OCR
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Wednesday 22 June 2016 – Morning

A2 GCE CHEMISTRY A

F325/01 Equilibria, Energetics and Elements

Candidates answer on the Question Paper.

OCR supplied materials:
- *Data Sheet for Chemistry A* (inserted)

Other materials required:
- Scientific calculator

Duration: 2 hours

* F 3 2 5 0 1 *

* 5 8 7 8 4 6 7 2 1 1 *

Candidate forename		Candidate surname	

Centre number						Candidate number				

INSTRUCTIONS TO CANDIDATES

- The Insert will be found inside this document.
- Write your name, centre number and candidate number in the boxes above. 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.
- Do **not** write in the bar codes.

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**.
- This document consists of **20** pages. Any blank pages are indicated.

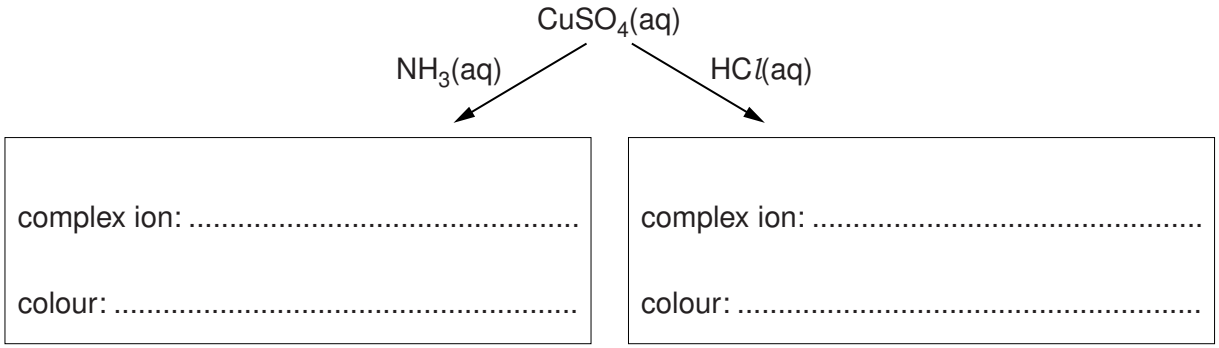
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Answer **all** the questions.

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.



[3]

(b) 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.

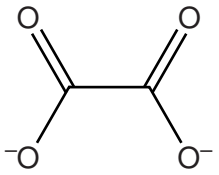


Fig. 1.1

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

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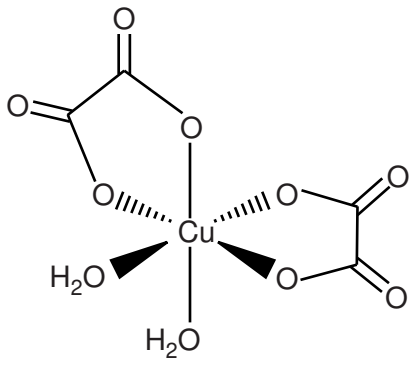
.....

..... **[1]**

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

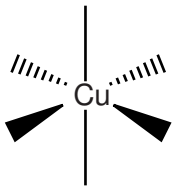
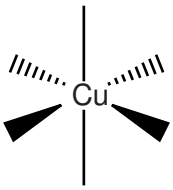
The shape of one of the stereoisomers is shown below. The charge has been omitted.



Complex A

Complete the 3D diagrams of the other two stereoisomers of **A**.
You do **not** need to include any charges.

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

Stereoisomer		
Type	*cis* ☐ *trans* ☐ optical ☐	*cis* ☐ *trans* ☐ optical ☐

[3]

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

..... **[2]**

[Total: 9]

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

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

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	$[H_2O_2(aq)]$ /mol dm^{-3}	$[I^-(aq)]$ /mol dm^{-3}	$[H^+(aq)]$ /mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}
1	0.0010	0.20	0.10	5.70×10^{-6}
2	0.0020	0.20	0.10	1.14×10^{-5}
3	0.0020	0.20	0.20	1.14×10^{-5}
4	0.0040	0.40	0.10	4.56×10^{-5}

(a) The rate equation is: $rate = k\,[H_2O_2(aq)]\,[I^-(aq)]$

- 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.

In your answer you should make clear how the experimental results provide evidence for the rate equation.

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..... **[6]**

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(b) The student concluded that $H^+(aq)$ 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*.

.....

..... **[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 3: $HIO + I^- \rightarrow I_2 + OH^-$

Step 4: .....

[3]

[Total: 11]

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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.

	Name of enthalpy change	Enthalpy change /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	

Table 3.1

(a) Define the term *enthalpy change of hydration*.

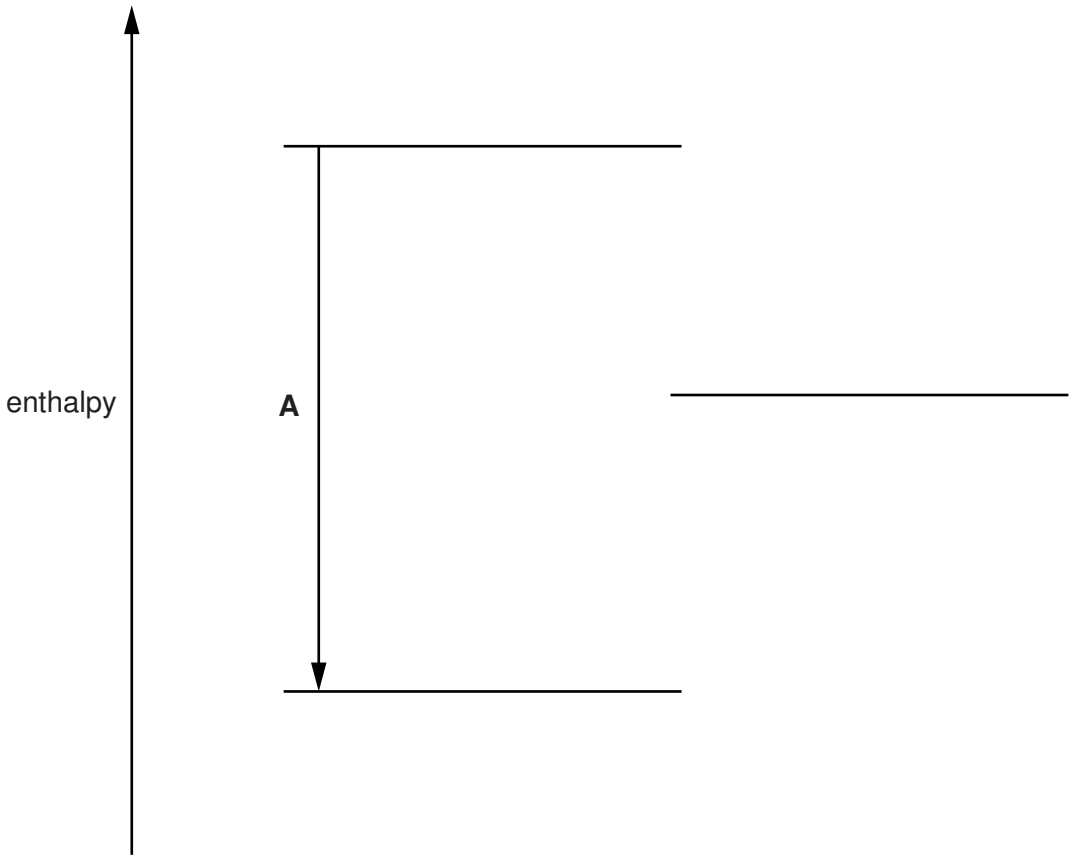
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..... **[2]**

(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.



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(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.

ΔH = ... $kJ\,mol^{-1}$ **[1]**

(c) The entropy change of solution of K_2SO_4 is $+225\,J\,K^{-1}\,mol^{-1}$.

(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 K_2SO_4 dissolves in water at 25 °C, despite the enthalpy change of solution being endothermic.

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..... **[3]**

[Total: 12]

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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.

$$I_2(s) \rightleftharpoons I_2(aq) \qquad \textbf{Equilibrium 1}$$

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

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad \textbf{Equilibrium 2}$$

(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 cm^3 equilibrium mixture contains:

4.00×10^{-5} mol $I_2(aq)$
9.404×10^{-2} mol $I^-(aq)$
1.96×10^{-3} mol $I_3^-(aq)$.

Calculate K_c for **equilibrium 2**.

Give your answer to an **appropriate** number of significant figures.

K_c = ... units ..... **[4]**

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(c) The student adds an excess of aqueous silver nitrate, $AgNO_3(aq)$, 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 $333.8\,g\,mol^{-1}$.

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:

.....

Reaction 2:

.....

[3]

[Total: 12]

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5 A chemist carries out some experiments using nitrous acid, $HNO_2(aq)$.

HNO_2 is a weak acid with a K_a value of $4.69 \times 10^{-4}\,mol\,dm^{-3}$ at the temperature of the chemist's experiments.

(a) Write the expression for K_a for $HNO_2(aq)$.

[1]

(b) Calculate the pH of $0.120\,mol\,dm^{-3}$ $HNO_2(aq)$.

Give your answer to **two** decimal places.

pH = ... **[2]**

(c) The chemist prepares $1\,dm^3$ of a buffer solution by mixing $200\,cm^3$ of $0.200\,mol\,dm^{-3}$ HNO_2 with $800\,cm^3$ of $0.0625\,mol\,dm^{-3}$ sodium nitrite, $NaNO_2$.

(i) Calculate the pH of the buffer solution.

Give your answer to **two** decimal places.

pH = ... **[4]**

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(ii) Explain how this buffer solution controls pH when:

- a small amount of HCl(aq) is added
- a small amount of NaOH(aq) is added.



*In your answer, include the equation for the equilibrium in the buffer solution and explain how **this** equilibrium system controls the pH.*

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..... **[4]**

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(d) The dissociation of water is shown below.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

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

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

(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, pKa and pH are logarithmic scales.

Calculate pK_w at 60 °C.

Give your answer to **two** decimal places.

pK_w = ... **[1]**

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

Calculate the pH of the diluted solution of NaOH at 60 °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** below.

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

Table 6.1

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

Include all standard conditions in your answer.

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..... **[2]**

(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]

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

standard cell potential = ... V **[1]**

(c) Explain what is meant by the terms *oxidising agent* and *reducing agent*.

Illustrate your answer by predicting reactions from redox systems **1**–**6** in which $Cr^{3+}(aq)$ behaves as an oxidising agent and as a reducing agent.

Include overall equations and explain why you have made your predictions.

State symbols are **not** required.

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..... **[6]**

[Total: 14]

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7 Hydroxide ions, OH^-, and cyanide ions, 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]

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(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, $[Au(CN)_2]^-$, with a bond angle of 180°. Hydroxide ions are also formed.

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

..... **[1]**

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

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..... **[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.

$CN^-(aq) + ClO^-(aq) + 2H_2O(l) \rightarrow NH_4^+(aq) + CO_3^{2-}(aq) + Cl^-(aq)$

The oxidation half-equation is:

$CN^- + 3H_2O \rightarrow NH_4^+ + CO_3^{2-} + 2H^+ + 2e^-$

Construct the reduction half-equation.

State symbols are **not** required.

..... **[1]**

[Total: 13]

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8 Hydrated copper(II) methanoate, $Cu(HCOO)_2 \cdot xH_2O$, is a copper salt.

A student carries out the procedure below to prepare $Cu(HCOO)_2 \cdot xH_2O$ and to determine the value of x in its formula.

Step 1
The student prepares $Cu(HCOO)_2 \cdot xH_2O$ by reacting a copper compound with aqueous methanoic acid to form $Cu(HCOO)_2(aq)$ and allowing the solvent to evaporate.

Step 2
The student dissolves 2.226 g of $Cu(HCOO)_2 \cdot xH_2O$ in water and makes up the solution to 250.0 cm^3.

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

The $Cu^{2+}(aq)$ ions react to form a precipitate of copper(I) iodide and $I_2(aq)$.
In this reaction, 2 mol Cu^{2+} form 1 mol I_2.

Step 4
The student titrates the iodine in the resulting mixture with 0.0420 mol dm^{-3} $Na_2S_2O_3$ (aq).

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

23.5 cm^3 0.0420 mol dm^{-3} $Na_2S_2O_3$ (aq) is required to reach the end point.

(a) Complete the electron configuration of copper in

$Cu(HCOO)_2 \cdot xH_2O$: $1s^2$ .....

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 $Cu(HCOO)_2(aq)$.

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]**

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(e) Determine the value of x in $Cu(HCOO)_2 \cdot xH_2O$.

Show your working.

[5]

[Total: 11]

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

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