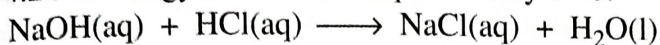


**Example 4.1****Calculating enthalpy from experimental data**

When 50.0 mL of 2.0 mol L<sup>-1</sup> sodium hydroxide solution neutralised 50.0 mL of 2.0 mol L<sup>-1</sup> hydrochloric acid solution, the temperature of the solution rose from 21 °C to 35 °C. Calculate the heat of the reaction assuming 1.0 mL of the combined solution required 4.2 J of energy to raise its temperature by 1 °C.



Calculate the temperature change.

$$\begin{aligned} \text{Temperature change} &= 35\text{ °C} - 21\text{ °C} \\ &= 14\text{ °C.} \end{aligned}$$

Calculate the energy change.

$$\begin{aligned} m(\text{water}) &= 100.0\text{ g} \quad \Delta T = 14\text{ °C} \quad s = 4.2\text{ J g}^{-1}\text{ °C}^{-1} \\ \Delta E &= m(\text{water}) \times \Delta T \times s \\ &= 100\text{ g} \times 14\text{ °C} \times 4.2\text{ J g}^{-1}\text{ °C}^{-1} \\ &= 5880\text{ J} \\ &= 5.9\text{ kJ (2 sig fig)} \end{aligned}$$

Calculate the enthalpy change in kJ mol<sup>-1</sup>

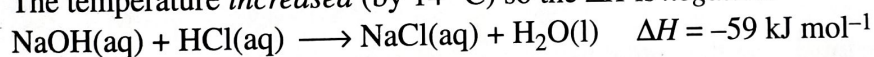
$$V(\text{NaOH}) = 50.0\text{ mL} \quad c(\text{NaOH}) = 2.0\text{ mol L}^{-1} \quad n(\text{NaOH}) = ?$$

$$\begin{aligned} n(\text{NaOH}) &= \frac{cV}{1000} \\ &= \frac{2.0\text{ mol L}^{-1} \times 50.0\text{ mL}}{1000} \\ &= 0.1\text{ mol} \end{aligned}$$

$$\begin{aligned} \Delta H(\text{reaction}) &= \frac{\Delta E}{n} \\ &= \frac{5.9\text{ kJ}}{0.1\text{ mol}} \\ &= 59\text{ kJ mol}^{-1} \end{aligned}$$

Write the thermochemical equation, including the appropriate sign for the  $\Delta H$ .

The temperature *increased* (by 14 °C) so the  $\Delta H$  is *negative*.



- Many students make the mistake of trying to calculate the energy change by using the mass of one of the reagents, rather than the mass of water (or aqueous solution) absorbing the energy.

## 2 Calculating enthalpy from heats of formation

If we know the standard enthalpies of formation for all the compounds in a given reaction, we can calculate the enthalpy of reaction using the following formula:

$$\Delta_r H^\circ = \Sigma \Delta_f H^\circ(\text{products}) - \Sigma \Delta_f H^\circ(\text{reactants})$$

(the symbol  $\Sigma$  means 'sum of').

These calculations are relatively straight-forward, providing you remember the following:

- the formula only works if the heats of *formation* for all the compounds are used.
- set your work out very carefully, paying close attention to the + and - signs.

If you have time during a test or exam, it is probably a good idea to repeat the calculation just to make sure you haven't made an arithmetical error.

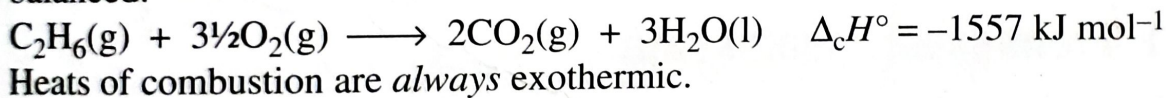
## Data book enthalpies

We can't measure enthalpies of specific reactants or products directly: all we can measure are enthalpy changes. Rather than list the enthalpy change for every possible chemical reaction, data books list the standard enthalpy of combustion and/or the standard enthalpy of formation for compounds. These figures can be used to calculate the enthalpy change for other reactions.

### $\Delta_c H^\circ$ —Standard enthalpy (heat) of combustion

*The standard enthalpy of combustion is the enthalpy change when one mole of the substance is completely burnt, with all reactants and products in their standard states.*

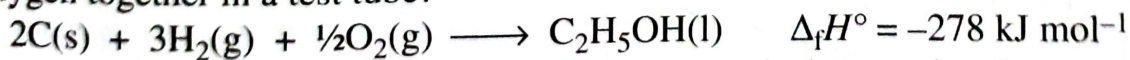
**Standard states** are the states at room temperature (25° C) and pressure—that is, oxygen is O<sub>2</sub>(g) and water is H<sub>2</sub>O(l) (even though the water forms as a gas first). Since we must start with one mole of the reactant, the equation may end up with fractional co-efficients (numbers) when it is balanced:



### $\Delta_f H^\circ$ —Standard enthalpy (heat) of formation

*The standard enthalpy of formation of a compound is the enthalpy change when one mole of the substance is formed from its elements, with all reactants and products in their standard states.*

Sometimes the equations for enthalpies of formation look rather strange—no-one would really make ethanol by shaking carbon, hydrogen and oxygen together in a test tube!



Data tables list heats of formation for compounds, but not for elements. Can you see why, by looking at the definition again? If we wanted the heat of formation for oxygen—O<sub>2</sub>(g), we'd have to start with O<sub>2</sub>(g), so the enthalpy change would be zero.

*The standard enthalpy of formation for all elements is zero.*

Heats of formation may be exothermic or endothermic, depending on the compound.



**REVISI**

4B 1a



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4B 1b



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## Test yourself 4B Data book enthalpies

- 1 Define the term *standard enthalpy of combustion*.
- 2 State why it is very important to include state symbols in all thermochemical equations.
- 3 Write equations for the enthalpies of combustion of:
  - a ethanol ( $\text{C}_2\text{H}_5\text{OH}$ )
  - b hydrogen
- 4 Define the term *standard enthalpy of formation*.
- 5 Write equations for the enthalpy of formation of:
  - a sodium chloride
  - b  $\text{CH}_3\text{OH}(\text{l})$
- 6 When would  $\Delta_f H$  for an element not be zero? Explain your answer.

## Calculating enthalpy


### 1 From experimental data

Determining the enthalpy change for test tube reactions is a relatively simple process, provided the system is closed (so that no heat is lost). Sometimes the reaction is done in a container which is surrounded by water. More usually at school, one of the reagents is a dilute aqueous solution, and we measure the temperature change of this solution which is assumed to have the same specific heat capacity as pure water. Remember that at room temperature 1.0 mL of water has a mass of 1.0 g, so for dilute aqueous solutions you can assume that 100 mL of solution has the same specific heat capacity as 100 g of water.


The method is:


- 1 Measure the temperature change for a known mass of water.
- 2 Calculate the energy absorbed by the water, using the specific heat capacity of water ( $4.18 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$ ).
- 3 Calculate the energy absorbed or released per mole of reactants.

### POWERPOINT

- 4C  Determining enthalpy experimentally

### PRACTICAL

- 4.2  Heats of combustion  
P 166

- 4.3  Finding the enthalpy change for redox reactions  
P 168

She noticed that after the reaction the liquid in the styrofoam cup was colourless, and that as well as the copper precipitate there was unreacted zinc in the cup.

Her teacher told her that the heat capacity of the liquid would be  $4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ .

a For which reagent ( $\text{Zn}$  or  $\text{CuSO}_4$ ) do you know the exact amount (in moles) which reacted? Give a reason for your answer.

b Calculate the  $\Delta H$  for the reaction between zinc and copper sulfate in  $\text{kJ mol}^{-1}$ .

### 3 Hess's law

The distance between your home and school is the same, no matter what route you use to get there. Likewise, the enthalpy change for a given chemical reaction is independent of the steps taken between reactants and products. This principle is called Hess's law. More formally it states that:

*the enthalpy change for a reaction is independent of the way in which a reaction proceeds and depends only on the initial conditions of the reactants and the final conditions of the products.*

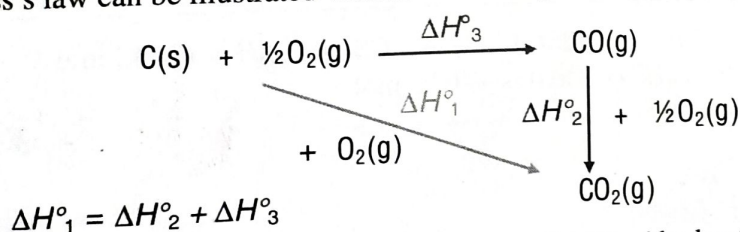


#### PRACTICAL

4.4  
P 170

Hess's law: the law of heat summation

Hess's law can be illustrated with the following:

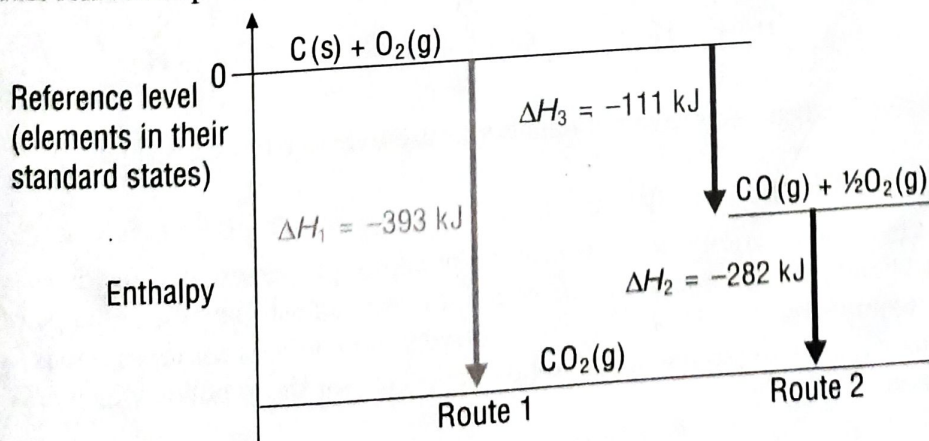


In practice, it is impossible to measure the value of  $\Delta H^\circ_3$  (the heat of formation of  $\text{CO(g)}$ ) directly as some  $\text{CO}_2(\text{g})$  is always formed as a by-product. However we can calculate it using the principle of Hess's law.

Given  $\Delta H^\circ_1 = -393 \text{ kJ mol}^{-1}$  and  $\Delta H^\circ_2 = -282 \text{ kJ mol}^{-1}$

$$\begin{aligned}
 \Delta H^\circ_3 &= \Delta H^\circ_1 - \Delta H^\circ_2 \\
 \Delta H^\circ_3 &= -393 - (-282) \\
 &= -111 \text{ kJ mol}^{-1}
 \end{aligned}$$

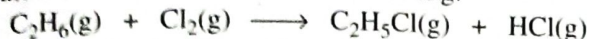
This relationship can also be seen on the following diagram.





**Example 4.4** Enthalpy calculation using bond energies

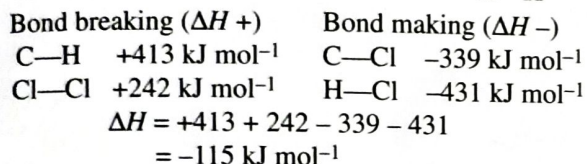
Calculate the heat of reaction for the following:



given the following bond energies:



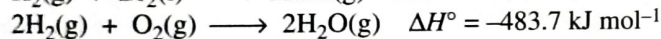
This kind of problem is simple once you write out the equation using graphic formulae, with every bond shown.



**Note:** In multiple bonds such as O=O we do not double the bond energy for the single bond (O—O). The double bond is a different kind of bond from the single bond.

**Test yourself 4D Thermochemical calculations (2)**

1 From the following equations and  $\Delta H^\circ$  values,



calculate the  $\Delta_r H^\circ$  for the following reaction:  $4\text{HBr}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{Br}_2(\text{l}) + 2\text{H}_2\text{O}(\text{g})$

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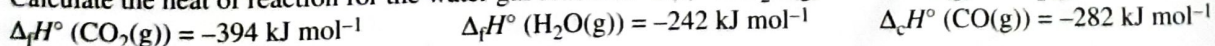
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2 Calculate the heat of reaction for the water gas reaction:  $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$




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**POWERPOINT**

4D 2 Bond energy calculations

Quiz 4D 2

**REVISION**

4D 3a Thermochemical processes

4D 3b Thermochemical definitions hangman