Edexcel

AS - Level

Chemistry

CODE: (WCH11)

Topic 6

Energetics

6A Introducing enthalpy and enthalpy change

CHEMICAL AND HEAT ENERGY

The first law of thermodynamics states that, during a chemical reaction, energy cannot be created or destroyed. However, one form of energy can be transferred into another form.

Various forms of energy are interesting to a chemist. Two of the most important ones are:

- chemical energy
- heat energy.

CHEMICAL ENERGY

Chemical energy is made up of two components:

- Kinetic energy, which is a measure of the motion of the particles (atoms, molecules or ions) in a substance.
- Potential energy, which is a measure of how strongly these particles interact with one another (i.e. both attract and repel one another).

HEAT ENERGY

Heat energy is the portion of the potential energy and the kinetic energy of a substance that is responsible for the temperature of the substance.

The heat energy of a substance is directly proportional to its absolute temperature (i.e. the temperature measured in Kelvin).

ENTHALPY AND ENTHALPY CHANGES

Enthalpy is a measure of the total energy of a system. When considering a chemical reaction, the 'system' refers to the reaction mixture. Everything outside of the system is called the 'surroundings', which in practice is the air in the room in which the reaction is taking place.

You cannot directly determine the enthalpy of a system, but you can measure the enthalpy change (ΔH) that takes place during a physical or a chemical change.

The enthalpy change of a process is the heat energy that is transferred between the system and the surroundings at *constant pressure.*

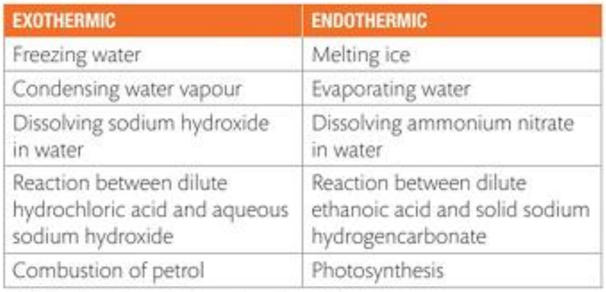
EXOTHERMIC AND ENDOTHERMIC PROCESSES AND REACTIONS

Two types of process can take place. These are:

- exothermic - where heat energy is transferred from the system to the surroundings
- endothermic - where heat energy is transferred from the surroundings to the system. Examples of exothermic and endothermic processes are given in table A.

Exothermic reactions increase temperature immediately, like adding hydrochloric acid to sodium hydroxide or burning natural gas in oxygen, while endothermic reactions decrease temperature, like adding sodium hydrogencarbonate to citric acid, and require continuous heating for execution.

For instance, the thermal decomposition of calcium carbonate into calcium oxide and carbon dioxide is an endothermic reaction:



EXOTHERMIC	ENDOTHERMIC
Freezing water	Melting ice
Condensing water vapour	Evaporating water
Dissolving sodium hydroxide in water	Dissolving ammonium nitrate in water
Reaction between dilute hydrochloric acid and aqueous sodium hydroxide	Reaction between dilute ethanoic acid and solid sodium hydrogencarbonate
Combustion of petrol	Photosynthesis

table A Examples of exothermic and endothermic processes.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad \Delta H = +178\,kJ\,mol^{-1}$$

STANDARD CONDITIONS

In 1982, the International Union of Pure and Applied Chemistry (IUPAC) recommended that all enthalpy changes should be quoted using standard conditions of 100 kPa pressure and a stated temperature. The temperature most commonly used is 298 K.

Under these conditions, the enthalpy change measured is called the 'standard enthalpy change', and is given the symbol $\Delta H^{\circ}_{298\text{K}}$ or simply ΔH°.

SUBJECT VOCABULARY

exothermic a reaction where heat energy is transferred from the system to the surroundings

endothermic a reaction where heat energy is transferred from the surroundings to the system

standard enthalpy change of reaction the enthalpy change which occurs when equation quantities of materials react under standard conditions

STANDARD ENTHALPY CHANGE OF REACTION, $\Delta_r H^{\circ}$

When looking at **standard enthalpy change of reaction** ($\Delta_r H^{\circ}$), it is important to recognise that the enthalpy change is for the reaction *as written*.

For the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta_r H^{\circ} = -92 \text{ kJ mol}^{-1}$$

But for the reaction when written as:

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightarrow NH_3(g) \qquad \Delta_r H^{\circ} = -46 \text{ kJ mol}^{-1}$$

In each case the 'per mole' refers to *one mole of equation*, and not to one mole of any reactant or product.

6B Enthalpy level diagrams

HOW TO DRAW AND INTERPRET ENTHALPY LEVEL DIAGRAMS

In an exothermic reaction, the final enthalpy of the system is less than its initial enthalpy. The reverse is true for an endothermic process. This is shown in the two **enthalpy level diagrams** in **fig A**.

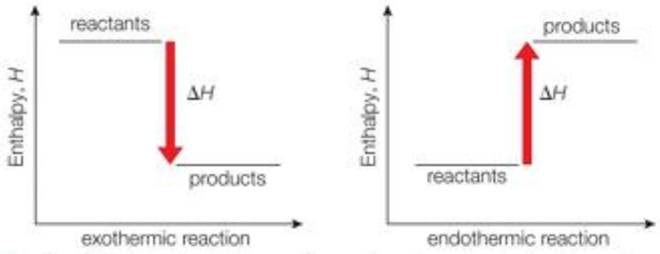


fig A Enthalpy level diagrams for exothermic and endothermic reactions.

The change in enthalpy, ΔH, is given by:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

For an exothermic reaction, $H_{\text{reactants}} > H_{\text{products}}$, so ΔH is negative.

For an endothermic reaction, $H_{\text{reactants}} < H_{\text{products}}$, so ΔH is positive.

Here are some points to remember when constructing enthalpy level diagrams.

- You only need to label the vertical axis. It is not necessary to label the horizontal axis in an enthalpy level diagram (if you did want to label it, you could use either 'Extent of reaction' or 'Progress of reaction'). It is, however, essential to label the horizontal axis in an enthalpy profile diagram (see Topic 9 on reaction kinetics).

- The formulae for both reactants and products should be given, including their state symbols.

- The values for AH should be given, including the correct sign.

- It is not essential to show the activation energy in an enthalpy level diagram, but it should be shown in an enthalpy profile diagram (see Topic 9 on reaction kinetics).

SUBJECT VOCABULARY

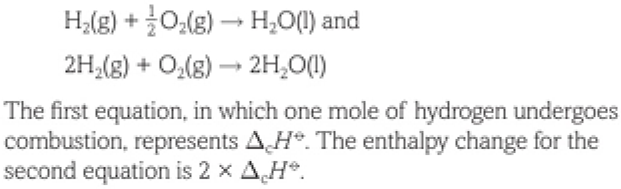
enthalpy level diagram a diagram that shows the relationship between the enthalpy of the reactants and the enthalpy of the products in a chemical reaction

6C Standard enthalpy change of combustion

WHAT IS MEANT BY STANDARD ENTHALPY CHANGE OF COMBUSTION

The standard enthalpy change of combustion (AH) is the enthalpy change measured at 100kPa and a specified temperature, usually 298 K, when one mole of a substance is completely burned in oxygen.

When you are writing an equation to represent the standard enthalpy change of combustion, it is important that you specify it is one mole of the substance that is being burned. Two common ways of writing the combustion of hydrogen are:



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

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

The first equation, in which one mole of hydrogen undergoes combustion, represents $\Delta_c H^{\circ}$. The enthalpy change for the second equation is $2 \times \Delta_c H^{\circ}$.

EXPERIMENTAL DETERMINATION OF ENTHALPY CHANGE OF COMBUSTION OF A LIQUID

To find the enthalpy change of combustion of a liquid, a known mass of the liquid is burned and the heat energy released is used to heat a known volume of water.

The following procedure is used.

- A spirit burner containing the liquid being tested is weighed.
- A known volume of water is added to a copper can.
- The temperature of the water is measured.
- The burner is lit.
- The mixture is constantly stirred with the thermometer.
- When the temperature of the water has reached approximately 20°C above its initial temperature, the flame is extinguished and the burner is immediately reweighed.
- The final temperature is measured.

The appropriate laboratory apparatus is shown in fig A.

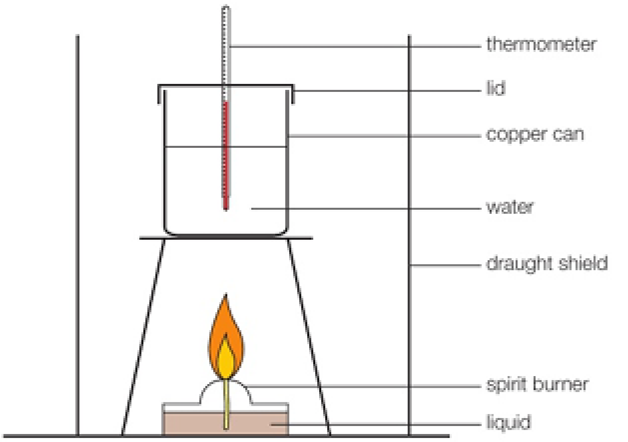
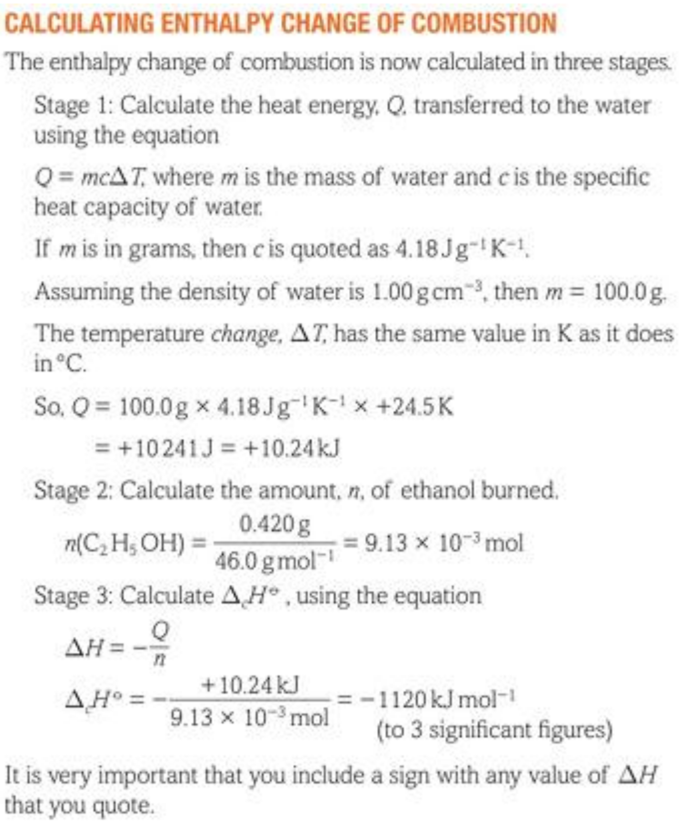


fig A Laboratory apparatus to find the enthalpy change of combustion of a liquid.



CALCULATING ENTHALPY CHANGE OF COMBUSTION

The enthalpy change of combustion is now calculated in three stages.

Stage 1: Calculate the heat energy, Q, transferred to the water using the equation

$Q = mc\Delta T$, where m is the mass of water and c is the specific heat capacity of water.

If m is in grams, then c is quoted as $4.18\,\text{J g}^{-1}\text{K}^{-1}$.

Assuming the density of water is $1.00\,\text{g cm}^{-3}$, then $m = 100.0\,\text{g}$.

The temperature *change*, ΔT, has the same value in K as it does in °C.

$$\text{So, } Q = 100.0\,\text{g} \times 4.18\,\text{J g}^{-1}\text{K}^{-1} \times +24.5\,\text{K}$$
$$= +10\,241\,\text{J} = +10.24\,\text{kJ}$$

Stage 2: Calculate the amount, n, of ethanol burned.

$$n(C_2H_5OH) = \frac{0.420\,\text{g}}{46.0\,\text{g mol}^{-1}} = 9.13 \times 10^{-3}\,\text{mol}$$

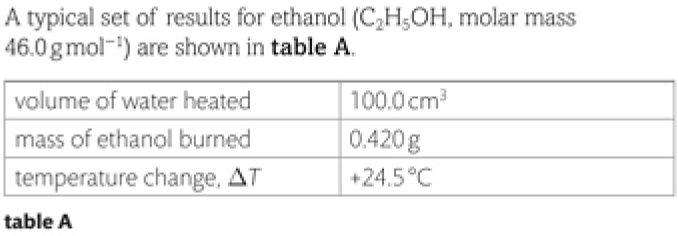
Stage 3: Calculate $\Delta_c H^\circ$, using the equation

$$\Delta H = -\frac{Q}{n}$$

$$\Delta_c H^\circ = -\frac{+10.24\,\text{kJ}}{9.13 \times 10^{-3}\,\text{mol}} = -1120\,\text{kJ mol}^{-1}$$

(to 3 significant figures)

It is very important that you include a sign with any value of ΔH that you quote.



A typical set of results for ethanol (C_2H_5OH, molar mass $46.0\,\text{g mol}^{-1}$) are shown in **table A**.

volume of water heated	$100.0\,\text{cm}^3$
mass of ethanol burned	0.420 g
temperature change, ΔT	+24.5 °C

table A

EVALUATING SOURCES OF ERROR AND ASSUMPTIONS MADE IN THE EXPERIMENTS

The value obtained from the above experiment is in reasonable agreement with the standard enthalpy change of combustion of ethanol, as obtained from a data book, of -1367 kJ mol1. This means that the errors in procedure were minimal.
Here are some possible sources of error.

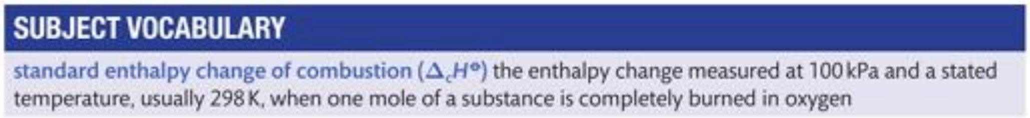
- Some of the heat energy produced in burning is transferred to the air and not the water.

- Some of the ethanol may not burn completely to form carbon dioxide and water. (Incomplete combustion would produce less heat energy and also cause soot to form on the bottom of the copper can.)

- Some of the heat energy produced in burning is transferred to the copper can and not to the water.

- The conditions are not standard. For example, water vapour, not liquid water, is produced.

- The experiment takes a long time. This means that not all of the heat energy transferred from the water to the surroundings is compensated for.



SUBJECT VOCABULARY

standard enthalpy change of combustion ($\Delta_c H^\circ$) the enthalpy change measured at 100 kPa and a stated temperature, usually 298 K, when one mole of a substance is completely burned in oxygen

6D Standard enthalpy change of neutralization

WHAT IS MEANT BY STANDARD ENTHALPY CHANGE OF NEUTRALISATION?

The standard enthalpy change of neutralisation (AneutH°) is the enthalpy change measured at 100kPa and a specified temperature, usually 298 K, when one mole of water is produced by the neutralisation of an acid with an alkali.

The following equation represents the standard enthalpy change of neutralisation of hydrochloric acid:

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

For sulfuric acid, it is the enthalpy change for:

$$\tfrac{1}{2}H_2SO_4(aq) + NaOH(aq) \rightarrow \tfrac{1}{2}Na_2SO_4(aq) + H_2O(l)$$

For certain combinations of acid and alkali, the standard enthalpy change of neutralisation is remarkably constant. Some values are shown in **table A**.

ACID	ALKALI	$\Delta_{neut}H^{\circ}$ / kJ mol^{-1}
HCl(aq)	NaOH(aq)	-57.9
HBr(aq)	KOH(aq)	-57.6
HNO_3(aq)	NaOH(aq)	-57.6

table A The standard enthalpy change of neutralisation is remarkably constant for certain combinations of acid and alkali.

All of the acids and alkalis in **table A** are classified as strong acids/alkalis. If we make the assumption that strong acids and alkalis are fully ionised in aqueous solution, then the reaction between them is simplified to:

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

Because the reaction is essentially the same in each case, it is not surprising that the enthalpy changes are so similar.

EXPERIMENTAL DETERMINATION OF ENTHALPY CHANGE OF NEUTRALISATION

Here is how to find the enthalpy change of neutralisation.

- Wear safety glasses and a lab coat.
- Using a pipette fitted with a safety filler, place 25.0 cm^3 of 1.00 mol dm^{-3} acid into an expanded polystyrene cup.
- Measure the temperature of the acid.
- Using a pipette fitted with a safety filler, place 25.0 cm^3 of the alkali (usually dilute sodium hydroxide of a concentration slightly greater than 1.00 mol dm^3 (to make sure all the acid is neutralised)) into a beaker.

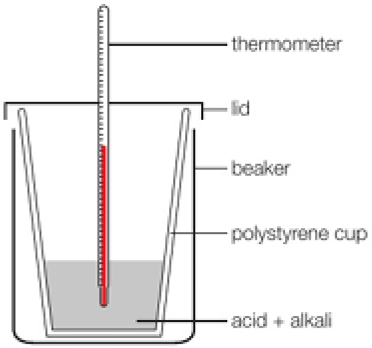
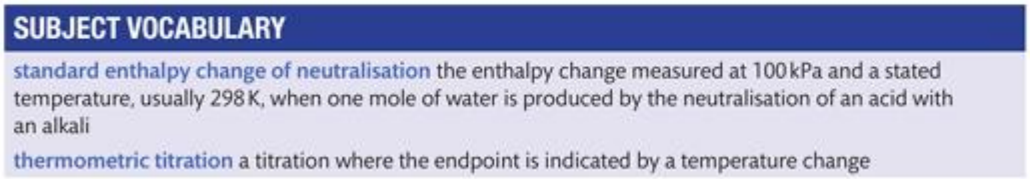


fig A Apparatus used to find the enthalpy change of neutralisation.

- Measure the temperature of the alkali.
- Add the alkali to the acid, stir with the thermometer and measure the maximum temperature reached.
- The appropriate laboratory apparatus is shown in fig A.

EVALUATING SOURCES OF ERROR AND ASSUMPTIONS MADE IN THE EXPERIMENTS

Answers should be given to only two significant figures. This is because AT is given to only two significant figures. There are the usual uncertainties of measurements involved with the use of the pipette and the thermometer. Additionally, some heat energy will be transferred to the thermometer and the polystyrene cup.



SUBJECT VOCABULARY

standard enthalpy change of neutralisation the enthalpy change measured at 100 kPa and a stated temperature, usually 298 K, when one mole of water is produced by the neutralisation of an acid with an alkali

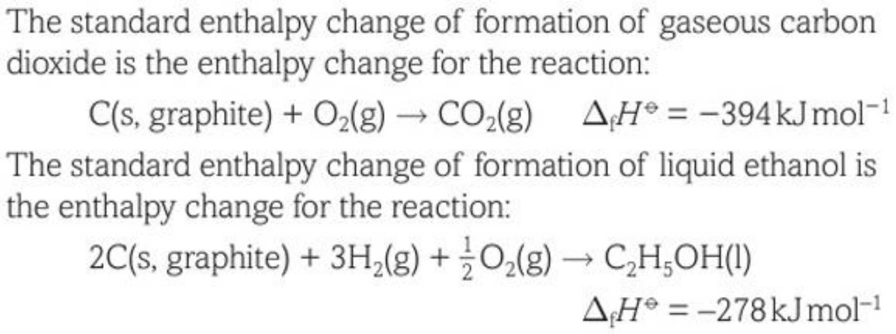
thermometric titration a titration where the endpoint is indicated by a temperature change

6E Standard enthalpy change of formation and Hess's Law

WHAT IS MEANT BY STANDARD ENTHALPY CHANGE OF FORMATION?

The standard enthalpy change of formation (A_fH®) is the enthalpy change measured at 100kPa and a specified temperature, usually 298 K, when one mole of a substance is formed from its elements in their standard states. For the purposes of this definition, the standard state of an element is the form in which it exists at the specified temperature, usually 298 K, and a pressure of 100 kPa.

The standard enthalpy change of formation of gaseous carbon dioxide is the enthalpy change for the reaction:



The standard enthalpy change of formation of gaseous carbon dioxide is the enthalpy change for the reaction:

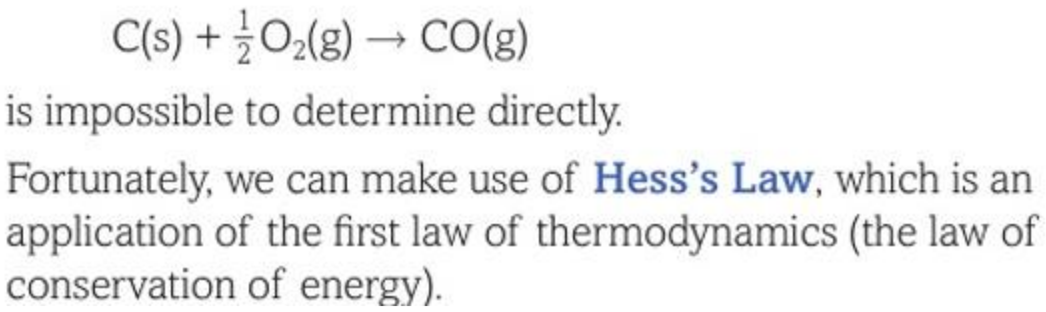
$$C(s, graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_f H^{\circ} = -394\,kJ\,mol^{-1}$$

The standard enthalpy change of formation of liquid ethanol is the enthalpy change for the reaction:

$$2C(s, graphite) + 3H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_5OH(l) \qquad \Delta_f H^{\circ} = -278\,kJ\,mol^{-1}$$

HESS'S LAW

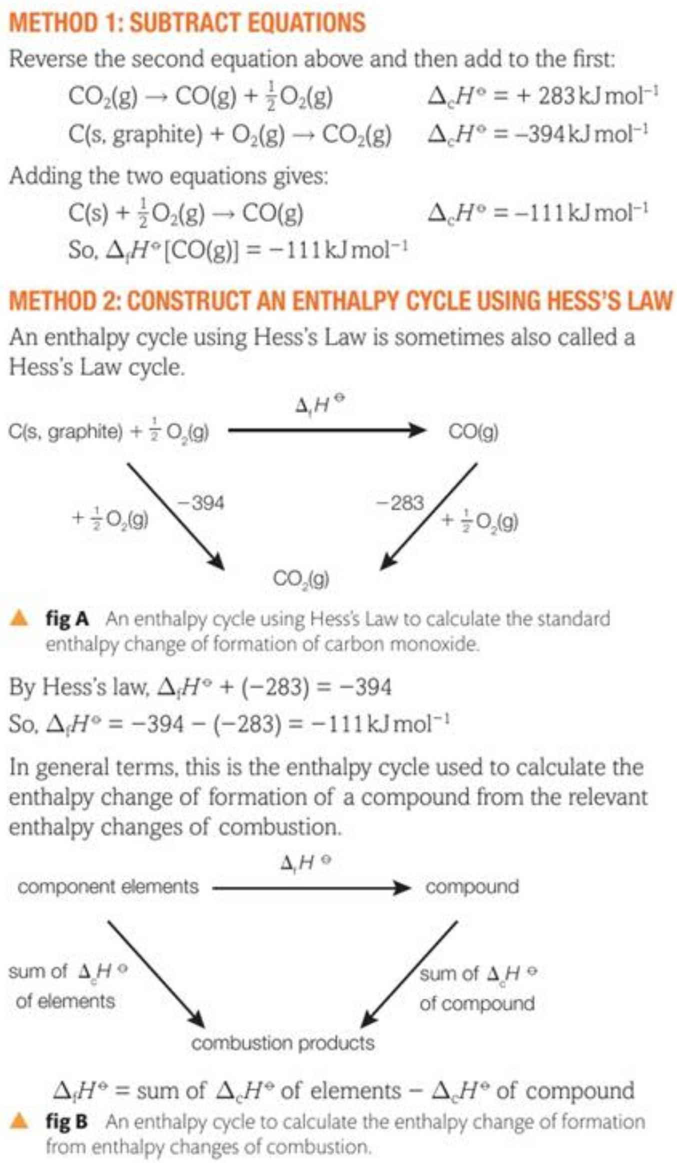
Most standard enthalpy changes of formation cannot be determined experimentally. For example, it is impossible to burn carbon in oxygen and form solely carbon monoxide. So, the enthalpy change for the reaction



$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$$

is impossible to determine directly.

Fortunately, we can make use of **Hess's Law**, which is an application of the first law of thermodynamics (the law of conservation of energy).



METHOD 1: SUBTRACT EQUATIONS

Reverse the second equation above and then add to the first:

$$CO_2(g) \rightarrow CO(g) + \tfrac{1}{2}O_2(g) \qquad \Delta_c H^\ominus = +283\,kJ\,mol^{-1}$$
$$C(s, graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_c H^\ominus = -394\,kJ\,mol^{-1}$$

Adding the two equations gives:

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta_c H^\ominus = -111\,kJ\,mol^{-1}$$

So, $\Delta_f H^\ominus[CO(g)] = -111\,kJ\,mol^{-1}$

METHOD 2: CONSTRUCT AN ENTHALPY CYCLE USING HESS'S LAW

An enthalpy cycle using Hess's Law is sometimes also called a Hess's Law cycle.

$$\begin{tikzcd}
C(s, graphite) + \frac{1}{2}O_2(g) \arrow[rr, "\Delta_f H^\ominus"] \arrow[dr, "-394", "+\frac{1}{2}O_2(g)"'] & & CO(g) \arrow[dl, "-283"', "+\frac{1}{2}O_2(g)"] \\
& CO_2(g) &
\end{tikzcd}$$

fig A An enthalpy cycle using Hess's Law to calculate the standard enthalpy change of formation of carbon monoxide.

By Hess's law, $\Delta_f H^\ominus + (-283) = -394$

So, $\Delta_f H^\ominus = -394 - (-283) = -111\,kJ\,mol^{-1}$

In general terms, this is the enthalpy cycle used to calculate the enthalpy change of formation of a compound from the relevant enthalpy changes of combustion.

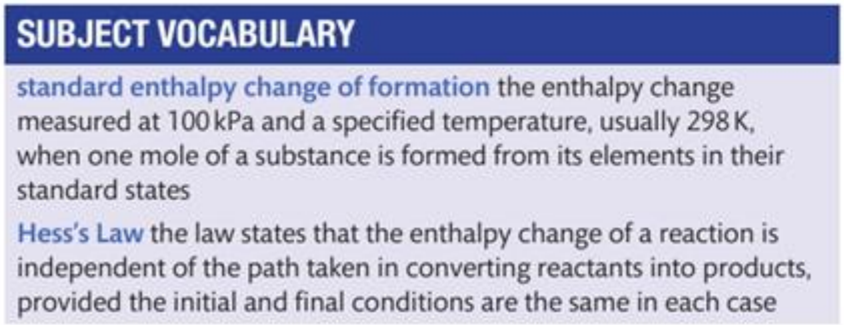
$$\begin{tikzcd}
\text{component elements} \arrow[rr, "\Delta_f H^\ominus"] \arrow[dr, "\text{sum of } \Delta_c H^\ominus \text{ of elements}"'] & & \text{compound} \arrow[dl, "\text{sum of } \Delta_c H^\ominus \text{ of compound}"] \\
& \text{combustion products} &
\end{tikzcd}$$

$$\Delta_f H^\ominus = \text{sum of } \Delta_c H^\ominus \text{ of elements} - \Delta_c H^\ominus \text{ of compound}$$

fig B An enthalpy cycle to calculate the enthalpy change of formation from enthalpy changes of combustion.

USING HESS'S LAW FOR OTHER REACTIONS

Hess's Law can be used to calculate the enthalpy change for many different types of reaction.

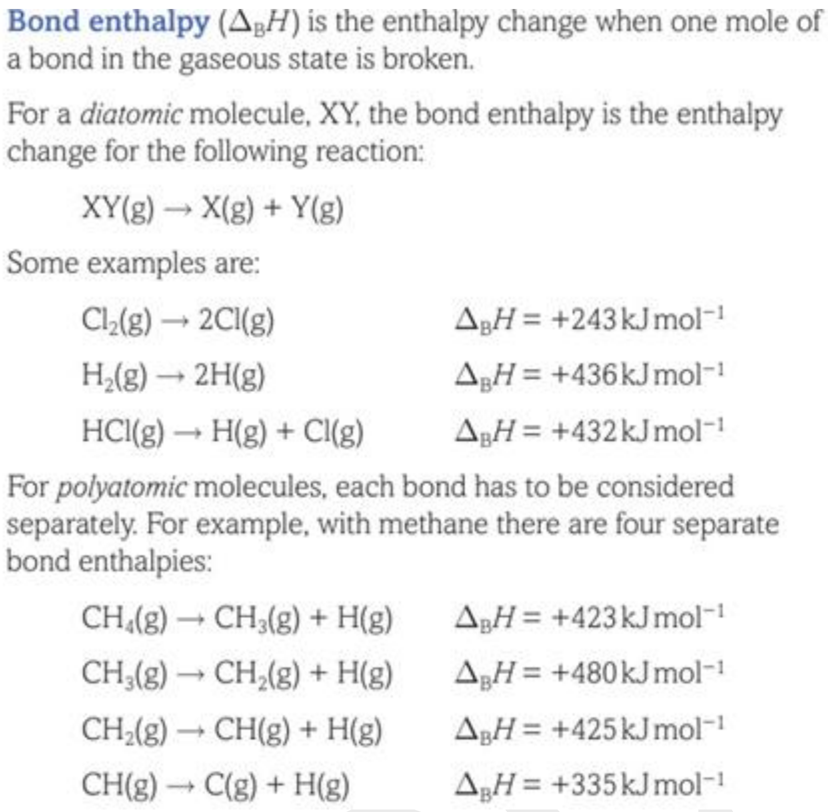


SUBJECT VOCABULARY

standard enthalpy change of formation the enthalpy change measured at 100 kPa and a specified temperature, usually 298 K, when one mole of a substance is formed from its elements in their standard states

Hess's Law the law states that the enthalpy change of a reaction is independent of the path taken in converting reactants into products, provided the initial and final conditions are the same in each case

6F Bond enthalpy and mean bond enthalpy



Bond enthalpy ($\Delta_B H$) is the enthalpy change when one mole of a bond in the gaseous state is broken.

For a *diatomic* molecule, XY, the bond enthalpy is the enthalpy change for the following reaction:

$$XY(g) \rightarrow X(g) + Y(g)$$

Some examples are:

$$Cl_2(g) \rightarrow 2Cl(g) \qquad \Delta_B H = +243\,kJ\,mol^{-1}$$

$$H_2(g) \rightarrow 2H(g) \qquad \Delta_B H = +436\,kJ\,mol^{-1}$$

$$HCl(g) \rightarrow H(g) + Cl(g) \qquad \Delta_B H = +432\,kJ\,mol^{-1}$$

For *polyatomic* molecules, each bond has to be considered separately. For example, with methane there are four separate bond enthalpies:

$$CH_4(g) \rightarrow CH_3(g) + H(g) \qquad \Delta_B H = +423\,kJ\,mol^{-1}$$

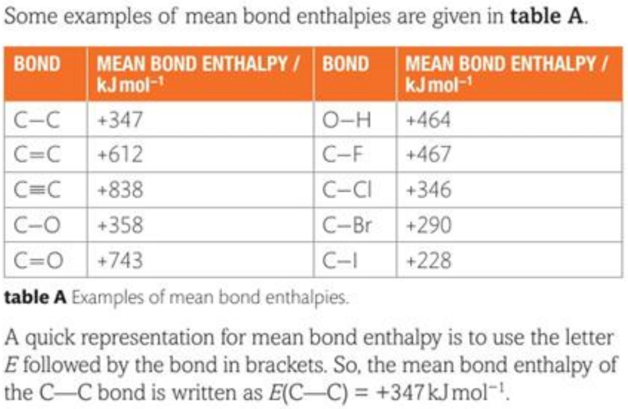
$$CH_3(g) \rightarrow CH_2(g) + H(g) \qquad \Delta_B H = +480\,kJ\,mol^{-1}$$

$$CH_2(g) \rightarrow CH(g) + H(g) \qquad \Delta_B H = +425\,kJ\,mol^{-1}$$

$$CH(g) \rightarrow C(g) + H(g) \qquad \Delta_B H = +335\,kJ\,mol^{-1}$$

WHAT IS MEAN BOND ENTHALPY?

You will notice that the bond enthalpy of the C-H bond varies with its environment. For this reason it is often useful to quote the mean bond enthalpy.
The mean bond enthalpy for the C-H bond in methane is approximately +416kJ mol^{-1}.

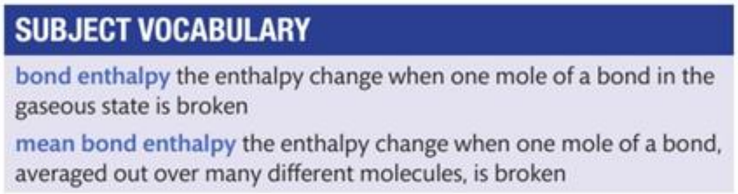


Some examples of mean bond enthalpies are given in **table A**.

BOND	MEAN BOND ENTHALPY / $kJ\,mol^{-1}$	BOND	MEAN BOND ENTHALPY / $kJ\,mol^{-1}$
C–C	+347	O–H	+464
C=C	+612	C–F	+467
C≡C	+838	C–Cl	+346
C–O	+358	C–Br	+290
C=O	+743	C–I	+228

table A Examples of mean bond enthalpies.

A quick representation for mean bond enthalpy is to use the letter *E* followed by the bond in brackets. So, the mean bond enthalpy of the C—C bond is written as *E*(C—C) = +347 kJ mol^{-1}.



SUBJECT VOCABULARY

bond enthalpy the enthalpy change when one mole of a bond in the gaseous state is broken

mean bond enthalpy the enthalpy change when one mole of a bond, averaged out over many different molecules, is broken

6G Using mean bond enthalpies

CALCULATING AN ENTHALPY CHANGE OF REACTION USING MEAN BOND ENTHALPIES

Here is the process for calculating an enthalpy change of reaction using mean bond enthalpies.

- Step 1: Calculate the sum of the mean bond enthalpies of the bonds broken, Σ(bonds broken).

- Step 2: Calculate the sum of the mean bond enthalpies of the bonds made, Σ(bonds made).

- Step 3: Calculate the enthalpy change of reaction using the equation:

$$\Delta_r H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$$

LIMITATIONS OF THIS METHOD OF CALCULATION

The measured value for the enthalpy change of this reaction is -98 kJ mol-1. The reason for the difference is that bond enthalpies are measured in the gaseous state, and both hydrogen peroxide and water are liquids in the reaction. Also, mean bond enthalpies have been used and these may not correspond to the bond enthalpies in the molecules themselves.

CALCULATING MEAN BOND ENTHALPIES FROM ENTHALPY CHANGES OF REACTION

For this type of calculation, you will be supplied with a value for the enthalpy change of a reaction, together with all the relevant mean bond enthalpies except one: the one you are asked to calculate. To solve the problem, simply substitute the known mean bond enthalpies and the unknown bond enthalpy into the expression:

$$\Delta_r H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$$

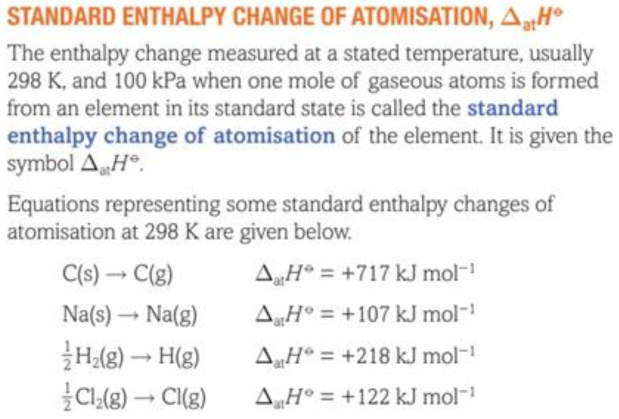
Rearrange the expression to make the unknown bond enthalpy the subject, and solve the problem.

BOND ENTHALPIES AND EASE OF REACTION

Bond enthalpies can be used to predict which bonds are most likely to break first in a reaction, and how easy it is to break the bond.

Bonds with high bond enthalpies require more energy to break them. Bonds with relatively low bond enthalpies require less energy to break them. This means that they are easier to break, and therefore are more likely to break first in a chemical reaction.

A reaction that involves breaking bonds with low bond enthalpies is more likely to take place at room temperature than reactions involving molecules with high bond enthalpies. Reactions involving the breaking of bonds with high bond enthalpies are more likely to require heating and/or the use of a catalyst.



STANDARD ENTHALPY CHANGE OF ATOMISATION, $\Delta_{at}H^{\circ}$

The enthalpy change measured at a stated temperature, usually 298 K, and 100 kPa when one mole of gaseous atoms is formed from an element in its standard state is called the **standard enthalpy change of atomisation** of the element. It is given the symbol $\Delta_{at}H^{\circ}$.

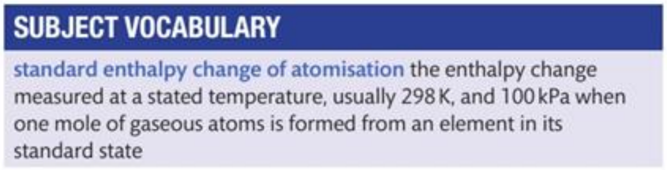
Equations representing some standard enthalpy changes of atomisation at 298 K are given below.

$C(s) \rightarrow C(g)$ $\Delta_{at}H^{\circ} = +717\ kJ\ mol^{-1}$

$Na(s) \rightarrow Na(g)$ $\Delta_{at}H^{\circ} = +107\ kJ\ mol^{-1}$

$\frac{1}{2}H_2(g) \rightarrow H(g)$ $\Delta_{at}H^{\circ} = +218\ kJ\ mol^{-1}$

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ $\Delta_{at}H^{\circ} = +122\ kJ\ mol^{-1}$



SUBJECT VOCABULARY

standard enthalpy change of atomisation the enthalpy change measured at a stated temperature, usually 298 K, and 100 kPa when one mole of gaseous atoms is formed from an element in its standard state

Revision questions

1.

A thermometric titration is a method for finding the end-point of a titration between aqueous solutions of ammonia and ethanoic acid.

A thermometric titration was carried out using the following steps:

- the temperatures of the aqueous ammonia and ethanoic acid solutions were measured and found to be 20.1 °C
- 30 cm^3 of the aqueous ammonia was placed in a polystyrene cup
- a 10 cm^3 portion of an ethanoic acid solution, concentration 1.10 mol dm^{-3} , was added to the polystyrene cup, the mixture stirred and the temperature measured
- further 10 cm^3 portions of ethanoic acid solution were added, the mixture stirred, and the temperature measured immediately after each addition, until a total of 80 cm^3 had been added.

Results for this experiment are shown in the table.

Volume of ethanoic acid added / cm^3	0	10	20	30	40	50	60	70	80
Temperature / °C	20.1	21.8	23.5	25.1	26.4	25.8	24.9	24.1	23.3

(i) The temperature of the reaction mixture initially increased because the reaction is

(1)

☒ **A** endothermic so energy is absorbed by the water
☒ **B** endothermic so energy is released by the water
☒ **C** exothermic so energy is absorbed by the water
☒ **D** exothermic so energy is released by the water

(ii) Give the main reason why, after the end-point was reached, the temperature of the solution decreased.

(1)

2.

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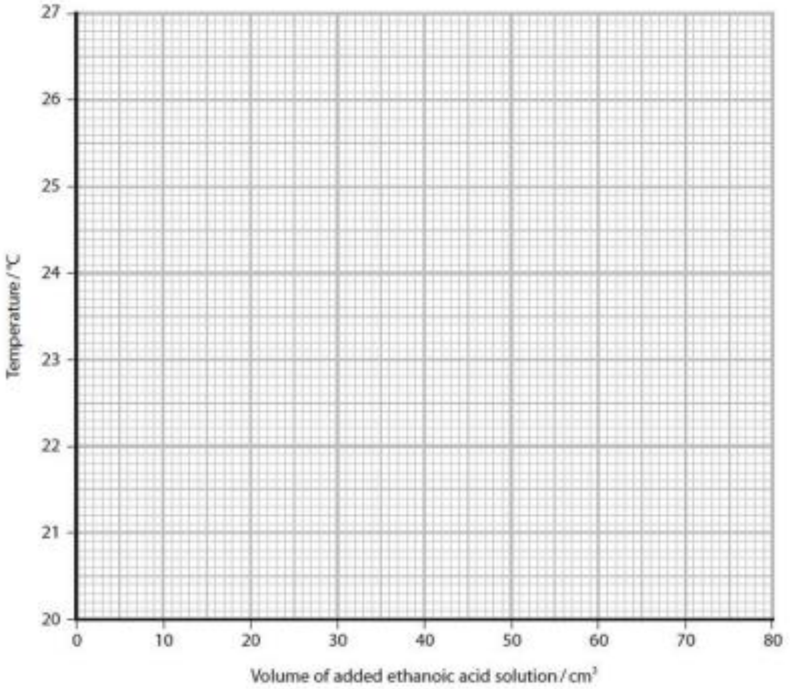
(i) Plot the results using the axes provided.

Include two straight lines of best fit, extrapolated until they meet.

(2)



(ii) Determine the maximum temperature rise from your graph.

(iii) Calculate the number of moles of ethanoic acid, with a concentration of 1.10 mol dm−3 , added at the end-point of the reaction.

(iv) The reaction that occurs is

$$NH_3(aq) + CH_3COOH(aq) \rightarrow NH_4^+(aq) + CH_3COO^-(aq)$$

Calculate the enthalpy change per mole for this reaction.
Include a sign and units in your answer.
[Assume:
specific heat capacity of the solution at the end-point = 4.18 J g^{-1} °C^{-1} 1.00 cm^3 of the solution at the end-point has a mass of 1.00 g]

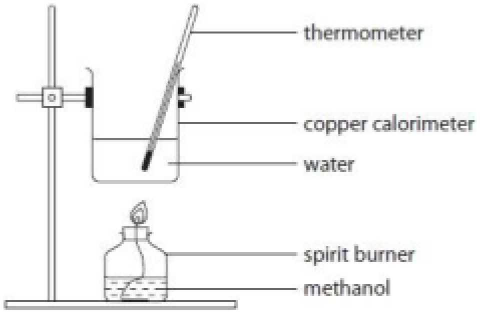
3.

This question is about the enthalpy change of combustion of methanol.

A teacher asked two students to carry out a practical task to determine the enthalpy change of combustion of methanol.
Both students were provided with the same apparatus and chemicals.
The following procedure was provided for the students.

Procedure

- Measure out 150 cm^3 of distilled water, using a 250 cm^3 measuring cylinder.
- Transfer the water to a copper calorimeter and note the initial temperature of the water (to the nearest 0.5°C) in **Table 1**.
- Weigh the spirit burner containing methanol and record its mass in **Table 1**.
- Place the spirit burner under the copper calorimeter, as shown in the diagram.
- Ignite the spirit burner and burn the methanol, whilst stirring the water with the thermometer.
- After heating the water for three minutes, extinguish the flame and immediately record the **highest** temperature reached by the water.
- As soon as possible, reweigh the spirit burner containing the methanol and record its mass in **Table 1**.



The results of Student 1 are recorded in **Table 1**.

Mass of spirit burner plus methanol before burning / g	213.47
Mass of spirit burner plus methanol after burning / g	211.87
Mass of methanol burned / g	
Highest temperature of the water / °C	64.5
Initial temperature of the water / °C	22.0
Temperature change of the water / °C	

Table 1

(a) Complete **Table 1**, giving the values to an appropriate number of decimal places.

(b) Write the equation that represents the reaction that occurs when the standard enthalpy change of combustion of methanol, $CH_3OH(l)$, is measured. Include state symbols.

(c) Use Student 1's result to calculate the enthalpy change of combustion of methanol in kJ mol^{-1}.
Give your answer to an appropriate number of significant figures.

Specific heat capacity of water = 4.18 J g^{-1} $°C^{-1}$
Density of water = 1.00 g cm^{-3}

(4)

(d) Student 1 compared the experimental value for the enthalpy change of combustion of methanol obtained in part (c) with the standard value given on the internet.
The student's value was **less exothermic** than the standard value.

Student 1 decided to evaluate the uncertainty in the measurements made in this experiment.

(i) Student 1 used a 250 cm^3 measuring cylinder to measure the volume of 150 cm^3 distilled water. The uncertainty in this volume measurement is ±1 cm^3.
Calculate the percentage uncertainty in the volume of distilled water that Student 1 measured in the experiment.

(1)

(ii) Compare and contrast the use of a 250 cm^3 measuring cylinder to measure out the 150 cm^3 distilled water with the use of a 25 cm^3 measuring cylinder (uncertainty ±0.2 cm^3 for each volume measurement) six times to measure the same volume.

(3)

(iii) Student 1 calculated the uncertainties in the remaining measurements. However, Student 1 realised that the measurement uncertainties did **not** explain the difference between the experimental value for the enthalpy change of combustion of methanol calculated in part (c) and the value obtained from the internet.
Other than human error, give **three** reasons for the difference in the values.

(3)

(e) Student 1 decided to repeat the experiment.

Student 1 used the copper calorimeter and water from the first experiment and recorded the initial temperature as 60.0°C.
Student 1 burned **exactly** the same mass of methanol as in the first experiment.
Explain, with a reason, how the value for the enthalpy change of combustion of methanol from this experiment would differ, if at all, from the value obtained in the first experiment.

(2)

(f) Student 2 followed the **original** instructions provided, but extinguished the flame after **four** minutes rather than after three minutes.

Explain how the value calculated by Student 2 for the enthalpy change of combustion of methanol compared with that obtained in Student 1's first experiment.

(2)

(g) Another student, Student 3, used the results from Student 1's first experiment to find the enthalpy change of combustion of methanol. Student 3 incorrectly used a value of 46.0 g mol^{-1} for the molar mass of methanol.

State and justify how this mistake would affect the calculated value for the enthalpy change of combustion of methanol.

(2)

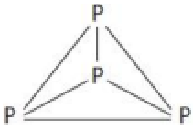
4.

The halogens are elements in Group 7 of the Periodic Table.

Chlorine compounds have many uses, including water treatment.

(i) Chlorine and phosphorus (P_4) can react to form phosphorus(V) chloride.

The structure of a molecule of phosphorus is



Some mean bond enthalpy values are shown in the table.

Bond	Mean bond enthalpy / kJ mol^{-1}
P—P	+198
Cl—Cl	+243
P—Cl	+326

Calculate the enthalpy change for the reaction between chlorine and phosphorus to form phosphorus(V) chloride.

$$10Cl_2 + P_4 \rightarrow 4PCl_5$$

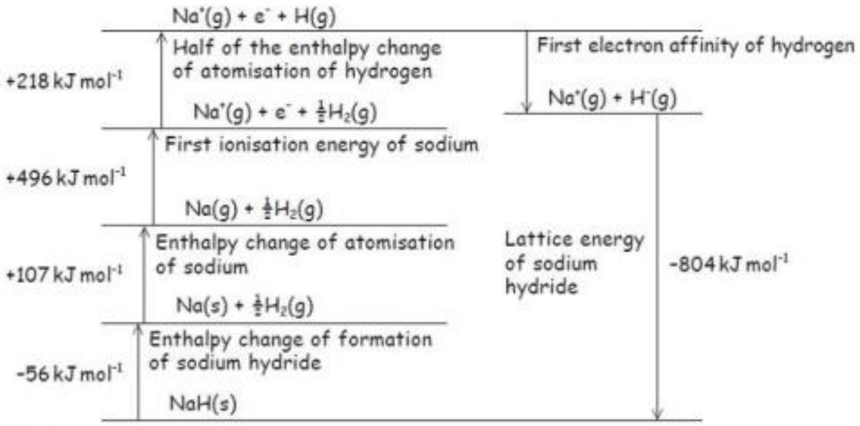
(ii) Give a reason why bond enthalpy values are always positive

5.

Sodium hydride, NaH, can be used to generate hydrogen for fuel cells.

In order to calculate the first electron affinity of hydrogen, a student was asked to draw a Born-Haber cycle for sodium hydride.

The cycle had **two** errors but the numerical data were correct.



(i) Identify and correct the **two** errors in this Born-Haber cycle.

(ii) Calculate the first electron affinity, in kJ mol–1 , of hydrogen, using the values given in the cycle.

6.

Nitrogen monoxide and chlorine gases react together to form a single product, nitrosyl chloride, NOCl.

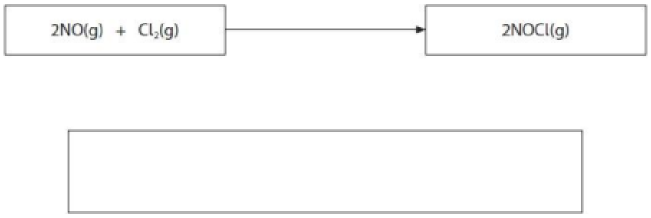
Below 100 °C the yield of NOCl is almost 100 %, but as the temperature rises the yield of NOCl decreases as the equilibrium position shifts to the left.

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad \Delta_r H^\ominus = -75.6 \text{ kJ mol}^{-1}$$

(i) Complete the Hess cycle to enable you to calculate the enthalpy change of formation, $\Delta_f H^\ominus_{298}$, of NOCl.

Include state symbols.

(2)



(ii) Calculate the enthalpy change of formation, $\Delta_f H^\ominus_{298}$, of NOCl given the data

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad \Delta_r H^\ominus_{298} = -75.6 \text{ kJ mol}^{-1}$$

enthalpy change of formation of NO, $\Delta_f H^\ominus_{298}$, $= +90.3$ kJ mol^{-1}

(2)

7.

When solid calcium sulfate dihydrate, $CaSO_4{\cdot}2H_2O$, is heated in a crucible, it forms solid calcium sulfate hemihydrate, $CaSO_4{\cdot}½H_2O$.

When water is added to calcium sulfate hemihydrate, there is a rise in temperature.

A student decided to investigate this reaction using the following procedure:

Step 1 10 cm^3 of distilled water is measured using a measuring cylinder having an uncertainty of ±0.5 cm^3, and is placed in an insulated cup with a lid.

Step 2 A thermometer with an uncertainty of ±0.5 °C is placed in the water.

Step 3 Exactly 10.00 g of calcium sulfate hemihydrate is weighed out using a balance with an uncertainty of ±0.005 g.

Step 4 The weighed quantity of calcium sulfate hemihydrate is added to the water in the insulated cup.

Step 5 The mixture in the insulated cup is stirred until no further temperature change is observed.

Results

Temperature of the water before adding the solid = 23.5 °C

Maximum temperature of the mixture after adding the solid = 26.3 °C

Other data

Molar mass of calcium sulfate hemihydrate, $CaSO_4{\cdot}½H_2O$ = 145.2 g mol^{-1}

Density of water = 1.00 g cm^{-3}

(i) Calculate the minimum volume of water needed to convert 10.00 g of $CaSO_4{\cdot}½H_2O$ into $CaSO_4{\cdot}2H_2O$.

(2)

(ii) Calculate the enthalpy change, in kJ mol^{-1}, for this reaction.
Include a sign in your answer and give your answer to an appropriate number of significant figures.

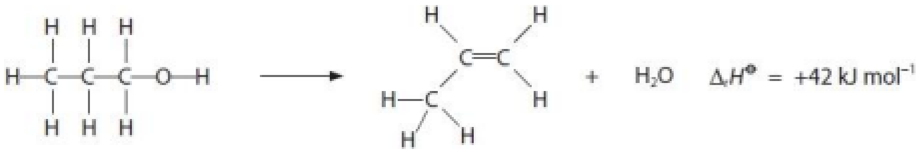
Assume that the liquid has a mass of 10.00 g and a specific heat capacity of 4.18 J g^{-1} °C^{-1}.

(4)

8.

This question is about enthalpy changes and entropy changes.

Propan-1-ol is dehydrated to form propene.



The relevant mean bond enthalpies are given in the table.

Bond	Mean bond enthalpy / kJ mol^{-1}
C—C	347
C═C	612
C—H	413
O—H	464

Calculate the C—O mean bond enthalpy, using the mean bond enthalpies given in the table and the enthalpy change of reaction.

(3)