

**OXFORD CAMBRIDGE AND RSA EXAMINATIONS**

**A2 GCE**

**F325/01**

**CHEMISTRY A**

**Equilibria, Energetics and Elements**

**WEDNESDAY 22 JUNE 2016: Morning**

**DURATION: 2 hours**

**plus your additional time allowance**

**MODIFIED ENLARGED**

<b>Candidate forename</b>		<b>Candidate surname</b>	
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<b>Centre number</b>						<b>Candidate number</b>				
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**Candidates answer on the Question Paper.**

**OCR SUPPLIED MATERIALS:**

**Data Sheet for Chemistry A (inserted)**

**OTHER MATERIALS REQUIRED:**

**Scientific calculator**

**READ INSTRUCTIONS OVERLEAF**



## **INSTRUCTIONS TO CANDIDATES**

**The Insert will be found inside this document.**

**Write your name, centre number and candidate number in the boxes on the first page. Please write clearly and in capital letters.**

**Use black ink. HB pencil may be used for graphs and diagrams only.**

**Answer ALL the questions.**

**Read each question carefully. Make sure you know what you have to do before starting your answer.**

**Write your answer to each question in the space provided. If additional space is required, you should use the lined page at the end of this booklet. The question number(s) must be clearly shown.**

## **INFORMATION FOR CANDIDATES**

**The number of marks is given in brackets [ ] at the end of each question or part question.**



**Where you see this icon you will be awarded marks for the quality of written communication in your answer.**

**This means, for example, you should:**

**ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear;**

**organise information clearly and coherently, using specialist vocabulary when appropriate.**

**You may use a scientific calculator.**

**A copy of the Data Sheet for Chemistry A is provided as an insert with this question paper.**

**You are advised to show all the steps in any calculations.**

**The total number of marks for this paper is 100.**

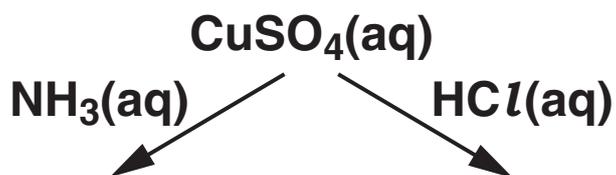
**Any blank pages are indicated.**

Answer ALL the questions.

1 This question is about the chemistry of copper compounds and complex ions.

(a) The flowchart shows two reactions of aqueous copper(II) sulfate.

In the boxes, write the formulae and colours of the complex ions formed.



complex ion:  
\_\_\_\_\_

colour:  
\_\_\_\_\_

complex ion:  
\_\_\_\_\_

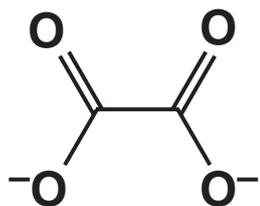
colour:  
\_\_\_\_\_

[3]

- (b)  $\text{Cu}^{2+}$  ions form a complex ion A with two ethanedioate ions and two water molecules. The ethanedioate ion is a bidentate ligand.

The skeletal formula of the ethanedioate ion is shown in FIG. 1.1 below.

Fig. 1.1



- (i) What is meant by the term 'bidentate ligand'?

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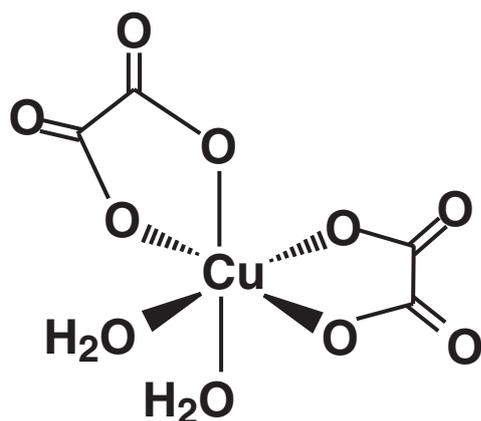
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[1]

- (ii) The complex ion A exists as three stereoisomers.

The shape of one of the stereoisomers is shown below. The charge has been omitted.

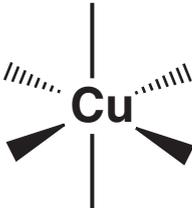
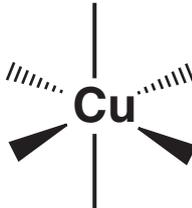
Complex A



Complete the 3D diagrams of the other two stereoisomers of A below.

You do NOT need to include any charges.

Indicate with ticks whether the stereoisomers are cis, trans, optical or a combination of these types.

STEREISOOMER														
TYPE	<table border="1" data-bbox="576 1205 959 1420"> <tbody> <tr> <td>cis</td> <td></td> </tr> <tr> <td>trans</td> <td></td> </tr> <tr> <td>optical</td> <td></td> </tr> </tbody> </table>	cis		trans		optical		<table border="1" data-bbox="1062 1205 1445 1420"> <tbody> <tr> <td>cis</td> <td></td> </tr> <tr> <td>trans</td> <td></td> </tr> <tr> <td>optical</td> <td></td> </tr> </tbody> </table>	cis		trans		optical	
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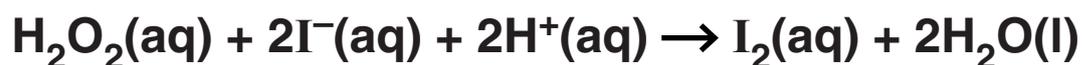
[3]

(iii) What is the empirical formula, including the charge, of the complex ion A?

\_\_\_\_\_ [2]

[TOTAL: 9]

2 Hydrogen peroxide reacts with iodide ions in acid conditions, as shown below.



A student investigates the rate of this reaction by carrying out four experiments at the same temperature. The student's results are shown below.

Experiment	$[\text{H}_2\text{O}_2(\text{aq})]$ / $\text{mol dm}^{-3}$	$[\text{I}^-(\text{aq})]$ / $\text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})]$ / $\text{mol dm}^{-3}$	Initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.0010	0.20	0.10	$5.70 \times 10^{-6}$
2	0.0020	0.20	0.10	$1.14 \times 10^{-5}$
3	0.0020	0.20	0.20	$1.14 \times 10^{-5}$
4	0.0040	0.40	0.10	$4.56 \times 10^{-5}$

(a) The rate equation is:  $\text{rate} = k [\text{H}_2\text{O}_2(\text{aq})] [\text{I}^-(\text{aq})]$

Show that the student's results support this rate equation.

Calculate the rate constant,  $k$ , for this reaction.

Give your answer to TWO significant figures, in standard form and with units.



**(b) The student concluded that  $\text{H}^+(\text{aq})$  ions act as a catalyst.**

**Explain why the student's conclusion is NOT correct.**

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[1]

**(c) A four-step mechanism has been proposed for this reaction.  
The rate-determining step is the first step.**

**(i) State what is meant by the term 'rate-determining step'.**

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[1]

- (ii) The equation for STEP 3 in the four-step mechanism is shown below.

Suggest equations for the other three steps.  
State symbols are NOT required.

STEP 1: \_\_\_\_\_

STEP 2: \_\_\_\_\_



STEP 4: \_\_\_\_\_

[3]

[TOTAL: 11]

- 3 This question is about four enthalpy changes, A–D, that can be linked to the dissolving of potassium sulfate,  $K_2SO_4$ , in water.

Table 3.1

	NAME OF ENTHALPY CHANGE	Enthalpy change / $\text{kJ mol}^{-1}$
A	lattice enthalpy of potassium sulfate	–1763
B	enthalpy change of solution of potassium sulfate	+24
C	enthalpy change of hydration of potassium ions	–320
D	enthalpy change of hydration of sulfate ions	

- (a) Define the term ‘enthalpy change of hydration’.

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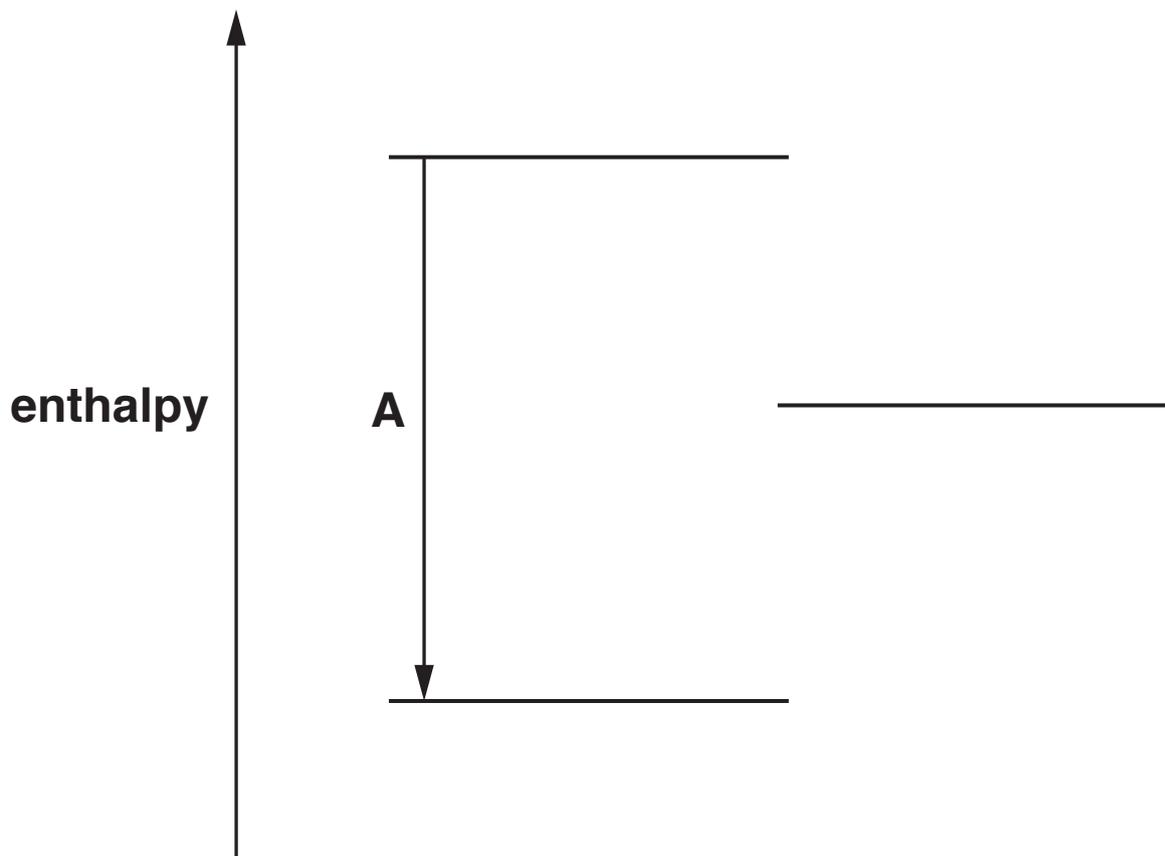
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[2]

- (b) The diagram below is an incomplete energy cycle linking the four enthalpy changes in TABLE 3.1. One of the four energy levels is missing.

Include state symbols for all species.



- (i) Complete the energy cycle as follows.

Add the missing energy level to the diagram.  
Add the species on all FOUR energy levels.

Add arrows to show the direction of the three missing enthalpy changes. Label these enthalpy changes using the letters B–D from TABLE 3.1.

[5]

- (ii) Calculate the enthalpy change of hydration of sulfate ions.

$$\Delta H = \text{_____} \text{ kJ mol}^{-1} \text{ [1]}$$

- (c) The entropy change of solution of  $\text{K}_2\text{SO}_4$  is  $+225 \text{ J K}^{-1} \text{ mol}^{-1}$ .

- (i) Suggest, in terms of the states of the particles involved, why this entropy change is positive.

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[1]

- (ii) Explain, using a calculation, why  $\text{K}_2\text{SO}_4$  dissolves in water at  $25^\circ\text{C}$ , despite the enthalpy change of solution being endothermic.

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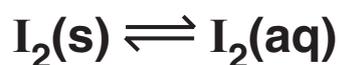
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[3]

[TOTAL: 12]

- 4 Iodine,  $I_2$ , is a grey-black solid that is not very soluble in water.  
EQUILIBRIUM 1 is set up with the equilibrium position well to the left.



EQUILIBRIUM 1

Solid iodine is much more soluble in an aqueous solution of potassium iodide,  $KI(aq)$ , than in water.  
EQUILIBRIUM 2 is set up.



EQUILIBRIUM 2

(a) Suggest why  $I_2$  is NOT very soluble in water.

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[1]

(b) A student dissolves  $I_2$  in  $KI(aq)$ .  
The resulting  $200\text{ cm}^3$  equilibrium mixture contains:

$4.00 \times 10^{-5}\text{ mol } I_2(aq)$

$9.404 \times 10^{-2}\text{ mol } I^-(aq)$

$1.96 \times 10^{-3}\text{ mol } I_3^-(aq)$ .

Calculate  $K_c$  for EQUILIBRIUM 2.

Give your answer to an APPROPRIATE number of significant figures.

$K_c =$  \_\_\_\_\_ units \_\_\_\_\_ [4]

**(c) The student adds an excess of aqueous silver nitrate,  $\text{AgNO}_3(\text{aq})$ , to the equilibrium mixture.**

**Predict what would be observed.**

**Explain the observations in terms of both EQUILIBRIUM 1 and EQUILIBRIUM 2 and any species formed.**

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**[4]**

**(d) Two redox reactions of iodine are described below.**

**REACTION 1: Iodine is reacted with oxygen to form a compound with a molar mass of  $333.8 \text{ g mol}^{-1}$ .**

**REACTION 2: In alkaline conditions, iodine disproportionates to form iodide ions, iodate(V) ions and water.**

**Construct equations for these TWO reactions.**

**State symbols are NOT required.**

**REACTION 1:**

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**REACTION 2:**

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**[3]**

**[TOTAL: 12]**

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- 5 A chemist carries out some experiments using nitrous acid,  $\text{HNO}_2(\text{aq})$ .

$\text{HNO}_2$  is a weak acid with a  $K_a$  value of  $4.69 \times 10^{-4} \text{ mol dm}^{-3}$  at the temperature of the chemist's experiments.

- (a) Write the expression for  $K_a$  for  $\text{HNO}_2(\text{aq})$ .

[1]

- (b) Calculate the pH of  $0.120 \text{ mol dm}^{-3}$   $\text{HNO}_2(\text{aq})$ .

Give your answer to TWO decimal places.

pH = \_\_\_\_\_ [2]

(c) The chemist prepares  $1\text{ dm}^3$  of a buffer solution by mixing  $200\text{ cm}^3$  of  $0.200\text{ mol dm}^{-3}$   $\text{HNO}_2$  with  $800\text{ cm}^3$  of  $0.0625\text{ mol dm}^{-3}$  sodium nitrite,  $\text{NaNO}_2$ .

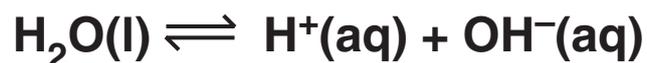
(i) Calculate the pH of the buffer solution.

Give your answer to TWO decimal places.

pH = \_\_\_\_\_ [4]



(d) The dissociation of water is shown below.



At 60 °C, the ionic product of water,  $K_w$ , is  $9.311 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ .

At 25 °C, the ionic product of water,  $K_w$ , is  $1.000 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ .

(i) Explain whether the dissociation of water is an exothermic or endothermic process.

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[1]

(ii) Predict, using a calculation, whether a pH of 7 at 60 °C is neutral, acidic or alkaline.

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[2]

(iii)  $pK_w$ ,  $pK_a$  and  $pH$  are logarithmic scales.

Calculate  $pK_w$  at  $60^\circ\text{C}$ .

Give your answer to TWO decimal places.

$pK_w =$  \_\_\_\_\_ [1]

(iv)  $20.0 \text{ cm}^3$  of  $0.0270 \text{ mol dm}^{-3}$  NaOH is diluted with water and the solution made up to  $100 \text{ cm}^3$  at  $60^\circ\text{C}$ .

Calculate the pH of the diluted solution of NaOH at  $60^\circ\text{C}$ .

Give your answer to TWO decimal places.

pH = \_\_\_\_\_ [3]

[TOTAL: 18]

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**6 Redox reactions can be used to generate electrical energy from electrochemical cells.**

**A student investigates the redox systems shown in TABLE 6.1 opposite.**

**(a) Define the term ‘standard electrode potential’.**

**Include all standard conditions in your answer.**

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**[2]**

**Table 6.1**

	<b>REDOX SYSTEM</b>	<b><math>E^\ominus/V</math></b>
<b>1</b>	<b><math>Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)</math></b>	<b>-1.66</b>
<b>2</b>	<b><math>Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)</math></b>	<b>-0.41</b>
<b>3</b>	<b><math>V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)</math></b>	<b>-0.26</b>
<b>4</b>	<b><math>Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)</math></b>	<b>+0.34</b>
<b>5</b>	<b><math>Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)</math></b>	<b>+1.33</b>
<b>6</b>	<b><math>FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightleftharpoons Fe^{3+}(aq) + 4H_2O(l)</math></b>	<b>+2.20</b>

**(b) The student sets up a standard cell based on redox systems 3 and 4.**

**(i) Draw a labelled diagram to show how the student could have set up this cell to measure the standard cell potential.**

**On your diagram,**

**show the charge carriers in the circuit joining the two half cells**

**label the signs of the electrodes.**

**[5]**

**(ii) What is the standard cell potential of this cell?**

**standard cell potential = \_\_\_\_\_ V [1]**



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**[TOTAL: 14]**

**7 Hydroxide ions,  $\text{OH}^-$ , and cyanide ions,  $\text{CN}^-$ , can react with some aqueous solutions of transition metal compounds.**

**(a) When nickel(II) sulfate is dissolved in water, a pale green solution forms containing a six-coordinate complex ion C.**

**Aqueous potassium hydroxide is added to aqueous nickel(II) sulfate.**

**A green solid D forms.**

**An excess of aqueous potassium cyanide is added to aqueous nickel(II) sulfate.**

**A yellow solution forms containing a four-coordinate complex ion E that contains ONLY nickel, carbon and nitrogen.**

**(i) In C, D and E, nickel has the +2 oxidation state. Suggest the formulae of C, D and E.**

**COMPLEX ION C: \_\_\_\_\_**

**SOLID D: \_\_\_\_\_**

**COMPLEX ION E: \_\_\_\_\_**

**[3]**

- (ii) Write equations, and name the types of reaction, for the formation of D and E.

Formation of solid D from aqueous nickel(II) sulfate.

Equation: \_\_\_\_\_

Type of reaction: \_\_\_\_\_

Formation of complex ion E from complex ion C.

Equation: \_\_\_\_\_

Type of reaction: \_\_\_\_\_

[4]

- (b) In some gold mines, cyanide is used to extract gold from its ore.

Gold metal in the ore reacts with cyanide ions, water and oxygen to form a water-soluble complex ion,  $[\text{Au}(\text{CN})_2]^-$ , with a bond angle of  $180^\circ$ . Hydroxide ions are also formed.

- (i) Name the shape of  $[\text{Au}(\text{CN})_2]^-$ .

\_\_\_\_\_ [1]

- (ii) Using oxidation numbers, show that a redox reaction takes place.

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_ [2]

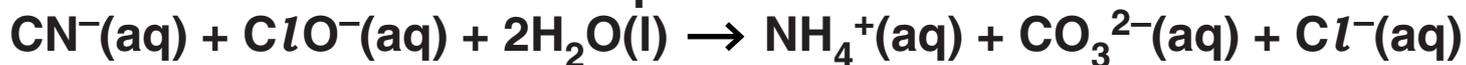
- (iii) Construct the overall equation for this reaction.

State symbols are NOT required.

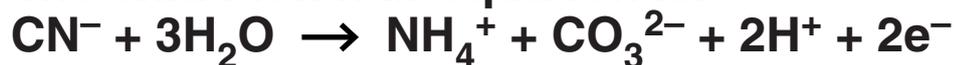
\_\_\_\_\_ [2]

- (iv) Some owners of gold mines remove cyanide ions from waste by adding oxidising agents, such as chlorate(I) ions, before discharge into watercourses.

The overall equation is shown below.



The oxidation half-equation is:



Construct the reduction half-equation.

State symbols are NOT required.

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[1]

[TOTAL: 13]

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8 Hydrated copper(II) methanoate,  $\text{Cu}(\text{HCOO})_2 \cdot x\text{H}_2\text{O}$ , is a copper salt.

A student carries out the procedure below to prepare  $\text{Cu}(\text{HCOO})_2 \cdot x\text{H}_2\text{O}$  and to determine the value of  $x$  in its formula.

### STEP 1

The student prepares  $\text{Cu}(\text{HCOO})_2 \cdot x\text{H}_2\text{O}$  by reacting a copper compound with aqueous methanoic acid to form  $\text{Cu}(\text{HCOO})_2(\text{aq})$  and allowing the solvent to evaporate.

### STEP 2

The student dissolves 2.226 g of  $\text{Cu}(\text{HCOO})_2 \cdot x\text{H}_2\text{O}$  in water and makes up the solution to  $250.0 \text{ cm}^3$ .

### STEP 3

Using a pipette, the student adds  $25.0 \text{ cm}^3$  of this solution to a conical flask followed by an excess of  $\text{KI}(\text{aq})$ .

The  $\text{Cu}^{2+}(\text{aq})$  ions react to form a precipitate of copper(I) iodide and  $\text{I}_2(\text{aq})$ .

In this reaction, 2 mol  $\text{Cu}^{2+}$  form 1 mol  $\text{I}_2$ .

### STEP 4

The student titrates the iodine in the resulting mixture with  $0.0420 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$ .



$23.5 \text{ cm}^3$   $0.0420 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3(\text{aq})$  is required to reach the end point.

(a) Complete the electron configuration of copper in

$\text{Cu}(\text{HCOO})_2 \cdot x\text{H}_2\text{O}$ :  $1s^2$  \_\_\_\_\_

copper(I) iodide:  $1s^2$  \_\_\_\_\_ [2]

(b) Choose a suitable copper compound for STEP 1, and write the full equation for the reaction that would take place to form  $\text{Cu}(\text{HCOO})_2(\text{aq})$ .

State symbols are NOT required.

\_\_\_\_\_ [1]

(c) Write an ionic equation, including state symbols, for the reaction in STEP 3.

\_\_\_\_\_ [1]

(d) In STEP 4, the student adds a solution to observe the end point accurately.

Name the solution and state the colour change at the end point.

Solution added: \_\_\_\_\_

Colour change: \_\_\_\_\_ [2]

**(e) Determine the value of  $x$  in  $\text{Cu}(\text{HCOO})_2 \cdot x\text{H}_2\text{O}$ .**

**Show your working.**

**[5]**

**[TOTAL: 11]**

**END OF QUESTION PAPER**




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