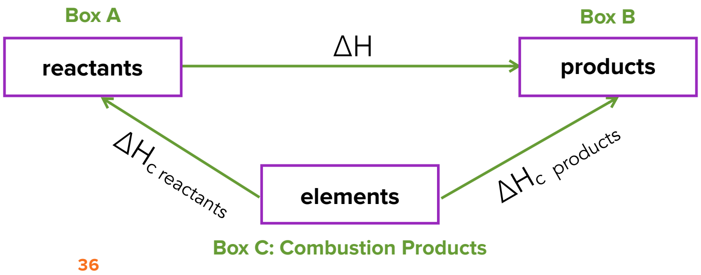
Start box: C **End box: B**

C ➜ A + A ➜ B = C ➜ B

FOR COMBUSTION REACTIONS

Start box: A **End box: C**

A ➜ B + B ➜ C = A ➜ C



EXAMPLE 1

Consider the following two reactions:

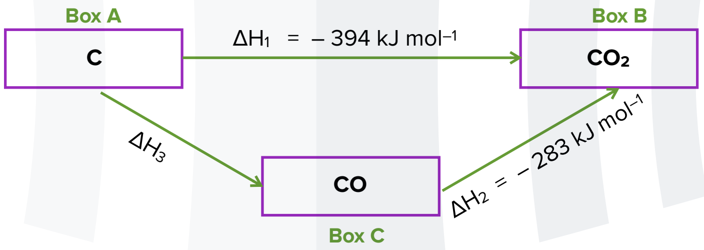
$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_1 = -394 \text{ kJ mol}^{-1}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_2 = -283 \text{ kJ mol}^{-1}$$

We can use Hess's Law to find the value of the incomplete combustion of carbon to form CO.

$$C_{(graphite)} + \tfrac{1}{2} O_2(g) \longrightarrow CO(g) \qquad \Delta H_3 = ?$$

EXAMPLE 1



$$A \rightarrow B = A \rightarrow C + C \rightarrow B$$

$$\Delta H_1 = \Delta H_3 + \Delta H_2$$

$$-394 = \Delta H_3 + (-283)$$

$$\Delta H_3 = ?$$

EXAMPLE 2

Calculate the standard enthalpy of formation of methane from the following data:

ΔH°_c (C) = —393 kJ mol^{-1}

ΔH°_c (H2) = —286 kJ mol^{-1}

ΔH°_c (CH4) = —890 kJ mol^{-1}

Step 1: form the equation of the formation of methane from its elements in their standard state.

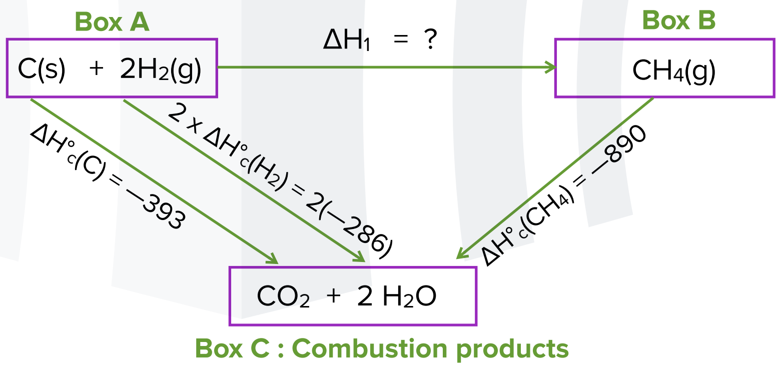
$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$$

EXAMPLE 2

Step 2: enter the reactants (in Box A) and products (in Box B) of Step 1 into the Hess cycle

Step 3: enter the combustion products of the Box A and Box B into Box C

Step 4: work out ΔH_1 from
$\Delta H_1 = \Delta H_2 + \Delta H_3$

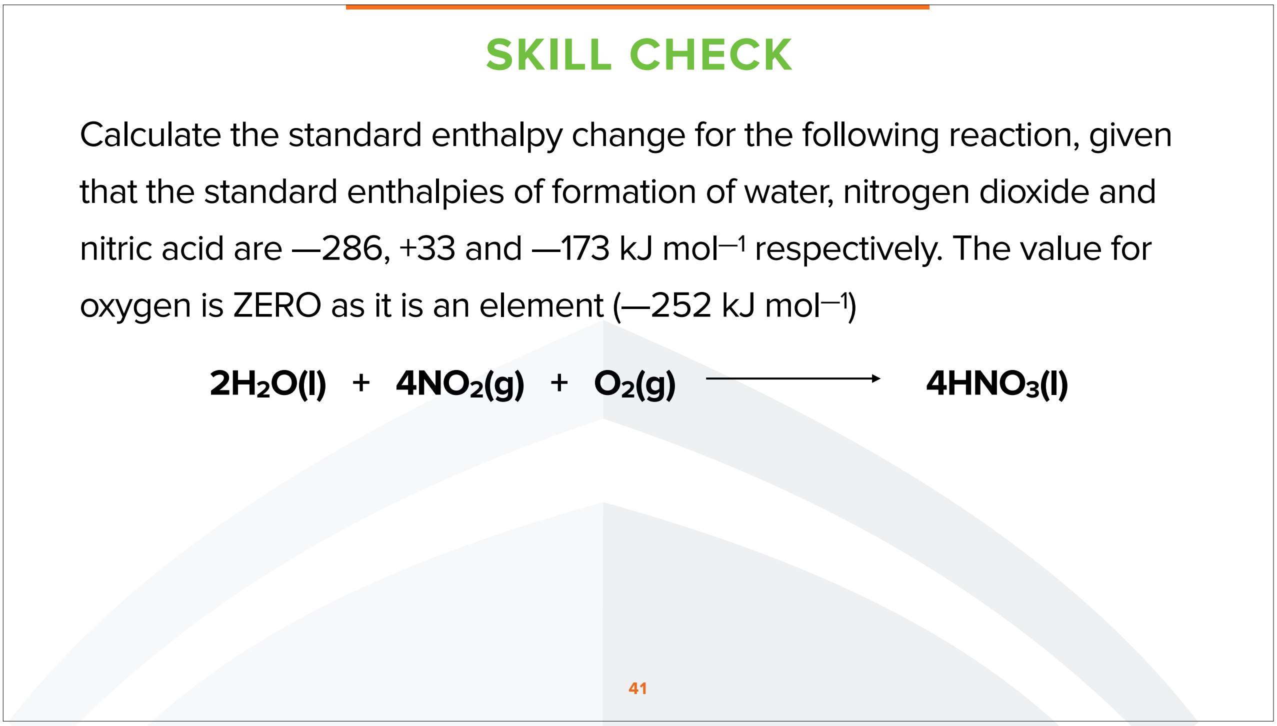


A ➜ B + B ➜ C = A ➜ C

$\Delta H_1 + \Delta H^\circ_c(CH_4) = \Delta H^\circ_c(C) + 2 \times \Delta H^\circ_c(H_2)$

$\Delta H_1 + (-890) = (-393) + 2(-286)$

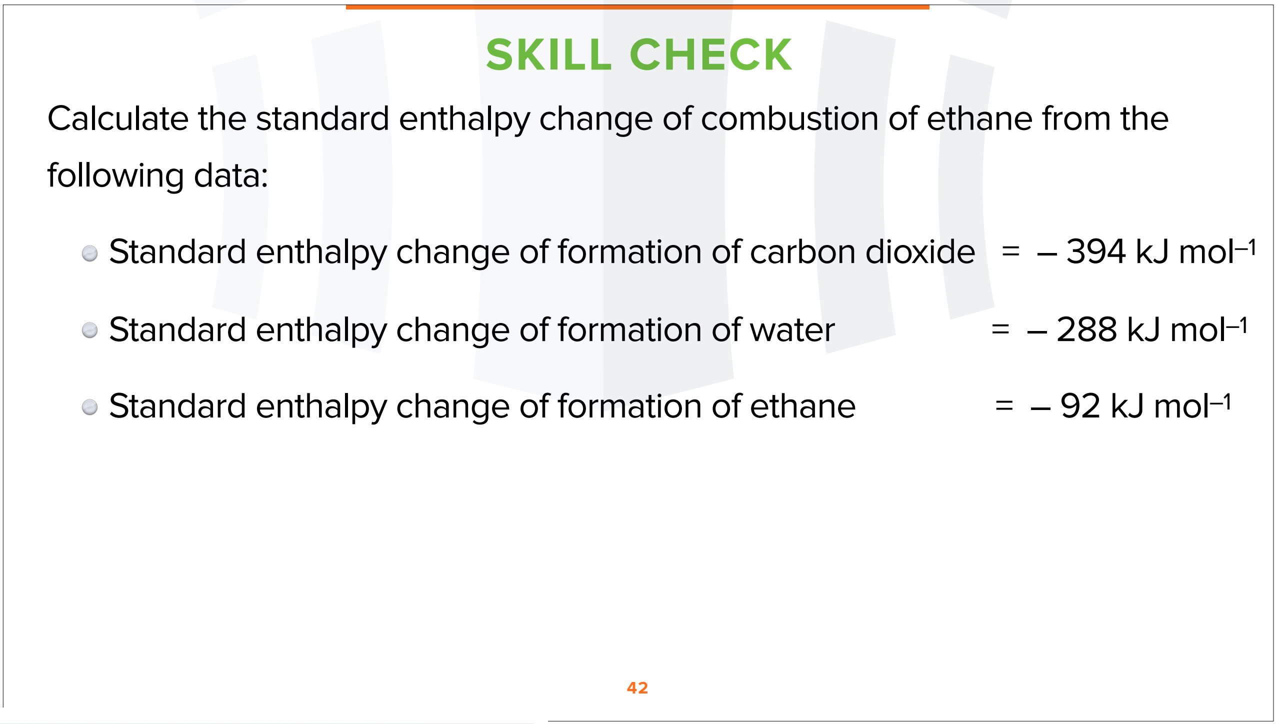
$\Delta H_1 = ?$



SKILL CHECK

Calculate the standard enthalpy change for the following reaction, given that the standard enthalpies of formation of water, nitrogen dioxide and nitric acid are —286, +33 and —173 kJ mol^{-1} respectively. The value for oxygen is ZERO as it is an element (—252 kJ mol^{-1})

$$2H_2O(l) \; + \; 4NO_2(g) \; + \; O_2(g) \longrightarrow 4HNO_3(l)$$



SKILL CHECK

Calculate the standard enthalpy change of combustion of ethane from the following data:

- Standard enthalpy change of formation of carbon dioxide = – 394 kJ mol^{-1}
- Standard enthalpy change of formation of water = – 288 kJ mol^{-1}
- Standard enthalpy change of formation of ethane = – 92 kJ mol^{-1}

SKILL CHECK

Calculate the enthalpy change for the reaction:

$$4CH_3NHNH_2(l) + 5N_2O_4(l) \longrightarrow 4CO_2 + 12H_2O + 9N_2$$

Given the following data:

- Standard enthalpy change of formation of carbon dioxide = – 394 kJ mol^{-1}
- Standard enthalpy change of formation of water = – 288 kJ mol^{-1}
- Standard enthalpy change of formation of CH_3NHNH_2 = +53 kJ mol^{-1}
- Standard enthalpy change of formation of N_2O_4 = – 20 kJ mol^{-1}

BOND ENTHALPY

Bond Enthalpy is the energy required to break one mole of a particular type of bond in gaseous molecules under standard conditions.

Bond enthalpy values are all positive, showing that bond enthalpies are endothermic (breaking bonds takes in energy).

The values found in the data booklet are average values for each type of bond. The same bond may have very slightly different bond enthalpies in different compounds.

The O—H bond has a slightly different enthalpy value in each compound.

BOND ENTHALPY

When a particular bond is broken, energy is taken in (*endothermic*):

$$\text{H—H(g)} \longrightarrow \text{H(g)} + \text{H(g)} \qquad \Delta H = +436 \text{ kJ mol}^{-1}$$

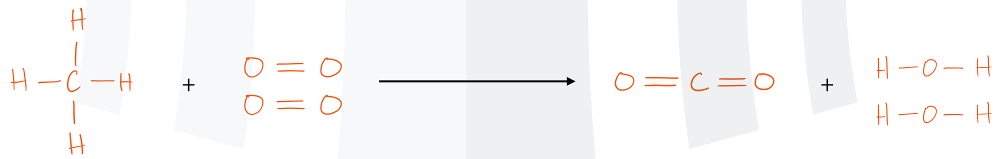
When the same bond is made, energy is given out (*exothermic*):

$$\text{H(g)} + \text{H(g)} \longrightarrow \text{H—H(g)} \qquad \Delta H = -436 \text{ kJ mol}^{-1}$$

Note: The amount of energy needed to break or form the same type of bond is the same.

EXAMPLE

Calculate the enthalpy change of reaction when 1 mole of methane, CH_4 , burns completely to form carbon dioxide and water.



4 x C—H bonds

2 x O=O bonds

2 x C=O bonds

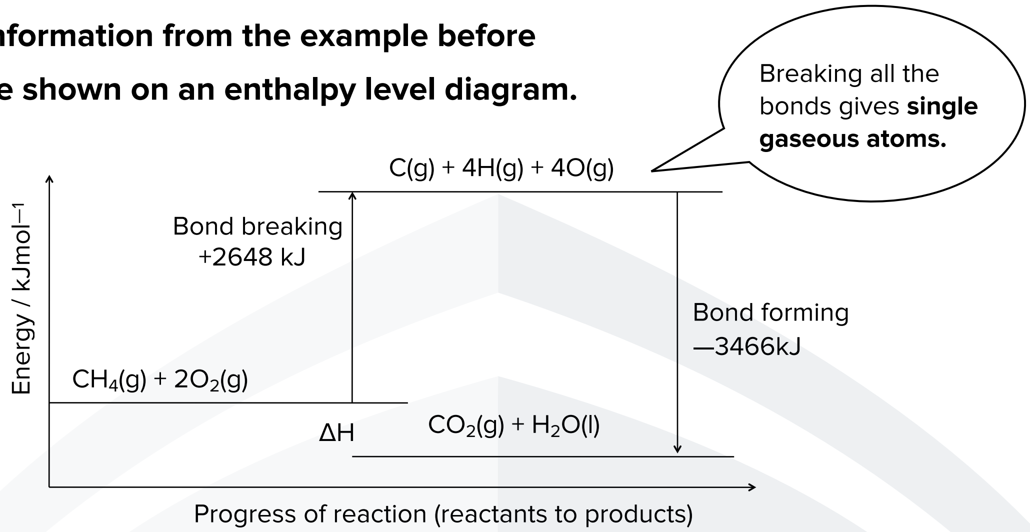
4 x O—H bonds

Reactant Bonds	Energy needed to break bonds /kJ mol^{-1}	Product bonds	Energy given out when bonds form /kJ mol^{-1}
4 x C—H	4 x +413 = +1652	2 x C=O	2 x —805 = —1610
2 x O=O	2 x +498 = +996	4 x O—H	4 x —464 = —1856
Total energy needed	= +2648	**Total energy given out**	= —3466

Enthalpy change of reaction = +2648 + (—3466) = —818 kJ mol^{-1}

EXAMPLE

The information from the example before can be shown on an enthalpy level diagram.



Breaking all the bonds gives **single gaseous atoms.**

$C(g) + 4H(g) + 4O(g)$

Energy / kJmol^{-1}

Bond breaking
+2648 kJ

Bond forming
—3466kJ

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

ΔH

$CO_2(g) + H_2O(l)$

Progress of reaction (reactants to products)

STANDARD ENTHALPY OF ATOMISATION

Standard enthalpy of atomisation (ΔH_{atm}) of an element is the enthalpy change when **1 mole** of **gaseous atoms** is formed from the elements in their **standard states**.

$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g) \quad \Delta H = +121\ kJ\ mol^{-1}$

For chlorine ΔH_{atm} = ½ bond dissociation energy

$Na(s) \longrightarrow Na(g) \quad \Delta H = +108\ kJ\ mol^{-1}$

For sodium ΔH_{atm} = energy of sublimation

STANDARD ENTHALPY OF ATOMISATION

$$\frac{1}{2}I_2(s) \longrightarrow I(g) \quad \Delta H = +107\ \text{kJ mol}^{-1}$$

For iodine ΔH_{atm} = ½(energy of sublimation + bond dissociation energy)

= ½(63 + 151) = ?

$$\frac{1}{2}Br_2(l) \longrightarrow Br(g) \quad \Delta H = +112\ \text{kJ mol}^{-1}$$

For bromine ΔH_{atm} = ½(enthalpy of vaporisation + bond dissociation energy)

SKILL CHECK

The equation for the combustion of ethanol is:

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

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

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

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.