



Calorimetry Experiments

To succeed in this topic you need to:-

- Have a good understanding of AS-level Energetics covered so far in Factsheet 08 - Energetics I - Hess's Law;
- be familiar with basic apparatus used in Chemistry.

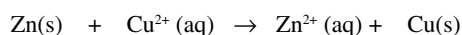
After working through this Factsheet you will:-

- be familiar with the main types of experiment used in calorimetry at AS-level;
- be able to calculate values of enthalpy changes from experimental data.

Experiment 1: Enthalpy changes on displacement and the reactivity series

Introduction

The relative positions of metals in the reactivity series can be investigated by adding metals to solutions of salts of other metals, for example



This confirms that zinc is 'above' copper in the reactivity series. The enthalpy change for this and similar reactions can lead to an illustration of Hess's Law.

Method

- Place 100 cm³ of copper(II) sulphate solution (0.2 mol dm⁻³) in a polystyrene cup (or vacuum flask if available).
- Record the temperature (to the nearest 0.1°C) of the solution every 30 seconds for two minutes.
- At the two minute mark add 2 g (an excess) of zinc powder and stir the mixture.
- Continue recording the temperature for a further five minutes.
- Plot a graph of temperature against time and use the plot to determine the maximum temperature change (ΔT).

Calculation

The heat energy exchanged in the experiment is $100 \times \Delta T \times 4.18$ joules.

In the reaction 0.02 (= $\frac{1}{50}$) mole of copper ions reacted so the heat exchanged per mole would be $50 \times (100 \times \Delta T \times 4.18)$ joules or $5 \times \Delta T \times 4.18$ kJ.

As the reaction is **exothermic** the value for ΔH (in kJ mol⁻¹) will need a **negative** sign.

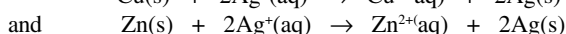
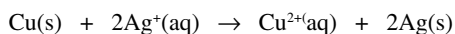
Alternative Method

Carry out the procedure above to determine the change in temperature.

- Then place a further 100 cm³ of copper(II) sulphate solution in the reaction vessel and insert a low voltage heater connected through a joulemeter.
- Switch on the current and allow the temperature to rise by the same number of degrees.
- Record the reading on the joulemeter to determine the heat exchanged in the experiment and thus calculate a value for ΔH .

Extension

If similar experiments are carried out to determine the enthalpy changes for (say)



then Hess's Law can be illustrated. For the zinc/copper reaction ΔH is -216 kJ mol⁻¹; for the copper/silver reaction ΔH is -147 kJ mol⁻¹;

The experiments outlined could be used in a school laboratory to collect data and thus determine values of ΔH .

Questions can be met requiring candidates to carry out calculations based on data from similar experiments. The calculations may involve the use of Hess's Law.

When a reaction is carried out in a calorimeter

the heat lost/gained by the reacting system = the heat gained/lost by the calorimeter and its contents

Changes in heat content are calculated using:

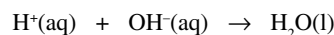
$$\Delta H = mc \Delta T \quad \text{where: } m = \text{mass}$$
$$c = \text{specific heat capacity}$$
$$\Delta T = \text{change in temperature}$$

and for the zinc/silver reaction ΔH is -363 kJ mol⁻¹.

Experiment 2: Enthalpy change of neutralisation

Introduction

Acidic and alkaline solutions mix exothermically. The ionic equation for neutralisation is



Method

- Put 50 cm³ of hydrochloric acid (1.0 mol dm⁻³) and 50 cm³ of sodium hydroxide solution (1.0 mol dm⁻³) into separate measuring cylinders
- Wait for the temperatures of the two solutions to equalise.
- Pour one of the solutions into a polystyrene cup.
- Add the second solution, stir well and record the maximum temperature reached.

The number of joules exchanged can be found by calculation or by the use of a joulemeter as in experiment 1.

Calculation

The heat energy exchanged in the experiment is $100 \times \Delta T \times 4.18$ joules.

As 0.05 (= $\frac{1}{20}$) mole of hydrochloric acid has been neutralised the heat exchanged per mole would be $20 \times (100 \times \Delta T \times 4.18)$ joules or $2 \times \Delta T \times 4.18$ kJ.

As the reaction is exothermic the value for ΔH (in kJ mol⁻¹) will need a negative sign.

Extension

The experiment can be repeated using nitric acid instead of hydrochloric acid and potassium hydroxide solution instead of sodium hydroxide solution.

In all four possible combinations a similar result should be found as the ionic equation for each is the same. The standard molar enthalpy change of neutralisation is -57.6 kJ mol⁻¹. A different, less negative value is obtained if a weak acid such as ethanoic acid is used as some heat energy is used in breaking bonds in the undissociated acid.

Experiment 3: Enthalpy of combustion**Introduction**

The complete combustion of hydrocarbons, alcohols and other organic compounds containing carbon, hydrogen and oxygen only produces carbon dioxide, water vapour and heat. In school laboratory experiments, results are not very reliable as, apart from heat losses, complete combustion is rarely achieved. The method described is usually restricted to liquid fuels such as alcohols.

For more accurate results a bomb calorimeter would be used.

Method

- Set up the apparatus filling the calorimeter with water.
- Stir the water in the calorimeter and record the temperature.
- Fill the spirit lamp with an alcohol and weigh it.
- Put the lamp in position, light the wick and quickly adjust the air flow to obtain a steady flame.
- Meanwhile stir the water.
- When a temperature rise of about 10°C has been obtained extinguish the flame but continue stirring and note the maximum temperature reached.
- Reweigh the lamp as quickly as possible.
- Use an electrical circuit to produce a similar temperature rise and note the number of joules required.

Calculation

From the mass of alcohol used (w) and its relative formula mass (M) the number of moles $\frac{w}{M}$ used can be found.

If the number of joules is known, then a value for the molar enthalpy of combustion can be calculated from $\frac{\text{(number of joules)}}{\text{(number of moles)}}$

Extension

If the experiment is repeated with a number of alcohols it can be shown that the values of the enthalpies of combustion of successive alcohols differ by a similar amount. This is because each member of an homologous series differs from the next by $-\text{CH}_2-$. The combustion of this unit should result in the same release of energy (about 650 kJ mol⁻¹) whatever the homologous series being investigated.

Experiment 4: Finding an enthalpy change that cannot be measured directly**Introduction**

For a vast number of reactions values of the enthalpy change cannot be determined directly. However, by using Hess's Law with values which can be experimentally determined, the missing values can be calculated.

Examples include the enthalpy change of reaction which occurs when an anhydrous salt becomes hydrated.

Method

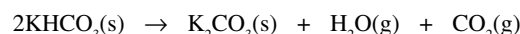
- Add 0.1 mol of the anhydrous salt to 100 cm³ of water and determine a value (ΔH_1) using procedures similar to Experiment 1 above.
- Then add 0.1 mol of the hydrated salt to water.
- The volume of water used should be less than 100 cm³ to allow for the water contained in the salt.
- A second value (ΔH_2) can then be calculated.

Calculation

Using Hess's Law, (ΔH_1) – (ΔH_2) will produce a value for the hydration reaction. Care must be taken over the signs for ΔH in each case.

Extension

The enthalpy change for the endothermic reaction



can be determined by adding appropriate masses of each solid to an excess of hydrochloric acid. Note that 2 mol of potassium hydrogencarbonate react to give 1 mol of potassium carbonate. Again a Hess's Law triangle or enthalpy level diagram will produce a value for the enthalpy change.

Practice Questions

1. A student wrote the following account:
A piece of zinc weighing 3 g was placed in a glass beaker. 50 cm³ of 0.5 mol dm⁻³ copper sulphate solution was measured using a measuring cylinder and added to the beaker. The temperature of the solution was taken before it was added and then every minute afterwards.

The results were:

Time in minutes	0	1	2	3	4	5
Temperature in °C	22	26	29	27	24	22

Suggest **three** improvements you would make to the experiment. Give reasons for each suggestion.

2. Outline the essential details of an experiment to determine the enthalpy of solution of ammonium nitrate.
Show how the experimental results would be used to calculate the molar enthalpy change.
3. 2.66 g of anhydrous copper(II) sulphate powder was added to 50.0 cm³ of distilled water in a polystyrene cup. The temperature of the water rose from 19.6°C to 25.4°C. Calculate the molar enthalpy change of solution of anhydrous copper(II) sulphate. You may assume that the specific heat capacity of copper(II) sulphate solution is 4.18 J g⁻¹ K⁻¹ and that there is negligible heat loss to the surroundings.

4. The enthalpy change for the precipitation of barium carbonate was investigated by mixing barium nitrate solution with sodium carbonate solution. Three experiments were used.

Expt 1: 10.0 cm³ of barium nitrate solution (1.0 mol dm⁻³) was added to 10.0 cm³ of sodium carbonate solution (1.0 mol dm⁻³). The temperature rose by 1.5°C.

Expt 2: 50.0 cm³ of barium nitrate solution (1.0 mol dm⁻³) was added to 50.0 cm³ of sodium carbonate solution (1.0 mol dm⁻³).

Expt 3: 50.0 cm³ of barium nitrate solution (0.2 mol dm⁻³) was added to 50.0 cm³ of sodium carbonate solution (0.2 mol dm⁻³).

- (a) Calculate the temperature rises to be expected in experiments 2 and 3.
- (b) Which of the experiments should give the **most** accurate result for the determination of the temperature change? Give a reason for your answer.
- (c) Which of the experiments should give the **least** accurate result for the determination of the temperature change? Give a reason for your answer.

Answers

- Any three of:
 - Use powdered zinc – reacts faster so heat losses are reduced
 - Use a polystyrene cup/vacuum flask – reduces heat loss
 - Use a burette/pipette – more accurate than a measuring cylinder
 - Put the solution in the polystyrene cup before the zinc is added – to enable initial temperature to be checked
 - Use a thermometer reading to 0.1°C – more accurate temperature change found
 - Measure the temperature of the solution for a few minutes before addition of the solid – gives a better value for the initial temperature
 - Stir the mixture – helps reduce reaction time
 - Measure temperatures more frequently during the reaction – produces a better graph and thus a more accurate figure for the change in temperature
- Use a polystyrene cup/vacuum flask of suitable size
 - Use a burette/pipette to measure 50 cm³ of water and add this to the polystyrene cup
 - Weigh accurately 0.05 mol of the powdered solid
 - Use a thermometer reading to 0.1°C to find the initial temperature
 - Add the solid, stir the mixture and record the maximum (or minimum) temperature reached (or note the temperature every 15 seconds)

Determine the change in temperature (ΔT) either by simple difference or graphically

Calculate the heat exchanged using $50 \times \Delta T \times 4.18$

As the resulting solution is 1.0 mol dm⁻³ this calculation gives a numerical value for the enthalpy of solution. If the reaction is exothermic a – sign will be needed; if the reaction is endothermic a + sign must be used.

- Temperature rise = 25.4 – 19.6 = 5.8 (K). Reaction is exothermic.

Heat exchanged in experiment = $50.0 \times 5.8 \times 4.18 = 1212.2 \text{ J}$

RFM CuSO₄ = 63.6 + 32.0 + (4 × 16.0) = 159.6

Heat exchanged per mol of CuSO₄ = $\frac{1212.2 \times 159.6}{2.66} = 72732 \text{ J}$

$\Delta H = -72.7 \text{ kJ mol}^{-1}$

- 1.5°C 0.3°C
 - Experiment 2 – large volume, minimises errors
 - Experiment 3 – temperature change too small

Acknowledgements: This Factsheet was researched and written by Phil Richardson. Curriculum Press, Bank House, 105 King Street, Wellington, Shropshire, TF1 1NU. ChemistryFactsheets may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher. ISSN 1351-5136