Answer **all** the questions in the spaces provided.

1 Determination of the kinetics of the decomposition of thiosulfate ions

FA 1 is 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.

You are also provided with 2.0 mol dm^{-3} hydrochloric acid, HC*l*.

Solid sulfur is one of the products formed in the reaction between sodium thiosulfate and hydrochloric acid, as shown in equation 1. The presence of sulfur causes the solution to become opaque.

equation 1 $S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$

In this experiment, the rate of this reaction is studied by measuring the time taken for the reaction mixture to become opaque.

You will perform a series of five experiments. Then, you will graphically analyse your results in order to determine the order with respect to the concentration of thiosulfate ions, $[S_2O_3^{2-}]$.

For each experiment, you will note the volume of **FA 1** added, $V_{FA\,1}$, and the time taken, *t*, for the reaction mixture to become opaque.

In each experiment, you will need to ensure that the same total volume of reaction mixture is used by adding deionised water as required.

You will then calculate values for

- $1/t$,
- $\lg(1/t)$,
- $\lg(V_{FA\,1})$.

(a) Prepare a table in the space provided on page 4 in which to record, to an appropriate level of precision:

- all volumes, except the volume of hydrochloric acid,
- all values of *t*,
- all calculated values of $1/t$, $\lg(1/t)$ and $\lg(V_{FA\,1})$.

Notes: In each of these experiments, you will need to place the conical flask containing the reaction mixture on the printed page on page 2 of the insert . You will view the page by looking vertically down through the mixture. You will stop the stopwatch when the mixture **first** becomes opaque. This will be the **first** instant when you can no longer see the printed numbers on the page.

Experiment 1

1. Fill the burette labelled **FA 1**, with **FA 1**.
2. Transfer 25.00 cm^3 of **FA 1** into a 100 cm^3 conical flask.
3. Fill a second burette with hydrochloric acid.
4. Rinse out a test-tube with hydrochloric acid and discard this solution.
5. Transfer 5.00 cm^3 of hydrochloric acid to this test-tube.

Note: Small amounts of SO_2 will be produced during the reaction. Minimise inhalation of SO_2.

6. Pour the hydrochloric acid rapidly into the conical flask. Start the stopwatch during this addition.
7. Mix the contents thoroughly by swirling the flask. Then place the flask on the printed page on page 2 of the insert.
8. Stop the stopwatch when the solution **first** becomes opaque.
9. Record the time taken, *t*, to 0.1 s in your table.
10. Discard the reaction mixture **immediately** down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.

Experiments 2 to 5

Repeat experiment 1 four times, adding 22.50, 20.00, 17.50 and 15.00 cm^3 respectively, of **FA 1** at point 2.

In each case, you will need to ensure that the **same total volume** of reaction mixture is used by adding deionised water as required.

You should alternate the use of the two 100 cm^3 conical flasks.

Record all required volumes, time taken and calculated values in your table.

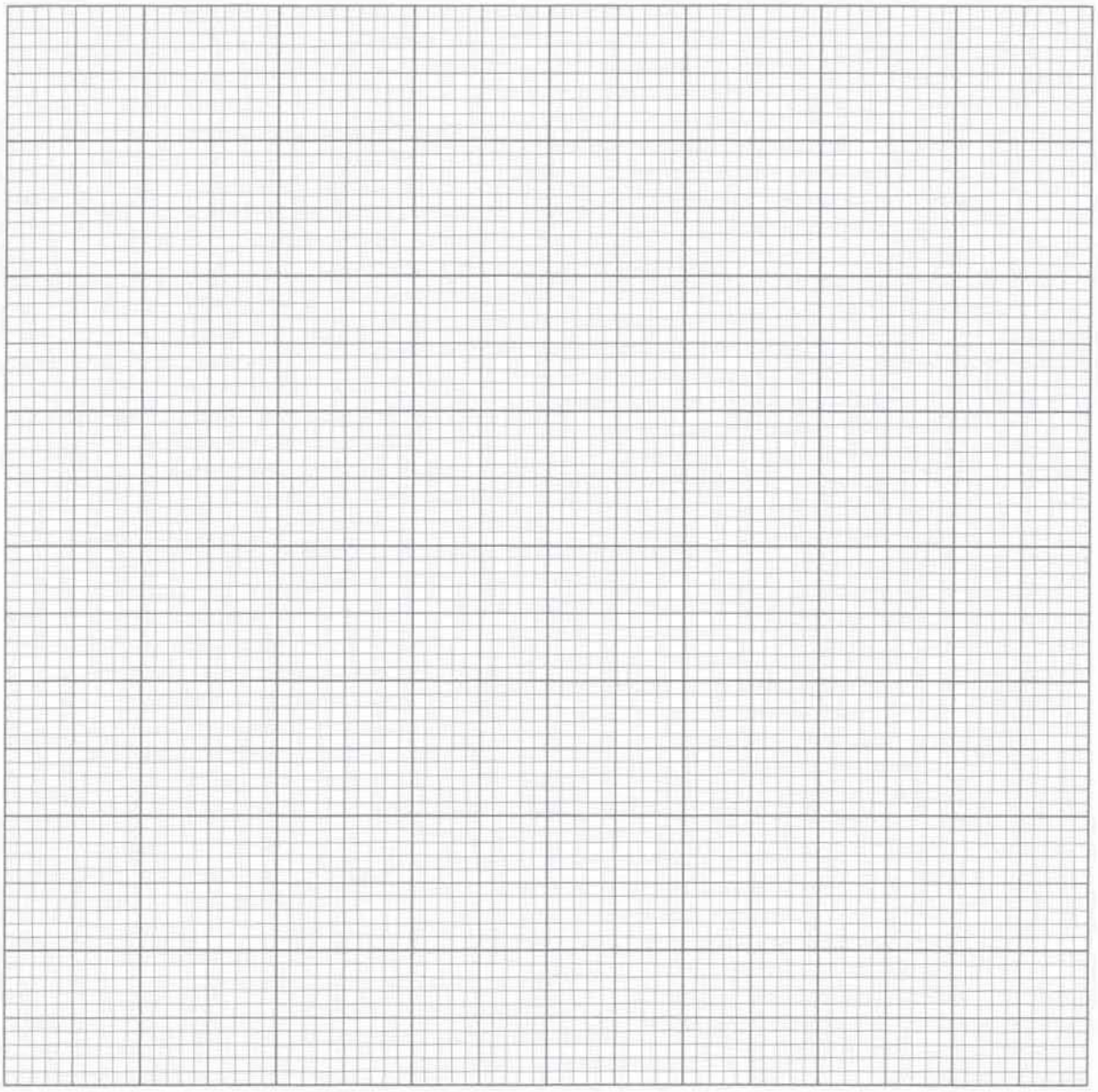
Results

Expt	V_{FA1} / cm^3	V_{water} / cm^3	t / s	1/t / s^{-1}	lg(1/t)	lg(V_{FA1})
1	25.00	0.0	27.9	0.0358	−1.45	1.40
2	22.50	2.5	30.2	0.0331	−1.48	1.35
3	20.00	5.0	34.0	0.0294	−1.53	1.30
4	17.50	7.5	38.9	0.0257	−1.59	1.24
5	15.00	10.0	45.7	0.0219	−1.66	1.18

Note: Measuring cylinder is used for distilled water hence precision is up to 0.5cm^3.

[4]

(b) (i) Plot a graph of lg(1/*t*) on the *y*-axis against lg($V_{FA\ 1}$) on the *x*-axis. Draw the best-fit straight line taking into account all of your plotted points.



[3]

(ii) Calculate the gradient of the line to three significant figures, showing clearly how you did this. Hence, deduce the order of the reaction with respect to $[S_2O_3^{2-}]$.

gradient = ...

order = ...

[3]

(c) When you performed this experiment, you were instructed to wash **and** drain a conical flask before using it again.

State and explain the likely effect on *t* of **not** draining a flask before it is reused.

effect on *t* .....

explanation .....

.....

.....

[1]

(d) The rate of this reaction relative to $[S_2O_3^{2-}]$ can be determined using the following expression.

$$\text{rate} = \left| \frac{\Delta[S_2O_3^{2-}]}{\Delta t} \right|$$

The data that you now have from your experiments is not sufficient to allow you to use this expression to calculate the rate of reaction.

Identify the other data you would need in order to calculate a rate for this experiment.

.....

.....[1]

(e) The following steps represent part of a possible mechanism for the formation of sulfur in the reaction shown in equation 1. In this mechanism, sulfur forms as the cyclic S_8 molecule in step 10.

The $HS–SO_3^-$ ion formed in step 1 is an intermediate that reacts with another $S_2O_3^{2-}$ ion, to produce the intermediate in step 2, and so on.

This process continues until the sulfur chain is long enough. This occurs in step 8 and a ring of elemental sulfur, S_8, is precipitated via steps 9 and 10.

step 1	$S_2O_3^{2-} + H^+$	$\rightleftharpoons$	$HS–SO_3^-$
step 2	$HS–SO_3^- + S_2O_3^{2-}$	$\rightarrow$	$HS–(S)_1–SO_3^- + SO_3^{2-}$
step 3	$HS–(S)_1–SO_3^- + S_2O_3^{2-}$	$\rightarrow$	$HS–(S)_2–SO_3^- + SO_3^{2-}$
steps 4 to 7		⋮	
step 8	$HS–(S)_6–SO_3^- + S_2O_3^{2-}$	$\rightarrow$	$HS–(S)_7–SO_3^- + SO_3^{2-}$
step 9	$HS–(S)_7–SO_3^-$	$\rightleftharpoons$	$H^+ + {}^-S–(S)_7–SO_3^-$
step 10	${}^-S–(S)_7–SO_3^-$	$\rightarrow$	$S_8 + SO_3^{2-}$

(i) Deduce the overall equation for the formation of one S_8 molecule from $S_2O_3^{2-}$ ions under acidic conditions.

.....[1]

(ii) Deduce the role of H^+ ions in the mechanism for the formation of sulfur. Explain your answer.

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.....

.....[1]

[Total: 14]

2 Determination of the percentage by mass of copper in an alloy

Copper forms compounds containing Cu^{2+} or Cu^{+} ions. Those compounds containing Cu^{2+} ions tend to be relatively stable.

The addition of an excess of potassium iodide, KI, to a solution of Cu^{2+} ions produces iodine, I_2, and a stable precipitate of CuI. For a titration to be accurate, it is necessary that all the Cu^{2+} ions are reduced to Cu^{+} ions. The I_2 turns the solution brown.

equation 2 $$2Cu^{2+} + 4I^{-} \rightarrow 2CuI + I_2$$

I_2 has a relatively low solubility in water. However, the presence of an excess of I^{-} ions in the reaction mixture allows the soluble tri-iodide ion, I_3^{-}, to form as shown by equation 3. This ensures that the I_2 formed as shown in equation 2 is fully dissolved.

equation 3 $$I_2 + I^{-} \rightarrow I_3^{-}$$

The I_3^{-} ions formed may be titrated against a standard solution of $Na_2S_2O_3$ as shown in equation 4.

equation 4 $$I_3^{-} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 3I^{-}$$

In **2(a)**, you will perform titrations to determine the percentage by mass of copper present in an alloy.

FA 2 is an aqueous solution containing 11.54 g dm^{-3} of the alloy in acid.

You are also provided with
- **FA 1**, 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$,
- 0.5 mol dm^{-3} potassium iodide, KI,
- aqueous sodium carbonate, Na_2CO_3,
- aqueous ethanoic acid, CH_3CO_2H,
- starch indicator.

The **FA 2** solution has been prepared using 11.54 g of the alloy containing copper and one other metal, in 1 dm^3 of the solution. **FA 2** contains residual traces of acid.

The presence of acid in the titration mixture will affect the accuracy of the results. The procedure described is designed to reduce these errors.

In this experiment, you will determine the percentage by mass of copper in the alloy used to prepare **FA 2**. You will titrate **FA 2** against **FA 1**.

(a) (i) Titration of FA 2 against FA 1

1. Refill the burette you used in **1(a)** with **FA 1**.
2. Use a pipette to transfer 25.0 cm^3 of **FA 2** into a 250 cm^3 conical flask.
3. Use a teat pipette to add $Na_2CO_3(aq)$, slowly, with shaking, to **FA 2** in the conical flask, until a slight permanent precipitate forms.
4. Use another teat pipette to add $CH_3CO_2H(aq)$ slowly, with shaking, until this precipitate **just** dissolves.
5. Use a measuring cylinder to add about 20 cm^3 of KI(aq) to this flask. A white precipitate forms in a brown solution.
6. Run **FA 1** from the burette into this flask. Near the end-point, when the brown solution becomes pale, add about 1 cm^3 of starch indicator.
7. Continue adding **FA 1** slowly. The end-point is reached when the **solution** first becomes colourless. The white precipitate remains.
8. Record your titration results, to an appropriate level of precision, in the space provided.
9. Swirl the reaction mixture and using two pieces of filter paper, filter the mixture into a test-tube until the test-tube is about half-full. Keep both the filtrate and the residue for use in **3(a)**. The filtrate is **FA 3** and the residue is **FA 4**.

While you are waiting for the mixture to filter, continue with step 10.

10. Repeat points 2 to 8 until consistent results are obtained.

Titration results

Titration number	1	2
Final burette reading / cm^3	25.80	25.00
Initial burette reading / cm^3	1.00	0.20
Volume of **FA 1** used / cm^3	24.80	24.80
	✓	✓

[3]

(ii) From your titrations, obtain a suitable volume of **FA 1**, $V_{FA\ 1}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{FA\ 1}$ = ...

[3]

(b) Calculate the mass of copper in the 11.54 g of the alloy used to prepare 1.00 dm^3 of **FA 2**, using your answer in **2(a)(ii)**.

Hence, determine the percentage by mass of copper in the alloy.

[A_r: Cu, 63.5]

mass of Cu in 11.54 g of the alloy = ...

percentage by mass of copper in the alloy = ...
[3]

(c) A large excess of potassium iodide is used in each titration.

(i) Calculate the ratio of the amount of iodide ions added in each titration to the minimum amount of iodide ions required to reduce the copper(II) ions used.

ratio = ...
[5]

(ii) Identify **two** different chemical processes that use iodide ions in this experiment.

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.....[1]

(d) In **2(a)(i)**, $Na_2CO_3(aq)$ was added to **FA 2** until a precipitate was formed, followed by $CH_3CO_2H(aq)$ to dissolve this precipitate.

(i) Explain the observations in terms of the chemistry involved.

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.....

.....[2]

(ii) Explain why it was necessary to add $Na_2CO_3(aq)$ to **FA 2**, and what effect failing to do it would have on the titre values.

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.....[1]

[Total: 18]

3 Investigation of some inorganic reactions

Note: You should complete **Question 2(a)(i)** before starting **Question 3**.

A reaction in which one species is both reduced and oxidised is known as a disproportionation reaction.

In aqueous solution, $Cu^+(aq)$ ions are unstable as they spontaneously undergo a disproportionation reaction. Stable Cu^+ compounds may, however, be prepared by precipitation or by forming complex ions. Examples of precipitates are copper(I) iodide, CuI, and copper(I) oxide, Cu_2O. Examples of stable complex ions are $[CuCl_2]^-$ and $[Cu(NH_3)_2]^+$, both of which form colourless aqueous solutions.

FA 3 is the filtrate from **2(a)(i)** and contains the second metal present in the alloy.
FA 4 is the residue from **2(a)(i)**. This solid is copper(I) iodide, CuI.

You are also provided with solid copper(I) oxide, Cu_2O.

Carry out the following tests. Carefully record your observations in Tables 3.1 and 3.2.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.1

		test	observations
(a)	(i)	Add 1 cm depth of **FA 3** to a test-tube. Add aqueous sodium hydroxide slowly, with shaking, until no further change is seen.	White ppt, soluble in excess NaOH(aq) to give a colourless solution
		Add 1 cm depth of **FA 3** to a test-tube. Add aqueous ammonia slowly, with shaking, until no further change is seen.	White ppt, soluble in excess NH_3 (aq) to give a colourless solution [1]
	(ii)	Place the filter funnel containing **FA 4** into a clean test-tube. Carefully add aqueous ammonia to the filter funnel so that it covers the precipitate. The filtrate will collect in the test-tube. Transfer 1 cm depth of this filtrate into a clean test-tube. Add dilute sulfuric acid slowly, with shaking, until no further change is seen.	White ppt CuI dissolves in NH_3(aq) to give a colourless filtrate that turns dark blue rapidly. When H_2SO_4(aq) is added dropwise, pale blue ppt is formed. [2] When more H_2SO_4(aq) is added, the pale blue ppt turns into a brown suspension. Upon leaving to stand, we can observe white ppt in the brown solution.

(iii) Identify the metal present in the alloy, other than copper. Use evidence from your observations in **3(a)(i)** to support your deduction.

metal .....

evidence .....

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.....

[1]

(iv) Suggest an explanation for your observations in **3(a)(ii)** in terms of the copper-containing complexes present.

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.....[1]

Table 3.2

		test	observations
(b)		Add about 3 cm depth of dilute sulfuric acid to the boiling tube containing Cu_2O. Gently shake the boiling tube for one minute. Leave to settle, then decant the liquid into a clean test-tube. This solution is **FA 5**.	When $H_2SO_4(aq)$ is added to the brick red solid Cu_2O, a blue solution and a pink solid is formed FA5 is a blue solution. [1]
(c)		Add 1 cm depth of **FA 5** to a test-tube. Add aqueous sodium hydroxide, slowly with shaking, until no further change is seen.	Pale blue ppt, insoluble in excess NaOH(aq)
		Add 1 cm depth of **FA 5** to a test-tube. Add aqueous ammonia, slowly with shaking, until no further change is seen.	Pale blue ppt, soluble in excess $NH_3(aq)$ to give a dark blue solution [2]

(d) Table 3.3 gives some standard electrode potential values involving copper and its ions.

Table 3.3

electrode reaction	$E^{\ominus}$ / V
$Cu^{+}(aq) + e^{-} \rightleftharpoons Cu(s)$	+0.52
$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$	+0.34
$Cu^{2+}(aq) + e^{-} \rightleftharpoons Cu^{+}(aq)$	+0.15

Consider your observations when dilute sulfuric acid was added to Cu_2O in **3(b)**, together with those you made in **3(c)** and the information in Table 3.3.

(i) Write an overall equation for the reaction that occurred when you added dilute sulfuric acid to Cu_2O in **3(b)**.

.....[1]

(ii) Use data from Table 3.3 to explain what happens to the copper in Cu_2O during this reaction.

.....

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.....[1]

[Total: 10]

4 Planning

When zinc powder is added to aqueous copper(II) sulfate, an exothermic reaction occurs.

equation 5 $\quad CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s) \qquad \Delta H_{reaction} < 0$

The maximum temperature change occurring during this reaction may be determined graphically.

The maximum temperature change, ΔT_{max}, obtained from the graph can be used to calculate the heat change, q, for this experiment.

Using q, a value for the molar enthalpy change of reaction, $\Delta H_{reaction}$, may be determined.

In this question, you are to plan a procedure that would provide sufficient data to allow you to determine an accurate and reliable value for the molar enthalpy change of reaction, $\Delta H_{reaction}$.

(a) Plan an investigation to determine the maximum temperature change, ΔT_{max}, **graphically** for the reaction between aqueous copper(II) sulfate and zinc powder.

Measurements should be taken:
- before the reaction starts,
- during the reaction,
- for some time after the reaction is complete.

You may assume that you are provided with:
- $150\,cm^3$ of $1.00\,mol\,dm^{-3}$ copper(II) sulfate,
- 10 g of powdered zinc,
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of:
- the apparatus you would use,
- the quantities you would use, so that there is an excess of zinc,
- the procedure you would follow,
- the measurements you would make to allow a suitable temperature-time graph to be drawn,
- how you would ensure that an **accurate** and **reliable** value of ΔT_{max} is obtained.

[A_r: Zn, 65.4; Cu, 63.5; S, 32.1; O, 16.0]

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[7]

(b) (i) Sketch, on Fig. 4.1, the graph you would expect to obtain using the measurements you planned to make in **4(a)**.

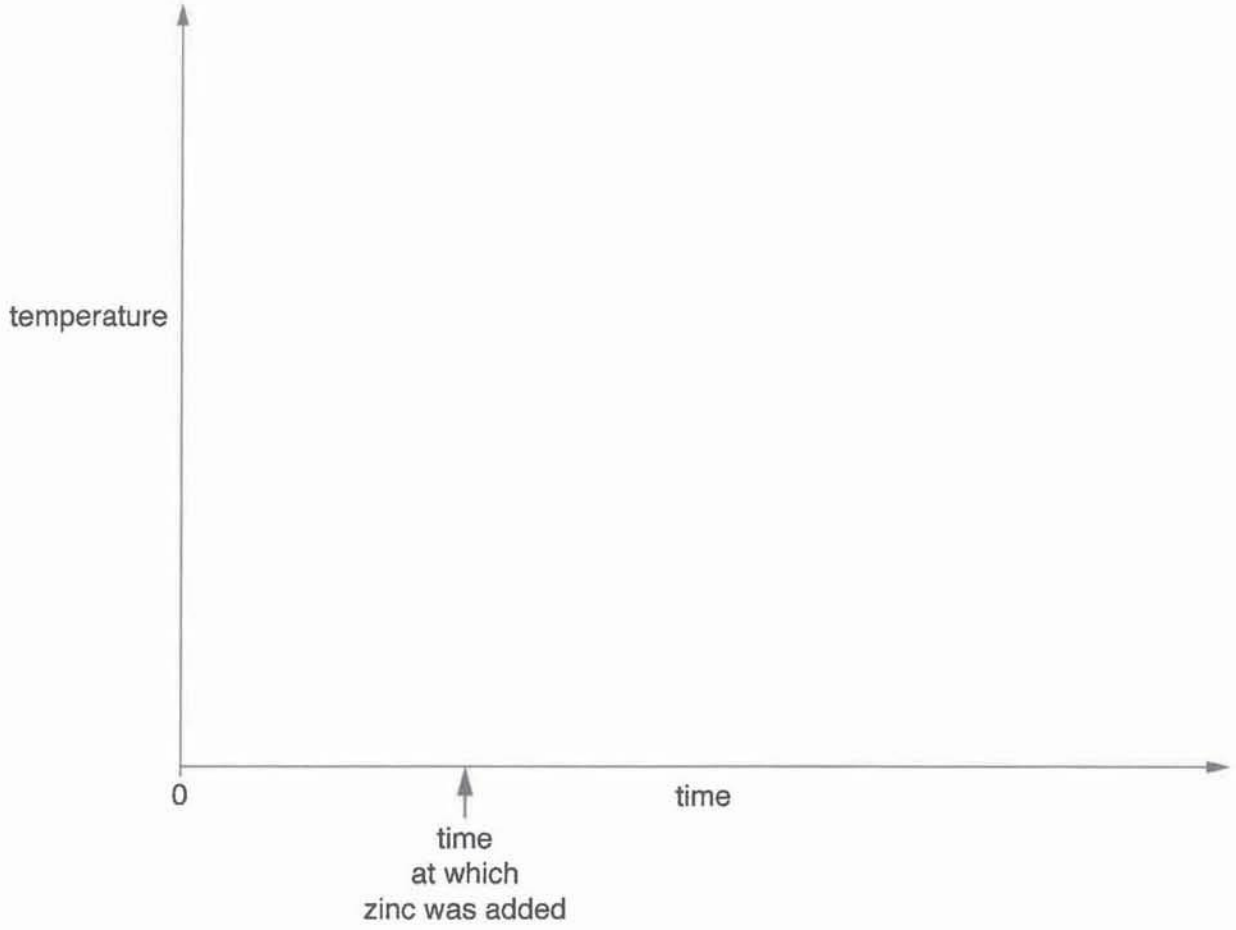

Fig. 4.1

[2]

(ii) Explain how the maximum temperature change, ΔT_{max}, can be determined. You may find it useful to show how this might be done on your graph in **4(b)(i)**.

.....

.....

.....[1]

(iii) Describe how you would use your ΔT_{max} value to calculate a value for q and hence determine a value for $\Delta H_{reaction}$ for this reaction.

You do not need to perform any calculations.

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.....[2]

(iv) The maximum temperature change, ΔT_{max}, can also be determined by direct measurement of the initial temperature and the maximum temperature reached only.

Explain why the graphical method is likely to give a more accurate value for ΔT_{max}, than the direct measurement method.

.....

.....

.....[1]

[Total: 13]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas/liquid	orange	orange-red
iodine, I_2	black solid/purple gas	brown	purple