SECOND EDITION

CHEMISTRY

COURSE COMPANION

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OXFORD

Contents

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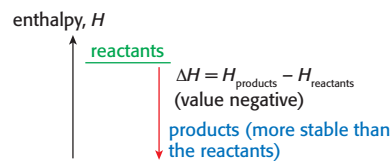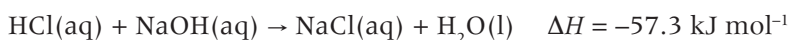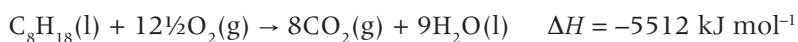
Exothermic and endothermic reactions

As we saw in the previous chapter, chemical reactions involve the breaking and making of bonds. It requires energy to break bonds, and energy is given out when new bonds are formed. If more energy is given out than needs to be put in, then this will be released as heat to the surroundings, and the reaction is said to be **exothermic**. If more energy is required to break the reactant bonds than is given out when the products are formed, then extra heat will need to be added, and the reaction is said to be **endothermic**.
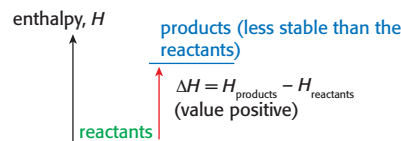

Figure 1 The "thermite reaction" is an example of an exothermic reaction. It is the reaction between a metal such as aluminium or magnesium with iron(III) oxide. The large amount of heat evolved can be used to weld sections of railway lines together.

The energy contained in chemical bonds that can be converted into heat is known as **enthalpy** and is given the symbol H. It is impossible to measure the actual heat content or enthalpy of a particular substance, but what can be readily measured is the enthalpy change for a reaction, ΔH. For exothermic reactions the heat content (enthalpy) of the products is less than that of the reactants. By convention the enthalpy change for the reaction, ΔH, is said to be negative (−). For endothermic reactions, where the enthalpy of the products is more than the enthalpy of the reactants, the enthalpy change, ΔH, will have a positive value (+). Note that the plus and minus symbols indicate the direction of heat flow; they do not imply positive or negative energy.

Examples of exothermic reactions include the combustion of fuels, such as hydrogen or gasoline (petrol), and the neutralization of an acid by a base:

$$C_8H_{18}(l) + 12\tfrac{1}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l) \qquad \Delta H = -5512 \text{ kJ mol}^{-1}$$

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \qquad \Delta H = -57.3 \text{ kJ mol}^{-1}$$

enthalpy, H

reactants

$\Delta H = H_{products} - H_{reactants}$
(value negative)

products (more stable than the reactants)

Representation of an exothermic reaction using an enthalpy diagram

enthalpy, H

products (less stable than the reactants)

$\Delta H = H_{products} - H_{reactants}$
(value positive)

reactants

Representation of an endothermic reaction using an enthalpy diagram

Figure 2 Use of enthalpy diagrams to represent: (a) an exothermic reaction; (b) an endothermic reaction.

An example of an endothermic reaction is the combination of nitrogen and oxygen to form nitrogen dioxide:

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad\qquad \Delta H = +33.9 \text{ kJ mol}^{-1}$$

Another interesting example of an endothermic reaction is the reaction between solid hydrated barium hydroxide and solid ammonium chloride:

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2.2H_2O(s) + 2NH_3(g/aq)$$
$$+ 8H_2O(l) \qquad \Delta H = +96.0 \text{ kJ}$$
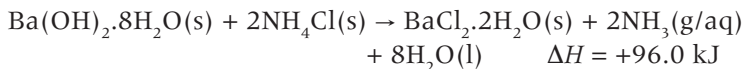
This is interesting not only because it is a reaction between two solids, but also because the temperature decrease is such that the flask will often stick to the bench after the reaction.

When there is a change of state from a solid to a liquid, a solid to a gas, or a liquid to a gas at a constant temperature, the process is also endothermic. For example:

$$Na(s) \rightarrow Na(g) \qquad\qquad \Delta H = +108 \text{ kJ mol}^{-1}$$

Standard enthalpy change of reaction

The actual amount of heat given out or taken in during a chemical reaction will depend on several factors:

- The nature of the reactants and products: different reactions have different values of enthalpy changes, ΔH, as different bonds with different strengths are being broken and formed.
- The amount (or concentration) of reactants: the greater the amount that reacts, the greater the heat change.
- The states of the reactants and products—changing state involves an enthalpy change, and so will affect the total amount of heat given out or taken in.
- The temperature of the reaction.
- The pressure at which the reaction is carried out.

All these factors are taken into account by referring to standard enthalpy changes. The **standard enthalpy change of reaction**, $\Delta H^{\ominus}$, is defined as the enthalpy change when molar quantities of reactants in their normal states react to form products in their normal states under standard conditions of temperature and pressure. Standard pressure is 101.3 kPa (1 atmosphere) and standard temperature is any specified temperature, but usually this is taken as 298 K (25 °C). The symbol $^{\ominus}$ signifies that the enthalpy change has been measured under standard conditions.

It is worth noting that enthalpy changes are normally carried out under **constant pressure**. If the volume is kept constant then the value for the heat change will be slightly different from that at constant pressure, because some work is involved in expanding or contracting a gas. Strictly speaking the enthalpy change, ΔH, is the heat change if the pressure is kept constant; if the volume is kept constant then the total heat change is designated by ΔU.

Calculation of enthalpy changes

Energy is defined as the ability to do work: that is, to move a force through a distance.

Energy = force $\times$ distance
(J)   (N $\times$ m)

$\Delta H^{\ominus}$ values are normally given in kJ mol^{-1}. However, the actual amount of heat evolved in an exothermic reaction is normally measured in practice by using the heat given out to the surroundings to increase the temperature of a known mass of water. Water has a high specific heat capacity and is able to absorb considerable quantities of heat without its temperature increasing significantly. One gram of water requires 4.18 J of heat energy for the temperature of the water to increase by 1 °C. This is known as the specific heat capacity of water, and is often quoted in SI units as 4180 J kg^{-1} K^{-1}.

Experiment: to determine the enthalpy change when 1 mol of ethanol is burned completely

The mass of a spirit lamp containing ethanol was determined accurately. The lamp was then lit and placed under a beaker containing 150 $\pm$ 1 g of pure water (Figure 3). The water was continually stirred. After the temperature of the water had increased by 12.0 $\pm$ 0.5 °C the flame was extinguished and the mass of the spirit lamp containing the unburnt ethanol was determined.
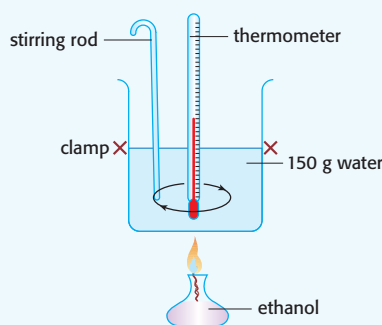

Figure 3 Determining the enthalpy change of combustion of ethanol

Data collection and processing

Observations:
The ethanol burned with a yellow flame. Some black soot was formed on the bottom of the beaker. It was noted that the spirit lamp was warm when it was weighed at the end of the experiment.

Quantitative results:
Mass of spirit lamp + ethanol before burning = 42.597 $\pm$ 0.001 g
Mass of spirit lamp + ethanol after burning = 42.200 $\pm$ 0.001 g
Mass of ethanol burned = 0.397 $\pm$ 0.002 g

Calculation:
Molar mass of ethanol, $C_2H_5OH = [(2 \times 12.01) + (6 \times 1.01) + 16.00] = 46.1$ g mol^{-1}

Amount of ethanol burned $= \dfrac{0.397 \text{ g}}{46.1 \text{ g mol}^{-1}} = 0.00861$ mol

Heat energy required to raise the temperature of 150 g of water by 12.0 °C
$= 150 \times 4.18 \times 12.0 = 7524$ J

Thus heat energy evolved by burning 0.0861 mol of ethanol = 7524 J

Heat energy evolved by burning 1 mol of ethanol $= \dfrac{7524}{0.00861} = 874\ 000\ \text{J} = 874\ \text{kJ}$

Since the reaction is exothermic, $\Delta H^{\ominus} = -874\ \text{kJ mol}^{-1}$

Total uncertainties:

Mass of water $= \dfrac{1}{150} \times 100 = 0.67\%$

Temperature $= \dfrac{0.5}{12} \times 100 = 4.17\%$

Mass of ethanol $= \dfrac{0.002}{0.397} \times 100 = 0.50\%$

Total percentage uncertainties $= 0.67\% + 4.17\% + 0.50\% = 5.34\%$

5.34% of 874 kJ mol^{-1} = 47 kJ mol^{-1}

Summary:

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H^{\ominus} = -874 \pm 47\ \text{kJ mol}^{-1}$

Figure 4 Alexia Leckie from S. Africa and David Wan from Wales, students at Atlantic College carrying out the combustion experiment

Conclusion and evaluation

The Data Booklet value for the standard enthalpy of combustion of ethanol is $-1371\ \text{kJ mol}^{-1}$. The percentage error for this experiment $= \dfrac{1371 - 874}{1371} \times 100$

$= 36.2\%$. This error is large, and cannot be accounted for by the uncertainties in the experimental measurements, although it is worth noting that the largest uncertainty will be due to the thermometer, and a more accurate thermometer could have been used.

The major uncertainties lie in the underlying assumptions used in the experiment. These are many. For example:

- Complete combustion of the ethanol occurred. In fact the ethanol was being burned in air, and the yellow flame and the black soot on the flask indicated that carbon, one of the products of incomplete combustion, was also formed.

- All the heat from the reaction was transferred to the water. Some of the heat would have been lost round the sides of the beaker, and from the water to the atmosphere.

- Only the water was being heated. The glass beaker, the stirrer and the thermometer were also being heated.

- None of the ethanol escaped through evaporation during the time the flame was extinguished and the spirit lamp and its contents were reweighed. Ethanol is a volatile liquid, and the fact that the spirit lamp was hot indicates that some of it would have evaporated.

The result from this experiment emphasises that it is good practice when considering uncertainties in an experiment to consider all the underlying assumptions made, not just simply list and quantify the experimental uncertainties due to the apparatus used to perform the measurements. If these assumptions are not true, then they may have a large effect on the reliability of the result.

?

1 Can you now devise a more accurate method to determine the enthalpy of combustion of ethanol in a school laboratory?

2 The Data Booklet values for enthalpies of combustion have been obtained using a bomb calorimeter. Use the Internet to discover how a bomb calorimeter works, and why it will give a more accurate value.

3 Ethanol is part of a series of alcohols, each having the general formula $C_nH_{(2n+1)}OH$. Use the Data Booklet to plot a graph of the enthalpy of combustion of the alcohol against the corresponding value of n for methanol, ethanol, propan-1-ol and butan-1-ol. Extrapolate the graph to predict the value for the enthalpy of combustion of pentan-1-ol.

Reactions carried out in solution

In the above experiment the heat evolved from an exothermic reaction was used to heat up water in a separate container. When the reaction takes place in aqueous solution the heat change of the solution can be measured directly.

WORKED EXAMPLE:

For example, when 50.0 cm³ of 1.00 mol dm⁻³ sodium hydroxide solution (NaOH(aq)) at 25.0 °C was added with stirring to 50.0 cm³ of 1.00 mol dm⁻³ hydrochloric acid solution (HCl(aq)), also at 25.0 °C, in a polystyrene "coffee cup" (acting as a simple calorimeter; Figure 5) the temperature of the resulting solution rose very quickly to 31.8 °C.
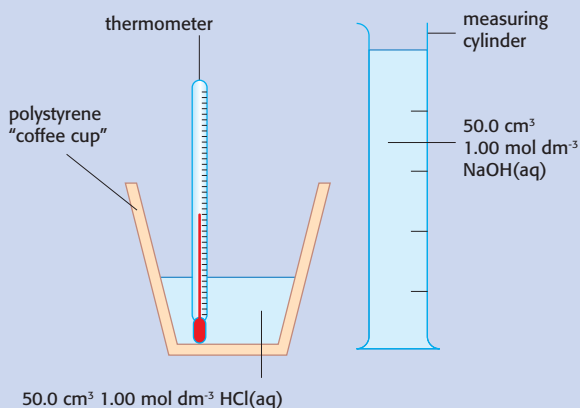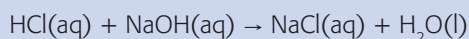

Figure 5 Experiment to measure the heat change of a solution

Figure 6 Irina Nadzarin from Malaysia, Marthe Oldernes from Norway and Chiara Prodani from Albania, students from Atlantic College, carrying out the neutralization experiment

The equation for the reaction is

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

The temperature rise = 31.8 − 25.0 = 6.8 °C

The total volume of final solution = 100 cm³

To calculate the heat evolved in this reaction two common assumptions are made. The first is that the resulting solution has the same specific heat capacity as pure water, whereas in reality it is a solution of sodium chloride in water. The second is that the density of the solution is 1.00 g cm⁻³ (i.e. the same as that of pure water). Assuming that the two volumes add cumulatively to give 100 cm³ this means that we can assume that the mass of the resulting solution is 100 g. In fact, upon reflection we know that the density of the salt solution will be greater than 1.00 g cm⁻³, because icebergs, which are basically pure water, float in the sea. Neither of these assumptions is actually true; however, within the confines of a school laboratory they are reasonable assumptions to make and do not affect the result greatly.

Heat evolved = mass of water × specific heat capacity of water × temperature rise

= 100 g × 4.18 J °C⁻¹ g⁻¹ × 6.8 °C = 2842 J = 2.842 kJ

Amount of hydrochloric acid = amount of sodium hydroxide = $\dfrac{50}{1000} \times 1 = 0.050$ mol

Thus enthalpy of neutralisation for this reaction = $\dfrac{-2.842}{0.050} = -56.8$ kJ mol⁻¹

That is:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \qquad \Delta H = -56.8 \text{ kJ mol}^{-1}$$
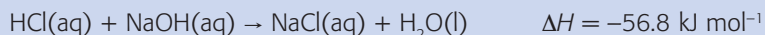
This compares quite favourably with the Data Booklet value of -57.3 kJ mol^{-1}. The error is less than 1%, which shows that very simple apparatus (in this case a "coffee cup") can often be used effectively in a school laboratory.

Neutralization reactions in solution are fast, because they involve oppositely charged ions, and so we can safely ignore any heat loss due to cooling during the reaction. The same is true of most precipitation reactions. However, if the reaction occurs at a slower rate then all the time the solution is being heated it is also losing heat to the surroundings. We can compensate for this heat loss to the surroundings by plotting a graph of temperature against time and extrapolating. A good example of this is the reaction between solid zinc metal and copper(II) sulfate solution, $CuSO_4(aq)$:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$
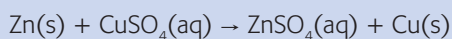
50.0 cm³ of 0.200 mol copper(II) sulfate solution, $CuSO_4$, was placed in a polystyrene "coffee cup" and the temperature was taken every 30 seconds for 2 minutes. This was to ensure that the solution was at the same temperature as the surroundings (room temperature), and that no heat was being lost or gained before the reaction started. 1.20 g of powdered zinc metal was then added, and the solution was continuously stirred. The temperature was recorded every 30 seconds until it was clear that the reaction had finished and the temperature had dropped back by one or two degrees as the solution started to cool down to room temperature. The graph shown in Figure 7 was obtained.
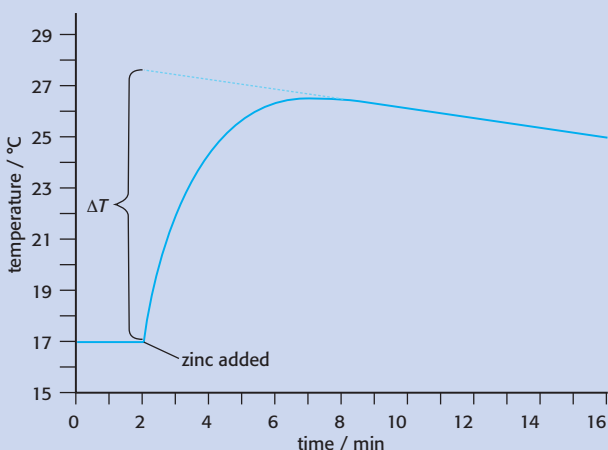

Figure 7

Answer the following questions:

1 Suggest a reason why the reaction is quite slow.

2 The highest temperature was reached 5 minutes after the zinc had been added. What exactly was happening at this point?

3 How high would the temperature have risen had there been no heat loss to the surroundings?

4 Calculate the amounts of zinc and copper(II) sulfate involved, and state which is the limiting reagent, and which is present in excess.

5 Copper(II) sulfate solution is blue; zinc sulfate solution is colourless. Zinc is a silver-grey metal, copper is a reddish-brown metal. State what you would expect to observe as the reaction proceeds.

6 Use the temperature increase from the extrapolation shown on the graph to calculate how much heat was given out in this reaction.

7 State the enthalpy change for the reaction in kilojoules per mole.

8 State three assumptions you have made in arriving at your answer.

9 The literature value for this reaction is -218 kJ mol-1. Calculate the percentage error, and comment on the validity of the assumptions you have stated.