OCR A-LEVEL CHEMISTRY A

CHEMISTRY



EXAM QUESTION PACK

UNIT F325 OLD SPECIFICATION PAPERS

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OCR
Oxford Cambridge and RSA

Monday 19 June 2017 – 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

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 barcodes.

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 Lattice enthalpies can be calculated indirectly using Born–Haber cycles.

Table 1.1 shows enthalpy changes that can be used to calculate the lattice enthalpy of magnesium bromide, $MgBr_2$.

Letter	Enthalpy change	Energy / kJ mol^{-1}
A	atomisation of magnesium	+146
B	1st ionisation energy of magnesium	+738
C	2nd ionisation energy of magnesium	+1451
D	atomisation of bromine	+112
E	1st electron affinity of bromine	–325
F	formation of magnesium bromide	–524
G	lattice enthalpy of magnesium bromide	

Table 1.1

(a) Define the term *lattice enthalpy*.

.....

.....

.....

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

(b) Lattice enthalpies are exothermic.

Explain why it is difficult to predict whether the lattice enthalpy of magnesium bromide would be more or less exothermic than the lattice enthalpy of sodium chloride.

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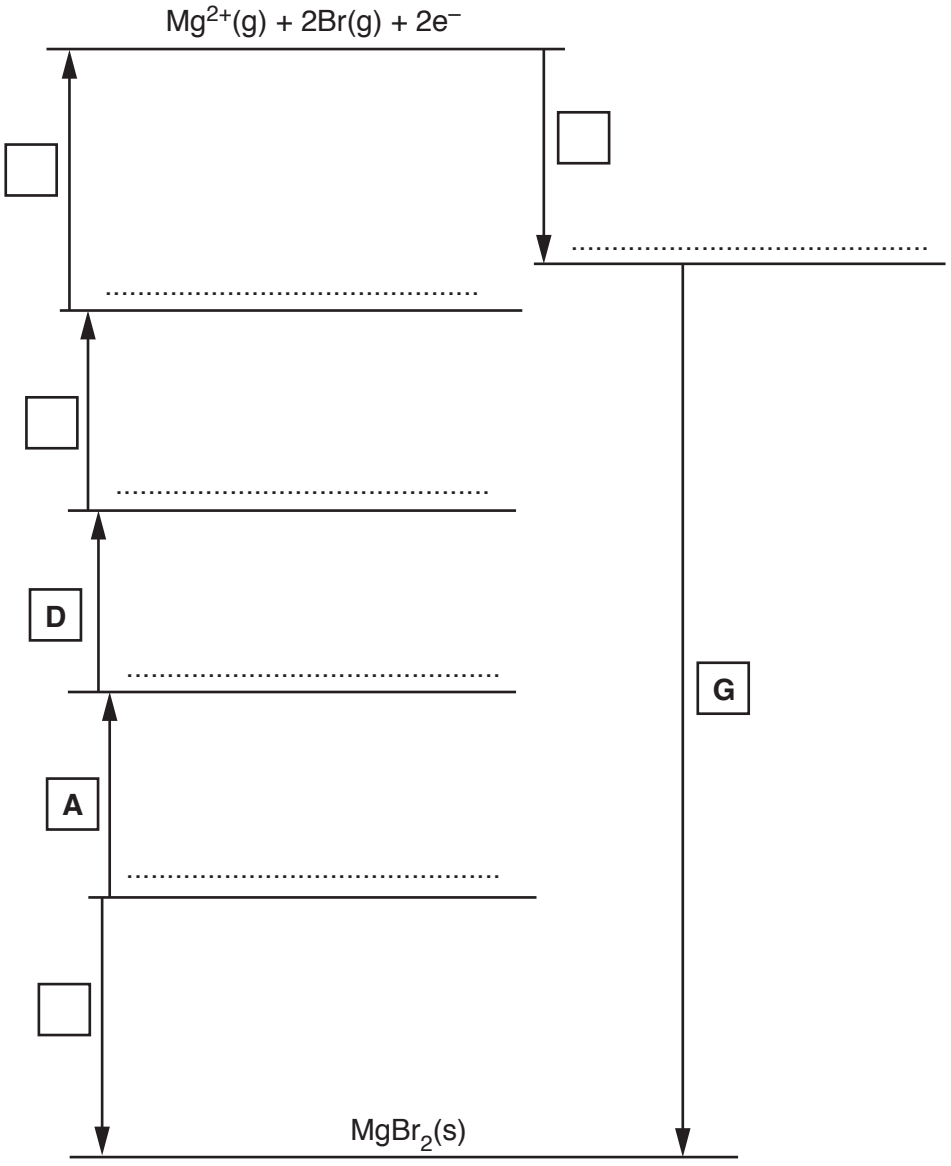
..... **[3]**

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(c) The Born–Haber cycle below links the lattice enthalpy of magnesium bromide with the enthalpy changes in **Table 1.1**.

(i) Add the correct letters from **Table 1.1** in the four empty boxes and write the correct species on the five dotted lines.



[6]

(ii) Calculate the lattice enthalpy of magnesium bromide.

lattice enthalpy = ... $kJ\,mol^{-1}$ **[2]**

[Total: 13]

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2 Entropy changes and free energy changes can be used to predict the feasibility of processes.

(a) Three processes are given below.

For each process, predict and explain whether the entropy change, ΔS, would be positive or negative.

- The melting of iron.

  ΔS: positive or negative .....

  explanation .....

  .....

  .....

- The reaction of magnesium with dilute sulfuric acid.

  ΔS: positive or negative .....

  explanation .....

  .....

  .....

- The complete combustion of ethane:

  $$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$$

  ΔS: positive or negative .....

  explanation .....

  .....

  .....

[3]

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(b) Ammonia can be oxidised as shown in the equation below.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

At 450 °C, $\Delta H = -907\,kJ\,mol^{-1}$ and $\Delta G = -1041\,kJ\,mol^{-1}$.

Calculate the standard entropy change, ΔS, in $J\,K^{-1}\,mol^{-1}$, for this reaction.

Show all your working.

ΔS = ... $J\,K^{-1}\,mol^{-1}$ **[2]**

(c) A reaction is **not** feasible at low temperatures but is feasible at high temperatures.

Deduce the signs of ΔH and ΔS for the reaction and explain why the feasibility changes with temperature.

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

[Total: 8]

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3 Nitrogen monoxide, NO, and hydrogen, H_2, react together.

The rate equation is shown below:

$$\text{rate} = k[NO(g)]^2 [H_2(g)]$$

(a) What are the orders of reaction shown below?

Order with respect to NO(g): .....

Order with respect to $H_2(g)$: .....

Overall order of reaction: .....

[1]

(b) Predict what would happen to the initial rate of the reaction between NO and H_2 for the following change in concentrations.

The concentrations of NO(g) and $H_2(g)$ are **both** increased by five times.

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

(c) Nitrogen monoxide and hydrogen are reacted together. The initial concentrations and initial rate are shown below.

$[NO(g)] / \text{mol dm}^{-3}$	3.24×10^{-3}
$[H_2(g)] / \text{mol dm}^{-3}$	5.45×10^{-2}
initial rate $/ \text{mol dm}^{-3} \text{s}^{-1}$	4.34×10^{-2}

Calculate the rate constant, k, for this reaction. State the units, if any.

Give your answer to **three** significant figures and in standard form.

k = ... units ..... **[3]**

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(d) Complete the table below to show the effect on the reaction rate and the rate constant, *k*, of the following changes in conditions.

Use the words **increases**, **decreases** or **none**.

Change	Effect on reaction rate	Effect on rate constant
Increase in pressure		
Increase in temperature		

[2]

(e) This reaction between NO(g) and $H_2(g)$ takes place by a two-step mechanism.

The rate equation is shown below:

$$\text{rate} = k[NO(g)]^2[H_2(g)]$$

- In the mechanism, **step 1** is much slower than **step 2**.
- The equation for **step 2** is shown below.

Write the equations for **step 1** and the **overall reaction**.

step 1: .....

step 2: $H_2(g) + N_2O(g) \rightarrow N_2(g) + H_2O(g)$

overall reaction: .....

[2]

[Total: 9]

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4 This question is about the chemistry of different transition elements.

(a) Vanadium, V, is a typical transition element in the d-block of the Periodic Table. In its compounds and ions, vanadium has several common oxidation numbers, +2, +3, +4 and +5.

(i) Show that vanadium is both a *d-block element* and *transition element*.

In your answer, include full electron configurations of vanadium in its 0 and +2 oxidation states.

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

(ii) An acidified solution containing VO_3^- ions reacts with zinc metal in a redox reaction. The resulting solution contains Zn^{2+} ions and V^{2+} ions.

The unbalanced half-equations are shown below.

Balance these half-equations and construct an overall equation for this reaction.

Half-equation 1: $VO_3^- + H^+ + e^- \rightarrow V^{2+} + H_2O$

Half-equation 2: $Zn \rightarrow Zn^{2+} + e^-$

Overall equation: .....

[3]

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(b) Platin, $Pt(NH_3)_2Cl_2$, is an uncharged complex of platinum(II) that has two stereoisomers. One of these stereoisomers is used in chemotherapy for the treatment of some cancers.

(i) Explain why platin has no charge.

.....

.....

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

(ii) Draw labelled diagrams of the two stereoisomers of platin, showing clearly the atoms involved in bonding, and describe the bonding involving Pt with its ligands.

.....

.....

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

(iii) Describe the action of one of the stereoisomers of platin in the treatment of cancer patients.

.....

.....

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

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(c) Aqueous cobalt(II) ions are reacted with aqueous sodium hydroxide and with concentrated hydrochloric acid.

Describe these reactions. Include colours of the cobalt-containing species, ionic equations and the types of reaction taking place.

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..... **[7]**

[Total: 19]

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5 This question is about acids, bases and buffer solutions.

(a) Ethanoic acid, CH_3COOH, and propanoic acid, C_2H_5COOH, are weak Brønsted–Lowry acids.

The acid dissociation constants, K_a, of the two acids are shown below.

Acid	K_a / mol dm^{-3}
CH_3COOH	1.70×10^{-5}
C_2H_5COOH	1.30×10^{-5}

(i) Explain the term *weak acid*.

.....

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

(ii) Write the expression for the acid dissociation constant, K_a, of ethanoic acid.

[1]

(iii) Calculate the pH of a 2.85×10^{-2} mol dm^{-3} solution of C_2H_5COOH.

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

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

(iv) Ethanoic acid is mixed with propanoic acid. An acid–base equilibrium is set up.

Complete the equation for the equilibrium.

Label the conjugate acid–base pairs using the labels **acid 1**, **base 1**, **acid 2**, **base 2**.

C_2H_5COOH + CH_3COOH $\rightleftharpoons$ ..... + ...

....

[2]

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(b) Barium hydroxide, $Ba(OH)_2$, is a strong Brønsted–Lowry base.

A student prepares 250.0 cm^3 of 0.1250 mol dm^{-3} barium hydroxide.

(i) Explain what is meant by the term *Brønsted–Lowry base*.

.....

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

(ii) Calculate the mass of $Ba(OH)_2$ that the student would need to weigh on a **two** decimal place balance to prepare 250.0 cm^3 of 0.1250 mol dm^{-3} $Ba(OH)_2$.

mass = ... (g) **[3]**

(iii) Calculate the pH of a 0.1250 mol dm^{-3} solution of $Ba(OH)_2$.

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

pH = ... **[3]**

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(c) The student attempts to prepare a buffer solution by mixing 200 cm^3 of 0.324 $mol\,dm^{-3}$ C_2H_5COOH with 100 cm^3 of the 0.1250 $mol\,dm^{-3}$ $Ba(OH)_2$ prepared in **(b)**.

The equation for the reaction that takes place is shown below.

$$2C_2H_5COOH(aq) + Ba(OH)_2(aq) \rightarrow (C_2H_5COO)_2Ba(aq) + 2H_2O(l)$$

Explain whether the student was successful in preparing a buffer solution.

Include all reasoning and any relevant calculations.

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

(d) Blood contains a mixture of carbonic acid, H_2CO_3, and hydrogencarbonate ions, HCO_3^-.

Explain how the carbonic acid–hydrogencarbonate mixture acts as a buffer.

In your answer include the equation for the equilibrium in this buffer solution and explain how this equilibrium system is able to control blood pH.

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..... **[5]**

[Total: 22]

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6 Ammonia can be manufactured from nitrogen and hydrogen gases in the Haber process. The equilibrium is shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

(a) Write an expression for K_c for this equilibrium.

[1]

(b) A chemist carries out a series of experiments to investigate the conversion of nitrogen and hydrogen into ammonia under different conditions.

- The chemist mixes together 10.40 mol N_2 and 22.50 mol H_2 and pressurises the gases so that the total gas volume is 5.00 dm^3.
- The mixture is allowed to reach equilibrium at constant temperature and without changing the total gas volume.
- The equilibrium mixture contains 5.60 mol NH_3.

Calculate K_c, including units, at this temperature.
Give your answer to **three** significant figures.

K_c = ... units ..... **[6]**

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(c) The chemist repeats the experiment several times. In each experiment, the chemist makes one change.

(i) The chemist heats the mixture to a higher temperature at constant pressure.

Explain whether the value of K_c would be greater, smaller or the same.

.....

.....

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

(ii) The chemist increases the pressure of the mixture at constant temperature.

Explain whether the value of K_c would be greater, smaller or the same.

.....

.....

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

[Total: 9]

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7 Redox reactions are used in electrochemical cells and in analysis.

(a) **Table 7.1** shows two redox systems, and their standard electrode potentials, $E^{\ominus}$.

	Redox system	$E^{\ominus}$/**V**
1	$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.74
2	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77

Table 7.1

(i) A student sets up a standard cell in the laboratory based on redox systems **1** and **2**.

Draw a labelled diagram to show how the student could set up this cell to measure its standard cell potential.

State the conditions needed to measure this standard cell potential.

conditions: .....

.....

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

(ii) Write down the overall cell reaction.

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

(iii) Write down the standard cell potential of this cell and state the sign of the chromium electrode.

standard cell potential = ... V

sign of chromium electrode = ... **[1]**

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(b) The student makes the following change to their standard cell set up in **(a)**.

The student adds solid $CrCl_3$ to the $Cr^{3+}(aq)/Cr(s)$ half-cell. The student stirs the solution to dissolve the $CrCl_3$.
The student finds that the cell potential has **decreased**.

Explain this observation, in terms of equilibrium and electrode potentials.

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

(c) A new type of fuel cell has been developed based on HCOOH and O_2.

The equation for the overall cell reaction is shown below.

$$2HCOOH(l) + O_2(g) \longrightarrow 2H_2O(l) + 2CO_2(g)$$

The half-equation at the oxygen electrode of this fuel cell is shown below.

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$$

(i) Deduce the half-equation at the other electrode of this fuel cell.

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

(ii) Suggest **one** advantage of this fuel cell over a hydrogen fuel cell.

.....

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

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(d) Redox reactions can be used in analysis.

Food additives containing sulfite ions, SO_3^{2-}, are often used as preservatives.

A student analyses a sample of hydrated sodium sulfite to find the formula of the hydrated salt.

The student titrates a solution of hydrated sodium sulfite with a standard solution of aqueous potassium manganate(VII), $KMnO_4$, under acidic conditions.

The method is outlined below.

- The student dissolves 2.400 g of hydrated sodium sulfite in water and makes the solution up to 250.0 cm^3.
- The student titrates 25.00 cm^3 volumes of this solution with 0.01500 mol dm^{-3} $KMnO_4$ under acidic conditions.

The mean titre is 25.40 cm^3.

In the titration, 2 mol of MnO_4^- reacts with 5 mol of SO_3^{2-}.

(i) Determine the formula of the hydrated sodium sulfite, showing clearly its water of crystallisation as a whole number.

formula = ... **[6]**

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(ii) In the titration, a redox reaction takes place between MnO_4^-, SO_3^{2-} and H^+ ions:

- MnO_4^- ions are reduced to manganese(II) ions,
- SO_3^{2-} ions are oxidised to sulfate(VI) ions.

Construct the overall equation for the redox reaction and the half-equations that take place in the titration.

Overall equation:

.....

Half-equations:

[3]

[Total: 20]

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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GCE

Chemistry A

Unit **F325:** Equilibria, Energetics and Elements

Advanced GCE

Mark Scheme for June 2017

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Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

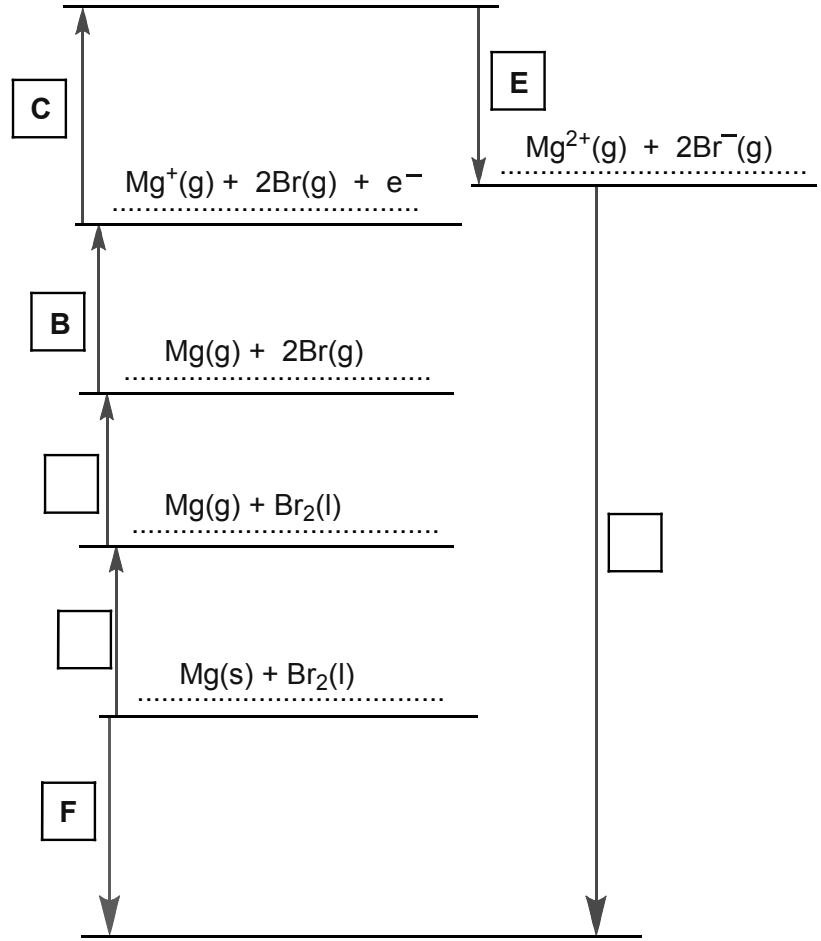
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Question			Answer	Marks	Guidance
1	(a)		**Formation** of **one mole** of a(n ionic) compound ✓ from its **gaseous ions** ✓ **IGNORE** standard conditions	2	**IGNORE** 'Energy needed' **OR** 'energy required' For '*compound*', **ALLOW**: lattice, crystal, substance, solid **Special case: 1 mark for gaseous ions ONLY** 'Formation of 1 mole of compound from 1 mole of gaseous ions.' Duplicate 1 mole is a **CON** for 1st marking point
1	(b)		***FULL ANNOTATIONS MUST BE USE*** For **ALL** marking points, assume the following: • For 'ions', **ALLOW** 'atoms', *e.g.* Na has a larger (atomic) radius • For Mg^{2+}, Na^{+}, Br^{-} and Cl^{-}, **ALLOW** symbols: *e.g.* Mg, Na, Br and Cl • **ALLOW** names: e.g. magnesium, sodium, bromine, bromide, chlorine, chloride • **DO NOT ALLOW** 'composite' particles, e.g. 'magnesium bromide/$MgBr_2$ has a larger ionic radius' **DO NOT ALLOW** molecules **IGNORE** idea of close packing of ions **IGNORE** electronegative		

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Question			Answer	Marks	Guidance
			Comparing cation size AND charge (ORA based on Na^+) Mg^{2+} is smaller **AND** Mg^{2+} has a greater charge **OR** Mg^{2+} has a greater charge density ✓ ***Comparing of anion size (ORA based on Cl^-)*** Br^- is larger **OR** Br^- has a smaller charge density ✓ ***Comparing cation ⇔ anion attraction*** Mg^{2+} has stronger attraction **AND** Cl^- has stronger attraction ✓ ***IGNORE*** *'nuclear' attraction*	**3**	**ALLOW** reverse argument throughout (**ORA**) --- For 'greater charge' part of mark, **ALLOW** Mg^{2+} **AND** Na^+ seen anywhere **ALLOW** Mg is 2+ **AND** Na is 1+ **IGNORE** just Mg^{2+} is small *comparison required* **IGNORE** just Br^- is large *comparison required* **ALLOW** pull for attraction **ALLOW** '**attracts** with more force' for greater attraction **BUT** … **IGNORE** just 'greater force' (*could be repulsion*) **OR** comparison of bond strength/energy to break bonds **IGNORE** comparisons of numbers of ions

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Question			Answer	Marks	Guidance
1	(c)	(i)	 **5 marks** for species **AND** state symbols on the dotted lines ✓✓✓✓✓ **1 mark** for **ALL** 4 correct letters in boxes ✓ *Place tick or cross by top right letter (E when correct)* **6** STEMUP.CO.UK	**6**	Correct species **AND** state symbols required for marks on dotted lines **ALLOW** e for e^- **TAKE CARE**: e^- may be in centre of response and more difficult to see than at end, e.g. $Mg^+(g) + e^- + 2Br(g)$ **ONE** correct response for each line **Mark each marking point independently** --- No **ECF** except for (g) and (s) state symbol of **Br_2**(l) i.e.: $Mg(g) + Br_2(g)$ ✓ **ECF** ↑ $Mg(s) + Br_2(g)$ × --- $Mg(g) + Br_2(s)$ ✓ **ECF** ↑ $Mg(s) + Br_2(s)$ × --- **DO NOT ALLOW ECF** for same change with (aq), i.e. $Mg(g) + Br_2(aq)$ × ↑ $Mg(s) + Br_2(aq)$ × ---

Question			Answer	Marks	Guidance
1	(c)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –2433 (kJ mol^{-1}) award 2 marks** --- **Cycle** (–524) = 146 + (2 × +112) + 738 + 1451 + (2 × –325) + LE **OR** LE = –524 – (146 + (2 × +112) + 738 + 1451 + (2 × –325) **OR** –524 – 1929 ✓ **Lattice energy** LE = **– 2433** ✓ (kJ mol^{-1})	**2**	For alternative answers, **ALLOW ECF** **See list below for marking of answers from common errors** --- **ALLOW** for 1 mark: +2433 wrong sign –2321 +112 used instead of **2 ×** 112 –2758 –325 used instead of **2 ×** –325 –3733 wrong sign for **2 ×** 325 –1385 wrong sign for 524 –2141 wrong sign for 146 –1985 wrong sign for 2 **×** 112 –957 wrong sign for 738 +469 wrong sign for 1451 Any other number: **CHECK** for **ECF** from 1st marking point for expressions with **ONE** error only e.g. one transcription error: e.g. +461 instead of +416
			Total	**13**	

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Question			Answer	Marks	Guidance
2	(a)		positive **OR** + **AND** solid forms liquid **OR** liquid has more disorder ✓	3	For 'liquid has more disorder': **ALLOW** liquid has more ways of arranging energy/ more freedom/ more random molecules
			positive **OR** + **AND** gas (H_2) forms **OR** Mg dissolves/disappears ✓		**ASSUME** gas is H_2 unless otherwise stated **BUT DO NOT ALLOW** an incorrect gas (e.g. CO_2) **IGNORE** liquid forms **IGNORE** equation with state symbols *Response should communicate why entropy increases*
			negative **OR** – **AND** **9** mol **gas** form **4** mol **gas OR** forms **5 fewer** mol of **gas** ✓		**Numbers and gas** are **essential** **IGNORE** 'forms fewer moles of gas' For mol, **ALLOW** molecules **IGNORE** numbers around equation *Treated as rough working*

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Question			Answer	Marks	Guidance
2	(b)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **185** (J K^{-1} mol^{-1}) award **2 marks** *Conversion of ºC to K* ***AND*** *substitution of values into* $\Delta G = \Delta H - T\Delta S$ $-1041 = -907 - 723 \times \Delta S$ ✓ *Calculation of* ΔS ***AND*** *conversion to J* K^{-1} mol^{-1} $\Delta S = \frac{1041 - 907}{723} \times 1000 = \frac{134}{723} \times 1000$ = 185 **OR** 185.3 (J K^{-1} mol^{-1}) ✓ ***ALLOW*** *3 SF up to calc value of 185.3388658 correctly rounded*	2	Conversion to J may be carried out at start but no mark **JUST** for this conversion **ALLOW ECF ONLY** from use of values from question: (–)907 **AND** (–)1041 **AND** 450/723 --- **COMMON ERRORS** **–185** wrong sign 1 mark **0.185** no conversion from kJ to J 1 mark **1.85 × 10^{-4}** ÷ by 1000 instead of × 1 mark **298/297.8 (calc 297.7 recurring)** Use of 450 ºC instead of 723 K 1 mark **–2694** wrong sign for 1041 1 mark **2694** wrong sign for 907 1 mark **±4329** Wrong sign **AND** 450ºC 0 marks

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Question			Answer	Marks	Guidance
2	(c)		**Signs of ΔH and ΔS** ΔH is positive **AND** ΔS is positive ✓ ***T*Δ*S* and temperature** 'Value of' $T\Delta S$ increases with temperature ✓ **Feasibility** At high temperatures, ΔG is –ve **OR** $\Delta G < 0$ **AND** At low temperatures, ΔG is +ve **OR** $\Delta G > 0$ **OR** $\Delta H - T\Delta S$ decreases with (increasing) temperature **OR** $\Delta H - T\Delta S$ from +ve to –ve with (increasing) temperature ✓ **OR** the idea: As temperature increases, $T\Delta S$ outweighs ΔH to make $\Delta G < 0$	3	***FULL ANNOTATIONS MUST BE USED*** **ALLOW** ΔH is endothermic for ΔH is positive **IGNORE** sign of $T\Delta S$ *(treated as $\lvert T\Delta S \rvert$)* *i.e.* ***ALLOW*** *$T\Delta S$ becomes more/less positive* ***OR*** *$T\Delta S$ becomes more/less negative* **IGNORE** ΔS increases with temperature **ONLY** award feasibility mark if signs of ΔH and ΔS are correct, i.e. ΔH +ve **AND** ΔS +ve (1st marking point) **ALLOW** $\Delta H - T\Delta S$ for ΔG, e.g. At high temperatures, $\Delta H - T\Delta S < 0$ **OR** $\Delta H < T\Delta S$ ***AND*** At low temperatures, $\Delta H - T\Delta S > 0$ **OR** $\Delta H > T\Delta S$
			Total	8	

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<table>
<tr><th colspan="3">Question</th><th>Expected answers</th><th>Marks</th><th>Additional guidance</th></tr>
<tr><td>3</td><td>(a)</td><td></td><td>NO: 2 /Second
AND H_2: 1 /First
AND Overall: 3 /Third ✓</td><td>1</td><td></td></tr>
<tr><td>3</td><td>(b)</td><td></td><td>rate × 125 ✓</td><td>1</td><td>**DO NOT ALLOW** just ‘increases by 5 and then by 25 / 5^2
OR increases by 5^3</td></tr>
<tr><td>3</td><td>(c)</td><td></td><td>**FIRST, CHECK THE ANSWER ON ANSWER LINE**
IF answer = **7.59×10^4** award **2 marks**
THEN IF units are **$dm^6\ mol^{-2}\ s^{-1}$**, award 1 further mark

Initial working
$k = \dfrac{4.34 \times 10^{-2}}{(3.24 \times 10^{-3})^2 \times 5.45 \times 10^{-2}}$

OR 75858.31764 to 3 SF or more ✓

3 SF and standard form
$= 7.59 \times 10^4$ ✓

units:
$dm^6\ mol^{-2}\ s^{-1}$ ✓</td><td>3</td><td>***FULL ANNOTATIONS MUST BE USED***

NO ECF from incorrectly rearranged *k* expression

ALLOW $mol^{-2}\ dm^6\ s^{-1}$ **OR** any order
DO NOT ALLOW other units from incorrect *k* expression
(Rate equation supplied on paper – **not** derived from data)</td></tr>
<tr><td>3</td><td>(d)</td><td></td><td><table><tr><td>Change</td><td>Effect on rate</td><td>Effect on k</td></tr><tr><td>Increase in pressure</td><td>increases</td><td>none</td></tr><tr><td>Increase in temperature</td><td>increases</td><td>increases</td></tr></table>Mark by **column**: ✓ ✓</td><td>2</td><td>**ALL** boxes are ‘increases’ **EXCEPT** top right is ‘none’.</td></tr>
</table>

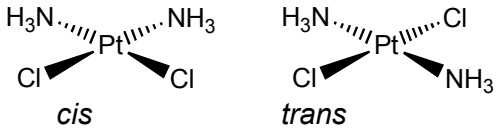
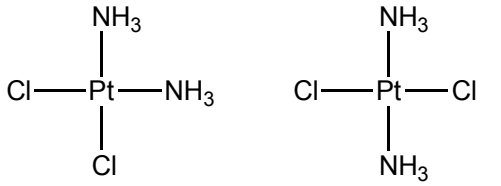
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Question			Expected answers	Marks	Additional guidance
3	(e)		**Overall equation must be sum of step 1 and step 2** **step 1**: $H_2(g) + 2\,NO(g) \rightarrow N_2O(g) + H_2O(g)$ ✓ **overall**: $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$ ✓ **NO ECF** for from **incorrect** step 1 equation	**2**	**IGNORE** any state symbols *For other possible correct responses, contact Team Leader*
			Total	**9**	

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Question			Answer	Marks	Guidance
4	(a)	(i)	**Note:** Examples must be for V, not other d block elements **d block element:** (3)d is **highest energy** sub-shell/orbital ✓ **Transition element:** has an **ion** with incomplete/partially-filled **d sub-shell/orbital** ✓ **V** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$ ✓ ***full*** *electron configuration required* **V^{2+}:** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ ✓ ***full*** *electron configuration required*	4	***FULL ANNOTATIONS MUST BE USED*** **DO NOT ALLOW highest energy** shell **ALLOW** 4s before 3d, ie $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ **ALLOW** upper case D, etc and subscripts, e.g. $[Ar]4S_2 3D_8$ **DO NOT ALLOW USE OF** [Ar] for $1s^2 2s^2 2p^6 3s^2 3p^6$ for configuration of V and V^{2+} **ALLOW** electron configuration with $4s^0$
4	(a)	(ii)	$VO_3^- + 6H^+ + 3e^- \longrightarrow V^{2+} + 3H_2O$ ✓ $Zn \longrightarrow Zn^{2+} + 2e^-$ ✓ $2VO_3^- + 12H^+ + 3Zn \longrightarrow 2V^{2+} + 6H_2O + 3Zn^{2+}$ ✓ **Multiples of this equation are the ONLY correct answer**	3	**ALLOW** multiples **NO ECF** from incorrect half equations **ALLOW** multiples, e.g. $VO_3^- + 6H^+ + 1½Zn \longrightarrow V^{2+} + 3H_2O + 1½Zn^{2+}$

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Question			Answer	Marks	Guidance
4	(b)	(i)	Pt: Pt^{2+} **OR** +2/2+ **AND** Cl: 2 × Cl^- **OR** 2 × –1 **OR** 2 Cl^-/Cl with oxidation number –1 ✓	1	**DO NOT ALLOW** response in terms of 'Cl_2'or 'Cl **molecule**', rather than Cl^- **DO NOT ALLOW** 'charges cancel' without the charges/oxidation numbers involved being stated **DO NOT ALLOW** if NH_3 shown to have charge
4	(b)	(ii)	 *cis* *trans* **OR**  *cis* *trans* ✓✓ For each structure **AND** correct *cis* and *trans* labels **AWARD** 1 mark for **TWO** correct structures with incorrect *cis* and *trans* labels **OR** no labels. --- Ligands **donates** electron pairs **OR** Pt/Pt^{2+}/metal (ion) **accepts** lone pairs ✓	3	**IGNORE** any charge, i.e. Pt^{2+} OR Cl^-, even if wrong Bonds **MUST** go to **N** of to **NH_3** **IGNORE** labelled bond angles (even if wrong) **DO NOT ALLOW any** structure that cannot be in one plane If ligands are orientated correctly in *cis* **AND** *trans*, but connectivity to N is poor **ALLOW** 1 mark for two diagrams --- **ALLOW** coordinate bonds shown on diagrams provide that they start from a lone pair on ligands
4	(b)	(iii)	***cis***-platin binds to DNA (of cancer cells) **OR *cis***-platin stops (cancer) cells dividing/replicating ✓	1	***ALLOW*** *cis-isomer:* ***cis*** is essential **IGNORE** simply '*cis*-platin used in cancer treatment'

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Question			Answer	Marks	Guidance
4	(c)		**Colour of $Co^{2+}(aq)$ OR $[Co(H_2O)_6]^{2+}$ 1 mark** Pink solution seen at least once **AND** not contradicted ✓ ***REACTION OF Co^{2+} with NaOH(aq) 3 marks*** **Correct equation** $Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$ ✓ state symbols **not** required **Observation** blue precipitate/solid ✓ **Type of reaction** precipitation ✓	7	***FULL ANNOTATIONS MUST BE USED*** **ALLOW equilibrium signs in all equations** **IGNORE state symbols** **IGNORE an incorrect formula for an observation** --- **ALLOW** '$Co^{2+}(aq)$ is pink' or similar wording (aq) **OR** $[Co(H_2O)_6]^{2+}$ is equivalent to 'solution' **DO NOT ALLOW** pink **precipitate** **ALLOW** $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2(H_2O)_4 + 2H_2O$ **ALLOW** 'hybrid' equations, e.g. $Co^{2+} + 2NaOH \rightarrow Co(OH)_2 + 2Na^+$ $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2 + 6H_2O$ **ALLOW** any shade of blue **IGNORE** changes in colour over time **DO NOT ALLOW** 'precipitate reaction' **IF** equation with $[Co(H_2O)_6]^{2+}$ has been shown, **ALLOW** acid–base **OR** neutralisation
			REACTION OF Co^{2+} WITH HCl(aq) 3 marks **Correct equation** $[Co(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CoCl_4]^{2-} + 6H_2O$ ✓ **Observation** blue (solution) ✓ **Type of reaction** ligand substitution ✓		**ALLOW** $CoCl_4^{2-}$ i.e. no brackets **OR** $Co(Cl)_4^{2-}$ **ALLOW** $[Co(H_2O)_6]^{2+} + 4HCl \longrightarrow [CoCl_4]^{2-} + 6H_2O + 4H^+$ **IGNORE** $Co^{2+} + 4Cl^- \longrightarrow CoCl_4^{2-}$ **ALLOW** any shades of blue **DO NOT ALLOW** blue **precipitate** **ALLOW** ligand exchange

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Question	Answer	Marks	Guidance
	Total	19	

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Question			Answer	Marks	Guidance
5	(a)	(i)	partlially dissociates ✓	1	For dissociates, **ALLOW** ionises
5	(a)	(ii)	$(K_a =) \frac{[H^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$ ✓ All species **MUST** have square brackets	1	**ALLOW** $[H_3O^+]$ for $[H^+]$ **IGNORE** $\frac{[H^+]^2}{[C_2H_5COOH]}$ **OR** $\frac{[H^+]\,[A^-]}{[HA]}$ **IGNORE** state symbols

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Question			Answer	Marks	Guidance
5	(a)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **3.22**, award **2 marks** --- $[H^+] = \sqrt{(1.30 \times 10^{-5}) \times (2.85 \times 10^{-2})}$ **OR** 6.09×10^{-4} (mol dm^{-3}) ✓ pH = –log 6.09×10^{-4} = **3.22** ✓ *Must be from a calculated $[H^+]$* **NOTE**: The marks are **ONLY** available from attempted use of K_a **AND** $[C_2H_5COOH]$	**2**	**ALLOW** 6.09×10^{-4} to calculator value of $6.086871117 \times 10^{-4}$ correctly rounded **ALLOW ECF** from incorrect $[H^+]$ derived from K_a **AND** $[H^+]$ **ALLOW** use of quadratic equation – gives same answer of 3.22 --- **COMMON ERRORS (MUST be to 2 DP)** Mark other errors by **ECF** **pH = 6.43 1 mark** –log $(1.30 \times 10^{-5}) \times (2.85 \times 10^{-2})$ *No* √ **pH = 3.16 1 mark** Wrong acid ($K_a = 1.70 \times 10^{-5}$) but all else correct **pH = 4.89 0 marks** $-\log(1.30 \times 10^{-5}) = 4.89$ *–log K_a* **pH = 1.55 0 marks** $-\log(2.85 \times 10^{-2}) = 4.87$ *–log $[H^+]$*

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Question			Answer	Marks	Guidance
5	(a)	(iv)	$C_2H_5COOH + CH_3COOH \rightleftharpoons \mathbf{C_2H_5COOH_2^+ + CH_3COO^-}$ ✓ **Base 2 Acid 1 Acid 2 Base 1** ✓ *1st mark for correct products, $C_2H_5COOH_2^+$ **AND** CH_3COO^-* *2nd mark for correct labels*	2	**ALLOW ECF** for 2nd mark if H^+ transfer shown other way round, i.e. $C_2H_5COOH + CH_3COOH \rightleftharpoons \mathbf{C_2H_5COO^- + CH_3COOH_2^+}$ **×** **Acid 1 Base 2 Base 1 Acid 2** ✓ **ECF** **NO OTHER ECF** **ALLOW** A1, B1, etc or any unambiguous labels
5	(b)	(i)	proton/H^+ acceptor ✓	1	**DO NOT ALLOW** OH^- donor
5	(b)	(ii)	**FIRST CHECK THE ANSWER ON THE ANSWER LINE** **IF** answer = 5.35 (g) award **3 marks** $n(Ba(OH)_2) = (250/1000) \times 0.1250 = 0.03125$ (mol) ✓ $M(Ba(OH)_2) = 171.3$ (g mol^{-1}) ✓ mass = $0.03125 \times 171.3 = 5.35$ (g) ✓ **NOTE**: Answer to **two** decimal places	3	**ALLOW ECF** but answer required to **two** decimal places

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Question			Answer	Marks	Guidance
5	(b)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **13.40** award **3 marks** $[OH^-] = 2 \times 0.1250 = 0.25(0)$ (mol dm^{-3}) ✓ $[H^+] = \frac{1.00\times10^{-14}}{0.25(0)}$ **OR** $4(.00) \times 10^{-14}$ (mol dm^{-3}) ✓ *Subsumes 1st mark* pH = –log 4.00×10^{-14} = **13.40** ✓ *Must be from a calculated $[H^+]$* --- **pOH variation (also worth 3 marks)** $[OH^-] = 2 \times 0.125 = 0.25(0)$ (mol dm^{-3}) ✓ pOH = –log 0.25(0) = 0.60 ✓ pH = 14.00 – 0.60 = 13.40 ✓ *Must be from a calculated pOH*	3	**Marks are for correctly calculated values. Working shows how values have been derived.** **ALLOW** by **ECF** $\frac{1.00\times10^{-14}}{\text{calculated value of } [OH^-]}$ **DO NOT ALLOW** 13.4 *not **two** decimal places* --- **COMMON ERRORS for pH** 13.4 ✓✓ *not 2 DP* 13.10 ✓✓ *no × 2 for $[OH^-]$* 13.1 ✓ *no × 2 for $[OH^-]$ **AND** 1 DP only* 12.80 ✓✓ ÷2 instead of × *2 for $[OH^-]$* 0.60 ✓ 2×0.1250 expressed as pH 0.90 **no marks** *–log 0.125*

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Question			Answer	Marks	Guidance
5	(c)		**Possible conclusion from mixing C_2H_5COOH and $Ba(OH)_2$** Buffer forms when • acid / C_2H_5COOH is in excess • **OR** buffer contains C_2H_5COOH **AND** $C_2H_5COO^-$ / $(C_2H_5COO)_2Ba$ ✓ Independent of calculations ***n*(Ba(OH)$_2$)** = (100/1000) × 0.1250 = 0.0125 (mol) ✓ ***n*(C_2H_5COOH)** = (200/1000) × 0.324 = 0.0648 (mol) ✓ **Correct calculation showing that C_2H_5COOH is in excess** **Must use** 2 × 0.0125 **OR** 0.0250 ✓ Possible calculations could show: • C_2H_5COOH is 0.0398 mol in excess • ratio $n(C_2H_5COOH)/n(Ba(OH)_2$ > 2/1 • $n(C_2H_5COOH) > n(OH^-)$	4	**ORA** Buffer does **not** form when • acid / C_2H_5COOH is **not** in excess/ $Ba(OH)_2$ is in excess • **OR** buffer does **not** contains C_2H_5COOH **AND** $C_2H_5COO^-$ / $(C_2H_5COO)_2Ba$ ✓ $n(C_2H_5COOH) = 0.0648 – 0.0250 = 0.0398$ ratio $n(C_2H_5COOH)/n(Ba(OH)_2) = 0.0648/0.0125 = 5.184/1$ $n(C_2H_5COOH) > n(OH^-) = 0.0648 > 0.0250$

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Question			Answer	Marks	Guidance
5	(d)		• **Quality of written communication, QWC** • 2 marks are available for explaining how the equilibrium system allows the buffer solution to control the pH on addition of H^+ and OH^- (see below) • ---------- • $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ ✓ • • ---------- • • H_2CO_3 reacts with added alkali /OH^- • **OR** $H_2CO_3 + OH^- \rightarrow$ • **OR** added alkali reacts with H^+ • **OR** $H^+ + OH^- \rightarrow$ ✓ Equilibrium → right **OR** Equilibrium → HCO_3^- ✓ (**QWC**) • • HCO_3^- reacts with added acid /H^+ ✓ Equilibrium → left **OR** Equilibrium → H_2CO_3 ✓ (**QWC**)	5	***FULL ANNOTATIONS MUST BE USED*** ---------- **Note: If there is no equilibrium equation then the two subsequent equilibrium marks are not available: max 2** **DO NOT ALLOW** HA $\rightleftharpoons$ $H^+ + A^-$ **DO NOT ALLOW** more than one equilibrium equation. ---------- **ALLOW** response in terms of H^+, A^- and HA **IF** more than one equilibrium shown, it **must** be clear which one is being referred to by labeling the equilibria. **ALLOW** weak acid reacts with added alkali **DO NOT ALLOW** acid reacts with added alkali **ALLOW** conjugate base reacts with added acid **DO NOT ALLOW** salt/base reacts with added acid
			Total	**22**	

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Question			Answer	Marks	Guidance
6	(a)		$(K_c =) \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$ ✓	1	Must be square brackets **IGNORE** state symbols

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Question			Answer	Marks	Guidance
6	(b)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 0.0368 $dm^6\ mol^{-2}$, award **6 marks** **IF** answer = 0.0368 with incorrect units, award **5 mark** --- **Equilibrium amounts in mol** **2 MARKS** $n(N_2)$ = 10.40 – 5.60/2 = 7.6(0) (mol) ✓ $n(H_2)$ = 22.50 – 1.5 × 5.60 = 14.1(0) (mol) ✓ **Equilibrium concentrations (moles ÷ 5)** **1 MARK** N_2 = 7.60/5 = 1.52 (mol dm^{-3}) **AND** H_2 = 14.1/5 = 2.82 (mol dm^{-3}) **AND** NH_3 = 5.60/5 = 1.12 (mol dm^{-3}) ✓ **Calculation of K_c and units** **3 MARKS** $K_c = \frac{1.12^2}{1.52 \times 2.82^3}$ ✓ K_c = 0.0368 ✓ $dm^6\ mol^{-2}$ ✓ ***3SF** required* --- ***NOTE**: If inverted K_c expression used, look back to Q6(a) Then apply ECF with ALL marks being available in 16(b).* *Expected answer = 27.2* *Expected units* = $mol^2\ dm^{-6}$ *See also Common errors* **24**	**6**	**FULL ANNOTATIONS NEEDED** **IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ALLOW ECF** from incorrect moles of SO_2, O_2 **AND** SO_2 **ALL three** concentrations required for this mark **ALLOW ECF** from incorrect concentrations or moles (if concentration stage is omitted) **ALLOW ECF** from wrong K_c expression for K_c value and units For units, **ALLOW** $mol^{-2}\ dm^6$ **DO NOT ALLOW** dm^6/mol^2 **Common errors for K_c** **1.47×10^{-3}** *missing ÷ 5 to calculate concentrations* *4 marks + units mark (i.e. just one mark dropped)* **0.0338** *Subtracting 5.60 from initial moles of N_2 and H_2* *3 marks + units mark* **6.62×10^{-3}** *Use of initial concentrations of N_2 and H_2* *(3 marks + units mark)* **2.65×10^{-4}** *Use of initial moles of N_2 and H_2 and no ÷5 for concs* *(2 marks + units mark)* **27.2** *Calculated value from inverted K_c* *4 marks + units mark for $mol^2\ dm^{-6}$*

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Question			Answer	Marks	Guidance
6	(c)	(i)	K_c is smaller **AND** (forward) reaction is **exothermic OR** ΔH is negative ✓	1	Link to ΔH/exothermic essential **ALLOW reverse** reaction is **endothermic** **DO NOT ALLOW** equilibrium shifts to the right (**CON**)
6	(c)	(ii)	K_c is the same **AND** K_c is temperature dependent/only changed by temperature **OR** K_c is not changed by pressure ✓	1	**ALLOW** K_c is **only** changed by temperature **IGNORE** same number of moles on both side
			Total	**9**	

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Question			Answer	Marks	Guidance
7	(a)	(i)	complete circuit with voltmeter **AND** salt bridge linking two half-cells ✓ Cr electrode in Cr^{3+} solution ✓ Pt electrode in solution containing Fe^{2+} **AND** Fe^{3+} ✓ **Conditions** *Units essential* (Temperature of) 298 K / 25ºC **AND** (solution concentrations of) 1 mol dm^{-3} ✓ (**may be on diagram**)	4	***FULL ANNOTATIONS MUST BE USED*** circuit shown **must** be complete, *ie* must be capable of working salt bridge **must** be labelled and must dip into both solutions Half cells can be drawn in either order Half cells must show electrodes dipping into solutions **ALLOW** small gaps in circuit **ALLOW** 1M and 1 mol/dm^3 **DO NOT ALLOW** 1 mol **IGNORE** pressure *(No gases in this cell)*
7	(a)	(ii)	$Cr(s) + 3Fe^{3+}(aq) \rightarrow Cr^{3+}(aq) + 3Fe^{2+}(aq)$ ✓ *State symbols **not** required*	1	**IGNORE** state symbols **ALLOW** equilibrium sign providing reactants and products are on correct sides of equation
7	(a)	(iii)	E = 1.51 (V) **AND** Sign of Cr electrode: – /negative ✓	1	**IGNORE** sign for E
7	(b)		**Assume Cr^{3+}|Cr OR Cr half-cell unless otherwise stated.** [Cr^{3+}] increases **OR** > 1 mol dm^{-3} ✓ Equilibrium (shown in table) shifts to right **OR** towards Cr ✓ Electrons are removed/used up/fewer electrons released **OR**	3	***FULL ANNOTATIONS MUST BE USED*** --- **ALLOW** [Cr^{3+}] more than standard concentration/1 mol dm^{-3} **IGNORE** $CrCl_3$ reacts **Take care:** Response may refer to a **reverse** half equation written by candidate. The equilibrium then shifts to left. **IGNORE** comments about $E^{\ominus}$ changing

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Question			Answer	Marks	Guidance
			E (for $Cr^{3+}|Cr$) is less negative / more positive **OR** The cell has a smaller **difference** in E ✓		**IGNORE** just 'cell potential decreases' (in the question)
7	(c)	(i)	$HCOOH(l) \rightarrow CO_2(g) + 2H^+ + 2e^-$	1	**ALLOW** multiples e.g. $2HCOOH(l) \rightarrow 2CO_2(g) + 4H^+ + 4e^-$
7	(c)	(ii)	HCOOH is a **liquid OR** is **less** volatile **AND** HCOOH is easier to store/transport/stored more safely **OR** H_2 is more explosive/more flammable ✓	1	Assume that '**it**' refers to HCOOH **ALLOW ORA** throughout **IGNORE** comments about efficiency **IGNORE** comments about biomass and renewable
7	(d)	(i)	amount MnO_4^- used = $0.01500 \times \frac{25.40}{1000}$ = **3.81×10^{-4}** (mol) ✓ amount SO_3^{2-} = **$3.81 \times 10^{-4} \times 2.5$** = **$9.525 \times 10^{-4}$** (mol) ✓ amount SO_3^{2-} in original 250 cm^3 = **10 ×** 9.525×10^{-4} = **9.525×10^{-3}** mol ✓ Mass of Na_2SO_3 in sample = **126.1** × 9.525×10^{-3} g = **1.20 g** ✓ $n(H_2O) = \frac{2.40 - 1.20}{18.0}$ = **6.67×10^{-2}** (mol) ✓	6	***FULL ANNOTATIONS MUST BE USED*** **IF** a step is omitted but subsequent step subsumes previous, then award mark for any missed step **Working: at least 3 SF throughout until final % mark** **BUT** ignore trailing zeroes, ie for 0.01500 allow 0.015/0.0150 --- **ALLOW ECF at all stages** **ALLOW** M(hydrated sodium sulfite) = $\frac{2.40}{9.525 \times 10^{-3}}$ = 252 ✓ Molar mass of H_2O = 252 – 126.1 = 125.9 ✓

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Question			Answer	Marks	Guidance
			$n(Na_2SO_3) : n(H_2O) = 9.525 \times 10^{-3} : 6.67 \times 10^{-2} = 1 : 7$ Formula = **$Na_2SO_3 \bullet 7H_2O$** ✓ *Formula is required. 1:7 ratio is insufficient*		*Number of* H_2O of crystallisation = $\frac{125.9}{18.0} = 7$ Formula = **$Na_2SO_3 \bullet 7H_2O$** ✓
	(d)	**(ii)**	***MARK INDEPENDENTLY*** ***Except for multiples, equations are only correct answers*** *Overall:* $2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$ ✓ *Half equations*: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ ✓ $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$ ✓	**3**	**ALLOW multiples and equilibrium signs throughout** **IGNORE** state symbols throughout e.g. $MnO_4^- + 3H^+ + 2½ SO_3^{2-} \rightarrow Mn^{2+} + 2½ SO_4^{2-} + 1½ H_2O$
			Total	**20**	

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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

F325/01

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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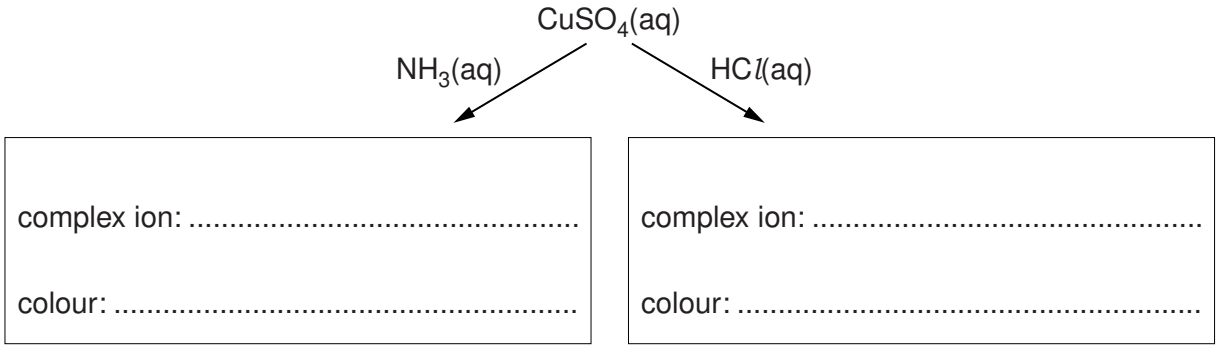
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Answer **all** the questions.

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.

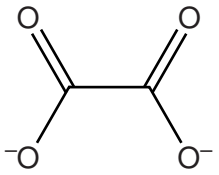


Fig. 1.1

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

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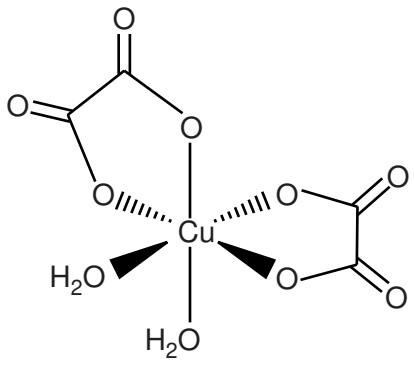
.....

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

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

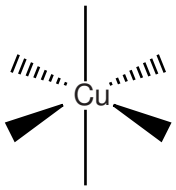
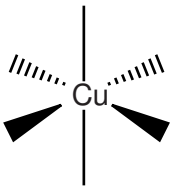
The shape of one of the stereoisomers is shown below. The charge has been omitted.



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.

.....

.....

.....

..... **[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*.

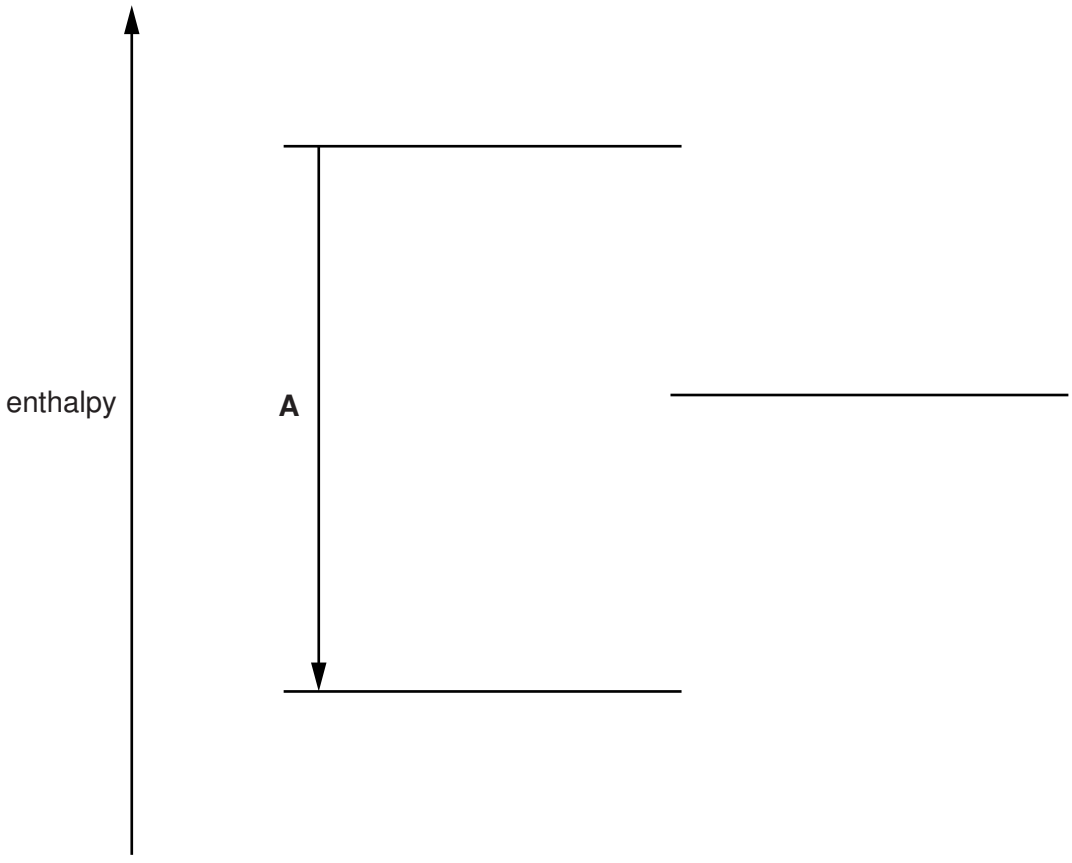
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..... **[2]**

(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.

.....

.....

.....

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

(ii) Explain, using a calculation, why K_2SO_4 dissolves in water at 25 °C, despite the enthalpy change of solution being endothermic.

.....

.....

.....

..... **[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.

.....

.....

..... **[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.

.....

.....

..... **[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.

.....

.....

.....

..... **[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.

.....

.....

.....

..... **[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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GCE

Chemistry A

Unit **F325:** Equilibria, Energetics and Elements

Advanced GCE

Mark Scheme for June 2016

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1. Annotations available in RM Assessor.

Annotation	Meaning
BOD	Benefit of doubt given
CON	Contradiction
	Incorrect response
ECF	Error carried forward
I	Ignore
NAQ	Not answered question
NBOD	Benefit of doubt not given
POT	Power of 10 error
^	Omission mark
RE	Rounding error
SF	Error in number of significant figures
	Correct response

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2. Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

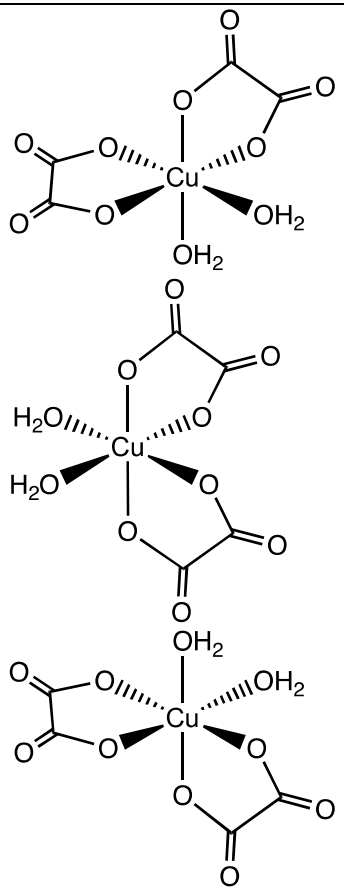
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

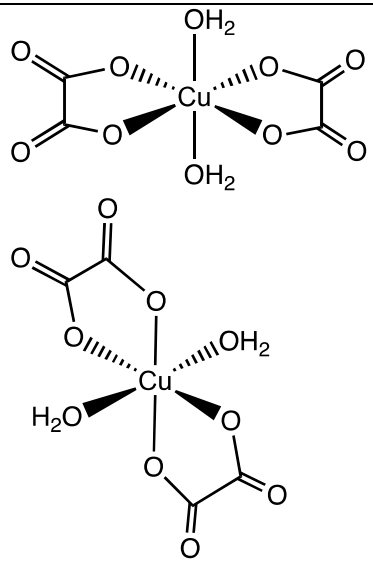
3. The following questions should be marked using **ALL** appropriate annotations to show where marks have been awarded in the body of the text:
2(a)
4(b)(ii)
4(c)
4(d)
5(c)(i)
5(c)(ii)
5(d)(iv)
6(c)
8(e)

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Question			Answer	Marks	Guidance
1	(a)		**IGNORE** any charges shown within complexes (treat as rough working) **Formulae** **2 marks** $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ✓ $[CuCl_4]^{2-}$ ✓ **Colours** **1 mark** blue **AND** yellow ✓ *Mark independently of formulae*	**3**	For charges, **ALLOW** +2 and –2 Square brackets **required**, i.e. **DO NOT ALLOW** $Cu(NH_3)_4(H_2O)_2^{2+}$ **ALLOW** Ligands in any order **ALLOW** $CuCl_4^{2-}$ i.e. no brackets **OR** $Cu(Cl)_4^{2-}$ For $CuCl_4^{2-}$, **ALLOW** green–yellow **OR** yellow–green **DO NOT ALLOW** green For $[Cu(NH_3)_4(H_2O)_2]^{2+}$ **DO NOT ALLOW** pale blue, light blue **DO NOT ALLOW** precipitate with blue **OR** yellow
1	(b)	(i)	**Donates two** electron **pairs** to a metal ion/metal/Cu^{2+} **AND** forms **two** coordinate **bonds** to a metal ion/metal/Cu^{2+} ✓	**1**	**ALLOW** lone pairs for electron pairs **ALLOW** molecule/atom/ion/substance for 'ligand' **ALLOW** dative (covalent) bonds for coordinate bonds **ALLOW** transition element for metal **Two is needed once only** e.g. **Donates two** electron **pairs** to form coordinate **bonds** to a metal ion/metal/Cu^{2+} **Donates** electron **pairs** to form **two** coordinate **bonds** to a metal ion/metal/Cu^{2+} **DO NOT ALLOW** donates **two** electron pairs to form **one/a** coordinate bond

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<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>Guidance</th></tr>
<tr><td>1</td><td>(b)</td><td>(ii)</td><td> 


</td><td>3</td><td>FULL ANNOTATIONS MUST BE USED
----
2 marks: one for each correct isomer ✓✓

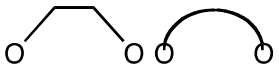
TAKE CARE: structures may be in different orientations and in different order

IF BOTH isomers are ‘correct’, but O connectivity wrong, AWARD 1 mark for both structures
Check H_2O ligands carefully for connectivity

ALLOW H_2O reversed shown as $–O_2H$

IGNORE charges (anywhere)

NOTE: For each structure, ALL O atoms must be shown AND For $(COO^–)_2$, ALLOW skeletal, structural or displayed formula

DO NOT ALLOW structures such as those shown below
  </td></tr>
<tr><td></td><td></td><td></td><td><table><tr><td>cis</td><td>✓</td></tr><tr><td>trans</td><td></td></tr><tr><td>optical</td><td>✓</td></tr></table></td><td><table><tr><td>cis</td><td></td></tr><tr><td>trans</td><td>✓</td></tr><tr><td>optical</td><td></td></tr></table></td><td></td><td>1 mark: for whole of 2nd row for whole of ‘Type’ row
i.e. (cis AND optical) AND trans only</td></tr>
</table>

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Question			Answer	Marks	Guidance
1	(b)	(iii)	$CuC_4H_4O_{10}^{2-}$ Formula ✓ 2– charge ✓ **MARK formula and charge INDEPENDENTLY**	2	**Empirical** formula essential, e.g. **DO NOT ALLOW** $Cu(COO)_2(H_2O)_2$ for formula mark **ALLOW** any order of elements in formula **ALLOW** –2 for charge
			Total	9	

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Question			Answer	Marks	Guidance
2	(a)		***initial rates data (3 marks)*** **NOTE**: Each comparison **MUST** relate to the **actual** change in concentration/rate in the experiments **EXPTS** **H_2O_2**: $[H_2O_2] \times 2$ rate $\times 2$ (1 & 2) **AND** 1st order ✓ **H^+**: $[H^+] \times 2$ rate does not change (2 & 3) **AND** Zero order ✓ **I^-**: $[I^-] \times 2$ **AND** $[H_2O_2] \times 2$ rate $\times 4$ (2 & 4) **OR** $[I^-] \times 2$ **AND** $[H_2O_2] \times 4$ rate $\times 8$ (1 & 4) **OR** $[I^-] \times 2$ **AND** $[H_2O_2] \times 2$ rate $\times 4$ (3 & 4) **AND** 1st order ✓	3	***FULL ANNOTATIONS MUST BE USED*** --- **THROUGHOUT**, • Square brackets **NOT REQUIRED** around H_2O_2, H^+ and I^- • **ALLOW** 'doubles' for × 2; quadruples for × 4 **ALLOW** direct comparison of concentrations and rate, e.g. $[H_2O_2]$ changes by $\frac{0.0020}{0.0010} = 2$, rate changes by $\frac{1.14 \times 10^{-5}}{5.70 \times 10^{-6}} = 2$ **AND 1**st order (Expts 1 & 2) **DO NOT ALLOW** I_2 for I^- **IGNORE** $[H^+]$ for Expts 3 & 4
			Calculation of rate constant (3 marks), **EITHER** $k = \frac{5.70 \times 10^{-6}}{0.0010 \times 0.20}$ **OR** 2.85×10^{-2} **OR** 0.0285 **OR** 0.029 ✓ $k = 2.9 \times 10^{-2}$ ✓ (2 SF in standard form) *Subsumes previous mark if no working shown* $dm^3\ mol^{-1}\ s^{-1}$ ✓	3	**IGNORE working** **DO NOT ALLOW** 0.03 **ALLOW ECF** from error in powers of 10 **ONLY** e.g. 2.9×10^{-3} by use of 0.010 instead of 0.0010 **DO NOT ALLOW 2.90** $\times 10^{-2}$ **(3 SF)** **OR 29** $\times 10^{-3}$ (Not standard form) **ALLOW** mol^{-1}, dm^3 and s^{-1} in any order, e.g. $mol^{-1}\ dm^3\ s^{-1}$

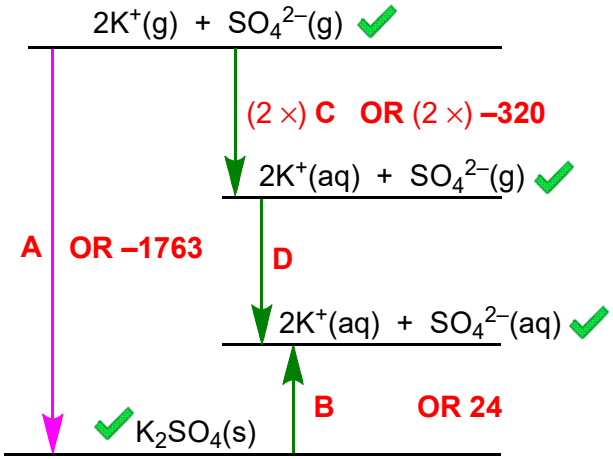
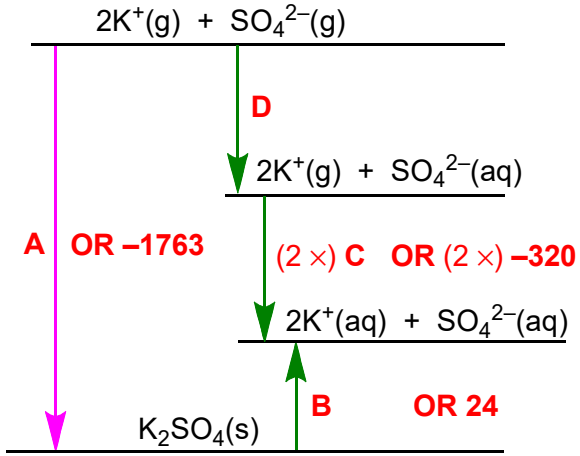
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Question			Answer	Marks	Guidance
2	(b)		H^+ ions are consumed/used up **OR** H^+ ions are in the (overall) equation ✓	1	**ALLOW** H^+ is **not** regenerated/reformed **ALLOW** H^+ is a reactant but not a product **ALLOW** 'it' for H^+ **IGNORE** H^+ is not in the rate equation/does not affect rate **IGNORE** does not take part in rate-determining step
2	(c)	(i)	The slowest/slow step ✓	1	**ALLOW** step that takes the longest time
2	(c)	(ii)	**NO ECF from incorrect rate equation** **Principles** • H_2O_2 and I^- **must be** the reactants in **1st step** • 2nd mark **only to be awarded** if 1st mark scored • Step 4 is independent **Reactants of Step 1 as H_2O_2 + I^-** **1 mark** **Step 1**: $H_2O_2 + I^- \rightarrow$ ✓ **Products of Step 1 AND all of Step 2** **1 mark** **Step 1** $\rightarrow$ $IO^- + H_2O$ **AND Step 2**: $H^+ + IO^- \rightarrow$ HIO ✓ **Step 4 (Independent mark)** **1 mark** $H^+ + OH^- \rightarrow H_2O$ ✓	3	**IGNORE state symbols** Elements can be in any order in formulae **Alternatives for 2nd mark** **Step 1:** $\rightarrow HIO + OH^-$ **AND Step 2**: $H^+ + OH^- \rightarrow H_2O$ ✓ **Step 1:** $\rightarrow H_2O_2I^-$ **AND Step 2**: $H^+ + H_2O_2I^- \rightarrow HIO + H_2O$ ✓ Other possibilities, contact TL **ALLOW** $2H^+ + 2OH^- \rightarrow 2H_2O$ $H_3O^+ + OH^- \rightarrow 2H_2O$
			Total	11	

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Question			Answer	Marks	Guidance
3	(a)		(enthalpy change for) 1 mole of gaseous ions **OR** 1 mole of hydrated ions/aqueous ions ✓ gaseous ions forming aqueous/hydrated ions ✓	2	**one mole** can be stated just once **EITHER** with gaseous ions **OR** with aqueous ions, e.g. • 1 mole of gaseous ions **forms** hydrated ions/aqueous ions • Gaseous ions **form 1 mole of** hydrated ions/aqueous ions **ALLOW** 1 mol for 1 mole **IGNORE** 'energy released' **OR** 'energy required' For 2nd mark **IGNORE** gaseous ions are hydrated **IGNORE** gaseous ions dissolve in water ***Particles formed not stated*** **ALLOW** 1 mark for: 1 mole of gaseous **IONS** forms aqueous/hydrated **atoms/ particles/ molecules**

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Question			Answer	Marks	Guidance
3	(b)	(i)	**4 marks** for species **AND** state symbols on all 4 energy levels (including added energy level)  **1 mark** for **B**, **C AND D** labels **OR** enthalpy values **AND** arrow directions correct ✓ **ALLOW** $K_2SO_4(aq)$ for $2K^+(aq) + SO_4^{2-}(aq)$ **ALLOW** arrows not touching lines. **Direction** is important: • **FROM** $2K^+(g) + SO_4^{2-}(g)$ line • **FROM** $K_2SO_4(s)$ line **See APPENDIX** '2 ×' is **NOT** required – *part of calculation mark*	5	**IF** extra energy level is **above** top line **OR below** bottom line, **DO NOT ALLOW** mark for species on this line. **See APPENDIX** **ALLOW C** and **D** with associated labels, the other way round:  State symbols are **essential** **IF** no extra energy level is shown with **C** and **D** combined forming $2K^+(aq) + SO_4^{2-}(aq)$, • No mark for the extra energy level with species • No mark for labels as **C** and **D** are combined Therefore 3 max for species on energy levels provided
3	(b)	(ii)	ΔH(hydration) SO_4^{2-} = **–1099** (kJ mol^{-1}) ✓	1	**ONLY** correct answer

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Question			Answer	Marks	Guidance
3	(c)	(i)	**Aqueous** particles are more disordered than **solid** (particles) **OR** **Solid** particles are more ordered than **aqueous** (particles) ✓	1	For particles, **ALLOW** ions **DO NOT ALLOW** molecules/atoms **ALLOW** 'When the state changes from solid to aqueous, disorder increases' For more disordered, **ALLOW** less ordered/ more freedom/ more ways of arranging energy/ more random For aqueous particles, **ALLOW particles in solution** **IGNORE** dissolved
3	(c)	(ii)	***Calculation (2 marks)*** ΔG = 24 – (298 × 0.225) **OR** 24 – 67.05 *(in kJ)* **OR** 24000 – (298 × 225) **OR** 24000 – 67050 *(in J)* ✓ **Calculation of ΔG (IGNORE UNITS)** ΔG = –43 (kJ mol^{-1}) **OR** –43000 (J mol^{-1}) ✓ *Subsumes 1st calculation mark* **Reason for solubility** Calculated value of ΔG that is **negative** **AND** Statement that: ΔG is negative **OR** ΔG < 0 **OR** –43 < 0 **OR** $\Delta H - T\Delta S$ < 0 **OR** $T\Delta S > \Delta H$ ✓	3	**Contact TL if solely entropy approach rather than ΔG** **ALLOW** –43.1 OR –43.05 (*calculator value*) **ALLOW 1 calculation mark (IGNORE units) for** –67.(026) **OR** –67026 ***ECF** from 225 instead of 0.225* 18.(375) **OR** +18.375 ***ECF** from 25* instead of 298 **ALLOW other ECF** from **ONE** error in 1st step of calc, e.g. incorrect value for ΔH such as –1099 from 3bii → –1166.05 **TAKE CARE** that same units used for ΔH and ΔS **NO reason mark from a +ve value of ΔG**
			Total	12	

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Question			Answer	Marks	Guidance
4	(a)		Iodine is non-polar **OR** Iodine does not form H bonds **with water** ✓	1	**IGNORE** iodine is slightly polar **IGNORE** 'cannot bond to water' (too vague) **IGNORE** 'Lack of a lone pair' **IGNORE** 'inability to induce a dipole
4	(b)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF K_c = 104 dm^3 mol^{-1} award 4 marks:** ***3 for calculation of 104 from data, 1 for units*** --- **Equilibrium concentrations (mol × 5) (1 mark)** I_2 = 4.00×10^{-5} × **5** = 2.00×10^{-4} (mol dm^{-3}) **AND** I^- = 9.404×10^{-2} × **5** = 0.4702 (mol dm^{-3}) ✓ **AND** I_3^- = 1.96×10^{-3} × **5** = 9.80×10^{-3} (mol dm^{-3}) **Calculation of K_c and units (3 marks)** $K_c = \frac{[I_3^-(aq)]}{[I_2(aq)] \times [I^-(aq)]}$ **OR** $\frac{9.80 \times 10^{-3}}{2.00 \times 10^{-4} \times 0.4702}$ ✓ = 104 ✓ **Must be 3 SF** dm^3 mol^{-1} **OR** mol^{-1} dm^3 ✓	4	***FULL ANNOTATIONS MUST BE USED*** --- Throughout, at least **3SF** but **ALLOW** absence of trailing zeroes e.g. for 9.80×10^{-3} **ALLOW** 9.8×10^{-3} **FOR I^-** 0.4702, **ALLOW** 0.47(0) (mol dm^{-3}) still →104 for calc State symbols **not** required in K_c expression **ALLOW ECF** from incorrect concentrations Any **ECF** value **MUST** be to **3 SF** for K_c value --- **COMMON ERRORS** **104.2 → 104.2109741 (calc)** *> 3 SF* **2 marks + units** **521** *no × 5 for concs* **2 marks + units** **521.1 → 521.0548703** as above and > 3SF **1 mark + units** **2610** *÷ 5 instead of × 5 for concs* **2 marks + units** **9.60×10^{-3}** K_c upside down, correct concs **2 marks + units** **1.92×10^{-3}** K_c upside down, no × *5 for concs* **1 mark + units** **NOTE**: With K_c upside down, units become mol dm^{-3} by **ECF**

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Question			Answer	Marks	Guidance
4	(c)		Ag^+/silver nitrate reacts with I^- to form AgI/silver iodide **OR** $Ag^+ + I^- \rightarrow AgI$ ✓ yellow precipitate/solid forms ✓ **Equilibrium 2** shifts to the left ✓ **Equilibrium 1** shifts to left **AND** I_2 comes out of solution/less I_2 dissolves/ I_2 precipitates/black solid /grey solid /violet solid ✓	4	***FULL ANNOTATIONS MUST BE USED*** --- **DO NOT ALLOW** cream **OR** cream–yellow **ALLOW** just 'yellow' if supported by AgI(s) somewhere
4	(d)		**in all equations ALLOW equilibrium signs** **IGNORE** state symbols --- **Reaction 1: 1 mark** $2I_2 + 5O_2 \rightarrow 2I_2O_5$ ✓ --- **Reaction 2: 2 marks** **1st mark: ALL CORRECT species** e.g.: $I_2 + OH^- \rightarrow I^- + IO_3^- + H_2O$ **2nd mark** for **CORRECT balanced equation** $3I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$ ✓✓	3	***FULL ANNOTATIONS MUST BE USED*** --- **ALLOW** correct multiples throughout, e.g. $I_2 + 2½O_2 \rightarrow I_2O_5$ --- **For 1st mark, IGNORE** e^- present **ALLOW** species/equation with NaOH or KOH, e.g. $3I_2 + 6NaOH \rightarrow 5I^- + IO_3^- + 3H_2O + 6Na^+$ $3I_2 + 6NaOH \rightarrow 5NaI + NaIO_3 + 3H_2O$ **ALLOW** Species: $I_2 + OH^- \rightarrow I^- + IO_2^+ + H_2O$ ✓ **OR** Equation: $3I_2 + 4OH^- \rightarrow 5I^- + IO_2^+ + 2H_2O$ ✓✓ Species: $I_2 + OH^- \rightarrow I^- + IO^{3+} + H_2O$ ✓ **OR** Equation: $3I_2 + 2OH^- \rightarrow 5I^- + IO^{3+} + H_2O$ ✓✓
			Total	12	

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Question			Answer	Marks	Guidance
5	(a)		$(K_a =) \frac{[H^+]\,[NO_2^-]}{[HNO_2]}$ ✓ **IGNORE** state symbols	1	**IGNORE** $\frac{[H^+]^2}{[HNO_2]}$ **OR** $\frac{[H^+]\,[A^-]}{[A]}$ **ALLOW** H_3O^+ for H^+ Square brackets **required**
5	(b)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 2.12 award **2 marks** --- $[H^+] = \sqrt{K_a \times [HNO_2]} = 7.502 \times 10^{-3}$ (mol dm^{-3}) ✓ pH = –log 7.502×10^{-3} = 2.12 ✓ **pH to 2 DP**	2	--- **ALLOW** intermediate value from 3 SF (7.50 up to calculator value of $7.501999733 \times 10^{-3}$ **ALLOW** 1 mark for 2.1 **OR** answer > 2 DP (i.e. not 2 DP) **ONLY ALLOW** pH mark by **ECF** if K_a **AND** 0.120 used and **AND** pH <7 --- **COMMON ERRORS (MUST be to 2 DP)** **pH = 4.25 No square root:1 mark** $[H^+] = (4.69 \times 10^{-4} \times 0.120) = 5.628 \times 10^{-5}$ (mol dm^{-3}) pH = –log 5.628×10^{-5} = 4.25 ✓ **pH = 0.92 no K_a used: zero marks** pH = –log 0.120 = 0.92 **pH = 13.08 K_w/pOH used: zero marks** pH = –log $\frac{1.00 \times 10^{-4}}{0.120}$ **OR** 14 – log 0.120 = 13.08

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Question			Answer	Marks	Guidance
5	(c)	(i)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **3.43**, **AWARD 4 marks** --- *Expression: K_a × acid/base ratio* Use of $K_a \times \frac{[HNO_2]}{[NO_2^-]}$ **OR** $4.69 \times 10^{-4} \times \frac{[HNO_2]}{[NO_2^-]}$ ✓ *Using correct concs/mol in expression* $[H^+] = 4.69 \times 10^{-4} \times \frac{0.0400}{0.0500}$ ✓ *Subsumes previous mark* *Calculation of* $[H^+]$ $[H^+] = 3.752 \times 10^{-4}$ (mol dm^{-3}) ✓ *pH to 2 DP (From 3.42573717)* pH = –log 3.752×10^{-4} = 3.43 ✓ **NO marks** are available using K_a square root approach (weak acid pH) $K_w / 10^{-14}$ approach (strong base pH) --- **ALLOW** alternative approach based on Henderson–Hasselbalch equation (**ALLOW** $-\log K_a$ for pK_a) $pH = pK_a + \log \frac{[NO_2^-]}{[HNO_2]}$ **OR** $pK_a - \log \frac{[HNO_2]}{[NO_2^-]}$ ✓ $pH = pK_a + \log \frac{0.0500}{0.0400}$ **OR** $pK_a - \log \frac{0.0400}{0.0500}$ ✓ $pH = pK_a + 0.097$ ✓ pH = 3.329 + 0.097 = 3.43 ✓	4	***FULL ANNOTATIONS MUST BE USED*** --- **ALLOW** just $K_a \times \frac{\text{acid}}{\text{salt}}$ *expression* **Mark** by **ECF** from $4.69 \times 10^{-4} \times \frac{[NO_2^-]}{[HNO_2]}$ *inverted expression* **Mark** by **ECF** from incorrect $[HNO_2]$ and $[NO_2^-]$ **ONLY** award **marks** for a pH calculation via K_a **AND** using concentrations/mol derived from the question **DO NOT ALLOW** final pH mark by **ECF** if pH > 7 --- **COMMON ERRORS BUT CHECK WORKING** **pH = 2.82 3 marks** initial concs: 0.200 and 0.0625 **pH = 3.23 3 marks** 0.0400 and 0.0500 acid/base ratio inverted **pH = 3.83 2 marks** initial concs: 0.200 and 0.0625 and ratio inverted **pH = 2.73 3 marks** Incorrect $[NO_2^-]$ = 0.01 and correct $[HNO_2]$ = 0.04 **pH = 4.03 3 marks** correct $[NO_2^-]$ = 0.05 and incorrect $[HNO_2]$ = 0.01

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Question			Answer	Marks	Guidance
5	(c)	(ii)	**Equilibrium: 1 mark** $HNO_2 \rightleftharpoons H^+ + NO_2^-$ ✓ (ignore state symbols) **Control of pH: 2 marks (QWC)** ***Added HCl*** NO_2^- reacts with added acid/HCl/H^+ **OR** $NO_2^- + H^+ \rightarrow$ **OR** more HNO_2 forms ✓ ***Added NaOH*** HNO_2 reacts with added alkali/NaOH/OH^- **OR** $HNO_2 + OH^- \rightarrow$ **OR** more NO_2^- forms **OR** H^+ reacts with added alkali/NaOH **OR** $H^+ + OH^- \rightarrow$ ✓ **Equilibrium shift:** **1 mark for shifts in $HNO_2 \rightleftharpoons H^+ + NO_2^-$ (See 1st mark)** Equilibrium for added **acid → left** **AND** Equilibrium for added **alkali → right** ✓ (**QWC**)	4	***FULL ANNOTATIONS MUST BE USED*** --- **IGNORE** $HA \rightleftharpoons H^+ + A^-$ Equilibrium sign **essential** **BUT ALLOW** small slips in its appearance if it is obviously an attempt to show an equilibrium sign rather than an arrow **QWC: Quality of written communication** **DO NOT ALLOW** HA and A^- for HNO_2 and NO_2^- **IGNORE just** acid reacts with added alkali **IGNORE just** conjugate base/salt/base reacts with added acid **DO NOT ALLOW** salt/base reacts with added acid **AWARD** 'shift mark' **ONLY** if correct equilibrium equation has been given **IGNORE** any other equilibria in response

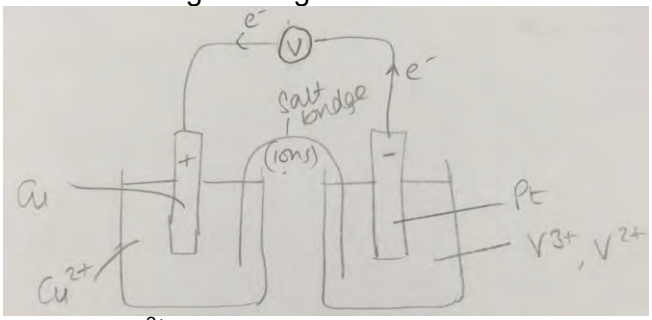
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Question			Answer	Marks	Guidance
5	(d)	(i)	Endothermic **AND** K_w increases with temperature **OR** Endothermic **AND** dissociation increases **with temperature** **OR** Endothermic **AND** (dissociation) involves breaking bonds ✓	1	Endothermic **and** reason required for the mark **ALLOW** Endothermic **AND** increasing temperature shifts equilibrium/reaction to the right/favours forward reaction **DO NOT ALLOW** breaking hydrogen bonds **OR** intermolecular bonds/forces
5	(d)	(ii)	***OH^- concentration*** $[OH^-] = \frac{9.311 \times 10^{-14}}{1.00 \times 10^{-7}} = 9.311 \times 10^{-7}$ (mol dm^{-3}) ✓ ***Explanation (dependent on 1st mark)*** $9.311 \times 10^{-7} > 1.(00) \times 10^{-7}$ **OR** $[OH^-] > [H^+]$ **OR** OH^- in excess **AND** Alkaline ✓	2	***H^+ OR OH^- concentration (neutral pH)*** $[H^+] = [OH^-] = \sqrt{(9.311 \times 10^{-14})} = 3.05 \times 10^{-7}$ (mol dm^{-3}) ✓ ***Explanation (dependent on 1st mark)*** pH = –log (3.05×10^{-7}) = 6.5 → 6.515501837 (calc) **AND** Alkaline ✓
5	(d)	(iii)	pK_w = 13.03 ✓	1	**ONLY** correct answer

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Question			Answer	Marks	Guidance
5	(d)	(iv)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **10.76**, award **3 marks** --- ***Dilution 1 mark*** $[OH^-(aq)] = [NaOH(aq)] = \frac{0.0270}{5} = 0.00540$ (mol dm^{-3}) ✓ ***[H^+] 1 mark*** $[H^+(aq)] = \frac{9.311 \times 10^{-14}}{0.00540} = 1.72 \times 10^{-11}$ (mol dm^{-3}) ✓ Calculator: $1.724259259 \times 10^{-11}$ ***pH 1 mark*** pH = –log 1.72×10^{-11} = **10.76** ✓ --- **ALLOW** pOH method for 2nd and 3rd mark: pOH = –log 0.00540 = 2.27 ✓ (calculator 2.26760624) pH = 13.03 – 2.27 = 10.76 ✓	**3**	***FULL ANNOTATIONS MUST BE USED*** --- **ALLOW** dilution **AFTER** calculation of $[H^+(aq)]$ i.e. original $[H^+] = \frac{9.311 \times 10^{-14}}{0.0270} = 3.45 \times 10^{-12}$ (mol dm^{-3}) ✓ After dilution, $[H^+] = 3.45 \times 10^{-12} \times 5 = 1.72 \times 10^{-11}$ (mol dm^{-3})✓ pH = –log 1.72×10^{-11} = **10.76** ✓ **ALLOW ECF** from incorrect $[H^+(aq)]$ provided that pH >7 --- **COMMON ERRORS (MUST be to 2 DP)** **pH = 11.73** At 25ºC (1.00×10^{-14}): **2 marks** pH = –log 1.85×10^{-12} = **11.73** **pH = 11.46** No dilution at 60ºC (9.311×10^{-14}) **2 marks** pH = –log(3.45×10^{-12}) = **11.46** **pH = 12.43** No dilution **AND** 25ºC (1.00×10^{-14}) **1 mark** pH = –log(3.70×10^{-13}) = **12.43** **pH = 12.16** ×5 instead of ÷ 5 at 60ºC (9.311×10^{-14}) **2 marks** pH = –log(6.879×10^{-13}) = **12.16** **pH = 13.13** ×5 instead of ÷ 5 at 25ºC (1.00×10^{-14}) **1 mark** pH = –log(7.407×10^{-14}) = **13.13** **NOTE:** Attempts at dilution → 0.0270 with error in powers of 10 → 12.46 from 0.00270, etc may give 2 marks by **ECF**
			Total	**18**	

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Question			Answer	Marks	Guidance
6	(a)		**Definition** The e.m.f. (of a half-cell) compared with/connected to a (standard**)** hydrogen half-cell/(standard**)** hydrogen electrode ✓ **Standard conditions** *Units essential* Temperature of 298 K / 25ºC **AND** (solution) concentrations of 1 mol dm^{-3} **AND** pressure of 100 kPa **OR** 10^5 Pa **OR** 1 bar ✓	**2**	For e.m.f., **ALLOW** voltage **OR** potential difference/p.d. **OR** electrode/reduction/redox potential **ALLOW** e.m.f. of a cell ….. **ALLOW** /(standard) hydrogen cell **IGNORE** S.H.E. (as abbreviation for standard hydrogen electrode) **DO NOT ALLOW** hydrogen fuel cell **ALLOW** 1M **OR** 1 mol/dm^3 **DO NOT ALLOW** 1 mol **OR** 1 mole **ALLOW** 1 atmosphere/1 atm **OR** 101 kPa **OR** 101325 Pa
6	(b)	(i)	**Complete** circuit with voltmeter **AND** labelled salt bridge linking two half-cells ✓  Cu electrode in Cu^{2+} ✓ Pt electrode in V^{2+} **AND** V^{3+} ✓ Cu shown as + **AND** Pt shown as – ✓ electrons in wire **AND** ions in salt bridge ✓ *On diagram or stated*	**5**	Half cells can be drawn in either order Half cells must show electrodes dipping into solutions **ALLOW** small gaps in circuit **DO NOT ALLOW** half-cell with H_2 added **IGNORE** any stated concentrations **IGNORE** ‘anode’ and ‘cathode’ In salt bridge, **ALLOW** any stated ion that may be present, e.g. K^+, NH_4^+, NO_3^-, Cu^{2+}, V^{2+}, V^{3+} **IGNORE** direction of travel of ions and electrons. **ALLOW** Cu half cell as + **AND** V half cell as –

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Question			Answer	Marks	Guidance
6	(b)	(ii)	0.60 **OR** 0.6 (V) ✓	1	**IGNORE** any sign
6	(c)		**Definitions:** ***1 mark*** Oxidising agent removes/accepts/gains electrons **OR** increases oxidation number (of another species) **AND** Reducing agent adds/donates/loses electrons **OR** decreases oxidation number (of another species) ✓ **Oxidising agent:** ***2 marks*** Cr^{3+} oxidises Al **OR** Cr^{3+} acts as oxidising agent **AND** $3Cr^{3+} + Al \rightarrow 3Cr^{2+} + Al^{3+}$ ✓ ***Explanation (dependent on Cr^{3+} oxidising Al above)*** *E* of redox system 2 (Cr^{3+}/Cr^{2+}) is **more** positive /**less** negative (than *E* of system 1 (Al^{3+}/Al)) **ORA**, i.e. in terms of 1 being more negative (than 2) ✓ **Reducing agent:** ***3 marks*** Cr^{3+} reduces $FeO_4^{2-}(/H^+)$ ✓ $2Cr^{3+} + 2FeO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + 2Fe^{3+} + H_2O$ ✓ ***Explanation (dependent on Cr^{3+} reducing FeO_4^{2-} above)*** *E* of redox system 5 ($Cr_2O_7^{2-}/Cr^{3+}$) is **less** positive/ **more** negative (than *E* of system 6 (FeO_4^{2-}/Fe^{3+})) **ORA**, i.e. in terms of 6 being more positive (than 5) ✓	6	***FULL ANNOTATIONS MUST BE USED*** --- **ALLOW** oxidising agent decreases its oxidation number **AND** reducing agent increases its oxidation number **IGNORE** oxidising agent oxidises/is reduced **OR** reducing agent reduces/is oxidised **In equations,** • **IGNORE** state symbols (even if incorrect) • **ALLOW** ⇌ in equation **IF** more than one equation shown for **Cr^{3+} as oxidising agent**, **CON** and **zero marks** for 2 oxidising agent marks **IGNORE** equations with Cr^{2+} as reactant Explanations **MUST** be in terms of positive/negative: **IGNORE** 'higher' *E* **OR** 'greater' **ALLOW** E_{cell} = +1.25 V (+ sign required) **IF** more than one equation shown for **Cr^{3+} as a reducing agent**, **CON** and **zero marks** for 3 reducing agent marks **IGNORE** equations with Cr^{2+} as reactant Explanations **MUST** be in terms of positive/negative: **IGNORE** 'higher' *E* **OR** 'greater' **ALLOW** E_{cell} = +0.87 V (+ sign required)
			Total	14	

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Question			Answer	Marks	Guidance
7	(a)	(i)	**IGNORE** any charges shown within complexes (treat as rough working) **Complex ion C**: $[Ni(H_2O)_6]^{2+}$ ✓ **Solid D**: $Ni(OH)_2$ ✓ **Complex ion E**: $[Ni(CN)_4]^{2-}$ ✓	3	**ALLOW** +2 and –2 for charges Square brackets required **ALLOW** $Ni(H_2O)_4(OH)_2$ $(H_2O)_4$ and $(OH)_2$ in any order **IGNORE** any square brackets Square brackets required **TAKE CARE** for round brackets within complex ion, i.e. (H_2O), (OH) and (CN)

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Question			Answer	Marks	Guidance
7	(a)	(ii)	**Mark independently of 7(a)(i)** **ALLOW** +2 and –2 for charges **IGNORE** any charges shown within complexes (treat as rough working) $Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$ ✓ Type of reaction: precipitation ✓ **INDEPENDENT of equation** $[Ni(H_2O)_6]^{2+} + 4CN^- \rightarrow [Ni(CN)_4]^{2-} + 6H_2O(l)$ ✓ Type of reaction: ligand substitution ✓ **INDEPENDENT of equation**	4	**For equations: IGNORE** state symbol (even if wrong) Square brackets **not** required for $Ni(OH)_2$ **ALLOW** $[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow [Ni(H_2O)_4(OH)_2] + 2H_2O$ **ALLOW** $[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + 6H_2O$ **ALLOW** $NiSO_4(aq) + 2OH^-(aq) \rightarrow Ni(OH)_2(s) + SO_4^{2-}(aq)$ **ALLOW** $NiSO_4(aq) + 2KOH(aq) \rightarrow Ni(OH)_2(s) + K_2SO_4(aq)$ **ALLOW** acid/base **OR** neutralisation **OR** deprotonation **ONLY IF** $[Ni(H_2O)_6]^{2+}$ **AND** $[Ni(H_2O)_4(OH)_2]$ used **ALLOW** precipitate **ALLOW** $[Ni(H_2O)_6]^{2+} + 4KCN \rightarrow [Ni(CN)_4]^{2-} + 6H_2O + 4K^+$ **LOOK** at formulae for **E** from **7(a)(i)** (copied at bottom) **ALLOW ECF** in **7aii** Equation for no round brackets around CN, i.e. $[NiCN_4]^{2-}$ in **7a(i)** This is the only **ECF** allowed from **7ai** structures. **ALLOW** ligand exchange
7	(b)	(i)	linear ✓	1	**IGNORE** planar

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Question			Answer	Marks	Guidance
7	(b)	(ii)	Au/Gold has been **oxidised** from 0 to +1 ✓ O/Oxygen/O_2 has been **reduced** from 0 to –2 ✓	2	**IF** Ag referred to, rather than Au, treat as a slip and apply **BOD** **ALLOW** 0 to 1 (i.e. no + sign for +1) **ALLOW** 1 mark for **ALL** oxidation numbers correct with no oxidised or reduced **OR** oxidation and reduction wrong way round, e.g. Au goes from 0 to +1 and O goes from 0 to –2 ✓ Au is reduced from 0 to +1 and O is oxidised from 0 to –2 ✓
7	(b)	(iii)	**IGNORE** any charges shown within complexes (treat as rough working) $4Au + 8CN^- + 2H_2O + O_2 \rightarrow 4[Au(CN)_2]^- + 4OH^-$ ✓✓ First mark for all 6 species Second mark for balancing	2	**IF** Ag referred to, rather than Au, treat as a slip and apply **BOD** **IGNORE** state symbols **CARE**: In $[Au(CN)_2]^-$, – sign is **OUTSIDE** square brackets **For 1st mark, IGNORE** e^- present **ALLOW** 1 mark for balanced equation with CN^- missing, i.e. $4Au + 2H_2O + O_2 \rightarrow 4Au^+ + 4OH^-$ **ALLOW** 1 mark rogue e^- on either side **ALLOW** multiples, e.g. $2Au + 4CN^- + H_2O + ½O_2 \rightarrow 2[Au(CN)_2]^- + 2OH^-$ $Au + 2CN^- + ½ H_2O + ¼ O_2 \rightarrow [Au(CN)_2]^- + OH^-$
7	(b)	(iv)	$ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O$ ✓	1	**IGNORE** state symbols **ALLOW** e for electron **ALLOW** multiples
			Total	13	

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Question			Answer	Marks	Guidance
8	(a)		Cu^{2+}: $(1s^2)\,2s^22p^63s^23p^63d^9$ ✓ Cu^{+}: $(1s^2)\,2s^22p^63s^23p^63d^{10}$ ✓	2	**IGNORE** repeated $1s^2$ after $1s^2$ prompt on answer line **ALLOW** $4s^0$, either before or after 3d **ALLOW** upper case D, etc and subscripts, e.g. ……$3S_23P^6$ **DO NOT ALLOW** [Ar] as shorthand for $1s^22s^22p^63s^23p^6$
8	(b)		**IGNORE** any charges shown within formulae (treat as rough working) $CuCO_3 + 2HCOOH \rightarrow Cu(HCOO)_2 + H_2O + CO_2$ **OR** $CuO + 2HCOOH \rightarrow Cu(HCOO)_2 + H_2O$ **OR** $Cu(OH)_2 + 2HCOOH \rightarrow Cu(HCOO)_2 + \mathbf{2}H_2O$ ✓	1	**IGNORE** state symbols In formula of HCOOH/HCOO, **ALLOW** H, C and O in **ANY** order **ALLOW** H_2CO_3 for H_2O and CO_2 in carbonate equation **ALLOW** $(HCOO)_2Cu$ for $Cu(HCOO)_2$ **DO NOT ALLOW** equation with $CuSO_4$
8	(c)		$2Cu^{2+} + 4I^- \rightarrow 2CuI\mathbf{(s)} + I_2$ ✓ State symbol for CuI(s) **ONLY** required	1	**ALLOW** multiples, e.g. $Cu^{2+} + 2I^- \rightarrow CuI\mathbf{(s)} + ½I_2$ **IGNORE** other state symbols, even if incorrect
8	(d)		Starch ✓ Blue/black to colourless/white ✓ **MARK INDEPENDENTLY**	2	**IGNORE** 'brown' in composite colour with blue or black, i.e. **ALLOW** blue/brown to colourless **ALLOW** black/brown to colourless **DO NOT ALLOW** just 'it turns colourless/is decoloured' *Initial colour required* **IGNORE** clear for colourless

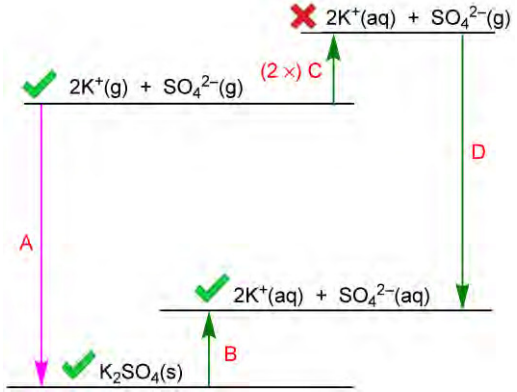
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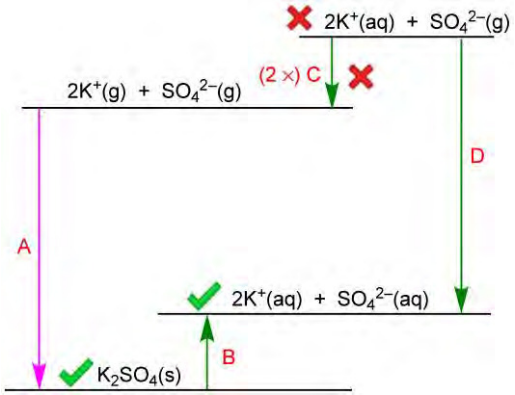
Question			Answer	Marks	Guidance
8	(e)		**WORKING REQUIRED** Correct answer: x = 4 required evidence of working --- $n(S_2O_3^{2-})$ **OR** $n(Cu^{2+}) = \frac{0.0420 \times 23.5}{1000} = 9.87 \times 10^{-4}$ (mol) ✓ In 250.0 cm^3 solution, $n(Cu^{2+}) = 9.87 \times 10^{-3}$ (mol) ✓ $M(Cu(HCOO)_2 \cdot 4H_2O) = \frac{2.226}{9.87 \times 10^{-3}} = 225.5$ (g mol^{-1}) ✓ $\boldsymbol{x}(H_2O)$ has mass of $225.5 - M(Cu(HCOO)_2)$ $= 225.5 - 153.5$ $= 72(.0)$ ✓ $\boldsymbol{x} = \frac{72(.0)}{18(.0)} = \mathbf{4}$ **WHOLE NUMBER** needed **AND** evidence of working ✓	5	***FULL ANNOTATIONS MUST BE USED*** --- At least **3 SF** required throughout *Alternative approach for final 3 marks based on mass:* mass $Cu(HCOO)_2 = 9.87 \times 10^{-3} \times 153.5 = 1.515$ g ✓ $n(H_2O) = \frac{2.226 - 1.515}{18(.0)} = \frac{0.711}{18(.0)} = 0.0395$ (mol) ✓ $\boldsymbol{x} = \frac{0.0395}{9.87 \times 10^{-3}} = 4$ ✓ **ALLOW** $Cu(HCOO)_2 \cdot 4H_2O$ --- **COMMON ERRORS for 4 marks** $\boldsymbol{x}$ = 117 (calc 116.78) *Use of 9.87×10^{-4} (no scaling × 10)* → *M* = 2255.319 $\boldsymbol{x}$ = 17 (calc 16.53) 4 marks *Use of 4.935×10^{-4} (Use of $0.5 \times 9.87 \times 10^{-3}$)* Check $n(Cu^{2+})$ for other **ECF**s Check for **ECF**s from incorrect *M*(anhydr salt) Actual = 153.5
			Total	**11**	

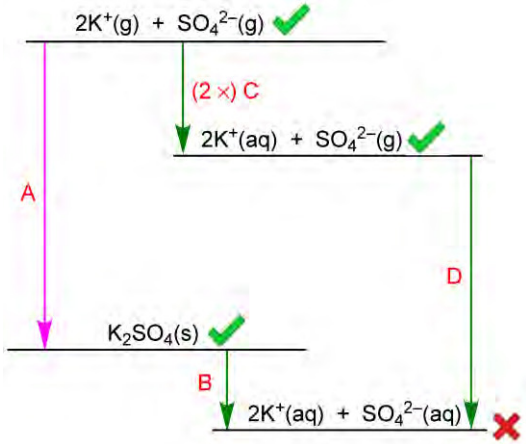
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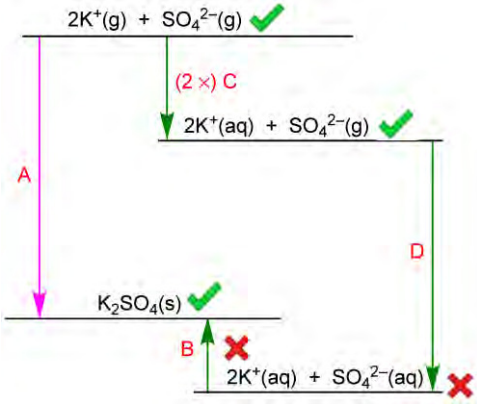
APPENDIX Q3(b)

<table>
<tr>
<td>Extra energy line placed ABOVE top line
3 out of 4 marks awarded for energy lines and species.

Top arrow is shown FROM $2K^+(g) + SO_4^{2-}(g)$ and arrow directions correct. Letter labels correct so last mark is awarded. 4/5 marks
 
</td>
<td>Same as left-hand response

BUT top arrow shown TO $2K^+(g) + SO_4^{2-}(g)$ so last mark not awarded 3/5 marks
 
</td>
</tr>
<tr>
<td>Extra energy line placed BELOW bottom line
3 out of 4 marks awarded for energy lines and species.

Top arrow is shown FROM $K_2SO_4(s)$ and arrow directions correct. Letter labels correct so last mark is awarded. 4/5 marks
 
</td>
<td>Same as left-hand response

BUT bottom arrow shown TO $K_2SO_4(s)$ so last mark not awarded 3/5 marks
 
</td>
</tr>
</table>

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Oxford Cambridge and RSA

Monday 15 June 2015 – Afternoon

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

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F3250 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 **24** pages. Any blank pages are indicated.

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Answer **all** the questions.

1 This question looks at properties of transition elements, ions and complexes.

(a) What is the oxidation number of Cr in the complex ion $[CrOCl_5]^{2-}$?

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

(b) Write the equation for a reaction catalysed by a named transition element, compound or ion.

Equation: .....

Catalyst: ..... **[1]**

(c) An octahedral complex ion **A**, $C_9H_{30}N_6Ni^{3+}$, exists as two optical isomers.

In complex ion **A**, Ni^{3+} is bonded to three molecules of a bidentate ligand **B**.

(i) State what is meant by a *bidentate ligand*.

.....

.....

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

(ii) What is the molecular formula of the bidentate ligand **B**?

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

(iii) Draw a possible structure for **B** and explain how **B** is able to act as a bidentate ligand.

.....

.....

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

(iv) What is the coordination number of complex ion **A**?

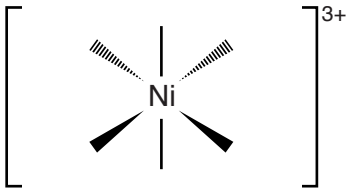
..... **[1]**

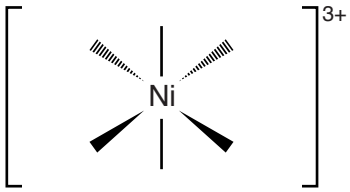
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(v) Complete the 3-D diagrams of the shapes of the optical isomers of complex ion **A**.

You can show the bidentate ligand simply as





[1]

(d) Describe the reactions of **EITHER** aqueous copper(II) ions **OR** aqueous cobalt(II) ions with:

- aqueous sodium hydroxide
- excess aqueous ammonia
- hydrochloric acid.



In your answer you should link observations with equations.

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

[Total: 14]

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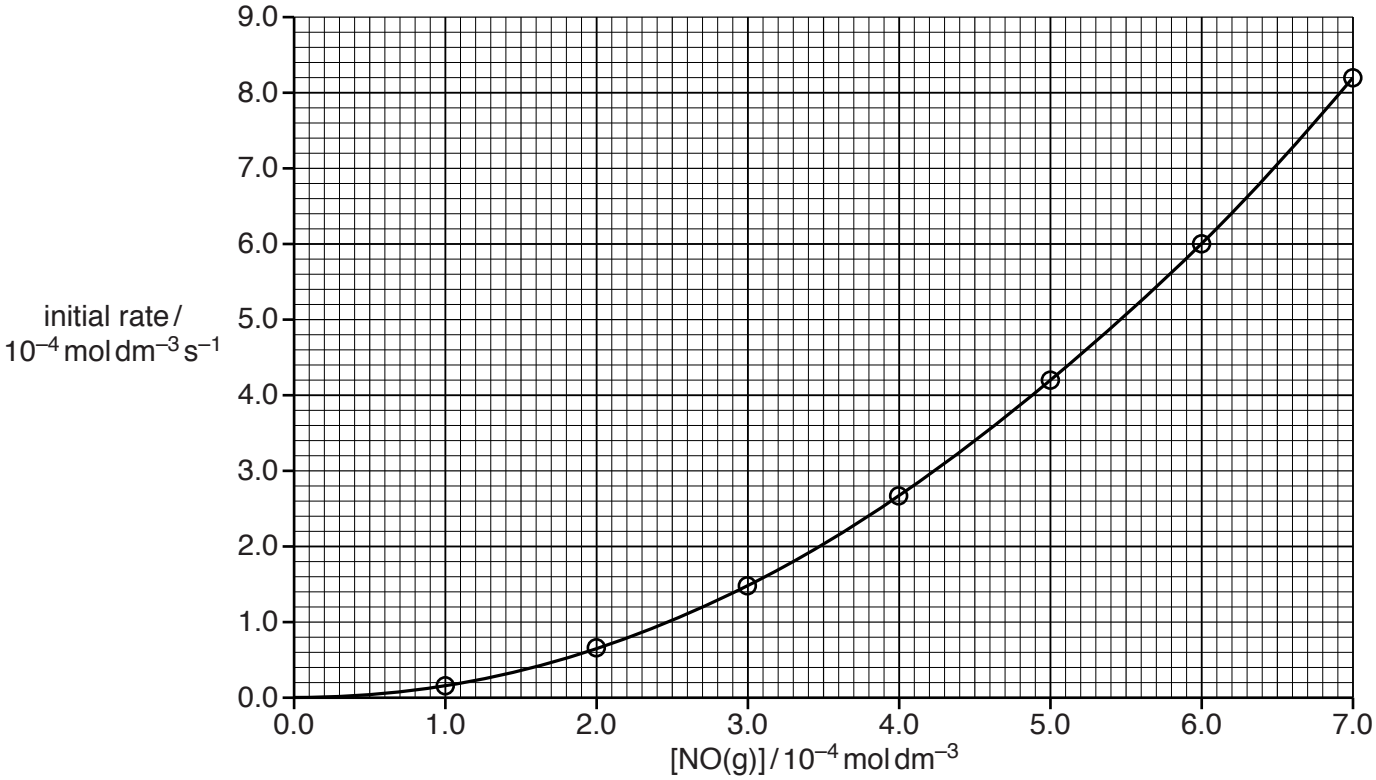
2 Hydrogen, H_2, reacts with nitrogen monoxide, NO, as shown below:

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

(a) The rate equation for this reaction is:

$$rate = k[H_2(g)][NO(g)]^2$$

The concentration of NO(g) is changed and a rate–concentration graph is plotted.



The chemist uses $H_2(g)$ of concentration 2.0×10^{-2} mol dm^{-3}.

Using values from the graph, calculate the rate constant, *k*, for this reaction.

Give your answer to **two** significant figures and in **standard form**.

Show your working.

k = ... units ..... **[4]**

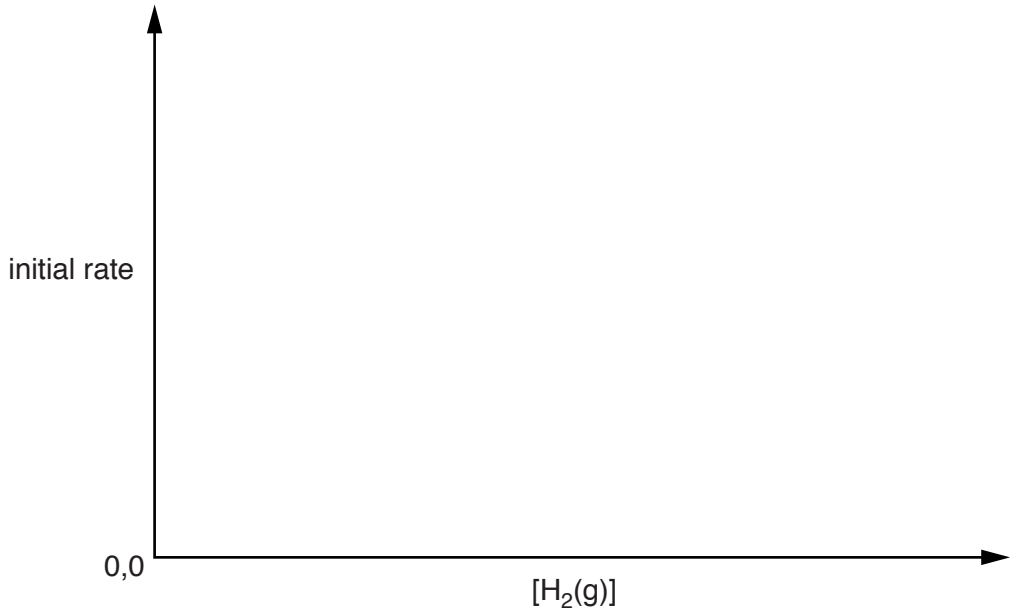
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(b) A chemist investigates the effect of changing the concentration of $H_2(g)$ on the initial reaction rate at two different temperatures.

The reaction is first order with respect to $H_2(g)$.

(i) Using the axes below, sketch **two** graphs of the results.

Label the graphs as follows:
- **L** for the lower temperature
- **H** for the higher temperature.



[2]

(ii) State the effect of the higher temperature on the rate constant, *k*.

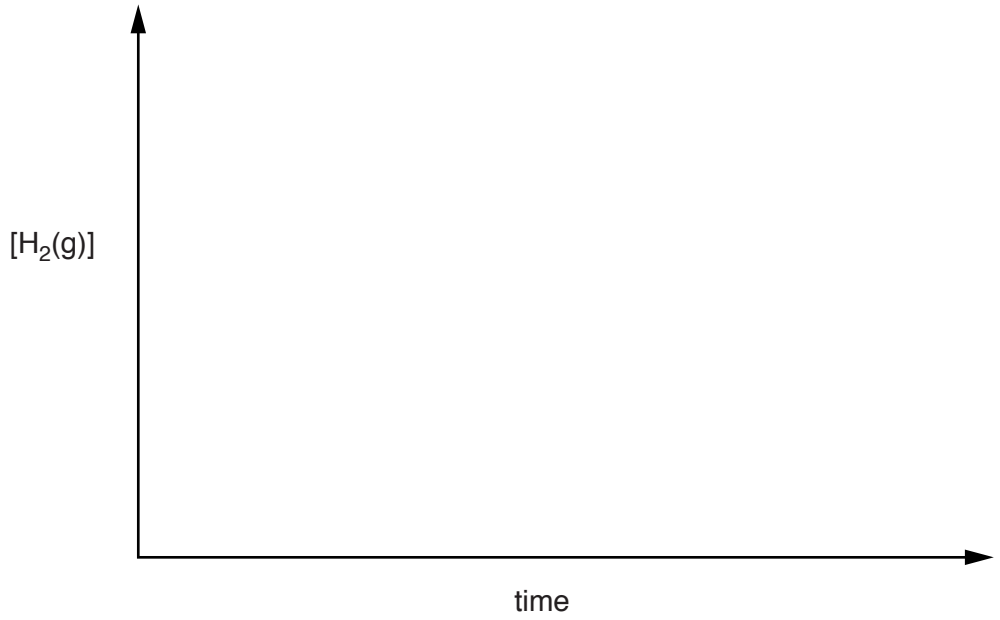
..... **[1]**

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(c) The reaction can also be shown as being first order with respect to $H_2(g)$ by continuous monitoring of $[H_2(g)]$ during the course of the reaction.

- Using the axes below, sketch a graph to show the results.
- State how you would use the graph to show this first order relationship for $H_2(g)$.



.....

.....

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

(d) The chemist proposes a three-step mechanism for the reaction:

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

(i) On the dotted line below, write the equation for step 3.

step 1:	$2NO \longrightarrow N_2O_2$	fast
step 2:	$H_2 + N_2O_2 \longrightarrow N_2O + H_2O$	slow
step 3:	.....	fast

[1]

(ii) Explain why this mechanism is consistent with the rate equation $rate = k[H_2(g)][NO(g)]^2$.

.....

.....

.....

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

[Total: 11]

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3 This question looks at two reactions involving sulfur compounds.

(a) Hydrogen reacts with carbon disulfide as shown below.

$$4H_2(g) + CS_2(g) \longrightarrow CH_4(g) + 2H_2S(g)$$

For this reaction, $\Delta H = -234\,kJ\,mol^{-1}$ and $\Delta S = -164\,J\,K^{-1}\,mol^{-1}$.

(i) Why does the reaction have a negative entropy change?

.....

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

(ii) Standard entropies are shown in the table below.

substance	**$CS_2(g)$**	**$CH_4(g)$**	**$H_2S(g)$**
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	238	186	206

Calculate the standard entropy for H_2.

$S^{\ominus}$ = ... $J\,K^{-1}\,mol^{-1}$ **[2]**

(iii) Explain, with a calculation, whether this reaction is feasible at 25 °C.

Show your working.

.....

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

(iv) Explain, with a calculation, the significance of temperatures above 1154 °C for this reaction.

.....

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

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(b) A chemist investigated methods to improve the synthesis of sulfur trioxide from sulfur dioxide and oxygen.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The chemist:

- mixed together 1.00 mol SO_2 and 0.500 mol O_2 with a catalyst at room temperature
- compressed the gas mixture to a volume of 250 cm^3
- allowed the mixture to reach equilibrium at constant temperature and without changing the total gas volume.

At equilibrium, 82.0% of the SO_2 had been converted into SO_3.

(i) Determine the concentrations of SO_2, O_2 and SO_3 present at equilibrium and calculate K_c for this reaction.

K_c = ... units ..... **[6]**

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(ii) Explain what would happen to the pressure as the system was allowed to reach equilibrium.

.....

.....

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

(iii) The value of K_c for this equilibrium decreases with increasing temperature.

Predict the sign of the enthalpy change for the forward reaction. State the effect on the equilibrium yield of SO_3 of increasing the temperature at constant pressure.

ΔH: .....

Effect on SO_3 yield: ..... **[1]**

(iv) The chemist repeated the experiment at the same temperature with 1.00 mol SO_2 and an excess of O_2.
The gas mixture was still compressed to a volume of 250 cm^3.

State and explain, in terms of K_c, how the equilibrium yield of SO_3 would be different from the yield in the first experiment.

.....

.....

.....

.....

.....

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

[Total: 19]

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4 A student is supplied with 0.500 mol dm^{-3} potassium hydroxide, KOH, and 0.480 mol dm^{-3} propanoic acid, C_2H_5COOH.

The acid dissociation constant, K_a, for C_2H_5COOH is 1.35×10^{-5} mol dm^{-3}.

(a) C_2H_5COOH is a weak Brønsted–Lowry acid.

What is meant by a *weak acid* and *Brønsted–Lowry acid*?

.....

.....

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

(b) Calculate the pH of 0.500 mol dm^{-3} potassium hydroxide.

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

(c) The student dilutes 25.0 cm^3 0.480 mol dm^{-3} C_2H_5COOH by adding water until the total volume is 100.0 cm^3.

(i) Write the expression for K_a for C_2H_5COOH.

[1]

(ii) Calculate the pH of the diluted solution.

pH = ... **[3]**

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(d) Aqueous propanoic acid, C_2H_5COOH, reacts with carbonates and alkalis.

(i) Write the full equation for the reaction of aqueous propanoic acid with sodium carbonate.

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

(ii) Write the **ionic** equation for the reaction of aqueous propanoic acid with aqueous potassium hydroxide.

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

(e) A student prepares a buffer solution containing propanoic acid C_2H_5COOH and propanoate ions, $C_2H_5COO^-$. The concentrations of C_2H_5COOH and $C_2H_5COO^-$ are both $1.00\,mol\,dm^{-3}$.

The following equilibrium is set up.

$$C_2H_5COOH(aq) \rightleftharpoons C_2H_5COO^-(aq) + H^+(aq)$$

The acid dissociation constant, K_a, for C_2H_5COOH is $1.35 \times 10^{-5}\,mol\,dm^{-3}$.

(i) Calculate the pH of this buffer solution.

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

pH = ... **[1]**

(ii) A small amount of aqueous ammonia, $NH_3(aq)$, is added to the buffer solution.

Explain, in terms of equilibrium, how the buffer solution would respond to the added $NH_3(aq)$.

.....

.....

.....

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

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(iii) The student adds 6.075 g Mg to 1.00 dm^3 of this buffer solution.

Calculate the pH of the new buffer solution.

Give your answer to **two** decimal places

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

[Total: 16]

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5 Iron(II) iodide, FeI_2, is formed when iron metal reacts with iodine.

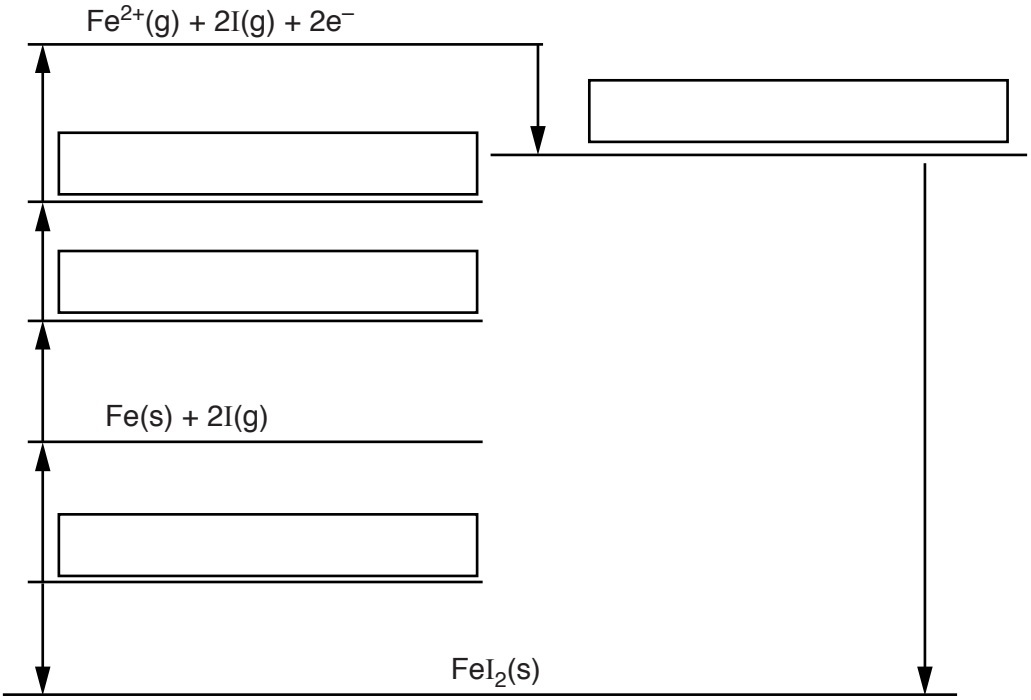
(a) The table below shows enthalpy changes involving iron, iodine and iron(II) iodide.

	Enthalpy change / kJ mol^{-1}
Formation of iron(II) iodide	–113
1st electron affinity of iodine	–295
1st ionisation energy of iron	+759
2nd ionisation energy of iron	+1561
Atomisation of iodine	+107
Atomisation of iron	+416

(i) The incomplete Born–Haber cycle below can be used to determine the lattice enthalpy of iron(II) iodide.

In the boxes, write the species present at each stage in the cycle.

Include state symbols for the species.



[4]

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(ii) Define the term *lattice enthalpy*.

.....

.....

.....

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

(iii) Calculate the lattice enthalpy of iron(II) iodide.

lattice enthalpy = ... $kJ\,mol^{-1}$ **[2]**

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(b) Some electrode potentials for ions are shown below.

$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$	$E^{\ominus} = -0.44\,V$
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	$E^{\ominus} = +0.77\,V$
$\frac{1}{2}I_2(aq) + e^-$	$\rightleftharpoons$	$I^-(aq)$	$E^{\ominus} = +0.54\,V$
$\frac{1}{2}Br_2(aq) + e^-$	$\rightleftharpoons$	$Br^-(aq)$	$E^{\ominus} = +1.09\,V$
$\frac{1}{2}Cl_2(aq) + e^-$	$\rightleftharpoons$	$Cl^-(aq)$	$E^{\ominus} = +1.36\,V$

(i) Complete the electron configurations for Fe^{2+} and Br^-.

Fe^{2+}: $1s^2$ .....

Br^-: $1s^2$ .....

[2]

(ii) Predict the products of reacting Fe(s) separately with $I_2(aq)$, $Br_2(aq)$ and $Cl_2(aq)$.

Explain your predictions using the electrode potential data above.

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

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(c) Fe^{2+} ions can be used to test for NO_3^- ions.
In this test, aqueous iron(II) sulfate is added to a solution containing NO_3^- ions, followed by slow addition of concentrated sulfuric acid. The sulfuric acid forms a layer below the aqueous solution.
In the presence of NO_3^- ions, a brown ring forms between the two layers.

Two reactions take place.

Reaction 1: In the acid conditions Fe^{2+} ions reduce NO_3^- ions to NO.
Fe^{2+} ions are oxidised to Fe^{3+} ions.
Water also forms.

Reaction 2: A ligand substitution reaction of $[Fe(H_2O)_6]^{2+}$ takes place in which one NO ligand exchanges with one water ligand. A deep brown complex ion forms as the brown ring.

Construct equations for these two reactions.

Reaction 1:

.....

Reaction 2:

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

[Total: 16]

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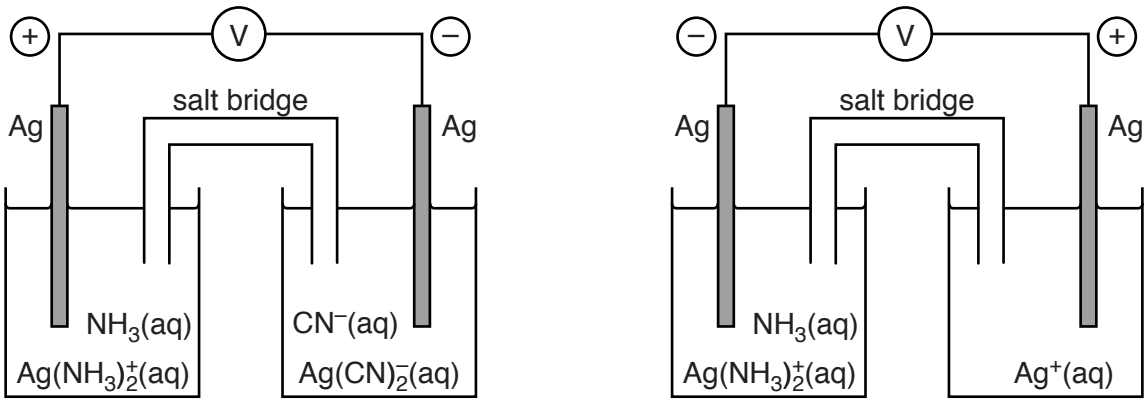
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6 Three redox systems, **C**, **D** and **E** are shown in Table 6.1.

C	$Ag(NH_3)_2^+(aq) + e^- \rightleftharpoons Ag(s) + 2NH_3(aq)$
D	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$
E	$Ag(CN)_2^-(aq) + e^- \rightleftharpoons Ag(s) + 2CN^-(aq)$

Table 6.1

The two cells below were set up in an experiment to compare the standard electrode potentials of redox systems **C**, **D** and **E**. The signs on each electrode are shown.



(a) List the three redox systems in order by adding the labels **C**, **D** and **E** to the table below.

$E^{\ominus}$	redox system
Most negative	
↑	
Least negative	

[1]

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(b) A standard cell is set up between redox system **D** in **Table 6.1** and a standard hydrogen half-cell. The standard cell potential of redox system **D** is +0.34 V.

The cell delivers a current for a length of time.
The pH of the solution in the standard hydrogen half-cell decreases.

(i) What is the pH of the solution in a standard hydrogen half-cell?

pH = ... **[1]**

(ii) Explain, in terms of electrode potentials and equilibrium, why the pH of the solution in the hydrogen half-cell decreases as this cell delivers current.

.....

.....

.....

.....

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

(iii) Write the equation for the overall cell reaction that takes place in this cell.

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

(c) The CN^- ion is the conjugate base of a very toxic weak acid.

In aqueous solutions of CN^- ions, an acid–base equilibrium is set up.

(i) Complete the equation for this equilibrium and label the conjugate acid–base pairs.

$$CN^- \quad + \quad H_2O \quad \rightleftharpoons \quad \text{.....} \quad + \quad \text{.....}$$

....

[1]

(ii) Explain, in terms of equilibrium, why acidic conditions should **not** be used with cells containing CN^-(aq) ions.

.....

.....

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

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(d) Direct-ethanol fuel cells (DEFCs) are being developed in which the fuel is ethanol rather than hydrogen.

The half-equation for the reaction at the ethanol electrode of the DEFC is shown below:

$$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 12H^+ + 12e^-$$

(i) State **one** important difference between a fuel cell and a modern storage cell.

.....

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

(ii) Suggest **one** advantage of using ethanol, rather than hydrogen, in a fuel cell for vehicles.

.....

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

(iii) The overall reaction in a DEFC is the same as for the complete combustion of ethanol.

Write the equation for the overall reaction in a DEFC.

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

(iv) Deduce the half-equation for the reaction at the oxygen electrode in a DEFC.

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

(v) Using oxidation numbers, show that oxidation and reduction take place in a DEFC.

Oxidation: .....

.....

Reduction: .....

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

[Total: 13]

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PLEASE DO NOT WRITE ON THIS PAGE

Turn over for the next question

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7 Chromite is the main ore of chromium. The chromium-containing compound in chromite is $Fe(CrO_2)_2$. The percentage of chromium in a sample of chromite can be determined using the method below.

Step 1

A 5.25 g sample of chromite ore is heated with sodium peroxide, Na_2O_2.

$$2Fe(CrO_2)_2 + 7Na_2O_2 \longrightarrow 2NaFeO_2 + 4Na_2CrO_4 + 2Na_2O$$

Water is added to the resulting mixture.
Na_2CrO_4 dissolves in the water forming a solution containing CrO_4^{2-} ions.

Step 2

The mixture from **Step 1** is filtered and the filtrate is made up to 1.00 dm^3 in a volumetric flask.
A 25.0 cm^3 sample of this alkaline solution is pipetted into a conical flask and an excess of aqueous potassium iodide is added.

- A redox reaction takes place between I^- ions, CrO_4^{2-} ions and H_2O.
- In this reaction 1 mol CrO_4^{2-} forms 1.5 mol I_2.

Step 3

The resulting mixture is titrated with 0.100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3(aq)$ to estimate the I_2 present:

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

The average titre of $Na_2S_2O_3(aq)$ is 25.5 cm^3.

(a) In **Step 1** Na_2O and $NaFeO_2$ react with water forming an alkaline solution containing a brown precipitate. This is **not** a redox reaction.

Write equations for:

- the reaction of Na_2O with water
- the reaction of $NaFeO_2$ with water.

.....

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

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(b) Determine the percentage, by mass, of chromium in the ore.

Give your answer to **one** decimal place.

[6]

(c) This part refers to **Step 2** of the method.

In the redox reaction between I^- ions, CrO_4^{2-} ions and H_2O:

- CrO_4^{2-} ions, are reduced to chromium(III) ions, Cr^{3+}
- I^- ions are oxidised to iodine, I_2
- Construct an overall equation for the redox reaction and write half equations for the oxidation and reduction.

Overall equation:

Half equations:

[3]

[Total: 11]

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

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

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GCE

Chemistry A

Unit **F325:** Equilibria, Energetics and Elements

Advanced GCE

Mark Scheme for June 2015

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1. These are the annotations, (including abbreviations), including those used in scoris, which are used when marking

Annotation	Meaning of annotation
BOD	Benefit of doubt given
CON	Contradiction
	Incorrect response
ECF	Error carried forward
I	Ignore
NAQ	Not answered question
NBOD	Benefit of doubt not given
POT	Power of 10 error
^	Omission mark
RE	Rounding error
SF	Error in number of significant figures
	Correct response

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2. Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

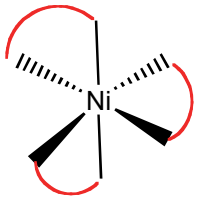
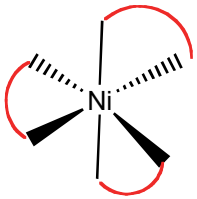
Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

3. The following questions should be annotated with **ALL annotations** to show where marks have been awarded in the body of the text:
1(d)
3(b)(i)
3(b)(iv)
4(e)(iii)
5(b)(ii)
7(b)

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Question			Answer	Marks	Guidance
1	(a)		(+)5 ✓	1	**ALLOW** 5+ **OR** V **OR** Cr^{5+}
1	(b)		For equations, **IGNORE** any state symbols; **ALLOW** multiples --- Any correct equation for a reaction catalysed by a transition element, compound or ion **AND** transition element, compound or ion (by formula or name) ✓	1	**EXAMPLES** $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (allow →) **AND** Fe/iron oxide $2SO_2 + O_2 \rightleftharpoons 2SO_3$ (allow →) **AND** V_2O_5/Pt $2CO + 2NO \rightarrow 2CO_2 + N_2$ **AND** Pt/Pd/Rh/Au Equation for any alkene + H_2 → alkane **AND** Ni/Pt/Pd $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$ **AND** Fe/$FeCl_3$/Fe^{3+} $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$ **AND** Fe/$FeBr_3$/Fe^{3+} $2H_2O_2 \rightarrow 2H_2O + O_2$ **AND** MnO_2 For other examples, **CHECK** with TL
1	(c)	(i)	**Donates two** electron **pairs** (to a metal ion) **AND** forms **two** coordinate **bonds** (to a metal ion) ✓ ***NOTE:*** *Metal ion not required as* Ni^{3+} *is in the question*	1	**ALLOW** lone pairs for electron pairs **ALLOW** dative (covalent) bonds for coordinate bonds **TWO** is only needed once, e.g. **Donates two** electron **pairs** to form coordinate **bonds** **Donates** electron **pairs** to form **two** coordinate **bonds**
1	(c)	(ii)	$C_3H_{10}N_2$ ✓	1	**ALLOW** in any order **IGNORE** structure
1	(c)	(iii)	**MARK INDEPENDENTLY** --- $H_2NCH_2CH_2CH_2NH_2$ ✓ Each N **OR** each NH_2 **OR** amine group has a lone pair/electron pair **OR** lone pairs shown on N atoms in structure ✓	2	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **ALLOW** $H_2NCH_2CH(CH_3)NH_2$ **OR** $H_2NCH(CH_2CH_3)NH_2$ **ALLOW** secondary or tertiary diamines or mixture **IGNORE** complex ion For other examples, **CHECK** with TL

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Question			Answer	Marks	Guidance
1	(c)	(iv)	6 ✓	1	
1	(c)	(v)	3–D diagrams of **BOTH** optical isomers required for the mark  **AND**  ✓	1	In this part, Charge **AND** Square brackets **NOT** required **IGNORE** N or attempts to draw structure of bidentate ligand Other orientations possible but all follow same principle with 2nd structure being a mirror image of the first

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Question			Answer	Marks	Guidance
1	(d)		*Quality of written communication* Observation must be linked to the correct **reaction** ***REACTIONS OF AQUEOUS Cu^{2+}*** --- **REACTION OF Cu^{2+} with NaOH(aq)** **Correct balanced equation** $Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$ ✓ state symbols **not** required **Observation** blue precipitate/solid ✓	**2**	***FULL ANNOTATIONS MUST BE USED THROUGHOUT*** **ALLOW some reactions for Cu^{2+} and some for Co^{2+}** **ALLOW equilibrium signs in all equations** **IGNORE any incorrect initial colours** **IGNORE state symbols** **IGNORE an incorrect formula for an observation** --- **ALLOW** $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$ **ALLOW** full or 'hybrid' equations, e.g. $Cu^{2+} + 2NaOH \rightarrow Cu(OH)_2 + 2Na^+$ $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$ $_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$ **ALLOW** any shade of blue ~~CuSO~~
1	(d)		**REACTION OF Cu^{2+} WITH excess NH_3(aq)** **Correct balanced equation** $[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$ ✓ **Observation** deep/dark blue (solution) ✓	**2**	**IGNORE initial precipitation of $Cu(OH)_2$** **IGNORE** $[Cu(NH_3)_4]^{2+}$ **ALLOW** royal blue, ultramarine blue or any blue colour that is clearly darker than for $[Cu(H_2O)_6]^{2+}$ **DO NOT ALLOW** deep blue precipitate for observation
1	(d)		**REACTION OF Cu^{2+} WITH HCl(aq)** **Correct balanced equation** $[Cu(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CuCl_4]^{2-} + 6H_2O$ ✓ **Observation** yellow (solution) ✓	**2**	**IGNORE** mention of different concentrations of HCl **ALLOW** $CuCl_4^{2-}$ i.e. no brackets **OR** $Cu(Cl)_4^{2-}$ **ALLOW** $[Cu(H_2O)_6]^{2+} + 4HCl \longrightarrow [CuCl_4]^{2-} + 6H_2O + 4H^+$ **IGNORE** $Cu^{2+} + 4Cl^- \longrightarrow CuCl_4^{2-}$ **ALLOW** green–yellow **OR** yellow–green **DO NOT ALLOW** yellow precipitate for observation

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Question			Answer	Marks	Guidance
1	(d)		*Quality of written communication* Observation must be linked to the correct **reaction** ***REACTIONS OF AQUEOUS Co^{2+}*** --- **REACTION OF Co^{2+} with NaOH(aq)** **Correct balanced equation** $Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$ ✓ state symbols **not** required **Observation** blue precipitate/solid ✓	2	***FULL ANNOTATIONS MUST BE USED THROUGHOUT*** **ALLOW some reactions for Cu^{2+} and some for Co^{2+}** **ALLOW equilibrium signs in all equations** **IGNORE any incorrect initial colours** **IGNORE state symbols** **IGNORE an incorrect formula for an observation** --- **ALLOW** $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2(H_2O)_4 + 2H_2O$ **ALLOW** full or 'hybrid' equations, e.g. $Co^{2+} + 2NaOH \rightarrow Co(OH)_2 + 2Na^+$ $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2 + 6H_2O$ $_4 + 2NaOH \rightarrow Co(OH)_2 + Na_2SO_4$ **ALLOW** any shade of blue CoSO **IGNORE** changes in colour over time
1	(d)		**REACTION OF Co^{2+} WITH excess $NH_3(aq)$** **Correct balanced equation** $[Co(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Co(NH_3)_6]^{2+} + 6H_2O$ ✓ **Observation** brown/yellow (solution) ✓	2	**IGNORE initial precipitation of $Co(OH)_2$** **ALLOW** any shade of brown or yellow **DO NOT ALLOW** brown/yellow precipitate for observation
1	(d)		**REACTION OF Co^{2+} WITH HCl(aq)** **Correct balanced equation** $[Co(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CoCl_4]^{2-} + 6H_2O$ ✓ **Observation** blue (solution) ✓	2	**IGNORE** mention of different concentrations of HCl **ALLOW** $CoCl_4^{2-}$ i.e. no brackets **OR** $Co(Cl)_4^{2-}$ **ALLOW** $[Co(H_2O)_6]^{2+} + 4HCl \longrightarrow [CoCl_4]^{2-} + 6H_2O + 4H^+$ **IGNORE** $Co^{2+} + 4Cl^- \longrightarrow CoCl_4^{2-}$ **ALLOW** any shades of blue **DO NOT ALLOW** blue precipitate for observation
			Total	14	

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<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>Guidance</th></tr>
<tr><td>2</td><td>(a)</td><td></td><td>
NOTE: First 3 marks are ONLY available from an expression using [NO]^2
Units are marked independently

Using values ON THE CURVE in CORRECT expression 1 mark
Use of any two correct values for rate and [NO] from graph
e.g. for 5.0×10^{-4} and 4.2×10^{-4},
$k = \dfrac{4.2 \times 10^{-4}}{(2.0 \times 10^{-2}) \times (5.0 \times 10^{-4})^2}$

OR $4.2 \times 10^{-4} = k\,(2.0 \times 10^{-2}) \times (5.0 \times 10^{-4})^2$ ✓

Calculation of k 2 marks

FOR 1 MARK
k calculated correctly from values obtained from graph
BUT NOT in standard form AND/OR more than 2 SF
e.g. $k = \dfrac{6.0 \times 10^{-4}}{(2.0 \times 10^{-2}) \times (6.0 \times 10^{-4})^2} = 83333.33$ ✓

OR FOR 2 MARKS
k calculated correctly from values obtained from graph
AND in standard form AND TO 2 SF
e.g. k = 83333.33 gives 8.3×10^4 ✓

UNITS FOR 1 MARK:
$dm^6\ mol^{-2}\ s^{-1}$ ✓
</td><td>4</td><td>
Note: rate and [NO] are any correct pair of readings from the graph,
The [NO] below are the most commonly seen.
For these [NO] values, these are the ONLY rates allowed

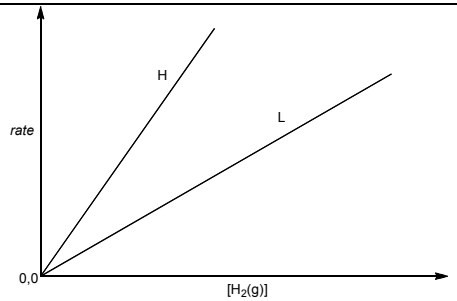
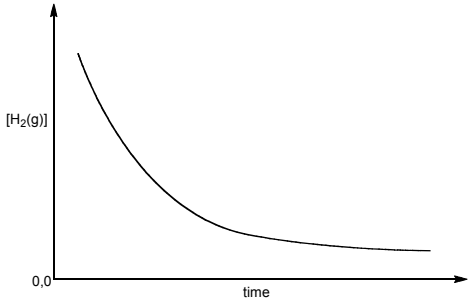
<table>
<tr><th>[NO]</th><th>rate</th><th>k</th><th>k</th></tr>
<tr><td>1.0×10^{-4}</td><td>0.1×10^{-4} to
0.2×10^{-4}</td><td>50000
100000</td><td>5.0×10^4
1.0×10^5</td></tr>
<tr><td>2.0×10^{-4}</td><td>0.6×10^{-4} to
0.7×10^{-4}</td><td>75000
87500</td><td>7.5×10^4
8.8×10^4</td></tr>
<tr><td>3.0×10^{-4}</td><td>1.5×10^{-4}</td><td>83333</td><td>8.3×10^4</td></tr>
<tr><td>4.0×10^{-4}</td><td>2.7×10^{-4}</td><td>84375</td><td>8.4×10^4</td></tr>
<tr><td>5.0×10^{-4}</td><td>4.2×10^{-4}</td><td>84000</td><td>8.4×10^4</td></tr>
<tr><td>6.0×10^{-4}</td><td>6.0×10^{-4}</td><td>83333</td><td>8.3×10^4</td></tr>
<tr><td>7.0×10^{-4}</td><td>8.2×10^{-4}</td><td>83673</td><td>8.4×10^4</td></tr>
</table>
IF OTHER values are given, mark using the same principle. If any doubt, contact TL.

NOTE: IGNORE any numbers used from tangents

SPECIAL CASES that ALLOW ECF for calculation of k from ONLY ONE of the following (2 marks)
1. Powers of 10 incorrect or absent in initial k expression
2. $[H_2]^2[NO]$ used instead of $[H_2][NO]^2$
3. Any value within ±0.2 of actual values from graph

ALLOW units in any order, e.g. $mol^{-2}\ dm^6\ s^{-1}$
</td></tr>
</table>

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Question			Answer	Marks	Guidance
2	(b)	(i)	 One straight upward line **AND** starting at 0,0 ✓ 2nd straight upward line starting at 0,0 and steeper **AND** Steeper line labelled H **OR** less steep line labelled L ✓	2	**ALLOW** 1 mark for two upward sloping curves starting at origin **AND** upper curve labelled H and lower curve labelled L **NOTE: ALLOW** some leeway for lines starting from origin **ALLOW** straight line not drawn with ruler, i.e. is a straight line rather than a curve **ALLOW** similar labelling as long as it is clear which line is which
2	(b)	(ii)	increases ✓	1	
2	(c)		**MARK INDEPENDENTLY** **----------**  Downward curve ✓ Half life is constant ✓	2	**ALLOW** curve touching y axis **ALLOW** curve touching x axis **ALLOW** Two half lives are the same **IGNORE** 'regular' half life (not necessarily the same)

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Question			Answer	Marks	Guidance
2	(d)	(i)	$H_2 + N_2O \rightarrow N_2 + H_2O$ ✓	1	**ONLY** correct answer **DO NOT ALLOW** multiples
2	(d)	(ii)	Steps 1 **AND** Step 2 together give $2NO + H_2$ ✓	1	**ALLOW** Step 1 **AND** Step 2 together give species in same ratio as in rate equation **ALLOW** rate-determining step/slow step for Step 2 **ALLOW** H_2 reacts with N_2O_2 which is formed from 2NO **NOTE**: The response must link Step 1 with Step 2 Steps can be referenced from the species in each step
			Total	11	

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Question			Answer	Marks	Guidance
3	(a)	(i)	5 mol/molecules (of gas) forms 3 mol/molecules (of gas) ✓	1	**ALLOW** reaction forms fewer moles/molecules **IF** stated, numbers of molecules **MUST** be correct **IGNORE** comments related to ΔG **OR** disorder (even if wrong)
3	(a)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer =(+)131 (J K^{-1} mol^{-1}) , award 2 marks** **----------** $-164 = (186 + 2 \times 206) - (4 \times S + 238)$ **OR** $4S = 164 + (186 + 2 \times 206) - 238$ ✓ S = (+)131 (J K^{-1} mol^{-1}) ✓	2	**NOTE:** IF any values are omitted, **DO NOT AWARD** any marks. e.g. –164 may be missing **ALLOW FOR 1 mark** –131 wrong final sign 49 wrong sign for 164 79.5 no use of 2 524 no division by 4 38 wrong sign for 186 –75 wrong sign for 206 250 wrong sign for 238 Any other number: **CHECK** for **ECF** from 1st marking point for expressions using **ALL** values with **ONE** error only e.g. one transcription error:, e.g.146 for 164

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Question			Answer	Marks	Guidance
3	(a)	(iii)	**NOTE: DO NOT ALLOW answer to 3(a)(ii) for ΔG calculation** --- **ΔG calculation: 2 marks** $\Delta G = -234 - 298 \times -0.164$ ✓ $= -185$ (kJ mol^{-1}) ✓ **IGNORE** units (even if wrong) –185 subsumes 1st mark) **Feasibility comment for negative ΔG answer: 1 mark** (Forward) reaction is feasible / spontaneous **AND** $\Delta G < 0$ / $\Delta H - T\Delta S < 0$ ✓	**2** **1**	**ALLOW** ΔG correctly calculated from 3 SF up to calculator value of –185.128 **ALLOW** working in J, *ie*: $\Delta G = -234000 - 298 \times -164$ ✓ $= -185000$ (J mol^{-1}) ✓ **ALLOW** 1 mark for use of 25 **OR** mixture of kJ and J, e.g. $\Delta G = -234 - 25 \times -0.164 = -229.9$ $\Delta G = -234 - 298 \times -164 = +48638$ **ALLOW ECF** if calculated value for ΔG is +ve Then 'correct' response for 3rd mark would be **not** feasible/not spontaneous **AND** $\Delta G > 0$ / $\Delta H - T\Delta S > 0$
3	(a)	(iv)	**(**ΔG =) $-234 - 1427 \times \frac{-164}{1000} = 0$ (calculator 0.028(kJ) OR 28 (J)) ✓ **2nd mark only available if 1st mark has been awarded** (Above 1427K/1154ºC), reaction is **not** feasible/**not** spontaneous✓ **OR** 1427 K is maximum temperature that reaction happens	**2**	**ALLOW** (When $\Delta G = 0$) $T = \frac{-234}{-0.164} = 1427$ K **OR** $\frac{-234000}{-164} = 1427$ K For 2nd mark, **IF** ΔG is +ve from **(a)(iii)** **ALLOW ECF** for: Above 1427 K, reaction is feasible / spontaneous **OR** 1427 K is minimum temperature that reaction happens **IGNORE LESS feasible** **IGNORE** comparisons of the signs of $T\Delta S$ and ΔH, *e.g IGNORE $T\Delta S$ is more negative than ΔH*

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Question			Answer	Marks	Guidance
3	(b)	(i)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 57.6 dm^3 mol^{-1}, award **6 marks** **IF** answer = 57.6 with incorrect units, award **5 mark** --- **Equilibrium amounts in mol 2 MARKS** $n(SO_2)$ = 0.180 (mol) **ALL 3** correct: ✓✓ $n(O_2)$ = 0.090 (mol) **ANY 2** correct: ✓ $n(SO_3)$ = 0.820 (mol) **Equilibrium concentrations (moles × 4) 1 MARK** SO_2 = 0.720 (mol dm^{-3}) **AND** O_2 = 0.360 (mol dm^{-3}) **AND** SO_3 = 3.28 (mol dm^{-3}) ✓ **Calculation of K_c and units 3 MARKS** $K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$ **OR** $\frac{3.28^2}{(0.720)^2 \times (0.360)}$ ✓ = 57.6 ✓ dm^3 mol^{-1} ✓ *At least 3SF is required*	6	**FULL ANNOTATIONS NEEDED** **IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ALLOW ECF** from incorrect moles of SO_2, O_2 **AND** SO_2 **ALL three** concentrations required for this mark **ALLOW ECF** from incorrect concentrations **NO ECF** for numerical value with a square missing For K_c, **ALLOW** 3 significant figures up to calculator value of 57.64746228 correctly rounded For units, **ALLOW** mol^{-1} dm^3 **DO NOT ALLOW** dm^3/mol **ALLOW ECF** from incorrect K_c expression for both calculation and units **COMMON ERRORS** 0.0294 ***3 marks + units mark*** from SO_2 = 0.820, O_2 = 0.410, SO_3 = 0.180 (mol)
3	(b)	(ii)	(Pressure) decreases **AND** fewer molecules/moles ✓	1	For fewer moles, **ALLOW** 3 mol → 2 mol **ALLOW** more moles **of reactants**

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Question			Answer	Marks	Guidance
3	(b)	(iii)	ΔH is negative / '– ' / –ve **AND** yield of SO_3 decreases ✓	1	**IGNORE** exothermic and endothermic
3	(b)	(iv)	**IGNORE** le Chatelier responses **----------** ***Each marking point is independent*** ***K_c*** K_c does not change (with pressure/ concentration) ✓ ***Comparison of conc terms with more O_2*** $[O_2]$/concentration of oxygen is greater **OR** denominator/bottom of K_c expression is greater ✓ ***QWC: yield of SO_3 linked to K_c*** (Yield of) SO_3 is greater/increases **AND** numerator/top of K_c expression is greater/increases ✓	3	**FULL ANNOTATIONS NEEDED** **ALLOW** K_c **only** changes with temperature **IF** 1st marking point has been awarded, **IGNORE** comments about 'K_c decreasing' or 'K_c increasing' and assume that this refers to how the ratio subsequently changes. i.e **DO NOT CON** 1st marking point. **IGNORE** O_2 is greater/increases **ALLOW** **(Yield of) SO_3 is greater/increases** **AND** to reach/restore K_c value ✓
			Total	**19**	

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Question			Answer	Marks	Guidance
4	(a)		Proton/H^+ donor **AND** Partially dissociates/ionises ✓	1	
4	(b)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 13.7(0), award **2 marks** --- $[H^+] = \frac{1.00 \times 10^{-14}}{0.5(00)}$ **OR** $2(.00) \times 10^{-14}$ (mol dm^{-3}) ✓ pH = $-\log 2(.00) \times 10^{-14}$ = **13.7(0)** ✓	2	For pOH method:, **ALLOW** pOH = $-\log[OH^-]$ = 0.3(0) ✓ (calculator 0.301029995) **ALLOW** pH = 14 – 0.3 = 13.7 ✓ **ALLOW** 13.7 up to calculator value of 13.69897 correctly rounded. **ALLOW ECF** from incorrect $[H^+(aq)]$ provided that pH >7
4	(c)	(i)	$(K_a =) \frac{[H^+]\,[C_2H_5COO^-]}{[C_2H_5COOH]}$ ✓	1	**IGNORE** $\frac{[H^+]^2}{[C_2H_5COOH]}$ **OR** $\frac{[H^+]\,[A^-]}{[HA]}$ **ALLOW** $[H_3O^+]$ for $[H^+]$ **IGNORE** state symbols

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Question			Answer	Marks	Guidance
4	(c)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **2.9(0)**, award **3 marks** --- [C_2H_5COOH] = 0.12(0) mol dm^{-3} ✓ $[H^+] = \sqrt{K_a \times [C_2H_5COOH]} = \sqrt{1.35\times10^{-5}\times0.12(0)}$ **OR** 1.27×10^{-3} (mol dm^{-3}) ✓ pH = –log 1.27×10^{-3} = **2.9(0)** ✓ **NOTE**: The final two marks are **ONLY** available from attempted use of K_a **AND** [C_2H_5COOH]	3	**ALLOW** HA for C_2H_5COOH and A^- for $C_2H_5COO^-$ **ALLOW ECF** from incorrectly calculated [C_2H_5COOH] **ALLOW** 1.27×10^{-3} to calculator value of $1.272792206 \times 10^{-3}$ correctly rounded **ALLOW** $2.9(0) \times 10^{-3}$ to calculator value of 2.895242493 correctly rounded **ALLOW** use of quadratic equation which gives same answer of 2.90 from 0.120 mol dm^{-3} --- **COMMON ERRORS (MUST be to AT LEAST 2 DP unless 2nd decimal place is 0)** **pH = 2.59 2 marks** –log√ $(1.35 \times 10^{-5} \times 0.480)$ *Original conc* **pH = 5.79 2 marks** –log$(1.35 \times 10^{-5} \times 0.120)$ *No √* **pH = 5.19 1 mark** –log $(1.35 \times 10^{-5} \times 0.480)$ *Original conc, no √* **pH = 4.87 0 marks** –log(1.35×10^{-5}) = 4.87 *–log K_a*

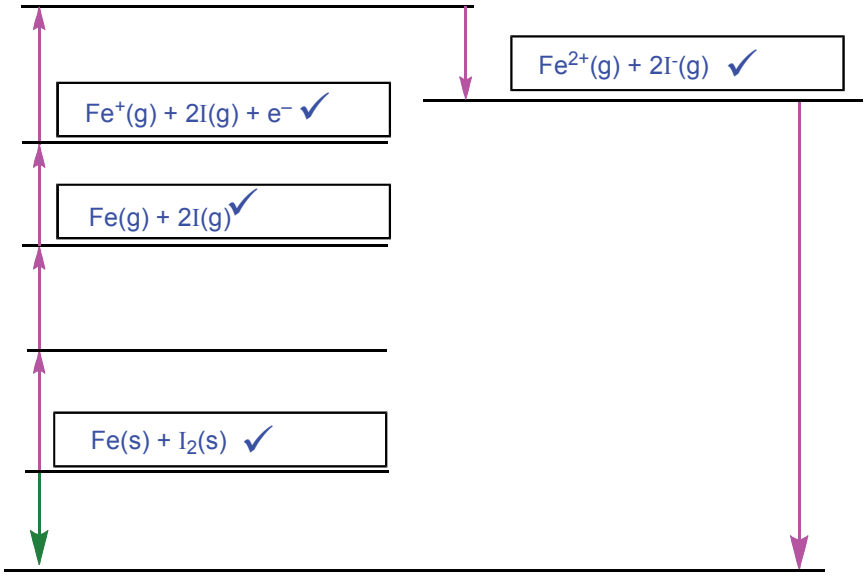
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Question			Answer	Marks	Guidance
4	(d)	(i)	$2C_2H_5COOH + Na_2CO_3 \rightarrow 2C_2H_5COONa + CO_2 + H_2O$ ✓	1	**IGNORE** state symbols and use of equilibrium sign **FOR** $CO_2 + H_2O$ **ALLOW** H_2CO_3 **ALLOW** $C_2H_5COO^-Na^+$ **OR** $C_2H_5COO^- + Na^+$ **BUT BOTH** + and – charges **must** be shown **ALLOW** NaC_2H_5COO
4	(d)	(ii)	$H^+ + OH^- \rightarrow H_2O$ ✓	1	**ALLOW** $C_2H_5COOH + OH^- \rightarrow C_2H_5COO^- + H_2O$ **IGNORE** state symbols
4	(e)	(i)	pH = –log 1.35×10^{-5} = **4.87** ✓	1	**ONLY** correct answer **DO NOT ALLOW** 4.9 (*Question asks for 2 DP)*
4	(e)	(ii)	**Added ammonia** C_2H_5COOH removes added NH_3/alkali/base **OR** $C_2H_5COOH + NH_3 / OH^- \rightarrow$ **OR** NH_3/alkali reacts with/accepts H^+ **OR** $H^+ + NH_3 \rightarrow$ **OR** $H^+ + OH^- \rightarrow$ ✓ Equlibrium → $C_2H_5COO^-$ **OR** Equilibrium → right ✓	 2	**ALLOW** use of HA/weak acid/acid for C_2H_5COOH; **ALLOW** use of NH_4OH for NH_3 **ALLOW** A^- for $C_2H_5COO^-$ **ASSUME** that equilibrium applies to that supplied in the question, i.e. **IGNORE** any other equilibria

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Question			Answer	Marks	Guidance
4	(e)	(iii)	***CHECK WORKING CAREFULLY AS CORRECT NUMERICAL ANSWER IS POSSIBLE FROM WRONG VALUES*** ========== **ALLOW** HA and A^- throughout **Amount of Mg (1 mark)** $n(Mg) = \frac{6.075}{24.3} = 0.25(0)$ mol ✓ --- **Moles/concentrations(2 marks)** $n(C_2H_5COOH) = 1.00 - (2 \times 0.25) = 0.50$ (mol) ✓ $(C_2H_5COO^-) = 1.00 + (2 \times 0.25) = 1.50$ (mol) ✓ ~~n~~--- **$[H^+]$ and pH (1 mark)** $[H^+] = 1.35 \times 10^{-5} \times \frac{0.50}{1.50}$ **OR** 4.5×10^{-6} (mol dm^{-3}) pH = –log 4.5×10^{-6} = **5.35** **2 dp required** ✓ **NOTE: IF there is no prior working,** **ALLOW 4 MARKS for** $[H^+] = 1.35 \times 10^{-5} \times \frac{0.50}{1.50}$ **AND** pH = **5.35** **IF the ONLY response is pH = 5.35, award 1 mark ONLY**	**4**	***FULL ANNOTATIONS MUST BE USED*** --- **For *n*(Mg), 1 mark** **ALLOW ECF** for **ALL** marks below from incorrect *n*(Mg) **ECF ONLY** available from concentrations that have • subtracted 0.50 **OR** 0.25 from 1 for $[C_2H_5COOH]$ • added 0.50 **OR** 0.25 to 1 for $[C_2H_5COO^-]$ ***i.e.*** **For moles/concentration 1 mark (1 mark lost)** **1.** $n(C_2H_5COOH) = 0.75$ **AND** $n(C_2H_5COO^-) = 1.25$ ***2.*** $n(C_2H_5COOH) = 0.50$ **AND** $n(C_2H_5COO^-) = 1.25$ ***3.*** $n(C_2H_5COOH) = 0.75$ **AND** $n(C_2H_5COO^-) = 1.50$ --- **ALLOW ECF ONLY** for the following giving 1 additional mark and a total of **3 marks** **1.** $[H^+] = 1.35 \times 10^{-5} \times \frac{0.75}{1.25}$ pH = –log 8.1×10^{-6} = **5.09** **2.** $[H^+] = 1.35 \times 10^{-5} \times \frac{0.50}{1.25}$ pH = –log 5.4×10^{-6} = **5.27** **3.** $[H^+] = 1.35 \times 10^{-5} \times \frac{0.75}{1.50}$ pH = –log 6.75×10^{-6} = **5.17**
			Award a maximum of 1 mark (for *n*(Mg) = 0.25 mol) for: pH value from K_a square root approach (weak acid pH) pH value from $K_w / 10^{-14}$ approach (strong base pH) --- **ALLOW** alternative approach based on Henderson–Hasselbalch equation for final 1 mark $pH = pK_a + \log \frac{1.5}{0.5}$ **OR** $pK_a - \log \frac{0.5}{1.5}$ pH = 4.87 + 0.48 = 5.35 ✓ **ALLOW** $-\log K_a$ for pK_a		
			Total	**16**	

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Question			Answer	Marks	Guidance
5	(a)	(i)	 **Mark each marking point independently**	4	Correct species **AND** state symbols required for each marks **ALLOW** e for e^{-} **TAKE CARE**: In top left box, e^{-} may be in centre of response and more difficult to see than at end. There is only **ONE** correct response for each line *From the gaps in the cycle, there is **NO** possibility of any **ECF***

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Question			Answer	Marks	Guidance
5	(a)	(ii)	(The enthalpy change that accompanies) the **formation** of **one mole** of a(n ionic) compound from its **gaseous ions** (under standard conditions) ✓✓ Award marks as follows. **1st mark: formation** of **compound** from **gaseous ions** **2nd mark: one mole** for compound **only** **DO NOT ALLOW** 2nd mark without 1st mark **DO NOT ALLOW** any marks for a definition for enthalpy change of **formation BUT** note the two concessions in guidance	**2**	**IGNORE** 'Energy needed' **OR** 'energy required' **ALLOW one mole** of compound is **formed/made** from its **gaseous ions** **ALLOW** as alternative for compound: lattice, crystal, substance, solid **IGNORE**: $Fe^{2+}(g) + 2I^{-}(g) \longrightarrow FeI_2(s)$ (Part of cycle) **ALLOW** 1 mark for absence of 'gaseous' only, i.e. the **formation** of **one mole** of a(n ionic) compound from its **ions** (under standard conditions) ✓ **ALLOW** 1 mark for ΔH_f definition with 'gaseous': the **formation** of **one mole** of a(n ionic) compound from its **gaseous** elements (under standard conditions) ✓

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Question			Answer	Marks	Guidance
5	(a)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –2473 (kJ mol^{-1}) award 2 marks** --- (–113) = 416 + (2 × +107) + 759 + 1561 + (2 × –295) + $\Delta H_{LE}(FeI_2)$ **OR** $\Delta H_{LE}(FeI_2)$ = –113 – (416 + (2 × +107) + 759 + 1561 + (2 × –295)) **OR** –113 – 2360 ✓ = – 2473 ✓ (kJ mol^{-1})	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. **See list below for marking of answers from common errors** --- **ALLOW** for 1 mark: +2473 wrong sign –2661 107 and –295 used instead of **2 ×** 107 and **2 ×** –295 –2366 +107 used instead of **2 ×** 107 –2768 –295 used instead of **2 ×** –295 –3653 wrong sign for 295 –2247 wrong sign for 113 –1641 wrong sign for 416 –2045 wrong sign for 2 **×** 107 –955 wrong sign for 750 +649 wrong sign for 1561 –3653 wrong sign for **2 ×** –295 Any other number: **CHECK** for **ECF** from 1st marking point for expressions with **ONE** error only e.g. one transcription error: e.g. +461 instead of +416
5	(b)	(i)	Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ ✓ Br^-: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ ✓	2	**ALLOW** 4s before 3d, ie $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ **ALLOW** $1s^2$ written after answer prompt (*ie* $1s^2$ twice) **ALLOW** upper case D, etc and subscripts, e.g. ……$4S_2 3D_1$ **ALLOW** for Fe^{2+} **……**$4s^0$ **DO NOT ALLOW** [Ar] as shorthand for $1s^2 2s^2 2p^6 3s^2 3p^6$ Look carefully at $1s^2 2s^2 2p^6 3s^2 3p^6$ – there may be a mistake

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Question			Answer	Marks	Guidance
5	(b)	(ii)	With Cl_2 **AND** Br_2 **AND** I_2 products are Fe^{2+} (AND halide ion) $FeCl_2$ **AND** $FeBr_2$ **AND** FeI_2 ✓ **OR** Evidence that **two** electrode potentials have been compared for at least **ONE** reaction, ✓ e.g. Fe –0.44 **AND** Cl_2 +1.36 e.g. Iron has more/most negative electrode potential With Cl_2 **AND** Br_2, products are Fe^{3+} (AND halide ion) $FeCl_3$ **AND** $FeBr_3$ ✓	3	**FULL ANNOTATIONS NEEDED** **ALLOW** products within equations (even if equations are not balanced) **IF stated, IGNORE reactants** **ALLOW** response in terms of positive 'cell reactions', e.g $Fe + Cl_2 \rightarrow Fe^{2+} + 2Cl^-$ E = (+)1.80 V **IGNORE** comments about reducing and oxidising agents and electrons
5	(c)		**BOTH EQUATIONS REQUIRE IONS PROVIDED IN QUESTION** **OR** **Reaction 1: 2 marks** **1st mark** for **ALL CORRECT species** e.g.: $Fe^{2+} + NO_3^- + H^+ \rightarrow Fe^{3+} + NO + H_2O$ **2nd mark** for **CORRECT balanced equation** $3Fe^{2+} + NO_3^- + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O$ ✓✓ --- **Reaction 2: 1 mark** $_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$ ✓	3	**ALLOW** correct multiples throughout **ALLOW equilibrium signs in all equations** **For 1st mark, IGNORE** e^- present **Check** carefully for correct **charges**
			[Fe(H **Total**	16	

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Question			Answer	Marks	
6	(a)		<table><tr><td>E^{o}</td><td>redox system</td></tr><tr><td>Most negative</td><td>**E**</td></tr><tr><td></td><td>**C**</td></tr><tr><td>Least negative</td><td>**D**</td></tr></table> ✓	1	**ALL** 3 correct for 1 mark
6	(b)	(i)	pH = 0 ✓	1	**Guidance**
6	(b)	(ii)	H redox system is more negative (e.g. has a more –ve *E* **OR** less +ve *E* **OR** is –ve electrode) **OR** H redox system releases electrons (May be in equation, e.g. $H_2 \rightarrow 2H^+ + 2e^-$) ✓ Equilibrium **shifts** to increase $[H^+]$ **OR** H^+ **OR** standard hydrogen equation **shifts** to increase $[H^+]$ **OR** H^+ ✓	2	**ALLOW ORA**, *ie* Ag redox system (D) has more positive *E* / less negative *E* **ALLOW** equilibrium sign **IGNORE** H is more reactive **ORA** **IGNORE** direction of equilibrium shift
6	(b)	(iii)	$H_2 + 2Ag^+ \rightarrow 2Ag + 2H^+$ ✓	1	**ALLOW** multiples e.g. $\frac{1}{2}H_2 + Ag^+ \rightarrow Ag + H^+$ State symbols **NOT** required **ALLOW** equilibrium sign
6	(c)	(i)	CN^- H_2O ⇌ **HCN** OH^- **AND** Base 2 Acid 1 Acid 2 Base 1 ✓ CN	1	State symbols **NOT** required **ALLOW** CNH and HO^- (i.e. any order) **ALLOW** 1 **and** 2 labels the other way around. **ALLOW** 'just acid' and 'base' labels throughout if linked by lines so that it is clear what the acid-base pairs are.

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Question			Answer	Marks	Guidance
6	(c)	(ii)	H^+ reacts with CN^- **OR** HCN forms **OR** equation: $H^+ + CN^- \rightarrow HCN$ (**ALLOW** $\rightleftharpoons$) **OR** CN^- accepts a proton/H^+ **OR** equilibrium shifts right **AND** CN^- is removed ✓	1	**ALLOW** Acid reacts with/removes OH^- ions (to form HCN) **ALLOW** CNH (i.e. any order) **IGNORE** other equilibrium comments
6	(d)	(i)	Fuel reacts with oxygen/oxidant to give **electrical** energy/voltage✓	1	**ALLOW** named fuel. e.g. hydrogen/H_2; ethanol; methanol, etc **ALLOW** fuel cell requires constant supply of fuel **AND** oxygen/an oxidant **OR** fuel cell operates continuously as long as a fuel **AND** oxygen/an oxidant are added **IGNORE** 'reactants' 'products' and comments about pollution and efficiency
6	(d)	(ii)	ethanol is a **liquid OR** is **less** volatile **OR** ethanol is easier to store/transport/stored more safely **OR** hydrogen is explosive/more flammable **OR** ethanol has more public/political acceptance ✓	1	Assume that '**it**' refers to ethanol **ALLOW** ORA throughout **IGNORE** ethanol has a higher boiling point **IGNORE** H_2 is a gas **IGNORE** 'produces no CO_2' **OR** less pollution **IGNORE** comments about efficiency **IGNORE** comments about biomass and renewable
6	(d)	(iii)	$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ ✓	1	Correct species **AND** balancing needed **ALLOW** multiples **ALLOW** C_2H_6O for formula of ethanol **IGNORE** state symbols
6	(d)	(iv)	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ✓	1	Correct species **AND** balancing needed **ALLOW** multiples, e.g. $3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O$ $_2 + 2H^+ + 2e^- \rightarrow H_2O$ **ALLOW** e (*ie* no + sign) ~~**ALLOW** $\frac{1}{2}O_2$~~ **ALLOW** $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ **OR** $3O_2 + 6H_2O + 12e^- \rightarrow 12OH^-$ **IGNORE** state symbols

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Question			Answer	Marks	Guidance
6	(d)	(v)	oxidation: C from –2 to +4 '+' sign **not** required ✓ reduction: O from 0 to –2 ✓	2	**ALLOW** 2– and 4+ **ALLOW** $C^{2-} \rightarrow C^{4+}$ **ALLOW** 0 and 2– **ALLOW** $O^{0} \rightarrow O^{2-}$ **ALLOW** 1 mark if correct oxidation numbers shown for **BOTH** C and O but wrong way around (*ie* C on reduction line and O on oxidation line) **IGNORE** O_2 reduced **IGNORE** any reference to electron transfer (*not in question*)
			Total	**13**	

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Question			Answer	Marks	Guidance
7	(a)		**Equations can be in either order** $Na_2O + H_2O \rightarrow 2NaOH$ ✓ $NaFeO_2 + 2H_2O \rightarrow Fe(OH)_3 + NaOH$ ✓	**2**	**ALLOW** multiples throughout **IGNORE** state symbols **ALLOW** $Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$ **DO NOT ALLOW** equations with uncancelled species. e.g. $Na_2O + 2H_2O \rightarrow 2NaOH + H_2O$ **ALLOW** $2NaFeO_2 + H_2O \rightarrow Fe_2O_3 + 2NaOH$ **OR** $_2 + H_2O \rightarrow Fe_2O_3 + 2Na^+ + 2OH^-$ ✓

2NaFeO

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Question			Answer	Marks	Guidance
7	(b)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 33.7%, award **6 marks.** **IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- amount $S_2O_3^{2-}$ used = $0.1000 \times \frac{25.50}{1000}$ = **2.550×10^{-3}** (mol) ✓ amount I_2 = 2.550×10^{-3} **÷ 2** **1.275×10^{-3}** (mol) ✓ amount CrO_4^{2-} **2/3 ×** 1.275×10^{-3} **OR** 1.275×10^{-3} **÷ 1.5** = **$8.5(00) \times 10^{-4}$** (mol) ✓ amount CrO_4^{2-} in original 1000 cm^3 = **40 ×** $8.5(00) \times 10^{-4}$ = **$3.4(00) \times 10^{-2}$** mol ✓ Mass of Cr/Cr^{3+} in ore = **52.0** × $3.4(00) \times 10^{-2}$ g **1.768 g** ✓ percentage Cr in ore = $\frac{1.768}{5.25} \times 100$ = **33.7%** ✓ **MUST** be to **one** decimal place (in the question)	**6**	***FULL ANNOTATIONS MUST BE USED*** **IF** a step is omitted but subsequent step subsumes previous, then award mark for any missed step **Working: at least 3 SF throughout until final % mark** BUT ignore trailing zeroes, ie for 0.490 allow 0.49 --- **ECF** answer above **÷ 2** **ECF** answer above **÷ 1.5** **ECF** answer above **× 40** **ECF** answer above × 52.0 **IMPORTANT**: The last two marks are **ONLY** available by using 52.0 for Cr --- **Common ECFs:** **0.8%** x 40 missing 5 marks (scaling error) **0.84%** x 40 missing 4 marks (scaling error and 2 DP) **33.68%** 5 marks (2 DP) **16.8%** 5 marks (divide Cr somewhere by 2) **144.9%; 72.5%** 4 marks (**Final 2 marks unavailable**) Use of $M(Fe(CrO_2)_2)$ = 223.8 instead of $M(Cr)$.

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Question	Answer	Marks	Guidance
(c)	*Overall*: $CrO_4^{2-} + 3I^- + 4H_2O \rightarrow Cr^{3+} + 1½\ I_2 + 8OH^-$ ✓ CrO *Half equations*: $CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr^{3+} + 8OH^-$ ✓ CrO $2I^- \rightarrow I_2 + 2e^-$ ✓	3	**ALLOW multiples and equilibrium signs throughout** **IGNORE** state symbols throughout e.g. $2CrO_4^{2-} + 6I^- + 8H_2O \rightarrow 2Cr^{3+} + 3I_2 + 16OH^-$ **ALLOW** equation using H^+. i.e. $CrO_4^{2-} + 3I^- + 8H^+ \rightarrow Cr^{3+} + 1½\ I_2 + 4H_2O$ **OR** $2CrO_4^{2-} + 6I^- + 16H^+ \rightarrow 2Cr^{3+} + 3I_2 + 8H_2O$ **ALLOW** CrO_4^{2-} half equation using H^+. i.e. $CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$ CrO
	Total	**11**	

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Tuesday 17 June 2014 – Afternoon

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 *

* 3 1 7 5 2 8 4 8 5 4 *

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 pages 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 **24** pages. Any blank pages are indicated.

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Answer **all** the questions.

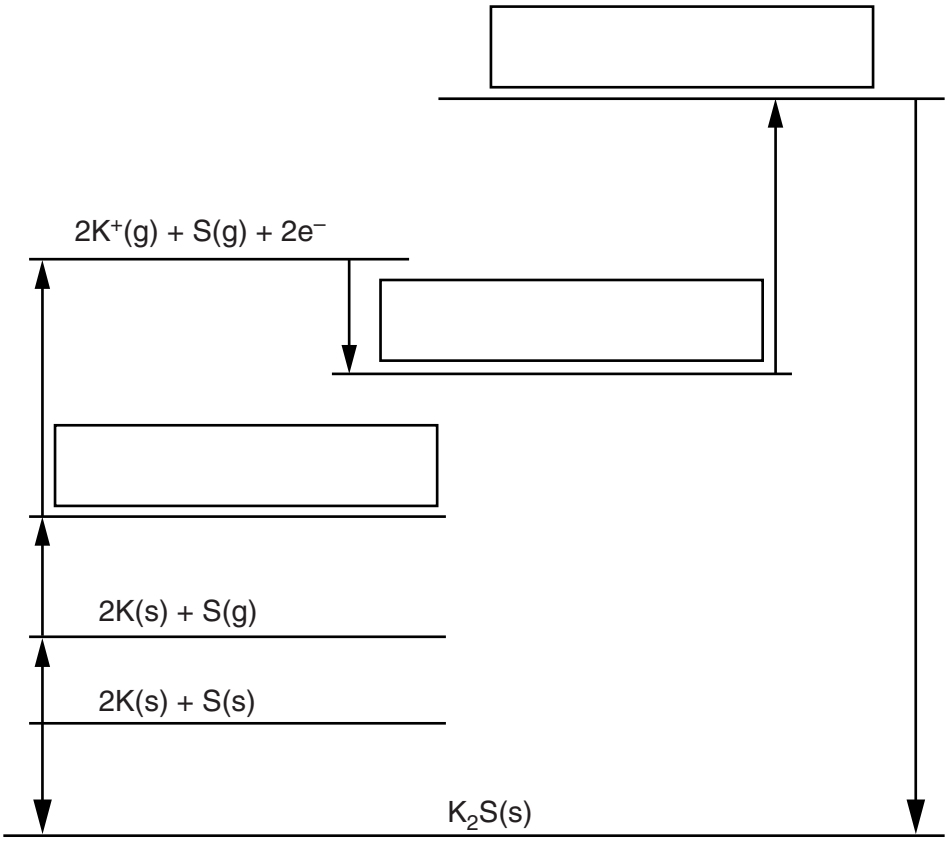
1 Born–Haber cycles can be used to calculate enthalpy changes indirectly.

(a) The table below shows enthalpy changes for a Born–Haber cycle involving potassium sulfide, K_2S.

	Enthalpy change /kJ mol^{-1}
Formation of potassium sulfide, K_2S	–381
1st electron affinity of sulfur	–200
2nd electron affinity of sulfur	+640
Atomisation of sulfur	+279
1st ionisation energy of potassium	+419
Atomisation of potassium	+89

(i) The incomplete Born–Haber cycle below can be used to determine the lattice enthalpy of potassium sulfide.

In the boxes, write the species present at each stage in the cycle.
Include state symbols for the species.



[3]

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(ii) Define, in words, the term *lattice enthalpy*.

.....

.....

.....

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

(iii) Using the Born–Haber cycle, calculate the lattice enthalpy of potassium sulfide.

lattice enthalpy = ... $kJ\,mol^{-1}$ **[2]**

(b) Several ionic radii are shown below.

Ion	Na^+	K^+	Rb^+	Cl^-	Br^-	I^-
Radius/pm	95	133	148	181	195	216

Predict the order of melting points for NaBr, KI and RbCl from lowest to highest.

Explain your answer.

Lowest melting point .....

.....

Highest melting point .....

Explanation .....

.....

.....

.....

.....

.....

[3]

[Total: 10]

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2 This question looks at different aspects of entropy.

(a) Three processes are given below.

For each process, state and explain whether the change would be accompanied by an increase or decrease in entropy.

(i) The freezing of water.

increase or decrease .....

explanation .....

.....

[1]

(ii) The reaction of calcium carbonate with hydrochloric acid.

increase or decrease .....

explanation .....

.....

[1]

(iii) The formation of $O_3(g)$ from $O_2(g)$.

increase or decrease .....

explanation .....

.....

[1]

(b) The enthalpy and entropy changes of a reaction both have a negative sign.

Discuss how the feasibility of this reaction will change as the temperature increases.

.....

.....

.....

.....

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

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(c) The metal tungsten is obtained on a large scale from its main ore, wolframite. Wolframite contains tungsten(VI) oxide, WO_3.

Tungsten is extracted from wolframite by reduction with hydrogen:

$$WO_3(s) + 3H_2(g) \longrightarrow W(s) + 3H_2O(g) \qquad \Delta H = +115\,kJ\,mol^{-1}$$

Standard entropies are given in the table below.

Substance	$WO_3(s)$	$H_2(g)$	W(s)	$H_2O(g)$
$S^{\ominus}$ **/ J K^{-1} mol^{-1}**	76	131	33	189

(i) Calculate the free energy change, ΔG, in kJ mol^{-1}, for this reaction at 25 °C.

Show your working.

ΔG at 25 °C = ... kJ mol^{-1} **[2]**

(ii) Calculate the minimum temperature, in K, at which this reaction becomes feasible.

Show your working.

minimum temperature = ... K **[2]**

[Total: 9]

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3 Ethyne gas, C_2H_2, is manufactured in large quantities for a variety of uses.

Much of this ethyne is manufactured from methane as shown in the equation below.

$$2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g) \qquad \Delta H = +377\,kJ\,mol^{-1}$$

(a) Write an expression for K_c for this equilibrium.

[1]

(b) A research chemist investigates how to improve the synthesis of ethyne from methane at a high temperature.

- The chemist adds CH_4 to a 4.00 dm^3 container.
- The chemist heats the container and allows equilibrium to be reached at constant temperature. The total gas volume does not change.
- The equilibrium mixture contains 9.36×10^{-2} mol CH_4 and 0.168 mol C_2H_2.

(i) Calculate the amount, in mol, of H_2 in the equilibrium mixture.

amount of H_2 = ... mol **[1]**

(ii) Calculate the equilibrium constant, K_c, at this temperature, including units.

Give your answer to **three** significant figures.

K_c = ... units .....**[3]**

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(iii) Calculate the amount, in mol, of CH_4 that the chemist originally added to the container.

amount of CH_4 = ... mol **[1]**

(c) The chemist repeats the experiment three times.
In each experiment the chemist makes **one** change but uses the **same** initial amount of CH_4.

Complete the table to show the predicted effect of each change compared with the original experiment.

Only use the words **greater**, **smaller** or **same**.

Change	K_c	Equilibrium amount of $C_2H_2(g)$/mol	Initial rate
The container is heated at constant pressure			
A smaller container is used			
A catalyst is added to CH_4 at the start			

[3]

(d) In this manufacture of ethyne, hydrogen is also produced. To improve the atom economy of the process, it is important to make use of the hydrogen. For example, hydrogen can be used in the extraction of some metals from their ores.

State **two** other large-scale uses of the hydrogen.

1 .....

2 .....

[1]

[Total: 10]

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4 A student carries out an initial rates investigation on the reaction below.

$$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$$

From the results, the student determines the rate equation for this reaction:

$$\text{rate} = k\,[I^-(aq)]^2\,[IO_3^-(aq)]\,[H^+(aq)]^2$$

(a) (i) What is the overall order of reaction?

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

(ii) A proposed mechanism for this reaction takes place in several steps.

Suggest **two** reasons why it is unlikely that this reaction could take place in one step.

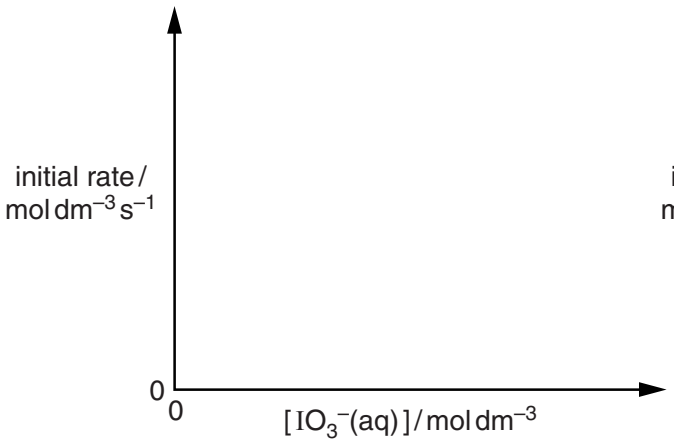
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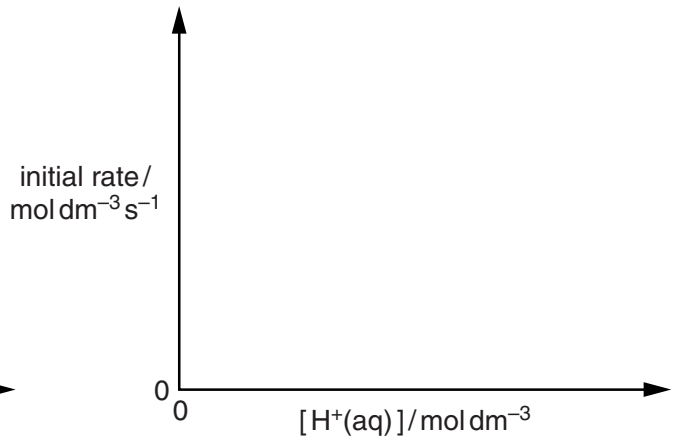
.....

.....

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

(b) On the rate–concentration graphs below, sketch lines to show the relationship between initial rate and concentration for $IO_3^-(aq)$ and $H^+(aq)$.





[2]

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(c) The table below shows some of the student's results.

(i) Complete the table by adding the missing initial rates in the boxes.

	$[I^-(aq)]$ / mol dm^{-3}	$[IO_3^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
Experiment 1	0.015	0.010	0.020	0.60
Experiment 2	0.045	0.010	0.020	
Experiment 3	0.060	0.040	0.080	

[2]

(ii) Calculate the rate constant, k, for this reaction. Include units.

Give your answer to **two** significant figures.

k = ... units .....**[3]**

(iii) The student repeats Experiment 1 using 0.020 mol dm^{-3} methanoic acid, HCOOH(aq) (pK_a = 3.75), instead of 0.020 mol dm^{-3} HCl(aq) as a source of H^+(aq).

Determine the initial rate in this experiment. Show your working.

initial rate = ... mol dm^{-3} s^{-1} **[3]**

[Total: 13]

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5 Elements in the d-block of the Periodic Table form ions that combine with ligands to form complex ions. Most d-block elements are also classified as transition elements.

(a) Explain why two of the Period 4 d-block elements (Sc–Zn) are **not** also transition elements.

In your answer you should link full electron configurations to your explanations.

.....

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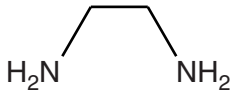
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.....

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

(b) The cobalt(III) ion, Co^{3+}, forms a complex ion **A** with two chloride ligands and two ethanediamine, $H_2NCH_2CH_2NH_2$, ligands.

The structure of ethanediamine is shown below.



(i) Explain how ethanediamine is able to act as a bidentate ligand.

.....

.....

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

(ii) Write the formula of complex ion **A**.

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

(iii) What is the coordination number of cobalt in complex ion **A**?

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

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(iv) Complex ion **A** has *cis* and *trans* stereoisomers. One of these stereoisomers also has an optical isomer.

Draw 3-D diagrams to show the three stereoisomers.

[3]

Question 5 continues on page 12

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(c) The equilibrium reaction for the transport of oxygen by haemoglobin (Hb) in blood can be represented as **equation 5.1**.

$$Hb(aq) + O_2(aq) \rightleftharpoons HbO_2(aq) \qquad \textbf{equation 5.1}$$

(i) Explain how ligand substitution reactions allow haemoglobin to transport oxygen in blood.

.....

.....

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

(ii) Write an expression for the stability constant, K_{stab}, for the equilibrium involved in the transport of oxygen by haemoglobin.

Use the simplified species in **equation 5.1**.

[1]

(iii) In the presence of carbon monoxide, less oxygen is transported in the blood.

Suggest why, in terms of bond strength and stability constants.

.....

.....

.....

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

[Total: 18]

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6 Ethanoic acid, CH_3COOH, is a weak Brønsted–Lowry acid.

(a) An acid–base equilibrium is set up when ethanoic acid is added to water.

Write the equation for the equilibrium that would be set up and label the two conjugate acid–base pairs.

..... + ... $\rightleftharpoons$ ..... + ...

....

[2]

(b) An aqueous solution of CH_3COOH has a pH of 3.060.
This solution contains both hydrogen ions and hydroxide ions.

(i) How can an aqueous solution of an acid contain hydroxide ions?

.....

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

(ii) Calculate the concentration of hydroxide ions in this solution of ethanoic acid.

concentration of hydroxide ions = ... $mol\,dm^{-3}$ **[2]**

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(c) A student adds an excess of aqueous ethanoic acid to solid calcium carbonate.
The resulting solution is able to act as a buffer solution.

(i) Write a full equation for the reaction between ethanoic acid and solid calcium carbonate.

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

(ii) Explain why this buffer solution has formed.

.....

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

(iii) Explain how this buffer solution controls pH when either an acid or an alkali is added.



In your answer you should explain how the equilibrium system allows the buffer solution to control the pH.

.....

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..... **[5]**

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(d) A biochemist plans to make up a buffer solution with a pH of 5.000.
The biochemist adds solid sodium ethanoate, CH_3COONa, to 400 cm^3 of 0.200 $mol\,dm^{-3}$ ethanoic acid.
K_a for ethanoic acid = $1.75 \times 10^{-5}\,mol\,dm^{-3}$

Calculate the mass of sodium ethanoate that the biochemist needs to dissolve in the ethanoic acid to prepare this buffer solution.

Assume that the volume of the solution remains constant at 400 cm^3 on dissolving the sodium ethanoate.

[5]

[Total: 17]

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7 Electrochemical cells contain two redox systems, one providing electrons and the other accepting electrons. The tendency to lose or gain electrons is measured using values called standard electrode potentials.

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

Include all standard conditions in your answer.

.....

.....

.....

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

(b) The table below shows two redox systems and their standard electrode potentials, $E^{\ominus}$.

Redox system	$E^{\ominus}$ / V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Ag^{+}(aq) + e^- \rightleftharpoons Ag(s)$	+0.80

A standard $Cu^{2+}(aq)/Cu(s)$ half-cell is connected to a standard $Ag^{+}(aq)/Ag(s)$ half-cell. The potential of the cell is measured.

Water is then added to the $Cu^{2+}(aq)/Cu(s)$ half-cell. This changes the position of equilibrium in the half-cell. The cell potential increases.

(i) Write down the equation for the overall cell reaction.

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

(ii) Explain, in terms of equilibrium, why the cell potential increases.

.....

.....

.....

.....

.....

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

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(c) Hydrogen fuel cells are being developed for powering vehicles.

(i) State **one** advantage of using hydrogen as a fuel compared with conventional fuels.

.....

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

(ii) In vehicles, hydrogen can be stored on the surface of a solid material or within a solid material.

State **one** other way that hydrogen can be stored as a fuel for vehicles.

.....

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

(d) Aluminium–oxygen cells are being investigated for powering vehicles.

The **reactions** at each electrode are shown below.

$$Al(s) + 4OH^-(aq) \longrightarrow Al(OH)_4^-(aq) + 3e^-$$

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

(i) The standard electrode potential for the O_2/OH^- redox system is +0.40 V.
The standard cell potential of an aluminium–oxygen cell is 2.71 V.

What is the standard electrode potential of the aluminium redox system in this cell?

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

(ii) Construct the overall cell equation for an aluminium–oxygen cell.

[2]

[Total: 11]

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8 A student carries out an investigation to prepare and analyse a sample of barium ferrate(VI), $BaFeO_4$. The steps in the investigation are shown below.

Step 1

The student adds solid iron(III) oxide to a hot aqueous solution containing an excess of hydroxide ions. The student bubbles chlorine gas through the mixture.
A solution forms containing aqueous ferrate(VI) ions, $FeO_4^{2-}(aq)$, and aqueous chloride ions.

Step 2

The student adds aqueous barium chloride to the resulting solution.
A precipitate of impure barium ferrate(VI) forms.
The precipitate is filtered, washed with distilled water and dried.
The student obtains 0.437 g of impure solid barium ferrate(VI).

Step 3

An excess of acidified aqueous potassium iodide is added to the solid from **step 2**.
The $BaFeO_4$ reacts as shown below, and the impurity does not react. A solution forms containing aqueous iodine, $I_2(aq)$.

$$BaFeO_4(s) + 8H^+(aq) + 3I^-(aq) \longrightarrow Fe^{3+}(aq) + Ba^{2+}(aq) + 1\tfrac{1}{2}I_2(aq) + 4H_2O(l)$$

Step 4

The student determines the amount of I_2 formed by carrying out a titration with aqueous sodium thiosulfate, $Na_2S_2O_3(aq)$.

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

26.4 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3(aq)$ are required to reach the end point.

(a) Construct an equation for the oxidation of iron(III) oxide (**step 1**).

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

(b) Write an **ionic** equation for the formation of barium ferrate(VI) (**step 2**).

Include state symbols.

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

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(c) In **step 3**, what is the reducing agent?

Explain your answer in terms of electrons.

reducing agent .....

explanation .....

.....

.....

[2]

(d) The solid sample of barium ferrate(VI) obtained in step 2 is impure.

Determine the percentage, by mass, of barium ferrate(VI) in the 0.437 g of solid formed in **step 2**.

Give your answer to **one** decimal place.

percentage of barium ferrate(VI) = ... % **[4]**

Question 8 continues on page 20

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(e) When the solution is not alkaline, ferrate(VI) ions react with water.
The reaction forms a gas with a density of 1.333×10^{-3} g cm^{-3}, measured at room temperature and pressure, and an orange–brown precipitate.

- Determine the formulae of the gas and the precipitate.
- Write an equation for the reaction that takes place.

gas .....

precipitate .....

equation

.....

[3]

[Total: 12]

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

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

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GCE

Chemistry A

Unit **F325:** Equilibria, Energetics and Elements

Advanced GCE

Mark Scheme for June 2014

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Annotations available in Scoris

Annotation	Meaning
BP	Blank Page – this annotation must be used on all blank pages within an answer booklet (structured or unstructured) and on each page of an additional object where there is no candidate response.
BOD	Benefit of doubt given
CON	Contradiction
	Incorrect response
ECF	Error carried forward
I	Ignore
NAQ	Not answered question
NBOD	Benefit of doubt not given
POT	Power of 10 error
^	Omission mark
RE	Rounding error
SF	Error in number of significant figures
	Correct response

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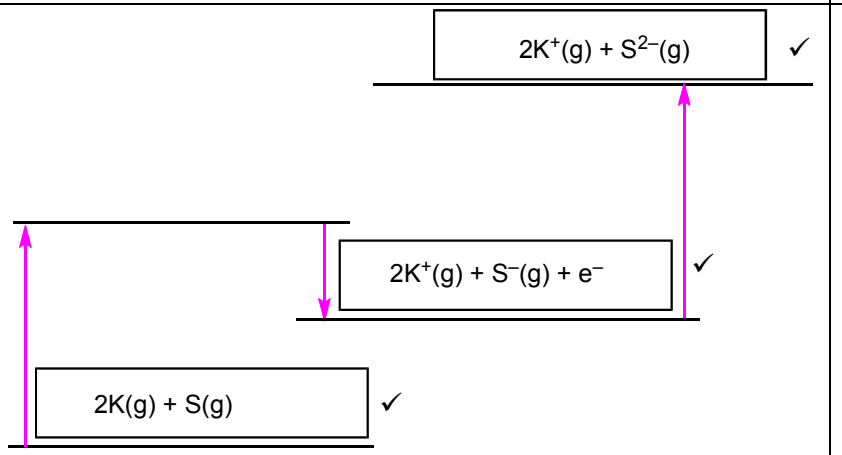
Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

The following questions should be marked using **ALL** appropriate annotations to show where marks have been awarded in the body of the text:

1(b),
2(b),
3(b)(ii),
4(c)(iii),
5(a),
5(b)(iv),
6c(iii),
6(d),
7(b)(ii)
8(d)

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Question			Answer	Marks	Guidance
1	(a)	(i)		3	Mark each marking point independently Correct species **AND** state symbols required for each mark For S^{2-}, **DO NOT ALLOW** S^{-2} For e^-, **ALLOW** e For e^- **only**, **IGNORE** any state symbols added **ALLOW** k and s *It can be very difficult distinguishing K from k; S from s*

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1	**(a)**	**(ii)**	(The enthalpy change that accompanies) the **formation** of **one mole** of a(n ionic) compound from its **gaseous ions** (under standard conditions) ✓✓ Award marks as follows. **1st mark: formation** of **compound** from **gaseous ions** **2nd mark: one mole** for compound **only** **DO NOT ALLOW** 2nd mark without 1st mark Note: A definition for enthalpy change of **formation** will receive **no** marks	**2**	**IGNORE** 'Energy needed' **OR** 'energy required' **ALLOW one mole** of compound is **formed/made** from its **gaseous ions** **ALLOW** as alternative for compound: lattice, crystal, substance, solid **IGNORE**: $2K^+(g) + S^{2-}(g) \longrightarrow K_2S(s)$ (question asks for words) **ALLOW** 1 mark (special case) for absence of 'gaseous' only, i.e. the **formation** of **one mole** of a(n ionic) compound from its **ions** (under standard conditions) ✓

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1	(a)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –2116 (kJ mol^{-1}) award 2 marks** --- –381 – (2 × +89 + 279 + 2 × +419 –200 + 640) ✓ –381 – 1735 = – 2116 ✓ (kJ mol^{-1})	**2**	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. **See list below for marking of answers from common errors** --- **ALLOW** for 1 mark **ONE** mistake with sign **OR** use of 2: –2027 (**2** × 89 not used for K) –1697 (**2** × 419 not used for K) –2516 (+200 rather than –200 for S 1st electron affinity) (+)2116 (wrong sign) –1354 (+381 instead of –381) (+)1354 (+1735 instead of –1735) –836 (–640 instead of +640) –1558 (–279 instead of +279) –1760 (–2 × 89 instead of +2 x 89) –439 (–2 × 419 instead of +2 x 419) –2120 (rounded to 3SF) **For other answers**, check for a **single** transcription error or calculator error which could merit 1 mark **DO NOT ALLOW** any other answers, e.g. –1608 (2 errors: **2** × 89 and **2 x** 419 not used for K) –846 (3 errors:)

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1	(b)		Lowest melting point **KI** **RbC*l*** Highest melting point **NaBr** Correct order ✓ **Mark 2nd and 3rd marking points independently** **Attraction and ionic size linked:** Greater attraction from smaller ions/closer ions/larger charge density ✓ *Comparison needed* **Energy AND attraction/breaking bonds linked:** More **energy**/**heat** to overcome attraction (between ions) **OR** More **energy**/**heat** to break (ionic) bonds ✓	**3**	***FULL ANNOTATIONS MUST BE USED*** **----------** **ORA** throughout Response must clearly refer to **ions** for explanation marks **2nd and 3rd marking point must be comparative** **DO NOT ALLOW incorrect named particles, e.g.** 'atoms', 'molecules', Na, Cl, Cl_2, 'atomic', etc **DO NOT ALLOW** responses using nuclear size or attraction **DO NOT ALLOW** responses linked with **loss** of electrons **IGNORE** larger **electron** density **ALLOW** smaller **sum** of radii gives a greater ionic attraction **IGNORE** NaBr has greater ionic attraction **IGNORE** NaBr has smallest ionic radius (*not focussing on size of **each** ion*) **ASSUME** bonds broken are ionic unless otherwise stated **DO NOT ALLOW incorrect named particles, e.g.** 'atoms', 'molecules', Na, Cl, Cl_2, 'atomic', etc **Note**: Comparison for energy **only** *(i.e. link between more energy and breaking bonds/overcoming attraction)*
			Total	**10**	

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Question			Answer	Marks	Guidance
2	(a)	(i)	(entropy) decreases **AND** (solid/ice has) less disorder/ more order/ fewer ways of arranging energy/ less freedom/ less random molecules ✓	1	**ORA** **decreases and reason required for mark** **ASSUME change is for freezing of water unless otherwise stated** **DO NOT ALLOW** atoms are more ordered
2	(a)	(ii)	(entropy) increases **AND** (CO_2) **gas** is **formed** ✓ *Could be from equation with $CO_2(g)$*	1	**increases and reason required for mark** **ASSUME** gas is CO_2 unless otherwise stated **BUT DO NOT ALLOW** an incorrect gas (e.g. H_2) **ALLOW** more gas
2	(a)	(iii)	entropy decreases **AND** 3 mol O_2 form 2 mol O_3 **OR** $3O_2 \rightarrow 2O_3$ **OR** 3 mol gas form 2 mol gas ✓	1	**decreases and reason required for mark** For mol, **ALLOW** molecules **ALLOW** multiples, e.g. $1½O_2 \rightarrow O_3$; $O_2 + ½O_2 \rightarrow O_3$ **ALLOW** $O_2 + O \rightarrow O_3$ **Note: DO NOT ALLOW** 2 mol gas forms 1 mol gas unless linked to $O_2 + O \rightarrow O_3$ **IGNORE** reaction forms fewer moles/molecules

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2	(b)		**CARE: responses involve changes of negative values** --- **Feasibility AND ΔG** Reaction becomes/is less feasible/not feasible **AND** ΔG increases **OR** ΔG becomes/is less negative/more positive **OR** $\Delta G > 0$ **OR** $\Delta H - T\Delta S > 0$ **OR** $\Delta H - T\Delta S$ becomes/is less negative/more positive **OR** $\Delta H > T\Delta S$ ✓ **OR** $T\Delta S$ becomes/is more negative than ΔH ✓ --- **Effect on $T\Delta S$** $T\Delta S$ becomes more negative **OR** $T\Delta S$ decreases **OR** $-T\Delta S$ becomes more positive **OR** $-T\Delta S$ increases **OR magnitude** of $T\Delta S$ increases **OR** $\lvert T\Delta S \rvert$ increases ✓ ---	**2**	***FULL ANNOTATIONS MUST BE USED*** --- As alternative for 'less feasible' **ALLOW 'less** spontaneous' **OR** a comment that implies 'reaction no longer take place' **ALLOW for ΔG increases** $\Delta G < 0$ **only** at low T **DO NOT ALLOW** $T\Delta S > \Delta H$ (*comparison wrong way round*) **NOTE: Last statement automatically scores 2nd mark ALSO** **IGNORE** significance **IGNORE** magnitude for 1st marking point --- **DO NOT ALLOW** $T\Delta S$ increases **IGNORE** significance --- ***APPROACH BASED ON TOTAL ENTROPY:*** **Feasibility with increasing temperature** Reaction becomes less feasible/not feasible **AND** $\Delta S - \Delta H/T$ **OR** ΔS_{total} decreases/ less positive ✓ **Effect on $\Delta H/T$** $\Delta H/T$ is less negative **OR** $\Delta H/T$ increases **OR** $-\Delta H/T$ decreases **OR** magnitude of $\Delta H/T$ decreases ✓

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2	(c)	(i)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 75.962 **OR** 75.96 **OR** 76.0 **OR** 76, award **2 marks** --- $\Delta S = (33 + 3 \times 189) - (76 + 3 \times 131)$ $= (+)131$ (J K^{-1} mol^{-1}) ✓ $\Delta G = 115 - (298 \times 0.131)$ = (+) 75.962 **OR** 75.96 **OR** 76.0 **OR** 76 (kJ K^{-1} mol^{-1}) ✓	**2**	**DO NOT ALLOW** –131 **ALLOW ECF** from incorrect calculated value of ΔS
2	(c)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 878 **OR** 877.9 **OR** 877.86, award **2 marks** --- (Minimum temperature when) $\Delta G = 0$ **OR** $\Delta H - T\Delta S = 0$ **OR** (For feasibility) $\Delta G = 0$ **OR** $\Delta G < 0$ **OR** $\Delta H - T\Delta S < 0$ **OR** $T = \frac{\Delta H}{\Delta S}$ ✓ $T = \frac{115}{0.131} = 878$ K ✓	**2**	**ALLOW** total entropy statement: ΔS(total) = 0 **OR** ΔS(total) >0 **ALLOW ECF** from incorrect calculated value of ΔS from **2(c)(i)** **ALLOW** 878 up to calculator value of 877.862595 correctly rounded
			Total	**9**	

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Question			Answer	Marks	Guidance
3	(a)		$(K_c =) \frac{[C_2H_2]\,[H_2]^3}{[CH_4]^2}$ ✓	1	Square brackets are **essential** State symbols **not** required. **IGNORE** incorrect state symbols
3	(b)	(i)	amount of $H_2 = 3 \times 0.168$ $= 0.504$ (mol) ✓	1	

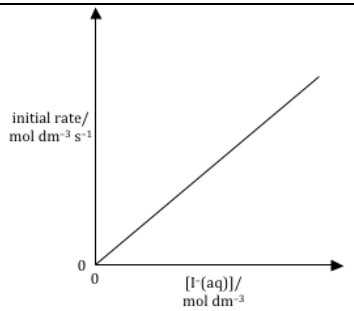
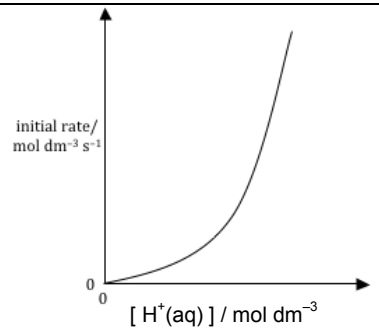
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3	(b)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 0.153 $mol^2\ dm^{-6}$, award **3 marks** **IF** answer = 0.153 with incorrect units, award **2 marks** --- **IF answer from 3(b)(i) for $n(H_2) \neq 0.504$, mark by ECF.** **Equilibrium concentrations** (from $n(H_2)$ = 0.504 mol dm^{-3}) $[CH_4] = 2.34 \times 10^{-2}$ (mol dm^{-3}) **AND** $[C_2H_2] = 4.20 \times 10^{-2}$ (mol dm^{-3}) **AND** $[H_2]$ = 0.126 (mol dm^{-3}) ✓ **Calculation of K_c and units** $K_c = \frac{4.20\times10^{-2}\times(0.126)^3}{(2.34\times10^{-2})^2}$ = 0.153 ✓ $mol^2\ dm^{-6}$ ✓ **3 significant figures** are required	**3**	***FULL ANNOTATIONS MUST BE USED*** --- **IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ALLOW** ÷ by 4 of equilibrium amounts in all expressions, i.e. **ALLOW** $[CH_4] = \frac{9.36\times10^{-2}}{4}$ mol dm^{-3} **AND** $[C_2H_2] = \frac{0.168}{4}$ mol dm^{-3} **AND** $[H_2] = \frac{0.504}{4}$ mol dm^{-3} ✓ **ALLOW ECF** from incorrect concentrations or from moles From moles: 9.36 $\times 10^{-2}$, 0.168 and 0.504, K_c = 2.45 by **ECF** **ALLOW** $dm^{-6}\ mol^2$ **DO NOT ALLOW** mol^2/dm^6 **ALLOW ECF** from incorrect K_c expression for both calculation and units --- **COMMON ECF** From **3(b)(i)** answer of 0.1404, K_c = 3.32 x 10^{-3} 2 marks + units K_c = 0.0531 No ÷ 4 throughout 1 mark + units
3	(b)	(iii)	**Initial amount of CH_4** amount of $CH_4 = 9.36 \times 10^{-2} + 2 \times 0.168$ = 0.4296 **OR** 0.43(0) (mol) ✓	**1**	**NO ECF** possible (all data given in question)

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3 (c)	<table><tr><th>Change</th><th>K_c</th><th>Equilibrium amount of C_2H_2 / mol</th><th>Initial rate</th></tr><tr><td>temperature increased</td><td>greater</td><td>greater</td><td>greater</td></tr><tr><td>smaller container</td><td>same</td><td>smaller</td><td>greater</td></tr><tr><td>catalyst added</td><td>same</td><td>same</td><td>greater</td></tr><tr><td></td><td>✓</td><td>✓</td><td>✓</td></tr></table>	3	Mark by **COLUMN** **ALLOW** obvious alternatives for greater/smaller/same, e.g. increases/decreases; more/less
3 (d)	**ONE** mark only **USE ONE TICK ONLY** ✓ from **TWO** uses: **1.** fuel cells **2.** manufacture of margarine **OR** hydrogenation of alkenes/unsaturated fats/unsaturated oils/unsaturated molecules **3.** making of ammonia **OR** Haber process **4.** making of HCl/hydrochloric acid **5.** making of methanol	1	**IGNORE** just 'fuel' **IGNORE** hydrogenation of margarine **ALLOW** hydrogenation of fats/oils **DO NOT ALLOW** explosives **OR** fertilisers
	Total	**10**	

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Question			Answer	Marks	Guidance
4	(a)	(i)	5 **OR** 5th (order) ✓	1	
4	(a)	(ii)	(stoichiometry in) rate equation does not match (stoichiometry) in **overall** equation ✓ Collision unlikely with more than 2 ions/species/particles ✓	2	**ALLOW** moles/ions/species/particles/molecules/atoms throughout (*i.e. emphasis on particles)* **IGNORE** more reactants in overall equation **If number of species is stated, ALLOW 3–5 only** *(rate equation contains 5 ions)* **DO NOT ALLOW** negative ions would repel (*there is a mixture of positive and negative ions*) **IGNORE** more than two **reactants** collide (*not related to rate equation*)
4	(b)		 Straight upward line **AND** starting at 0,0 ✓  Curve with increasing gradient, **AND** starting at 0,0 ✓	2	**ALLOW** lines starting close to 0,0 **ALLOW** 2nd order line with 'straight' section early or late as long as an upward curve is seen between.
4	(c)	(i)	5.4(0) ✓ 614.4(0) ✓	2	**IGNORE** sign **ALLOW** 614 **OR** 610

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4	(c)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 6.7×10^8 **OR** 670000000 $dm^{12}\ mol^{-4}\ s^{-1}$, award **3 marks** **IF** answer = 6.7×10^8 **OR** 670000000 with incorrect units, award **2 marks** *k* to >2 SF: 666666666.7 ✓ **OR** *k* to 2 SF: 6.7×10^8 **OR** 670000000 ✓✓ units: $dm^{12}\ mol^{-4}\ s^{-1}$ ✓	**3**	**ALLOW ECF** from incorrect initial rates if 1st experimental results have **not** been used. **(Look to 4(c)(i) to check)** *i.e.* **IF** other rows have been used, then calculate the rate constant from data chosen. For *k*, **ALLOW** 1 mark for the following: 6.6×10^8 recurring 6.6×10^8 2 SF answer for *k* **BUT** one power of 10 out i.e. 6.7×10^9 **OR** 6.7×10^7 **ALLOW** units in any order, e.g. $mol^{-4}\ dm^{12}\ s^{-1}$
4	(c)	(iii)	(K_a =) $10^{-3.75}$ **OR** 1.78×10^{-4} ($mol\ dm^{-3}$) ✓ $[H^+]$ = $\sqrt{1.78\times10^{-4}\times0.0200}$ = 1.89×10^{-3} ($mol\ dm^{-3}$) ✓ initial rate = 6.7×10^8 x 0.01 x 0.015^2 x $(1.89 \times 10^{-3})^2$ = 5.33×10^{-3} to 5.38×10^{-3} ($mol\ dm^{-3}\ s^{-1}$) **OR** 5.3×10^{-3} to 5.4×10^{-3} ($mol\ dm^{-3}\ s^{-1}$) ✓ Actual value will depend on amount of acceptable rounding in steps and whether figures kept in calculator even if rounding is written down. **ALLOW** any value in range given above.	**3**	***FULL ANNOTATIONS MUST BE USED*** **----------** **For ALL marks, ALLOW 2 SF** up to calculator value correctly rounded $1.77827941 \times 10^{-4}$ **ALLOW** $\sqrt{10^{-3.75}\times0.0200}$ for first marking point **ALLOW** 1.88×10^{-3} ($mol\ dm^{-3}$) **ALLOW ECF** from calculated $[H^+(aq)]$ and calculated answer for *k* from **4(c)(ii)** e.g. If no square root taken, $[H^+]$ = 3.56 x 10^{-6} $mol\ dm^{-3}$ and *rate* = 1.91 x 10^{-8} **OR** 1.9 x 10^{-8} by **ECF**
			Total	**13**	

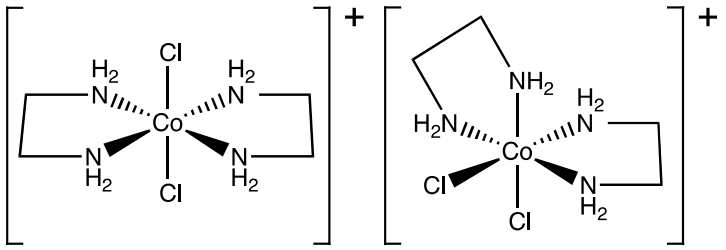
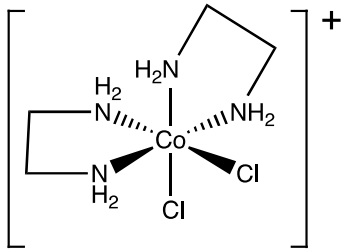
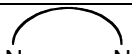
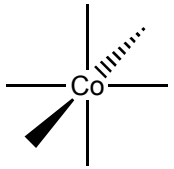
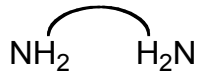
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Question			Answer	Marks	Guidance
5	(a)		(Transition element) has **an ion** with an incomplete/partially-filled d **sub-shell/d-orbital** ✓ Scandium/Sc and zinc/Zn are not transition elements ✓ *Electron configurations of ions* Sc^{3+} **AND** $1s^2 2s^2 2p^6 3s^2 3p^6$ ✓ Zn^{2+} **AND** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ ✓ Sc^{3+} **AND** d **sub-shell** empty **/ d orbital(s) empty** ✓ ***Note**: Sc^{3+} must be the **ONLY** scandium ion shown for this mark* Zn^{2+} **AND** d **sub-shell** full **/ALL d-orbitals** full ✓ ***Note**: Zn^{2+} must be the **ONLY** zinc ion shown for this mark*	**6**	***FULL ANNOTATIONS MUST BE USED*** **----------** **ALLOW** capital 'D' within definition **DO NOT ALLOW** d shell **ALLOW** if **ONLY** Sc and Zn are used to illustrate d block elements that are **NOT** transition elements This can be from anywhere in the overall response in terms of Sc, Sc^{3+}, Zn, Zn^{2+} **OR** incorrect charges, i.e. only Sc^{+}, Sc^{2+}, Zn^{+} In electron configurations, **IF** subscripts **OR** caps used, **DO NOT ALLOW** when first seen but credit subsequently **ALLOW** $4s^0$ in electron configurations **IGNORE** [Ar] **IGNORE** electron configurations for other Sc and Zn ions **ALLOW** for Sc^{3+}: Sc forms a 3+ ion; **ALLOW** Sc^{+3} **ALLOW** for Zn^{2+}: Zn forms a 2+ ion; **ALLOW** Zn^{+2} **ALLOW** Sc^{3+} has no d sub-shell **DO NOT ALLOW** 'd sub-shell is incomplete' *(in definition)* **DO NOT ALLOW** 'd sub-shell is incomplete' *(in definition)*

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5	(b)	(i)	Donates **two** electron/lone pairs to a metal ion **OR** Co^{3+} ✓ ***DO NOT ALLOW*** *metal (complex contains Co^{3+})* Electron/lone pair on N **OR** NH_2 (groups) ✓	**2**	**ALLOW** 'forms **two** coordinate bonds/dative covalent/dative bonds' as an alternative for 'donates **two** electron/lone pairs' *Two is required for 1st marking point* *Two can be implied using words such as 'both' or 'each'* For metal ion, **ALLOW** transition (metal) ion Second mark is for the atom that donates the electron/lone pairs **ALLOW** both marks for a response that communicates the same using N as the focus: e.g. The two N atoms each donate an electron pair to metal ion
5	(b)	(ii)	$[Co(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ ✓	**1**	Square brackets **AND** + charge required **DO NOT ALLOW** any charges included within square brackets **ALLOW** $[Co(C_2H_8N_2)_2Cl_2]^+$ **OR** $[CoC_4H_{16}N_4Cl_2]^+$ **ALLOW** structural **OR** displayed **OR** skeletal formula **OR** mixture of the above (as long as unambiguous) **IGNORE** $[Co(en)_2Cl_2]^+$ *simplifies question* Within formula, **ALLOW** ….$(Cl)_2$, (Cl_2) **ALLOW** CO Within the context of the question, CO is Co
5	(b)	(iii)	6 ✓	**1**	

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5	(b)	(iv)	 ✓ ✓  ✓ Note: For each structure, **ALL** NH_2 groups must be shown **AND** bonding between Co **AND** N of NH_2. For $H_2NCH_2CH_2NH_2$, **ALLOW** C–C without Hs and  --- **IF** NH_2 shown without Hs, e.g.  , penalise first time **ONLY** --- **IF ALL** 3 isomers are 'correct', but 2 x Cl **AND** no Ns, e.g.  **AWARD** 1 mark	**3**	***FULL ANNOTATIONS MUST BE USED*** --- **IGNORE** charges (**anywhere**) and labels (even if wrong) Square brackets **NOT** required Must contain 2 'out wedges', 2 'in wedges' and 2 lines in plane of paper **OR** 4 lines, 1 'out wedge' and 1 'in wedge': For bond into paper, **ALLOW**:  **ALLOW** following geometry throughout:  **TAKE CARE**: structures may be in different orientations. For $H_2NCH_2CH_2NH_2$, **ALLOW**  *(connectivity within 'loop' only)* **If Cl_2s are shown instead of Cl, penalise 1st time only**

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5	(c)	(i)	O_2/oxygen **bonds** to Fe^{2+}/Fe(II) ✓ *Fe^{2+}/Fe(II) essential for 1st marking point* (When required,) O_2 substituted **OR** O_2 released ✓ *Fe^{2+} not required for 2nd marking point (e.g. **IGNORE** Fe)*	**2**	**ASSUME that 'it' refers to oxygen** **ALLOW** O_2 **binds** to Fe^{2+} **OR** O_2 donates electron pair to Fe^{2+} **OR** O_2 is a ligand with Fe^{2+} **IGNORE** O_2 reacts with Fe^{2+} **OR** O_2 is around Fe^{2+} **ALLOW** bond to O_2 breaks when O_2 required **OR** H_2O replaces O_2 **OR** vice versa **ALLOW** CO_2 replaces O_2 **OR** vice versa **ALLOW** O_2 bonds/binds reversibly
5	(c)	(ii)	$(K_{stab} =) \frac{[HbO_2(aq)]}{[Hb(aq)]\,[O_2(aq)]}$ ✓ **ALL Square brackets essential**	**1**	**ALLOW** expression without state symbols (*given in question*)
5	(c)	(iii)	**Both marks require a comparison** Stability constant/K_{stab} value with CO is **greater** (than with complex in O_2) ✓ (Coordinate) bond with CO is **stronger** (than O_2) **OR** CO binds more strongly ✓	**2**	**IGNORE** (complex with) CO is more stable **ALLOW** bond with CO is less likely to break (than O_2) **OR** CO is a stronger ligand (than O_2) **OR** CO has greater affinity for ion/metal/haemoglobin (than O_2) **ALLOW** CO bond formation is irreversible **OR** CO is not able to break away **IGNORE** CO bonds more easily **OR** CO complex forms more easily
			Total	**18**	

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Question			Answer	Marks	Guidance
6	(a)		CH_3COOH + H_2O ⇌ H_3O^+ + CH_3COO^- ✓ Acid 1 Base 2 Acid 2 Base 1 ✓	2	**IGNORE** state symbols (even if incorrect) **ALLOW** 1 **AND** 2 labels the other way around. **ALLOW** 'just acid' and 'base' labels if linked by lines so that it is clear what the acid–base pairs are **ALLOW** A and B for 'acid' and 'base' **IF** proton transfer is wrong way around **ALLOW** 2nd mark for idea of acid–base pairs, *i.e.* CH_3COOH + H_2O ⇌ $CH_3COOH_2^+$ + OH^- ✗ Base 2 Acid 1 Acid 2 Base 1 ✓ **NOTE** For the 2nd marking point (acid–base pairs), this is the **ONLY** acceptable **ECF** *i.e., **NO ECF** from impossible chemistry*
6	(b)	(i)	Water dissociates/ionises **OR** $H_2O \rightleftharpoons H^+ + OH^-$ **OR** $2H_2O \rightleftharpoons H_3O^+ + OH^-$ ✓	1	**ALLOW** $K_w = [H^+]\,[OH^-]$ **OR** $[H^+]\,[OH^-] = 10^{-14}$ ($mol^2\ dm^{-6}$) **IGNORE** breaking for dissociation **IGNORE** water contains H^+ and OH^- **IGNORE** $H_2O \rightarrow H^+ + OH^-$ *i.e. no equilibrium sign* **IGNORE** $2H_2O \rightarrow H_3O^+ + OH^-$ *i.e. no equilibrium sign*

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6	(b)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = 1.15 × 10^{-11}, award 2 marks** --- $[H^+] = 10^{-3.06} = 8.71 \times 10^{-4}$ (mol dm^{-3}) ✓ $[OH^-] = \frac{1.00 \times 10^{-14}}{8.71 \times 10^{-4}} = 1.15 \times 10^{-11}$ (mol dm^{-3}) ✓ **ALLOW** answer to two or more significant figures 2SF: 1.1 × 10^{-11}; 4SF: 1.148 × 10^{-11}; calculator 1.148153621 × 10^{-11}	**2**	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. --- **ALLOW 2 SF:** 8.7 × 10^{-4} up to calculator value of 8.7096359 × 10^{-4} correctly rounded **ALLOW** alternative approach using pOH: pOH = 14 – 3.06 = 10.94 ✓ $[OH^-] = 10^{-10.94} = 1.15 \times 10^{-11}$ (mol dm^{-3}) ✓
6	(c)	(i)	$2CH_3COOH + CaCO_3 \rightarrow (CH_3COO)_2Ca + CO_2 + H_2O$ ✓	**1**	**IGNORE** state symbols **ALLOW** ⇌ provided that reactants on LHS For $CO_2 + H_2O$, **ALLOW** H_2CO_3 **ALLOW** $Ca(CH_3COO)_2$ **ALLOW** $(CH_3COO^-)_2Ca^{2+}$ **BUT DO NOT ALLOW** if either charge is missing or incorrect

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6	**(c)**	**(ii)**	solution contains CH_3COOH **AND** CH_3COO^- ✓	**1**	**ALLOW** names: ethanoic acid for CH_3COOH ethanoate for CH_3COO^- **ALLOW** calcium ethanoate **OR** $(CH_3COO)_2Ca$ for CH_3COO^- **IGNORE** 'acid, salt, conjugate base; responses must identify the acid and conjugate base as ethanoic acid and ethanoate **IGNORE** ethanoic acid is in excess (*in question*) **BUT DO ALLOW** some ethanoic acid is left over/present/some ethanoic acid has reacted **IGNORE** equilibrium: $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ *Dissociation of ethanoic acid only*

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6	(c)	(iii)	**Quality of written communication, QWC** 2 marks are available for explaining how the equilibrium system allows the buffer solution to control the pH on addition of H^+ and OH^- (see below) --- $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ ✓ --- CH_3COOH reacts with added alkali **OR** $CH_3COOH + OH^- \rightarrow$ **OR** added alkali reacts with H^+ **OR** $H^+ + OH^- \rightarrow$ ✓ Equilibrium → right **OR** Equilibrium → CH_3COO^- ✓ (**QWC**) CH_3COO^- reacts with added acid ✓ Equilibrium → left **OR** Equilibrium → CH_3COOH ✓ (**QWC**)	**5**	***FULL ANNOTATIONS MUST BE USED*** **---** **Note: If there is no equilibrium equation then the two subsequent equilibrium marks are not available: max 2** **DO NOT ALLOW** $HA \rightleftharpoons H^+ + A^-$ **DO NOT ALLOW** more than one equilibrium equation. **---** **ALLOW** response in terms of H^+, A^- and HA **IF** more than one equilibrium shown, it **must** be clear which one is being referred to by labeling the equilibria. **ALLOW** weak acid reacts with added alkali **DO NOT ALLOW** acid reacts with added alkali **ALLOW** conjugate base reacts with added acid **DO NOT ALLOW** salt/base reacts with added acid

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6	(d)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = 11.48 OR 11.5 (g), award 5 marks** --- $[H^+] = 10^{-5}$ (mol dm^{-3}) ✓ --- **$[CH_3COO^-]$** = $\frac{1.75 \times 10^{-5}}{10^{-5}}$ ✓ × 0.200 = 0.350 mol dm^{-3} ✓ *n*(**CH_3COONa/CH_3COO^-**) in 400 cm^3 = 0.350 × $\frac{400}{1000}$ = 0.14(0) (mol) ✓ --- mass **CH_3COONa** = 0.140 × 82.0 = 11.48 **OR** 11.5 (g) ✓ For **ECF**, ***n*(CH_3COONa/CH_3COO^-) must** have been calculated in step before	**5**	***FULL ANNOTATIONS MUST BE USED*** --- **IF** there is an alternative answer, check to see if there is any **ECF** credit possible. **Incorrect use of $[H^+] = \sqrt{([CH_3COOH] \times K_a)}$ scores zero** **BUT IGNORE** if an alternative successful method is present **Incorrect use of K_w, 1 max for $[H^+] = 10^{-5}$ (mol dm^{-3})** **BUT IGNORE** if an alternative successful method is present --- **ALLOW** *n*(**CH_3COONa/CH_3COO^-**) = $\frac{1.75 \times 10^{-5}}{10^{-5}}$ ✓ × 0.08 = 0.14(0) (mol) ✓✓ **Note: There is no mark just for** *n*(**CH_3COOH**) in 400 cm^3 = 0.200 × $\frac{400}{1000}$ = 0.08 (mol) --- As alternative for the 4th and 5th marks, **ALLOW**: mass of CH_3COONa in 1 dm^3 = 0.350 × 82.0 = 28.7 g ✓ mass of CH_3COONa in 400 cm^3 = 28.7 × $\frac{400}{1000}$ = 11.48 g ✓ --- **COMMON ECF** 4.592 **OR** 4.6 g **AWARD** 4 marks *use of 400/1000 twice*

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					ALLOW variants of Henderson–Hasselbalch equation. $pK_a = -\log(1.75 \times 10^{-5}) = 4.757$ ✓ *Calc: 4.75696…..* $\log \frac{[CH_3COO^-]}{[CH_3COOH]} = pH - pK_a = 5 - 4.757 = 0.243$ $\frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{0.243} = 1.75$ ✓ $[CH_3COO^-] = 1.75 \times 0.200 = 0.350$ mol dm^{-3} ✓ *n*(**CH_3COONa/CH_3COO^-**) in 400 cm^3 $= 0.350 \times \frac{400}{1000} = 0.14(0)$ (mol) ✓ --- mass **CH_3COONa** = 0.140 × 82.0 = 11.48 **OR** 11.5 (g) ✓
			Total	**17**	

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Question			Answer	Marks	Guidance
7	(a)		**Definition** The e.m.f. (of a half-cell) compared with/connected to a (standard**)** hydrogen half-cell/(standard**)** hydrogen electrode ✓ **Standard conditions** *Units essential* Temperature of 298 K / 25ºC **AND** (solution) concentrations of 1 mol dm^{-3} **AND** pressure of 100 kPa **OR** 10^5 Pa **OR** 1 bar ✓	**2**	As alternative for e.m.f., **ALLOW** voltage **OR** potential difference **OR** p.d. **OR** electrode potential **OR** reduction potential **OR** redox potential **ALLOW** /(standard) hydrogen cell **IGNORE** S.H.E. (as abbreviation for standard hydrogen electrode) **ALLOW** 1M **DO NOT ALLOW** 1 mol **ALLOW** 1 atmosphere/1 atm **OR** 101 kPa **OR** 101325 Pa
7	(b)	(i)	$2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$ ✓	**1**	State symbols **not** required **ALLOW** ⇌ provided that reactants on LHS
7	(b)	(ii)	**Assume Cu^{2+}|Cu OR Cu half cell unless otherwise stated.** $[Cu^{2+}]$ decreases **OR** < 1 mol dm^{-3} **AND** Equilibrium (shown in table) shifts to left ✓ more electrons are released by Cu ✓ The cell has a bigger **difference** in *E* ✓	**3**	***FULL ANNOTATIONS MUST BE USED*** --- **ALLOW** $[Cu^{2+}]$ less than standard concentration/1 mol dm^{-3} **DO NOT ALLOW** water reacts with Cu^{2+} **OR** Cu **ALLOW** *E* (for Cu^{2+}|Cu) is less positive / more negative /decreases **IGNORE standard** electrode potential (*Cell no longer standard*) **IGNORE** $E^{\ominus}$ decreases **CARE** **DO NOT ALLOW** statements about silver *E* changing (**CON**) **IGNORE** just 'cell potential increases' (in the question) *The final mark is more subtle and is a consequence of the less positive E value of the copper half cell*

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7	(c)	(i)	no/less CO_2 **OR** H_2O is **only** product **OR** greater efficiency ✓	1	**IGNORE** less pollution **IGNORE** less carbon emissions **IGNORE** less fossil fuels used **IGNORE** no/less greenhouse gas **OR** no global warming (*H_2O vapour is a greenhouse gas)*
7	(c)	(ii)	liquefied/as a liquid **AND** under pressure/pressurised ✓	1	**IGNORE** adsorption or absorption **IGNORE** low temperature **DO NOT ALLOW** liquidise *processes are described in the question*
7	(d)	(i)	E = –2.31 (V) ✓	1	– sign **AND** 2.31 **required** for the mark
7	(d)	(ii)	$4Al(s) + 4OH^-(aq) + 3O_2(g) + 6H_2O(l) \rightarrow 4Al(OH)_4^-(aq)$ species ✓ balance ✓	2	**IGNORE** state symbols **ALLOW** multiples **ALLOW** 1 mark for an equation in which OH^- are balanced but have not been cancelled, e.g. $4Al(s) + 16OH^-(aq) + 3O_2(g) + 6H_2O(l) \rightarrow 4Al(OH)_4^-(aq) + 12OH^-(aq)$ **ALLOW** 1 mark if charge on $Al(OH)_4$ is omitted, i.e $4Al(s) + 4OH^-(aq) + 3O_2(g) + 6H_2O(l) \rightarrow 4Al(OH)_4(aq)$ **ALLOW** 1 mark for an 'correct equation' reversed, i.e. $4Al(OH)_4^-(aq) \rightarrow 4Al(s) + 4OH^-(aq) + 3O_2(g) + 6H_2O(l)$
			Total	11	

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Question			Answer	Marks	Guidance
8	(a)		$Fe_2O_3 + 3Cl_2 + 10OH^- \rightarrow 2FeO_4^{2-} + 6Cl^- + 5H_2O$ ✓✓ First mark for all 6 species Second mark for balancing	2	**ALLOW** multiples **ALLOW** oxidation half equation for two marks $Fe_2O_3 + 10OH^- \rightarrow 2FeO_4^{2-} + 5H_2O + 6e^-$ Correct species would obtain 1 mark – *question: equation for oxidation* **ALLOW variants forming H^+ for 1 mark, e.g:** $Fe_2O_3 + 3Cl_2 + 5OH^- \rightarrow 2FeO_4^{2-} + 6Cl^- + 5H^+$ $Fe_2O_3 + 3Cl_2 + 5OH^- \rightarrow 2FeO_4^{2-} + 5HCl + Cl^-$
8	(b)		$Ba^{2+}(aq) + FeO_4^{2-}(aq) \rightarrow BaFeO_4(s)$ ✓	1	Balanced **ionic** equation **AND** state symbols required **DO NOT ALLOW** +2 or –2 for ionic charges
8	(c)		**Reason can ONLY be correct from correct reducing agent** **----------** ***reducing agent***: I^- **OR** KI ✓ I^- adds/donates/loses electrons **AND** to FeO_4^{2-} **OR** to $BaFeO_4$ **OR** to Fe(VI) or to Fe(+6) ✓ ***ALLOW** Fe(6+) **OR** Fe^{6+}*	2	**IGNORE** H^+ **OR** acidified **ALLOW** iodide/potassium iodide but **DO NOT ALLOW** iodine **ALLOW** I^- loses electrons **AND** to form I_2 **ALLOW** Fe(6+) **OR** Fe^{6+}

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8	(d)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 51.8%, award **4 marks.** --- $n(S_2O_3^{2-})$ used = $0.1000 \times \frac{26.4}{1000} = 2.64 \times 10^{-3}$ (mol) ✓ $n(FeO_4^{2-}) = ½ \times 2/3 \times 2.64 \times 10^{-3} = 8.8(0) \times 10^{-4}$ (mol) ✓ Mass $BaFeO_4$ in sample $= 8.8 \times 10^{-4} \times 257.1$ g = 0.226248 g ✓ % purity = $\frac{0.226248}{0.437} \times 100 = 51.8\%$ ✓ **MUST** be to **one** decimal place (in the question) --- As an alternative for the final two marks, **ALLOW**: Theoretical amount of $BaFeO_4 = \frac{0.437}{257.1} = 0.00170$ (mol) ✓ % purity = $\frac{8.8 \times 10^{-4}}{1.70 \times 10^{-3}} \times 100 = 51.8\%$ ✓	**4**	***FULL ANNOTATIONS MUST BE USED*** --- For alternative answers, look first at common **ECFs** below. Then check for **ECF** credit possible using working below **IF** a step is omitted but subsequent step subsumes previous, then award mark for any missed step --- **Working must be to at least 3 SF throughout until final % mark** **BUT** ignore trailing zeroes, ie for 0.880 allow 0.88 **ECF** answer above × ½ × 2/3 This mark may be seen in 2 steps via I_2 but the mark is for both steps combined **ECF** 257.1 × answer above **ECF** $\frac{\text{answer above}}{0.437} \times 100$ **ALLOW** 51.7% FROM 0.226 g $BaFeO_4$ (earlier rounding) --- **Common ECFs:** No × 2/3 for $n(FeO_4^{2-})$: % purity = 77.7%/77.6% 3 marks No ÷ 2 for $n(FeO_4^{2-})$: % purity = 25.9% 3 marks 24.6 used instead of 26.4: % purity = 48.2% 3 marks

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8	(e)		**gas**: O_2 ✓ **precipitate**: $Fe(OH)_3$ ✓ **equation**: $2FeO_4^{2-} + 5H_2O \rightarrow 1½O_2 + 2Fe(OH)_3 + 4OH^-$ **OR** $2FeO_4^{2-} + H_2O + 4H^+ \rightarrow 1½O_2 + 2Fe(OH)_3$ ✓	**3**	**DO NOT ALLOW** names **IGNORE** a balancing number shown before a formula **ALLOW** $Fe(OH)_3(H_2O)_3$ **ALLOW** multiples **ALLOW** $2FeO_4^{2-} + 11H_2O \rightarrow 1½O_2 + 2Fe(OH)_3(H_2O)_3 + 4OH^-$
			Total	**12**	

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RECOGNISING ACHIEVEMENT

Wednesday 12 June 2013 – Afternoon

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 *

* F 3 1 4 7 5 0 6 1 3 *

Candidate forename		Candidate surname	

Centre number						Candidate number				

INSTRUCTIONS TO CANDIDATES

- The Insert will be found in the centre of 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 pages 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 **24** pages. Any blank pages are indicated.

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Answer **all** the questions.

1 Born–Haber cycles can be used to determine lattice enthalpies of ionic compounds.

(a) Define, in words, the term *lattice enthalpy*.

.....

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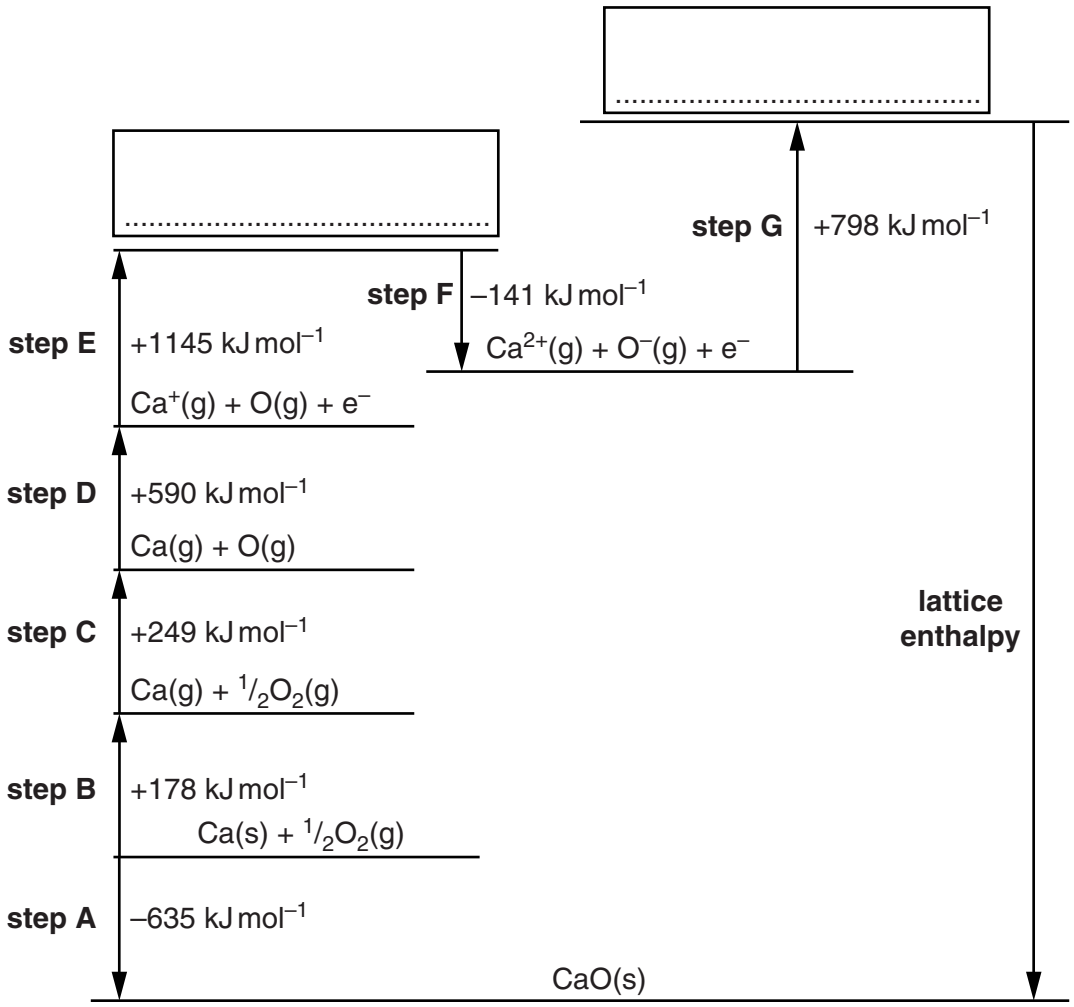
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..... **[2]**

(b) The Born–Haber cycle below can be used to determine the lattice enthalpy of calcium oxide. The cycle includes the values for the enthalpy changes of the steps labelled **A–G**.

(i) Complete the Born–Haber cycle by adding the species present on the two dotted lines.

Include state symbols.



[2]

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(ii) Name the enthalpy changes for the following steps in the Born–Haber cycle.

- **step A**

.....

- **step C**

.....

- **step G**

.....

[3]

(iii) Calculate the lattice enthalpy of calcium oxide.

answer = ... $kJ\,mol^{-1}$ **[2]**

(c) Describe and explain the factors that affect the values of lattice enthalpies.

.....

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

[Total: 12]

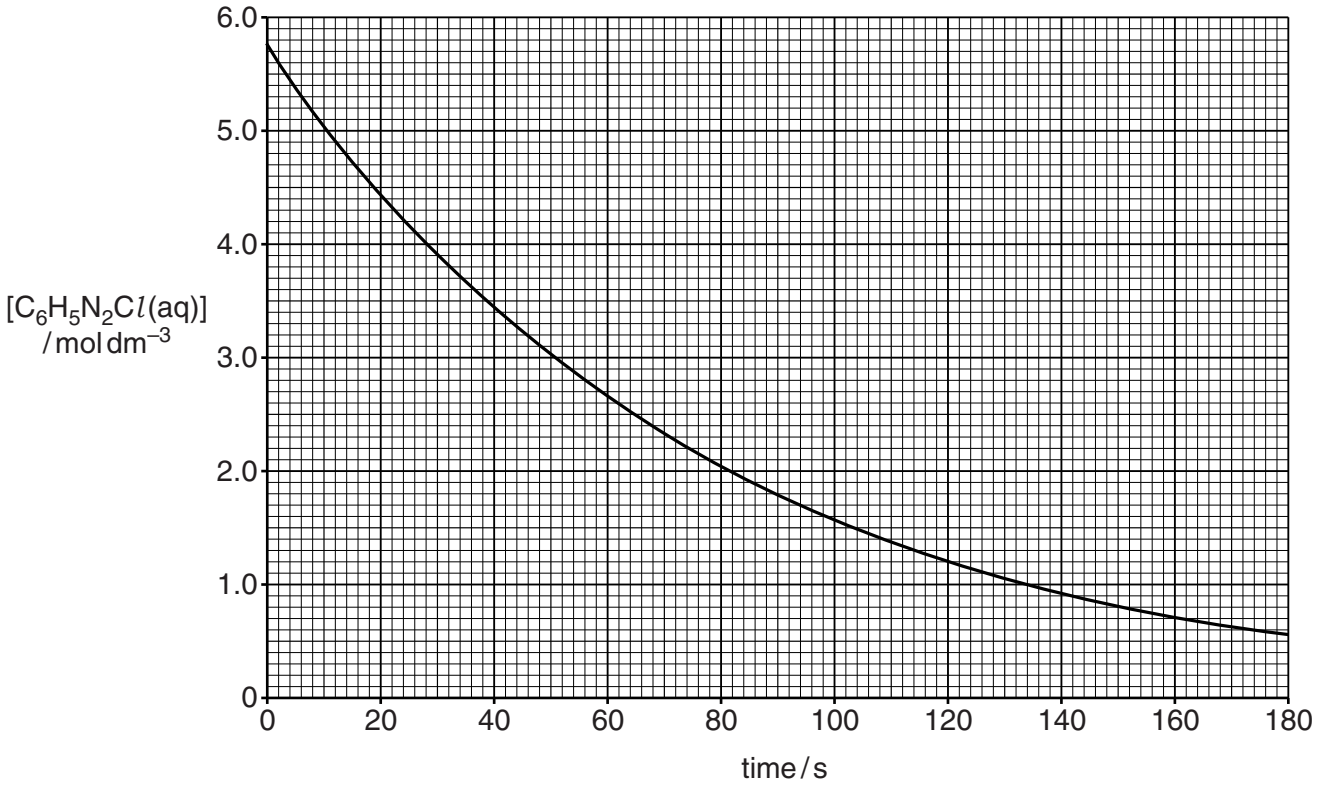
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2 In aqueous solution, benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes above 10 °C.

$$C_6H_5N_2Cl(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

A student investigates the rate of this reaction using an excess of water at 50 °C. The student takes measurements at intervals during the reaction and then plots his experimental results to give the graph shown below.



(a) The student uses half-life to suggest the order of reaction with respect to $C_6H_5N_2Cl$.

(i) What is meant by the *half-life* of a reaction?

.....

.....

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

(ii) Confirm the order of reaction with respect to $C_6H_5N_2Cl$.

Show your working on the graph.

.....

.....

.....

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

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(iii) What would be the effect, if any, on the half-life of this reaction of doubling the initial concentration of $C_6H_5N_2Cl$?

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

(b) The student predicts that the rate equation is: rate = $k[C_6H_5N_2Cl]$.

(i) Using the graph and this rate equation, determine the rate of reaction after 40 s.

Show your working on the graph.

rate = ... units ..... **[3]**

(ii) Calculate the rate constant, k, for this reaction and give its units.

k = ... units ..... **[2]**

(c) The order of this reaction with respect to H_2O is effectively zero.

Explain why.

.....

.....

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

[Total: 10]

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3 Hydrogen and iodine react together in a reversible reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H = -9\,kJ\,mol^{-1}$$

A chemist mixes together 2.00×10^{-3} mol $H_2(g)$ and 4.00×10^{-3} mol $I_2(g)$ in a 1.00 dm^3 container.
The chemist seals the container.
The mixture is heated and left to reach equilibrium.

At equilibrium, the mixture contains 3.00×10^{-4} mol of H_2.

(a) Calculate the equilibrium constant, K_c, including units, if any, for this equilibrium.

Give your answer to **three** significant figures.

K_c = ... units ..... **[5]**

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(b) The chemist repeats the experiment several times. In each experiment, the chemist makes one change.

(i) The chemist uses 3.00×10^{-3} mol $H_2(g)$ instead of 2.00×10^{-3} mol $H_2(g)$.

Predict whether the amounts of $H_2(g)$, $I_2(g)$ and HI(g) in the equilibrium mixture would be greater, smaller or the same as in the original experiment.

Answer by placing ticks in the appropriate boxes of the table below.

	$H_2(g)$	**$I_2(g)$**	**HI(g)**
Greater			
Smaller			
The same			

[2]

(ii) The chemist heats the mixture to a higher temperature at constant pressure.

Explain whether the value of K_c would be greater, smaller or the same.

.....

.....

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

(iii) The chemist increases the pressure of the mixture at constant temperature.

Explain whether the value of K_c would be greater, smaller or the same.

.....

.....

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

[Total: 9]

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4 This question looks at pH values and reactions of acids, bases and buffers.

(a) 0.14 mol dm^{-3} solutions of hydrochloric acid, HC*l*, and chloric(I) acid, HC*l*O (pK_a = 7.43), have different pH values.

Explain why the pH values are different and calculate the pH of 0.14 mol dm^{-3} solutions of HC*l* and HC*l*O to **two decimal places**.

Show any working in calculations.

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..... **[5]**

(b) Aluminium powder is added to aqueous ethanoic acid, CH_3COOH.

Write full and ionic equations for the reaction that takes place.

full equation .....

ionic equation ..... **[2]**

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(c) Calculate the pH of a 0.40 mol dm^{-3} solution of NaOH.

[2]

(d) In biochemistry, buffer solutions based on methanoic acid can be used in the analysis of urine samples.

(i) Explain what is meant by the term *buffer solution*.

Describe how a buffer solution based on methanoic acid can act as a buffer.

In your answer you should explain how the equilibrium system allows the buffer solution to control the pH.

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..... **[7]**

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(ii) A chemist prepares a buffer solution by mixing together the following:

200 cm^3 of 3.20 $mol\,dm^{-3}$ HCOOH ($K_a = 1.70 \times 10^{-4}\,mol\,dm^{-3}$) and
800 cm^3 of 0.500 $mol\,dm^{-3}$ NaOH.

The volume of the buffer solution is 1.00 dm^3.

- Explain why a buffer solution is formed when these two solutions are mixed together.
- Calculate the pH of this buffer solution.

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

.....

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.....

[6]

[Total: 22]

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5 Iron is heated with chlorine to form an orange–brown solid, **A**.

Solid **A** is dissolved in water to form an orange–brown solution, **X**, containing the complex ion $[Fe(H_2O)_6]^{3+}$.

Separate portions of solution **X** are reacted as shown in **Experiments 1–4** below.

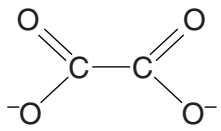
Experiment 1
Aqueous sodium hydroxide is added to solution **X**. An orange–brown precipitate **B** forms.

Experiment 2
Excess zinc powder is added to solution **X** and the mixture is heated. The excess zinc is removed leaving a pale-green solution containing the complex ion **C** and aqueous Zn^{2+} ions.

Experiment 3
An excess of aqueous potassium cyanide, KCN(aq), is added to solution **X**.
The solution turns a yellow colour and contains the complex ion **E**.
E has a molar mass of $211.8\,g\,mol^{-1}$.

Experiment 4
An aqueous solution containing ethanedioate ions, $(COO^-)_2$, is added to solution **X**.
A coloured solution forms containing a mixture of optical isomers **F** and **G**.

The structure of the ethanedioate ion is shown below.



(a) Write an equation for the formation of solid **A**.

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

(b) In **Experiment 1**, write an ionic equation for the formation of precipitate **B**.

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

(c) In **Experiment 2**,

(i) write an equation for the formation of complex ion **C**

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

(ii) state the type of reaction taking place.

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

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(d) In **Experiment 3**,

(i) write an equation for the formation of complex ion **E**

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

(ii) state the type of reaction taking place.

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

(e) In **Experiment 4**, optical isomers **F** and **G** are formed.

Show the 3-D shapes of **F** and **G**.
In your diagrams, show the ligand atoms that are bonded to the metal ions and any overall charges.

[3]

(f) In a separate experiment, iron metal is heated with potassium nitrate, KNO_3, a strong oxidising agent. A reaction takes place and the resulting mixture is poured into water. A dark red solution forms containing ferrate(VI) ions. The ferrate(VI) ion has a 2– charge.

Suggest a possible formula for the ferrate(VI) ion.

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

[Total: 12]

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6 The equation for the reaction of CO_2 and H_2O to produce glucose, $C_6H_{12}O_6$, and O_2 is shown below.

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g) \quad \Delta H = +2879\,kJ\,mol^{-1};\ \Delta S = -256\,J\,K^{-1}\,mol^{-1}$$

Standard entropies are given in the table below.

Substance	$CO_2(g)$	$H_2O(l)$	$O_2(g)$
$S^{\ominus}$ **/ J K^{-1} mol^{-1}**	214	70	205

(a) (i) Calculate the standard entropy of glucose.

$S^{\ominus}$ = ... J K^{-1} mol^{-1} **[2]**

(ii) Calculate ΔG, in kJ mol^{-1}, at 25 °C.

Show all your working.

ΔG = ... kJ mol^{-1} **[2]**

(iii) Explain why this reaction is **not** feasible at **any** temperature.

.....

.....

.....

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

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(b) Although the reaction between CO_2 and H_2O to form $C_6H_{12}O_6$ and O_2 appears not to be feasible, plants are able to make the reaction take place spontaneously by photosynthesis.

Each year, 3.4×10^{18} kJ of solar energy is taken in by all the plants on the Earth to make photosynthesis take place.

Calculate the mass of carbon dioxide that is removed each year from the atmosphere by photosynthesis on Earth.

mass of CO_2 = ... **[2]**

[Total: 7]

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7 Standard electrode potentials for seven redox systems are shown in **Table 7.1**.
You may need to use this information in parts **(a)–(d)** of this question.

Redox system				$E^{\ominus}$ / V
1	$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$	–2.37
2	$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34
3	$Al^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Al(s)$	–1.66
4	$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.77
5	$I_2(aq) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$	+0.54
6	$Cl_2(g) + 2e^-$	$\rightleftharpoons$	$2Cl^-(aq)$	+1.36
7	$ClO^-(aq) + 2H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}Cl_2(g) + H_2O(l)$	+1.63

Table 7.1

(a) Define the term *standard electrode potential*.
Include all standard conditions in your answer.

.....

.....

.....

.....

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

(b) An electrochemical cell can be made based on redox systems **1** and **2**.

Write down the standard cell potential of this cell.

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

(c) Using redox systems **3**, **4** and **5 only** in **Table 7.1**, predict **three** reactions that might be feasible.

(i) Write the overall equation for each predicted reaction.

.....

.....

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

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(ii) Give **two** reasons why it is uncertain whether reactions predicted from $E^{\ominus}$ values may actually take place.

.....

.....

.....

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

(d) In aqueous acid, Cl^-(aq) ions react with ClO^-(aq) ions to form chlorine gas, Cl_2(g).
In aqueous alkali, chlorine gas, Cl_2(g), reacts to form Cl^-(aq) and ClO^-(aq) ions.

Explain this difference.
Use **Table 7.1** to help you with your answer.

.....

.....

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.....

.....

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

(e) In acidic conditions, Sn^{2+} ions react with IO_3^- ions to produce iodine and Sn^{4+} ions.

(i) What is the oxidising agent in this reaction?
Explain your answer.

.....

.....

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

(ii) Construct an equation for this reaction.

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

[Total: 15]

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8 Dimethylglyoxime, DMGH, can be used to analyse nickel(II) compounds.

An excess of a solution of DMGH is added to an acidic solution of a nickel(II) compound. Aqueous ammonia is added which precipitates out a nickel(II) complex, $Ni(DMG)_2$, as a red solid.

A sample of a hydrated nickel(II) salt is analysed using the procedure below.

Step 1
2.50 g of the hydrated nickel(II) salt is dissolved in dilute acid.
An excess of an aqueous solution of DMGH is added.

Step 2
An excess of aqueous ammonia is added and the mixture is heated.
A red precipitate of $Ni(DMG)_2$ forms.

An equation for the reaction is shown below.

$$Ni^{2+}(aq) + 2DMGH(aq) + 2NH_3(aq) \longrightarrow \underset{\textbf{red precipitate}}{Ni(DMG)_2(s)} + 2NH_4^+(aq)$$

Step 3
The red precipitate is filtered, washed with water, dried and then weighed.
The precipitate of $Ni(DMG)_2$ has a mass of 2.57 g.
Assume that all $Ni^{2+}(aq)$ ions have been converted into $Ni(DMG)_2(s)$.
$M[Ni(DMG)_2] = 288.7\,g\,mol^{-1}$.

Step 4
A second 2.50 g sample of the hydrated nickel(II) salt is heated in a crucible to remove the water of crystallisation.
1.38 g of the anhydrous salt remains.

(a) Complete the electron configurations of nickel as the element and in the +2 oxidation state.

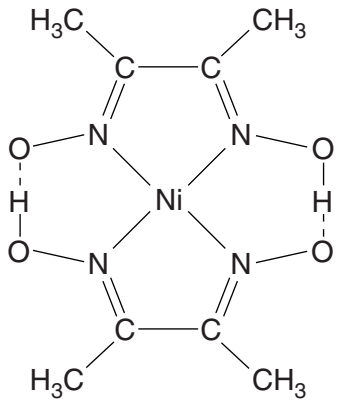
nickel as the element: $1s^2\ 2s^2 2p^6$ .....

nickel in the +2 oxidation state: $1s^2\ 2s^2 2p^6$ ..... **[2]**

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(b) The structure of $Ni(DMG)_2$ is shown below.



(i) State and explain the role of ammonia in **step 2** of this experiment.

.....

.....

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

(ii) State the coordination number of Ni in $Ni(DMG)_2$.

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

(iii) Why does the $Ni(DMG)_2$ complex have no overall charge?

.....

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

(iv) Draw the structure of dimethylglyoxime, DMGH.

[1]

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(c) Determine a possible formula of the hydrated nickel(II) salt.

Your answer **must** show relevant working.

[7]

[Total: 13]

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

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

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OCR
RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

Unit **F325:** Equilibria, Energetics and Elements

Mark Scheme for June 2013

Oxford Cambridge and RSA Examinations

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OCR (Oxford Cambridge and RSA) is a leading UK awarding body, providing a wide range of qualifications to meet the needs of candidates of all ages and abilities. OCR qualifications include AS/A Levels, Diplomas, GCSEs, Cambridge Nationals, Cambridge Technicals, Functional Skills, Key Skills, Entry Level qualifications, NVQs and vocational qualifications in areas such as IT, business, languages, teaching/training, administration and secretarial skills.

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This mark scheme is published as an aid to teachers and students, to indicate the requirements of the examination. It shows the basis on which marks were awarded by examiners. It does not indicate the details of the discussions which took place at an examiners' meeting before marking commenced.

All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

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Annotations

Annotation	Meaning
BOD	Benefit of doubt given
CON	Contradiction
✗	Incorrect response
ECF	Error carried forward
I	Ignore
NAQ	Not answered question
NBOD	Benefit of doubt not given
POT	Power of 10 error
^	Omission mark
RE	Rounding error
SF	Error in number of significant figures
✓	Correct response
...	Noted but no credit given
REP	Repeat

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Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

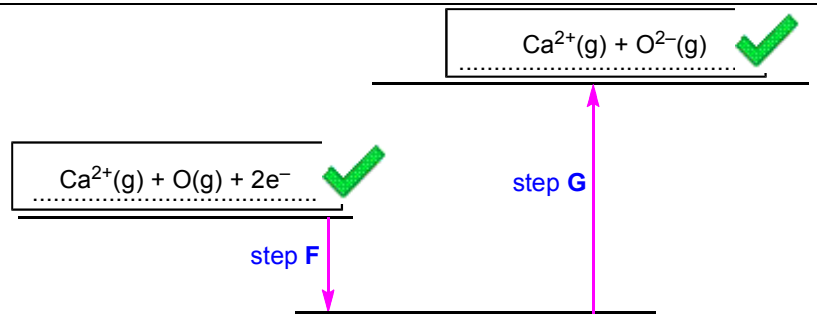
All questions should be annotated with ticks to show where marks have been awarded in the body of the text.

All questions where an ECF has been applied should also be annotated with the ECF annotation.

Use the omission mark where the answer is not sufficient to be awarded a mark.

The following questions should be annotated with full annotation (ie ticks, crosses etc) to show where marks have been awarded in the body of the text: **1(c)**, **3(a), 4(a), 4(d)(i), 4(d)(ii), 7(d), 8(c)**

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Question			Answer	Marks	Guidance
1	(a)		(The enthalpy change that accompanies) the formation of **one mole** of a(n ionic) compound ✓ from its **gaseous ions** (under standard conditions) ✓	2	**IGNORE** 'energy needed' **OR** 'energy required' **ALLOW** as alternative for compound: lattice, crystal, substance, solid **Note:** **1st mark** requires **1 mole** **2nd mark** requires **gaseous ions** **IF** candidate response has '1 mole of gaseous ions', award 2nd mark but **NOT** 1st mark
	(b)	(i)		2	Correct species **AND** state symbols required for both marks $2e^-$ required for left-hand response **ALLOW** e for e^- Mark each marking point independently
		(ii)	(enthalpy change of) formation (of calcium oxide) ✓ (enthalpy change of) atomisation of oxygen ✓ Second electron affinity (of oxygen) ✓	3	calcium oxide **not** required for this mark **DO NOT ALLOW** 'lattice formation' (*confusion with LE*) atomisation **AND** oxygen/O_2/½O_2/O both required (*atomisation of calcium is also in cycle)* **IGNORE** oxygen or oxygen species, e.g. O^- **DO NOT ALLOW** calcium

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Question			Answer	Marks	Guidance
1	(b)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –3454 (kJ mol^{-1}) award 2 marks** --- –635 = 178 + 249 + 590 + 1145 + (–141) + 798 + ΔH_{LE}(CaO) **OR** ΔH_{LE}(CaO) = –635 – [178 + 249 + 590 + 1145 + (–141) + 798] **OR** –635 – 2819 ✓ = –3454 ✓ (kJ mol^{-1})	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. **See list below for marking of answers from common errors** --- 1st mark for expression linking ΔH_{LE}(CaO) with ΔH values **ALLOW** LE for ΔH_{LE} **ALLOW** for 1 mark: –3736 use of +141 instead of –141 (+)3454 all signs reversed (+)2184 wrong sign before 2819 –2184 wrong sign for 635 –1858 wrong sign for +798 Any other number:**CHECK** for **ECF** from 1st marking point Award 1 mark for **one** transcription error only and everything else correct: e.g. +187 instead of +178 **IF** any value has been omitted, award zero

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Question			Answer	Marks	Guidance
1	(c)		**For first 2 marks,** • **IGNORE** nuclear attraction **OR** proton attraction • Property **AND** effect required • **IGNORE** 'atomic' and 'atoms' and 'molecules' and assume that 'size' and 'charge' refers to ions • **IGNORE** LE increases **OR** LE decreases • **IGNORE** bond strength; strength of ionic bonds		
			First 2 marks Decrease in (ionic) size **AND** **more negative** LE **OR** more **exo**thermic **OR** more attraction ✓ Increase in (ionic) charge **OR** charge density **AND** **more negative** LE **OR** more **exo**thermic **OR** more attraction ✓ --- *Link between LE and attraction* Lattice enthalpy correctly linked to attraction between **IONS** at least once ✓ *e.g. Greater attraction between **ions** gives **more negative** LE*	3	**ANNOTATE WITH TICKS AND CROSSES, etc** **ORA** throughout **ALLOW** pull for attraction **IGNORE** just 'greater force' (*could be repulsion*) **IGNORE** responses in terms of packing **IGNORE** electron density **IGNORE** lower/higher LE --- **For 3rd marking point ONLY, IONS is essential;** **DO NOT ALLOW** attraction between atoms or molecules **DO NOT ALLOW** nuclear attraction
			Total	**12**	

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Question			Answer	Marks	Guidance
2	(a)	(i)	Time for concentration (of reactant) to fall to half original value ✓	1	**ALLOW** time for concentration to fall by half **DO NOT ALLOW** concentration of **product** to fall by half **ALLOW** mass **OR** amount as alternative to concentration **ALLOW** time for reactant/substance/atoms to decrease by half
		(ii)	At least two half-lives correctly shown on graph **AND** half-life stated as approx. 54 s ✓ 1st order has a constant half-life ✓	2	**ALLOW** half-life in range 50–56 s **ALLOW** half-life shown on graph **Care**: Initial concentration is ~5.8 and **NOT** 6.0 For constant half-life, **ALLOW** 'half lives are the same', 'two half-lives are 54 s', etc. **ALLOW** 2 tangents drawn, one at half conc of first **AND** evidence that gradient (≡ rate) halves
		(iii)	No change ✓	1	
	(b)	(i)	*Tangent* On graph, tangent drawn to curve at t ~ 40 s ✓ *Calculation of rate from the tangent drawn* e.g. rate = $\frac{5.2}{116}$ = 0.045 **OR** 4.5 x 10^{-2} ✓ *Units* mol dm^{-3} s^{-1} ✓ *Independent mark*	3	Annotate tangent on graph **Note**: This mark can only be awarded from a tangent ***ALLOW ECF*** *for tangent drawn at different time from 40 s* **ALLOW** ±10% of gradient of tangent drawn **ALLOW** 2 SF up to calculator value **ALLOW** trailing zeroes, e.g. 0.04 for 0.040 **IGNORE** '–' sign for rate **Note: IF** candidate calculates rate via ln 2 method (shown in **(ii)**, consult with TL)

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Question			Answer	Marks	Guidance
2	(b)	(ii)	$k = \frac{\text{answer to (b)(i)}}{3.45}$ ✓ units: s^{-1} ✓ *Independent mark*	2	From 0.045, $k = \frac{0.045}{3.45} = 0.013$ **ALLOW** concentration range 3.4–3.5 **ALLOW** use of unrounded calculator answer from **(b)(i)** even if different from answer given on **(b)(i)** answer line *Many will keep this value in calculator for **(b)(ii)*** **ALLOW** k = ln 2/$t_{1/2}$ = 0.693/half life from **(a)(iii)** For 54 s, k = 0.693/54 = 0.013 **ALLOW** 2 SF up to calculator value
	(c)		water is in excess **OR** concentration of H_2O is very large/does not change ✓	1	**IGNORE** water does not affect the rate
			Total	**10**	

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Question	Answer	Marks	Guidance
3 (a)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 16.8 with 'no units', award **5 marks** --- At equilibrium, $n(I_2)$ **OR** $[I_2(g)]$ = $4.00 \times 10^{-3} - 1.70 \times 10^{-3} = 2.30 \times 10^{-3}$ (mol / mol dm^{-3}) ✓ $n(HI)$ **OR** $[HI(g)]$ = $2 \times 1.70 \times 10^{-3}$ = 3.40×10^{-3} (mol / mol dm^{-3}) ✓ (K_c =) $\frac{(3.40 \times 10^{-3})^2}{3.00 \times 10^{-4} \times 2.30 \times 10^{-3}}$ ✓ **IGNORE** $K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$ = 16.8 (**3 SF** required) ✓ no units ✓	5	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW ECF** throughout For **all** parts, **ALLOW** numerical answers from 3 significant figures up to the calculator value **ALLOW** omission of trailing zeroes, i.e. 3.40 as 3.4 but final numerical answer for K_c must be to 3 SF **ALLOW ECF** using incorrect values for $[I_2]$ **AND** [HI] **BUT** $[H_2]$ in K_c expression must be 3.00×10^{-4} (given in Q) **ALLOW ECF** from incorrect K_c expression for calculation to 3 SF and units **For 'no units' ALLOW 'none' (ORA) OR '—'** **DO NOT ALLOW** space to be left blank **Common errors:** Use of 1.70×10^{-3} for $n(HI)$ (no factor of x 2) K_c = 4.19 (3SF) and no units: 4 marks Use of K_c expression used is upside down K_c = 0.0597 (3SF) and no units: 4 marks No square for $[HI]^2$ K_c = 4930 and $dm^3\ mol^{-1}$ 4 marks **Note:** different ECF units

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<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Marks</th><th>Guidance</th></tr>
<tr><td>3</td><td>(b)</td><td>(i)</td><td>
<table>
<tr><th></th><th>$H_2(g)$</th><th>$I_2(g)$</th><th>HI(g)</th></tr>
<tr><td>greater</td><td>✓</td><td></td><td>✓</td></tr>
<tr><td>smaller</td><td></td><td>✓</td><td></td></tr>
<tr><td>the same</td><td></td><td></td><td></td></tr>
</table>
Each column should have only one box ticked

Correct ticks for $H_2(g)$ AND $I_2(g)$ AND HI(g) two marks ✓✓
i.e. all three columns correct

Ticks for two of $H_2(g)$, $I_2(g)$ and HI(g) correct one mark ✓
i.e. two columns correct
</td><td>2</td><td>DO NOT ALLOW more than one box ticked in a column (response is a CON)</td></tr>
<tr><td></td><td></td><td>(ii)</td><td>K_c is smaller
AND
(forward) reaction is exothermic OR ΔH is negative ✓</td><td>1</td><td>Link to ΔH/exothermic essential
ALLOW reverse reaction is endothermic
DO NOT ALLOW equilibrium shifts to the right (CON)</td></tr>
<tr><td></td><td></td><td>(iii)</td><td>K_c is the same
AND
K_c is temperature dependent OR K_c is not changed by pressure ✓</td><td>1</td><td>ALLOW K_c is only changed by temperature
IGNORE same number of moles on both side</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>9</td><td></td></tr>
</table>

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Question	Answer	Marks	Guidance
4 (a)	HC*l* is a strong acid **AND** HC*l*O is a weak acid ✓ **HC*l***: pH = –log 0.14 = 0.85 (**2 DP** required) ✓ **HC*l*O**: **CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 4.14, award all three calculation marks --- $K_a = 10^{-7.43}$ **OR** 3.7×10^{-8} (mol dm^{-3}) ✓ $[H^+] = \sqrt{K_a \times [HClO]}$ **OR** $\sqrt{K_a \times [HA]}$ **OR** $\sqrt{K_a \times 0.14}$ **OR** $\sqrt{3.7 \times 10^{-8} \times 0.14}$ ✓ pH = 4.14 (**2 DP** required) ✓	5	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** HC*l* completely dissociates **AND** HC*l*O partially dissociates **ALLOW** HC*l* $\rightarrow$ H^+ + C*l* **AND** HC*l*O $\rightleftharpoons$ H^+ + C*l*O$^-$ **IGNORE** HC*l* is a stronger acid than HC*l*O **IGNORE** HC*l* produces more H^+ **IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ALLOW** 2 SF to calculator value: $3.715352291 \times 10^{-8}$, correctly rounded **IGNORE** 'HC*l*' if it is clear that it is a 'slip' Always **ALLOW** calculator value irrespective of working as number may have been kept in calculator. ***Note**: pH = 4.14 is obtained from all three values above* *From no square root, pH = 8.28. Worth K_a mark only*

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Question			Answer	Marks	Guidance
4	(b)		$2Al + 6CH_3COOH \longrightarrow 2(CH_3COO)_3Al + 3H_2$ ✓ $2Al + 6H^+ \longrightarrow 2Al^{3+} + 3H_2$ ✓	2	**IGNORE** state symbols **ALLOW** correct multiples, e.g.: $Al + 3CH_3COOH \longrightarrow (CH_3COO)_3Al + 1.5H_2$ **ALLOW** any unambiguous formula for $(CH_3COO)_3Al$, *i.e.* $(CH_3CO_2)_3Al$, $Al(CH_3CO_2)_3$, $(CH_3COO^-)_3Al^{3+}$, etc. **Note**: **IF** charges are shown, they **must** be correct with **both** – and 3+ shown **ALLOW** multiples, e.g.: $Al + 3H^+ \longrightarrow Al^{3+} + 1.5H_2$
	(c)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 13.6(0), award **2 marks** --- $[H^+] = \frac{K_w}{[OH^-]}$ **OR** $\frac{1.0 \times 10^{-14}}{[OH^-]}$ **OR** $\frac{1.0 \times 10^{-14}}{0.4(0)}$ **OR** 2.5×10^{-14} (mol dm^{-3}) ✓ Correctly calculates pH = $-\log 2.5 \times 10^{-14} = 13.6(0)$ ✓	2	**ALLOW** alternative approach using pOH: pOH = 0.4(0) ✓ pH = 14 – 0.40 = 13.6(0) ✓ **ALLOW ECF** from $[H^+]$ derived using K_w and $[OH^-]$ BUT **DO NOT ALLOW** an acid pH. **ALLOW** one or more decimal places

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Question			Answer	Marks	Guidance
4	(d)	(i)	A buffer solution minimises pH changes ✓ on addition of **small** amounts of acid/H^+ or alkali/OH^-/base ✓ --- $HCOOH \rightleftharpoons H^+ + HCOO^-$ ✓ *Equilibrium sign essential*	7	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** resists pH changes **ALLOW** buffer solutions maintains a **nearly**/**virtually** constant pH **DO NOT ALLOW** a response that implies that the pH is actually constant, e.g. does not change pH; maintains pH --- **DO NOT ALLOW** $COOH^-$ **OR** CHOOH **OR** COOH **DO NOT ALLOW** $HA \rightleftharpoons H^+ + A^-$
			For effect of acid and alkali, **ALLOW** wrong carboxylic acid (e.g. CH_3COOH) **OR** HA; **ALLOW** CHOOH for acid (effectively **ECF**) **ALLOW** $COOH^-$ for base **ALLOW** responses based on $COOH \rightleftharpoons H^+ + COO^-$ **DO NOT ALLOW** other incorrect formula, e.g. CH_3OOH		**<u>Quality of written communication, QWC</u>** *2 marks are for explaining how the equilibrium system allows the buffer solution to control the pH on addition of H^+ and OH^-*
			Added alkali HCOOH reacts with added alkali/base/OH^- **OR** added alkali/OH^- reacts with H^+ ✓ **QWC**: Equilibrium shifts forming $HCOO^-$ **OR** H^+ **OR** (HCOOH) Equilibrium → right ✓ **Added acid** $HCOO^-$ reacts with added acid/H^+ ✓ **QWC**: Equilibrium shifts forming HCOOH **OR** (HCOOH) Equilibrium → left ✓		**ALLOW** HA **OR** weak acid reacts with added alkali **DO NOT ALLOW** this mark if there is no equilibrium system shown, e.g. $HCOOH \rightleftharpoons H^+ + HCOO^-$ is absent **ALLOW** A^- **OR** conjugate base reacts with added acid **IGNORE** salt reacts with added acid **DO NOT ALLOW** this mark if there is no equilibrium system shown, e.g. $HCOOH \rightleftharpoons H^+ + HCOO^-$ is absent

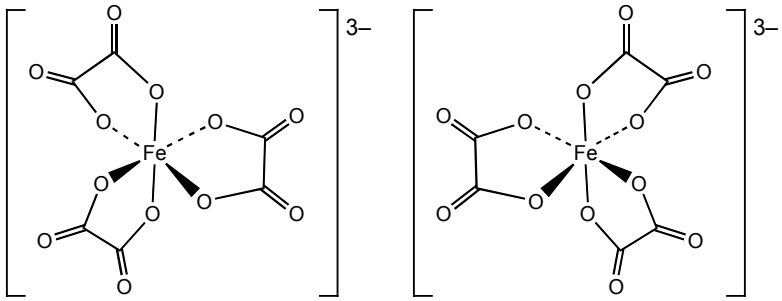
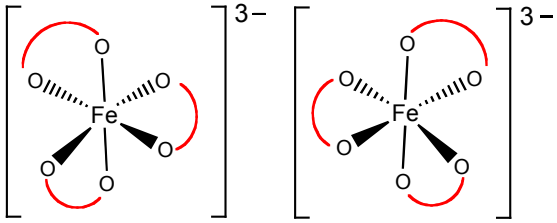
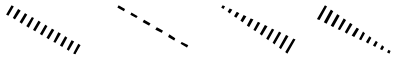
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Question			Answer	Marks	Guidance
4	(d)	(ii)	**HCOOH** reacts with **NaOH** forming **$HCOO^-$/HCOONa** **OR** $HCOOH + NaOH \rightarrow HCOONa + H_2O$ ✓ *Equilibrium sign allowed* (Some) HCOOH/(weak) acid remains **OR** HCOOH/(weak) acid is in excess ✓	6	**ANNOTATE WITH TICKS AND CROSSES, etc** **DO NOT ALLOW** just 'methanoate/$HCOO^-$ forms' *formulae or names of reactants also required* **ALLOW** $HCOOH + OH^- \rightarrow HCOO^- + H_2O$ ✓ **IGNORE** conjugate base/**salt forms** **IGNORE** HCOOH has been partially neutralised
			Calculation **CHECK THE ANSWER** **IF** answer = 3.99, award all **four** calculation marks		
			n(HCOOH) **OR** [HCOOH] = 0.24(0) (mol / mol dm^{-3}) ✓ $n(HCOO^-)$ **OR** $[HCOO^-]$ **OR** [HCOONa] = 0.4(00) (mol / mol dm^{-3}) ✓ $[H^+] = K_a \times \frac{[HCOOH]}{[HCOO^-]}$ ✓ $pH = -\log [H^+] = -\log(1.70 \times 10^{-4} \times \frac{0.24}{0.4}) = 3.99$ ✓ --- **OR** use of Henderson–Hasselbalch equation: $pH = pK_a + \log \frac{[HCOO^-]}{[HCOOH]}$ **OR** $pH = -\log K_a + \log \frac{[HCOO^-]}{[HCOOH]}$ ✓ = 3.77 + 0.22 = 3.99 ✓		**Note:** There must be a clear statement that 0.24 and 0.4 apply to moles or concentrations of HCOOH and $HCOO^-$. **DO NOT ALLOW** these values if unlabelled **ALLOW** HA/acid and A^-/salt for HCOOH and $HCOO^-$ **DO NOT ALLOW ECF for this mark:** **3.99 is the ONLY correct answer** --- **ALLOW** HA/acid and A^-/salt for HCOOH and $HCOO^-$ **ALLOW** $pH = pK_a - \log \frac{[HCOOH]}{[HCOO^-]}$ **OR** $pH = -\log K_a - \log \frac{[HCOOH]}{[HCOO^-]}$ **ALLOW** = 3.77 – (–0.22) = 3.99 **DO NOT ALLOW ECF for this mark:** **3.99 is the ONLY correct answer**
			Total	**22**	

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Question			Answer	Marks	Guidance
5	(a)		$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$ ✓	1	**ALLOW** $2Fe + 3Cl_2 \longrightarrow Fe_2Cl_6$ **ALLOW** multiples, e.g. $Fe + 1½Cl_2 \longrightarrow FeCl_3$ **IGNORE** state symbols **DO NOT ALLOW** $2Fe + 3Cl_2 \longrightarrow 2Fe^{3+} + 6Cl^-$
	(b)		$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$ ✓	1	**IGNORE** state symbols **ALLOW** $[Fe(H_2O)_6]^{3+} + 3OH^- \longrightarrow Fe(H_2O)_3(OH)_3 + 3H_2O$ **ALLOW** $[Fe(H_2O)_6]^{3+} + 3OH^- \longrightarrow Fe(OH)_3 + 6H_2O$
	(c)	(i)	$2[Fe(H_2O)_6]^{3+} + Zn \longrightarrow 2[Fe(H_2O)_6]^{2+} + Zn^{2+}$ All chemical species correct (**IGNORE** e^- for 1st mark) ✓ Balancing with '2' in front of **both** Fe complex ions ✓	2	**IGNORE** state symbols **For 1 mark,** **ALLOW** balancing if (aq) species have been used instead of complex ions: $2Fe^{3+} + Zn \longrightarrow 2Fe^{2+} + Zn^{2+}$
		(ii)	redox ✓	1	**ALLOW** reduction **AND** oxidation **CARE**: possible confusion with **(d)(ii)**
	(d)	(i)	Formula of **E** as $[Fe(CN)_6]^{3-}$ shown as product in equation ✓ Correct balanced equation: $[Fe(H_2O)_6]^{3+} + 6CN^- \longrightarrow [Fe(CN)_6]^{3-} + 6H_2O$ ✓ Notice different charges on complex ions: LHS 3+, RHS 3– state symbols **not** required	2	**ALLOW** equations with KCN, i.e.: $[Fe(H_2O)_6]^{3+} + 6KCN \rightarrow [Fe(CN)_6]^{3-} + 6K^+ + 6H_2O$ $[Fe(H_2O)_6]^{3+} + 6K^+ + 6CN^- \rightarrow [Fe(CN)_6]^{3-} + 6K^+ + 6H_2O$ **ALLOW** ECF for an equation showing formation of $[Fe(CN)_6]^{4-}$ from $[Fe(H_2O)_6]^{2+}$: $[Fe(H_2O)_6]^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-} + 6H_2O$ Notice different charges on complex ions: LHS 2+, RHS 4–
		(ii)	ligand substitution ✓	1	**ALLOW** ligand exchange **OR** ligand replacement **CARE**: possible confusion with **(c)(ii)**

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Question			Answer	Marks	Guidance
5	(e)		**F** and **G**:  1 mark for each isomer ✓✓ *Bonds **must** go to O ligand atoms on **EACH** structure* ***IGNORE** charges on Fe^{3+} and O^{-} at this stage* 3– charge outside brackets of **BOTH** isomers **AND NO** charges shown on Fe or O within brackets **Note**: This mark is only available from structures with three bidentate ligands bonded to Fe via two Os on each ligand ✓	3	**ALLOW** any attempt to show bidentate ligand Bottom line is the diagram below.  **IGNORE** structure between two Os in ligand even if slightly different Must contain 2 out wedges, 2 in wedges and 2 lines in plane of paper. For bond into paper, **ALLOW**: 
	(f)		FeO_4^{2-} ✓	1	Formula **AND** charge needed **ALLOW** other 2– ions containing: Fe **AND** O **AND** Fe has ox no of +6 i.e. **ALLOW** $Fe_2O_7^{2-}$, $Fe_3O_{10}^{2-}$, etc.
			Total	**12**	

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Question			Answer	Marks	Guidance
6	(a)	(i)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 218, award **2 marks** --- $-256 = (6 \times 205) + S(C_6H_{12}O_6) - (6 \times 214 + 6 \times 70)$ **OR** $S(C_6H_{12}O_6) = -256 - (6 \times 205) + (6 \times 214 + 6 \times 70)$ **OR** –256 + 474 ✓ = 218 (J K^{-1} mol^{-1}) ✓	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible. Note that **ALL** 4 S values must be used for **ECF** --- **ALLOW** 1 mark for –218 **ALLOW** 1 mark for +730 (*products – reactants*) **Note:** –3190 for simple addition of products + reactants scores zero marks
		(ii)	ΔG = +2879 – 298 × –0.256 ✓ = (+)2955 (kJ mol^{-1}) ✓	2	**ALLOW** 3 SF: 2960 to calculator value of 2955.288 **Award 1 mark for the following:** • ΔG = 2890 to calculator value of 2885.4 *25 °C used rather than 298 K:* • ΔG = 79200 to calculator value of 79167 *ΔS not converted from J K^{-1} mol^{-1} to kJ $K^{-1}mol^{-1}$* • expressions with **one** transcription error: e.g. +2897 instead of +2879; 0.265 instead of 0.256 • ΔG = 2814.036 *use of 218 rather than –256* • Use of 'answer to **(a)(i)**'/1000 (by **ECF**)
		(iii)	ΔH is positive **OR** $\Delta H > 0$ **AND** ΔS is negative **OR** $T\Delta S$ is negative **OR** $\Delta S < 0$ **OR** $T\Delta S < 0$ **AND** ΔG will always be positive **OR** $\Delta G > 0$ ✓	1	**ALLOW** ΔH is endothermic for ΔH is +ve **ALLOW** ΔG will never be less than 0 **DO NOT ALLOW** *S* or *H* i.e. **change** in entropy, ΔS and change in enthalpy ΔH are essential

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Question			Answer	Marks	Guidance
6	(b)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 3.12 x 10^{17} g, award **2 marks** --- amount of CO_2 removed = $3.4 \times 10^{18} \times 6 / 2879$ **OR** 7.09×10^{15} (mol) ✓ mass of $CO_2 = 44.0 \times 7.09 \times 10^{15} = 3.12 \times 10^{17}$ g ✓	2	**ALLOW** 2 SF (7.1×10^{15} (mol)) up to calculator value of 7.085793678, correctly rounded **ALLOW** 2 SF (3.1×10^{17} g) up to calculator value, correctly rounded **Correct units required for 2nd mark** e.g. 3.12×10^{14} kg; 3.12×10^{11} tonne **ALLOW** 1 mark for 3.1×10^{17} with no unit **ALLOW** ECF from incorrectly calculated amount of CO_2 provided that both 3.4 x 10^{18} **AND** 2879 have been used e.g. Omission of x 6 gives 1.181 x 10^{15} mol CO_2 and 5.196 x 10^{16} g CO_2
			Total	**7**	

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Question			Answer	Marks	Guidance
7	(a)		**Definition** The e.m.f. (of a half-cell) compared with a (standard) hydrogen half-cell/(standard) hydrogen electrode ✓ **Standard conditions** Temperature of 298 K / 25ºC **AND** (solution) concentrations of 1 mol dm^{-3} / 1M **AND** pressure of 101 kPa **OR** 100 kPa ✓	2	**ALLOW** voltage **OR** potential difference **OR** p.d. **OR** electrode potential **OR** reduction potential **OR** redox potential as alternative for e.m.f. **IGNORE** S.H.E. (as abbreviation for standard hydrogen electrode) **ALLOW** 1 atmosphere/1 atm **OR** 10^5 Pa **OR** 1 bar
	(b)		2.71 V ✓	1	**IGNORE** any sign
	(c)	(i)	$Al + 3Fe^{3+} \longrightarrow Al^{3+} + 3Fe^{2+}$ ✓ $2Al + 3I_2 \longrightarrow 2Al^{3+} + 6I^-$ ✓ $2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$ ✓	3	Correct species **AND** balancing needed for each mark **IGNORE** state symbols **ALLOW** equilibrium sign (i.e. assume reaction is to right) **ALLOW** correct multiples **IF** there are **more than** three equations • mark a maximum of three equations • mark incorrect equations first
		(ii)	High activation energy **OR** slow rate ✓ Conditions not standard **OR** concentrations not 1 mol dm^{-3} ✓	2	 **DO NOT ALLOW** 'standard conditions' are different

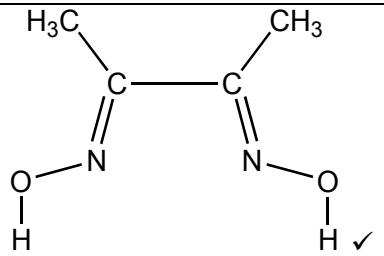
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Question			Answer	Marks	Guidance
7	(d)		**ANNOTATE WITH TICKS, CROSSES, etc**	4 max	**ORA** throughout Minimum identification for system **6** is Cl^- Minimum identification for system **7** is ClO^- **Note**: Cl_2 is unsuitable as an identifier as it features in both system **6** and system **7** **IGNORE** reference to gaining and losing electrons; oxidation and reduction
			General (2 marks – assumed to be acid) • (E of) **7** (ClO^-/Cl_2) is more positive/less negative (than **6**) **OR** E_{cell} is (+)0.27 (V) **OR** E_{cell} is positive ✓ • **6** (Cl_2/Cl^-) moves to left **AND 7** (ClO^-/Cl_2) to right ✓		**Note**: identification of systems 6 and 7 could be from use of relevant half equations/overall equation **ALLOW** 'greater' or 'higher' for 'more positive' **ALLOW** correct eqn: $Cl^- + ClO^- + 2H^+ \rightarrow Cl_2 + H_2O$ **IGNORE** uncancelled electrons **ALLOW** multiples, e.g. $2Cl^- + 2ClO^- + 4H^+ \rightarrow 2Cl_2 + 2H_2O$ **Note**: **IF** equilibrium shifts are correct, **IGNORE** incorrectly balanced equation but **CON** an equation in wrong direction
			In alkali (3 marking points), • H^+ in **7** (ClO^-/Cl_2) is removed by/reacts with OH^-/alkali ✓ • (E of) **7** (ClO^-/Cl_2) less positive/more negative (than **6**) ✓ • **6** (Cl_2/Cl^-) moves to right **AND 7** (ClO^-/Cl_2) to left ✓		**ALLOW** correct eqn: $Cl_2 + H_2O \rightarrow Cl^- + ClO^- + 2H^+$ **IGNORE** uncancelled electrons **ALLOW** multiples, e.g. $2Cl_2 + 2H_2O \rightarrow 2Cl^- + 2ClO^- + 4H^+$ **Note**: **IF** equilibrium shifts are correct, **IGNORE** incorrectly balanced equation but **CON** an equation in wrong direction

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Question			Answer	Marks	Guidance
	(e)	(i)	IO_3^- has removed/gained electrons from Sn^{2+} **OR** IO_3^- has been reduced to I_2 / reduced to 0 **OR** IO_3^- has oxidised Sn^{2+} ✓	1	**ALLOW** IO_3^- is the oxidising agent as I has been reduced **DO NOT ALLOW** just IO_3^- has been reduced **DO NOT ALLOW** I is the oxidising agent
		(ii)	$5Sn^{2+} + 2IO_3^- + 12H^+ \longrightarrow I_2 + 5Sn^{4+} + 6H_2O$ All chemical species correct with **no extra** chemical species ✓ Correct balancing with no electrons shown ✓	2	**ALLOW** correct multiples eg $2½\ Sn^{2+} + IO_3^- + 6H^+ \rightarrow ½\ I_2 + 2½\ Sn^{4+} + 3H_2O$ **IGNORE** e^- for 1st marking point
			Total	**15**	

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Question			Answer	Marks	Guidance
8	(a)		$(1s^2 2s^2 2p^6)\ 3s^2 3p^6 3d^8 4s^2$ ✓ $(1s^2 2s^2 2p^6)\ 3s^2 3p^6 3d^8$ ✓	2	**ALLOW** 4s before 3d, i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$ **IF** candidate has used subscripts **OR** caps, **DO NOT ALLOW** when first seen but credit subsequently, i.e. $1s_2 2s_2 2p_6 3s_2 3p_6 3d_8 4s_2$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3D^8$ For Ni^{2+} **ALLOW** $4s^0$ in electron configuration
	(b)	(i)	Acts as a base **OR** alkali **AND** removes/accepts a proton (from DMGH) ✓	1	
		(ii)	4 ✓	1	
		(iii)	(Each) DMG has 1– charge which **cancel** 2+ charge on Ni^{2+} ✓	1	**ALLOW** 2 x –1 + 2 = 0 For Ni^{2+}, **ALLOW** Ni has an oxidation number of (+)2 **ALLOW** Ni^{2+} cancelled out by 2 DMG^- **ALLOW** 'balanced' for cancelled
		(iv)	 ✓	1	**ALLOW** OH for O—H **ALLOW** CH_3— **DO NOT ALLOW** —H—O

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Question			Answer	Marks	Guidance
8	(c)		**Marks are for correctly calculated values** *amount of Ni* ---------- amount $Ni(DMG)_2$ **OR** amount hydrated salt **OR** amount Ni^{2+} $= \frac{2.57}{288.7}$ = **$8.9(0) \times 10^{-3}$** mol ✓ *M values* ---------- *M*(hydrated salt) $= \frac{2.50}{8.90 \times 10^{-3}}$ = **280.9** ($g\ mol^{-1}$) ✓ *M*(anhydrous salt) $= \frac{1.38}{8.90 \times 10^{-3}}$ = **155.0** ($g\ mol^{-1}$) ✓ *H_2O* ---------- mass H_2O = 2.50 – 1.38 = **1.12 g** ✓ *n*(H_2O) from mass or *M* values $= \frac{1.12}{18.0}$ = **$6.2(2) \times 10^{-2}$ OR** 280.9 – 155.0 **~125.9** ✓ waters of crystallisation $= \frac{6.22 \times 10^{-2}}{8.90 \times 10^{-3}}$ = **7** **OR** $\frac{125.9}{18.0}$ = **7** ✓ *Anion* ---------- Molar mass of anion = 280.9 – (58.7 + 7 x 18) = **96.1** ($g\ mol^{-1}$) **OR** Molar mass of anion = 155.0 – 58.7 = **96.3** ($g\ mol^{-1}$) ✓ *Formula* ---------- Formula of salt is **$NiSO_4 \cdot 7H_2O$** ✓	**7 max**	**ANNOTATE WITH TICKS AND CROSSES, etc** **Note:** The answers incorporate three different approaches to solving this problem. **IF candidate attempts calculation via another method, consult your TL** **ECF** answer above **ALLOW** numerical answers 280.8 – 280.9 (**ALLOW** 281) **IGNORE** further figures **ALLOW** numerical answers 155.0 – 155.1 (**ALLOW** 155) **IGNORE** further figures **ASSUME** that 'unlabelled 1.12 g' applies to H_2O unless contradicted **ALLOW** numerical answers 125.7 – 125.9 (**ALLOW** 126) **ECF** answer above **7** as whole number is required **Note:** Mark for 7 can be credited within formula **BUT** there must be some relevant working to derive ~7, e.g. 6.99 **ALLOW** numerical answers 96.0 – 96.4 (**ALLOW** 96)
			Total	**13**	

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RECOGNISING ACHIEVEMENT

Tuesday 22 January 2013 – Afternoon

A2 GCE CHEMISTRY A

F325/01 Equilibria, Energetics and Elements

F3144801 13

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

Candidate forename		Candidate surname	

Centre number						Candidate number				

INSTRUCTIONS TO CANDIDATES

- The Insert will be found in the centre of 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 refers to chemistry of d-block elements in Period 4 (Sc–Zn).

(a) For each statement below, select the symbols of the correct element(s).

(i) The element that has atoms containing six electrons in the 3d sub-shell.

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

(ii) Two elements that have atoms with two unpaired d electrons.

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

(iii) The element with ions that form a blue complex with chloride ions.

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

(iv) The element **X** that forms an oxide with the formula $\mathbf{X}_3O_4$ with the molar mass of $228.7\,g\,mol^{-1}$.

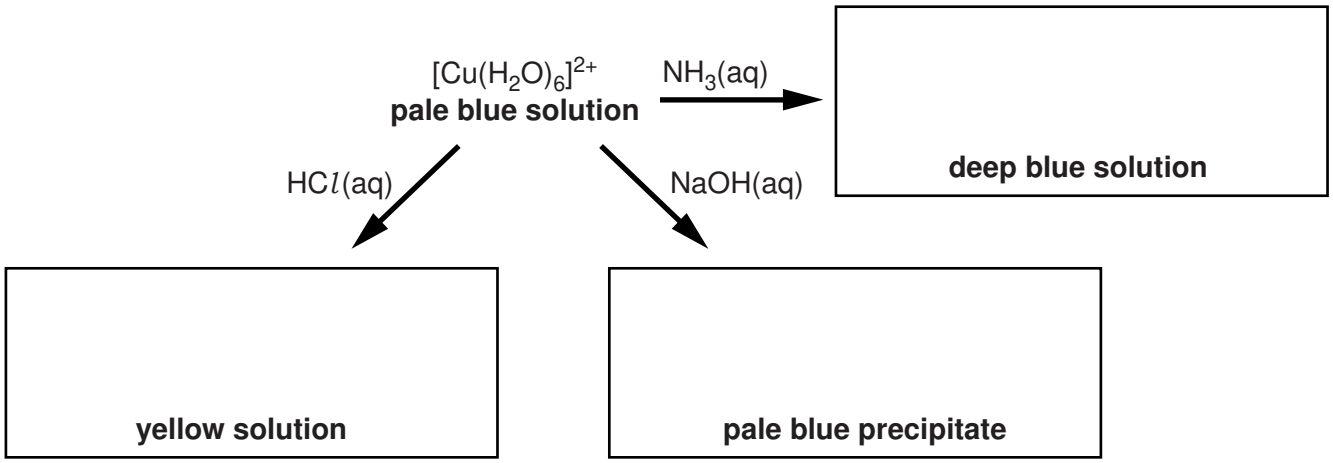
..... **[1]**

(v) The element that has atoms with an average mass of $8.64 \times 10^{-23}\,g$.

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

(b) The flowchart below shows three reactions of the complex ion $[Cu(H_2O)_6]^{2+}$.

In the boxes below, write down the formulae of the species formed.



[3]

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(c) The answers to this question all refer to complex ions of nickel.

(i) State the shape of the complex ion $[Ni(H_2O)_6]^{2+}$.

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

(ii) What is the formula of the complex ion of Ni^{2+} containing six fluoride ligands?

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

(iii) Show the 3-D shapes of the stereoisomers of the complex ion $[Ni(en)_3]^{2+}$.
(en = $H_2NCH_2CH_2NH_2$)

[2]

[Total: 13]

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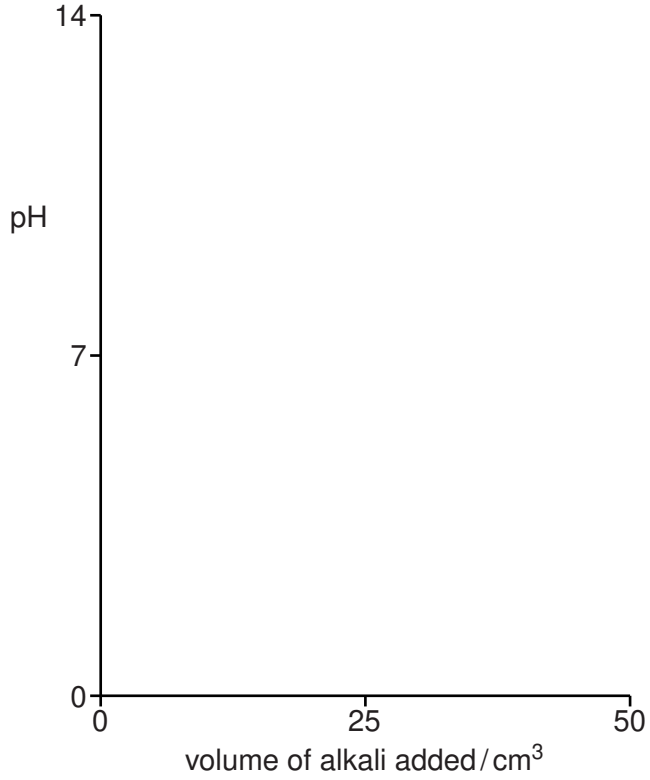
2 This question looks at different aspects of neutralisation.

(a) Acid–base titration pH curves can be used to help choose suitable indicators for the following titrations:

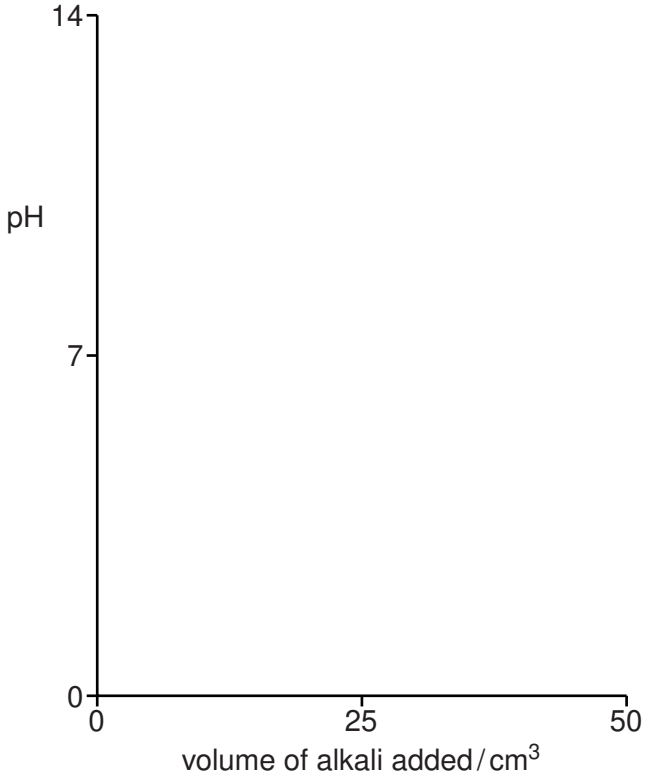
- 25.0 cm^3 of 0.100 mol dm^{-3} HC*l*(aq) with 0.100 mol dm^{-3} NaOH(aq)
- 25.0 cm^3 of 0.100 mol dm^{-3} CH_3COOH(aq) with 0.100 mol dm^{-3} NaOH(aq).

(i) On the axes below, sketch pH acid–base titration curves to show how the pH changes when the alkali is added from a burette until the alkali is in excess.

25.0 cm^3 of 0.100 mol dm^{-3} HC*l*(aq) with 0.100 mol dm^{-3} NaOH(aq)



25.0 cm^3 of 0.100 mol dm^{-3} CH_3COOH(aq) with 0.100 mol dm^{-3} NaOH(aq)



[4]

(ii) Explain how the choice of indicator is linked to the pH curve.

.....

.....

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

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(b) A student carries out an experiment to measure the enthalpy change of neutralisation.

(i) Define the term e*nthalpy change of neutralisation*.

.....

.....

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

(ii) The student measures out 35.0 cm^3 of 2.40 mol dm^{-3} NaOH and 35.0 cm^3 of 2.40 mol dm^{-3} HC*l*. The temperature of each solution is the same.

The student mixes the two solutions. The temperature rises by 16.5 °C.

The specific heat capacity of the mixture is 4.18 J g^{-1} K^{-1}. Assume that the density of the mixture is 1.00 g cm^{-3}.

Calculate the enthalpy change of neutralisation, in kJ mol^{-1}.

enthalpy change of neutralisation = ... kJ mol^{-1} **[3]**

(iii) The student repeats the experiment using 70.0 cm^3 of 1.20 mol dm^{-3} HC*l* instead of 35.0 cm^3 of 2.40 mol dm^{-3} HC*l*.

Explain why the temperature rise is less, and predict what the temperature rise will be.

.....

.....

.....

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

[Total: 11]

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3 Energy changes take place when water dissolves compounds and when water changes its physical state.

(a) You are provided with the following information.

Ion	$\Delta H_{hydration}$ /kJ mol^{-1}
Na^+	–405
Mg^{2+}	–1926
OH^-	–460

The enthalpy change of solution of $Mg(OH)_2$ is –152 kJ mol^{-1}.

(i) Define, in words, the terms *enthalpy change of solution* and *enthalpy change of hydration*.

enthalpy change of solution .....

.....

.....

.....

enthalpy change of hydration .....

.....

.....

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

(ii) Explain the difference between the $\Delta H_{hydration}$ values for Na^+ and Mg^{2+}.

.....

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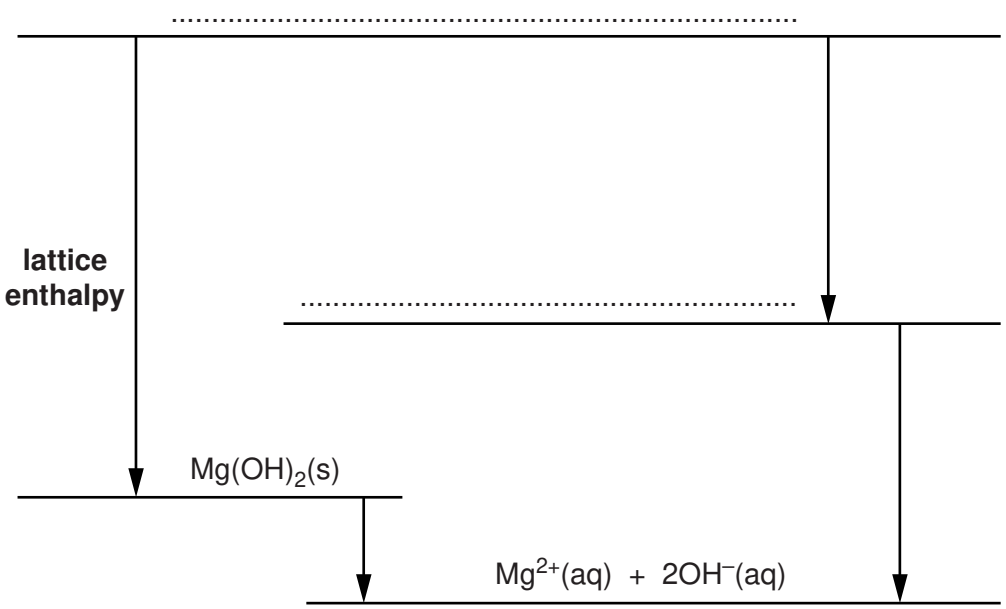
.....

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

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(iii) A Born–Haber cycle can be drawn to link the lattice enthalpy and enthalpy change of solution of $Mg(OH)_2$ with hydration enthalpies.

On the two dotted lines, add the species present, including state symbols.



[2]

(iv) Calculate the lattice enthalpy of $Mg(OH)_2$.

lattice enthalpy = ... $kJ\,mol^{-1}$ **[2]**

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(b) Energy changes for the melting and boiling of H_2O are shown below.

$H_2O(s) \rightarrow H_2O(l)$ $\quad \Delta H = +6.01\,kJ\,mol^{-1}$
$H_2O(l) \rightarrow H_2O(g)$ $\quad \Delta H = +40.7\,kJ\,mol^{-1}$

Standard entropies of H_2O in its three physical states are given in the table below.

	$H_2O(s)$	$H_2O(l)$	$H_2O(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	+48.0	+70.0	+188.7

(i) Explain the following:

- When water melts or boils, ΔH is positive
- When water melts or boils, $S^{\ominus}$ increases.

In your answer, you should explain why the increase in $S^{\ominus}$ is much greater when water boils than when water melts.

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

(ii) Using the data in the table above, show that ice melts at 0 °C (at standard pressure).

[3]

[Total: 16]

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9

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4 Iodide ions, I^-, react with $S_2O_8^{2-}$ ions as shown in the equation below.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

A student investigates the rate of this reaction using the initial rates method.

The student measures the time taken for a certain amount of iodine to be produced.

(a) Outline a series of experiments that the student could have carried out using the initial rates method.

How could the results be used to show that the reaction is first-order with respect to both I^- and $S_2O_8^{2-}$?

In your answer you should make clear how the results are related to the initial rates.

.....

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

(b) In one of the experiments, the student reacts together:

- 8.0×10^{-2} mol dm^{-3} $I^-(aq)$
- 4.0×10^{-3} mol dm^{-3} $S_2O_8^{2-}(aq)$.

The initial rate of this reaction is 1.2×10^{-3} mol dm^{-3} s^{-1}.

The reaction is first-order with respect to I^- and first-order with respect to $S_2O_8^{2-}$.

Calculate the rate constant, *k*, for this reaction.
State the units, if any.

k = ... units ..... **[3]**

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(c) This reaction between I^- ions and $S_2O_8^{2-}$ ions can be catalysed by either $Fe^{2+}(aq)$ ions or $Fe^{3+}(aq)$ ions.

Standard electrode potentials are shown below.

$S_2O_8^{2-}(aq) + 2e^-$	$\rightleftharpoons$	$2SO_4^{2-}(aq)$	$E^\ominus = +2.01\,V$
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	$E^\ominus = +0.77\,V$
$I_2(aq) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$	$E^\ominus = +0.54\,V$

(i) Using this information, write two equations to show how the reaction of I^- ions and $S_2O_8^{2-}$ ions can be catalysed by **Fe^{2+}** ions.

equation 1: .....

equation 2: ..... **[2]**

(ii) Suggest why the reaction of I^- ions and $S_2O_8^{2-}$ ions is also catalysed by **Fe^{3+}** ions.

.....

.....

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

[Total: 10]

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5 Methanol can be prepared industrially by reacting together carbon monoxide and hydrogen. This is a reversible reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -94\,kJ\,mol^{-1}$$

- A chemist mixes together 0.114 mol CO(g) and 0.152 mol $H_2(g)$ in a container.
- The container is pressurised and then sealed. The total volume is 200 cm^3.
- The mixture is heated to 500 K and left to reach equilibrium.
  The volume of the sealed container is kept at 200 cm^3.
- The chemist analyses the equilibrium mixture and finds that 0.052 mol CH_3OH has formed.

(a) Calculate the value of K_c, including units, for the equilibrium at 500 K.

Give your answer to **three** significant figures.

K_c = ... units ..... **[6]**

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(b) The chemist repeats the experiment using the same initial amounts of CO and H_2.
The same procedure is used but the mixture is heated in the 200 cm^3 sealed container to a higher temperature than 500 K.

As the gas volume is kept at 200 cm^3, the increased temperature also increases the pressure.

- Explain why it is difficult to predict how the yield of CH_3OH would change.
- Explain what happens to the value of K_c.

.....

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.....

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

[Total: 10]

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6 Storage cells and fuel cells are types of electrochemical cell used as sources of energy.

Information about five redox systems that could be used in electrochemical cells is shown below. You may need to use this information throughout this question.

redox system					$E^{\ominus}$ / V
1	$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$		–0.44
2	$2H_2O(l) + 2e^-$	$\rightleftharpoons$	$2OH^-(aq) + H_2(g)$		–0.83
3	$2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2(g)$		0.00
4	$O_2(g) + 2H_2O(l) + 4e^-$	$\rightleftharpoons$	$4OH^-(aq)$		+0.40
5	$O_2(g) + 4H^+(aq) + 4e^-$	$\rightleftharpoons$	$2H_2O(l)$		+1.23

(a) The standard electrode potential of redox system **1** can be measured by constructing an electrochemical cell.

- Draw a diagram below to show how the standard electrode potential could be measured for redox system **1**.
- State the conditions needed to measure this standard electrode potential.

conditions: .....

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

(b) When an **alkaline** hydrogen–oxygen fuel cell is being used to produce electrical energy, chemical changes take place within the cell.

(i) Write half-equations for the changes that take place at each electrode.

oxygen electrode: .....

hydrogen electrode: ..... **[2]**

(ii) Write the overall equation for the cell reaction.

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

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(iii) What is the standard cell potential of this fuel cell?

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

(c) State **one** important difference between a fuel cell and a conventional storage cell.

.....

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

(d) People often assume that hydrogen–oxygen fuel cells are a source of energy that is carbon neutral, *i.e.* there is no net increase in carbon dioxide from using the fuel cell.

Suggest **one** reason why this assumption may **not** be correct.

.....

.....

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

(e) A student constructs a cell as follows.

- A half-cell is made from a strip of chromium metal and a solution of aqueous chromium(III) sulfate.
- A second half-cell is made from a strip of a metal **X** and a solution of **X**SO_4(aq).
- The two half-cells are connected together and a current is allowed to pass for a length of time.

The chromium electrode gains 1.456 g in mass.
The electrode made of metal **X** loses 1.021 g in mass.

Determine the identity of metal **X**.
Show all your working.

X = ... **[4]**

[Total: 14]

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7 This question looks at two weak acids that are used as food additives to preserve food:

- calcium hydrogensulfate(IV), $Ca(HSO_3)_2$
- a carboxylic acid, **HA**.

(a) $Ca(HSO_3)_2$ can be made by reacting an excess of sulfur dioxide gas with a suspension of calcium carbonate in water.

Write the equation for this reaction.

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

(b) Calcium hydrogensulfate(IV), $Ca(HSO_3)_2$, dissolves in water forming an aqueous solution containing $Ca^{2+}(aq)$ and $HSO_3^-(aq)$ ions. This solution is weakly acidic.

(i) What is meant by a *weak acid*?

Write an equation to show why this solution is weakly acidic.

weak acid: .....

.....

equation: ..... **[2]**

(ii) An aqueous solution of $Ca(HSO_3)_2$ oxidises magnesium forming hydrogen gas.

Construct full and ionic equations for the oxidation of magnesium metal by $Ca(HSO_3)_2(aq)$.

full equation: .....

ionic equation: .....
[2]

(iii) $HSO_3^-(aq)$ can act as either a Brønsted–Lowry acid or a Brønsted–Lowry base.

Explain this statement.
Include equations for the reaction of $HSO_3^-(aq)$ with $H^+(aq)$ and with $OH^-(aq)$.

.....

.....

.....

.....

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

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(c) A carboxylic acid **HA** is a food additive used as a preservative in cakes.

The K_a value of **HA** is 1.51×10^{-5} mol dm^{-3}.

A student analyses a sample of **HA** using the procedure below.

- A student dissolves 0.7369 g of **HA** in water and makes the solution up to 1.00 dm^3.
- The student measures the pH of the resulting solution as 3.52.

(i) Determine the molar mass of **HA** and suggest a possible formula for **HA**.
HA has one carboxylic acid group and contains C, H and O only.
Show all your working.

molar mass of **HA** = ... g mol^{-1}

possible formula for **HA** = ... **[6]**

(ii) The student had considered analysing the solution of **HA** by carrying out a titration with an alkaline solution of known concentration.

The student rejects this method as being invalid because **HA** is a weak acid and only a small proportion of H^+ ions would be neutralised.

Explain whether the student was correct in rejecting the titration method.

.....

.....

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

[Total: 16]

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8 Vanadium is a transition element that forms compounds and ions in which vanadium has oxidation states +2, +3, +4 and +5.

(a) Complete the electron configuration of a vanadium ion in the +3 oxidation state:

$1s^2 2s^2 2p^6$ ..... **[1]**

(b) Suggest why vanadium does **not** form ions in which vanadium has an oxidation state greater than +5.

.....

.....

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

(c) A student carries out an investigation into the oxidation states of vanadium as outlined below.

Stage 1 A 0.126 g sample of vanadium metal is completely reacted with acid to form a yellow solution. The solution is made up to 50.0 cm^3 in a volumetric flask.
This yellow solution contains VO_3^- ions with vanadium in the +5 oxidation state.

Stage 2 The yellow solution is reduced to form a violet solution containing V^{n+} ions.
This 50.0 cm^3 violet solution contains vanadium in the $+n$ oxidation state.

Stage 3 10.0 cm^3 of the violet solution is titrated with 2.25×10^{-2} mol dm^{-3} $KMnO_4(aq)$.
13.2 cm^3 of $KMnO_4(aq)$ are required to reach the end-point.

In the titration,

- V^{n+} ions are oxidised back to VO_3^- ions.
- MnO_4^- ions are reduced:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

(i) Why is there no clear colour change at the end-point of this titration?

.....

.....

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

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(ii) Analyse the student's results as follows:

- Determine the value of n in the V^{n+} ions formed in **Stage 2**
- Construct an equation for the reaction that takes place during the titration.

Show all your working.

n = ...

equation:

[7]

[Total: 10]

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

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

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RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

Unit **F325:** Equilibria, Energetics and Elements

Mark Scheme for January 2013

Oxford Cambridge and RSA Examinations

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Annotations available in scoris

Annotation	Meaning
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

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Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

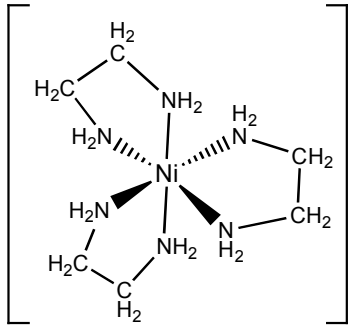
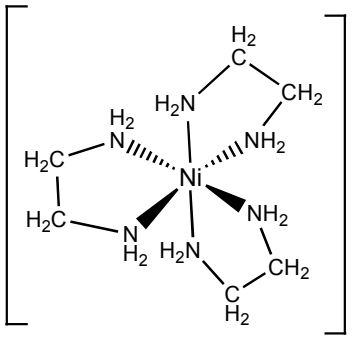
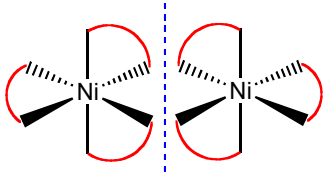
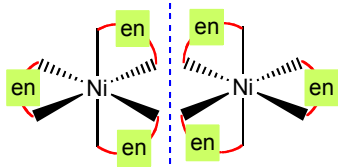
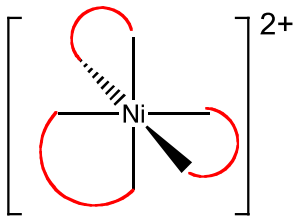
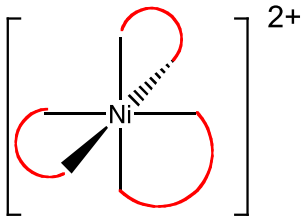
Subject-specific Marking Instructions

The following questions should be fully annotated to show where marks have been awarded in the body of the text: **2(a)(i), 2(b)(ii), 3(b)(ii)**, **4(a), 5(a), 6(e)**, **7(c)(i) and 8(c)(ii)**.

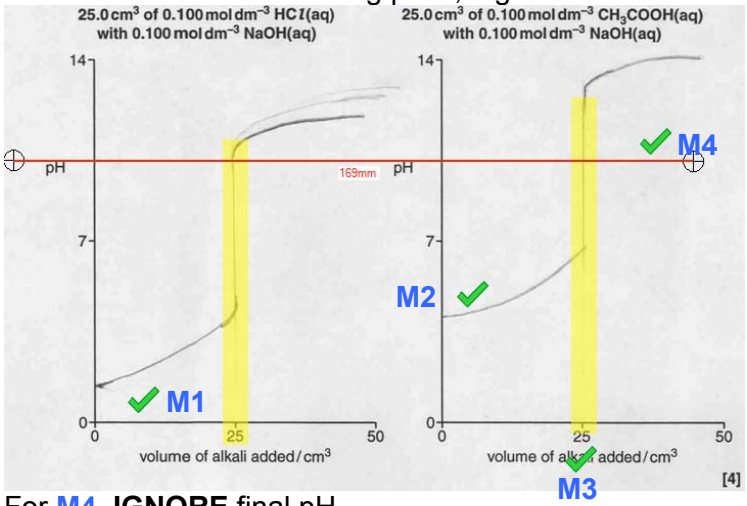
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Question			Answer	Marks	Guidance
					Throughout Q1 **IGNORE** variations in caps and small letters
1	(a)	(i)	Fe ✓	1	**ALLOW** name: iron **DO NOT ALLOW** ions, e.g. Fe^{2+}
1	(a)	(ii)	Ti ✓ Ni ✓	2	**ALLOW** names: titanium and nickel **DO NOT ALLOW** ions
1	(a)	(iii)	Co ✓	1	**ALLOW** name: cobalt **ALLOW** Co^{2+}
1	(a)	(iv)	Mn ✓	1	**ALLOW** name: manganese **ALLOW** Mn_3O_4
1	(a)	(v)	Cr ✓	1	**ALLOW** name: chromium
1	(b)		deep-blue solution: $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ✓ yellow solution: $CuCl_4^{2-}$ ✓ pale-blue precipitate: $Cu(OH)_2$ ✓	3	**DO NOT ALLOW** $[Cu(NH_3)_4]^{2+}$ **OR** $[Cu(NH_3)_6]^{2+}$ **[ ] not required** **ALLOW round brackets around any atom** **e.g. ALLOW** $[CuCl_4]^{2-}$**;** $Cu(Cl_4)^{2-}$ **DO NOT ALLOW** $[Cu(Cl^-)_4]^{2-}$ **OR** $[Cu^{2+}(Cl^-)_4]^{2-}$ **ALLOW** $Cu(OH)_2(H_2O)_4$ **OR** $[Cu(OH)_2(H_2O)_4]$
1	(c)	(i)	octahedral ✓	1	
1	(c)	(ii)	NiF_6^{4-} **OR** $[NiF_6]^{4-}$ ✓	1	**4–** charge **required** **ALLOW** $[Ni(F)_6]^{4-}$; **ALLOW** NiF_6^{-4} **ALLOW** round brackets **DO NOT ALLOW** F*l* for F **DO NOT ALLOW** $[Ni(F^-)_6]^{4-}$ **OR** $[Ni^{2+}(F^-)_6]^{4-}$

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Question			Answer	Marks	Guidance
1	(c)	(iii)	 2+  2+ ✓ ✓ one mark for each structure *2nd structure must be correct mirror image of 1st structure*	2	1 mark for 3D diagram with ligands attached for ONE stereoisomer Must contain 2 out wedges, 2 in wedges or dotted lines and 2 lines in plane of paper **IGNORE** any charges shown **ALLOW** any attempt to show bidentate ligand. Bottom line shown in diagrams below. **IGNORE** connectivity: ——H_2N OK   **ALLOW**  2+  2+ **ALLOW** 2 x en seen in each bridge
			Total	**13**	

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Question			Answer	Marks	Guidance
2	(a)	(i)	**M1 Shape** On **one** graph (can be either), shape: slight rise/flat, then vertical, then slight rise/flat ✓ **M2 pH at start for acid** Weak acid pH curve starts at higher pH and below pH 7 ✓ **M3 End point** On both graphs, vertical section approximately 25 cm^3 alkali have been added ✓ **M4 pH when alkaline** On both graphs, vertical section is **still vertical** through a ruler line aligned with the top of the pH axis label on left-hand axis ✓	4	**FULL ANNOTATIONS MUST BE USED** --- Use ruler tool for 4th marking point, e.g.  For **M4**, **IGNORE** final pH For **M1** and **M2**, **IGNORE** small gap before curve starts **Note**: If pH curves wrong way round (i.e. adding acid to alkali), **ONLY M3** (25 cm^3) can be awarded
2	(a)	(ii)	pH range (of the indicator) matches vertical section/**rapid** pH change **OR** end point/colour change matches vertical section/rapid pH change ✓	1	**ALLOW** pH range (of the indicator) matches equivalence point **ALLOW** end point/colour change matches equivalence point **IGNORE** colour change matches end point *Colour change is the same as end point*
2	(b)	(i)	(enthalpy change for) the formation of **1 mole H_2O** from reaction of an acid/H^+ with an alkali/base/OH^- ✓	1	**ALLOW** (enthalpy change for) the reaction of 1 mol H^+ with 1 mol of OH^- **DO NOT ALLOW** formation of 1 mol H_2O from *1 mole* of acid and/or *1 mole* of alkali **DO NOT ALLOW** formation of 1 mol H_2O from an acid and its *conjugate* base

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Question			Answer	Marks	Guidance
2	(b)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –57.5 (kJ mol^{-1}) award 3 marks** --- energy change = 70.0 x 4.18 x 16.5 = 4827.9 (J) **OR** 4.8279 (kJ) ✓ amount of H_2O formed = $2.4(0) \times \frac{35.0}{1000}$ = 0.084(0) mol ✓ $\Delta H_{neut} = -\frac{4.8279}{0.084(0)}$ = –57.475 **OR** –57.48 **OR** –57.5 (kJ mol^{-1}) ✓	3	**FULL ANNOTATIONS MUST BE USED** --- **IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **IGNORE** any sign shown **ALLOW** 4830 **AND** 4828 (J) **ALLOW** amount of HC*l* **OR** amount of NaOH (same value) – sign **required** **ALLOW ECF** from $\frac{\text{calculated energy change}}{\text{calculated moles } H_2O}$ **ALLOW** 3 significant figures up to calculator value correctly rounded **Common errors** Use of 289.5 K can give up to 2 marks by **ECF:** = 70.0 x 4.18 x 289.5 = 84.71 **x** amount of H_2O formed = $2.4(0) \times \frac{35.0}{1000}$ = 0.084(0) mol ✓ $\Delta H_{neut} = -\frac{84.71}{0.084(0)}$ = –1008 **OR** –1010 (kJ mol^{-1}) ✓ Use of 35 can give up to 2 marks by **ECF:** = 35.0 x 4.18 x 16.5 = 2413.95 (J) **x** amount of H_2O formed = $2.4(0) \times \frac{35.0}{1000}$ = 0.084(0) mol ✓ $\Delta H_{neut} = -\frac{2.41395}{0.084(0)}$ = –28.7375 **OR** –28.7 (kJ mol^{-1}) ✓

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Question			Answer	Marks	Guidance
2	(b)	(iii)	**Same** energy is spread over larger volume ✓ --- 11 ºC ✓	2	**ALLOW same** energy heats **greater** volume /mass **ALLOW** the following alternatives for '**energy'**: Heat, *q*, *mc*∆*T*, enthalpy **change**, ∆*H* **ALLOW** use to '105 cm^3/105 g' as evidence of 'greater volume/ mass' **ALLOW** use of same energy value as in **2(b)(ii)** as evidence for 'same energy' *May need to refer to previous part, 2(b)(ii)* **IGNORE** more energy heats a greater volume --- **ASSUME** units are ºC unless told otherwise
			Total	**11**	

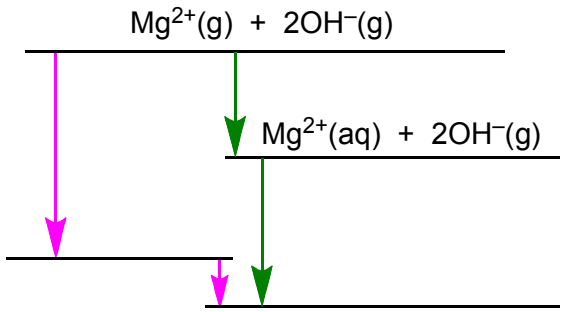
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Question			Answer	Marks	Guidance
3	(a)	(i)	**solution**: (enthalpy change for) 1 mole of a compound/substance/solid/solute dissolving ✓ **----------** **hydration**: (enthalpy change for) 1 mole of gaseous ions **OR** 1 mole of hydrated/aqueous ions ✓ gaseous ions forming aqueous/hydrated ions ✓	3	**IGNORE** 'energy released' **OR** 'energy required' For dissolving, **ALLOW** forms aqueous/hydrated ions **DO NOT ALLOW** dissolving elements **IGNORE** ionic **OR** covalent **DO NOT ALLOW** response that implies formation of **1 mole** of aqueous ions **----------** **IGNORE** 'energy released' **OR** 'energy required' For final mark **IGNORE** gaseous ions are hydrated **IGNORE** gaseous ions dissolve *Particles formed not stated*

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Question			Answer	Marks	Guidance
3	(a)	(ii)	**For 1st two marking points (*Charge* and *Size*),** **IGNORE** 'atomic' and 'atoms' and assume that Mg or Na refer to ions, e.g. **ALLOW** Mg has a smaller (atomic) radius **----------** *Charge* Magnesium ion/Mg^{2+} has greater charge **OR** Mg^{2+} has greater charge density ✓ **----------** *Size* Magnesium ion **OR** Mg^{2+} is smaller ✓ **----------** *Attraction* **Note:** Correct particles required for this mark i.e. **DO NOT ALLOW** Mg; Mg atoms; Na; Na atoms Mg^{2+} has a stronger attraction/ force/ bonding to H_2O /$O^{\delta-}$ ✓	3	**Note:** Charge density can be used to credit the charge mark but **not** size mark **----------** **ORA** Sodium ion/Na^+ has smaller charge **OR** Na^+ has smaller charge density **----------** **ORA:** Sodium ion **OR** Na^+ is larger **IGNORE** smaller charge density (*'charge mark above'*) **IGNORE** idea of close packing of ions **----------** **Note:** Response must refer to attraction/bonding with H_2O or this must be implied from the whole response **ALLOW** Mg^{2+} has a stronger ion–dipole attractions **ORA:** Na^+ has weaker attraction/bonding to H_2O **DO NOT ALLOW** a response implying that *ionic* bonds (between ions) **OR** *covalent* bonds **OR** *hydrogen* bonds are formed

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Question			Answer	Marks	Guidance
3	(a)	(iii)	 ✓ ✓	2	Correct species **AND** state symbols required for both marks **Mark each marking point independently** **ALLOW** response on lower line: $Mg^{2+}(g) + 2OH^-(aq)$ (i.e. OH^- hydrated before Mg^{2+})
3	(a)	(iv)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –2694 (kJ mol^{-1}) award 2 marks** --- Lattice enthalpy $(Mg(OH)_2)$ = [–1926 + (2 x – 460)] – (–152) **OR** – 2846 + 152 ✓ = –2694 ✓ (kJ mol^{-1})	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. **See list below for marking of answers from common errors** --- **ALLOW** for 1 mark: –2234: *use of OH^- rather than 2 x OH^-* (+)2694: *signs all reversed* –2998: *sign wrong for 152* (+)1158: *sign wrong for 1926* –854: *sign wrong for 2 x 460* (+)2998: *sign wrong for 2846* **IF ALL 3 relevant values from the information at the start of Q3 have NOT been used, award zero marks unless one number has a transcription error, where 1 mark can be awarded ECF**

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Question			Answer	Marks	Guidance
3	(b)	(i)	• ΔH **positive** (Intermolecular) bonds/forces are being broken ✓ • ΔS Increase in disorder/ randomness/ number of arrangements (of particles/molecules/energy) ✓ • **Comparison of ΔS (QWC)** In a gas, molecules/particles are **much** more disordered/ random (than in liquids and solids) ✓	3	**ALLOW** hydrogen bonds **DO NOT ALLOW** breaking of ionic **OR** covalent bonds **IGNORE** a response comparing bonds made and bonds broken (*boiling involves just breaking bonds*) **ALLOW** liquids are more disordered than solids **OR** gases are more disordered than liquids **ALLOW** in a gas, molecules are **much** further apart (than in liquids and solids) **IGNORE** ΔS is much greater (*in question*)
3	(b)	(ii)	$\Delta S = \Sigma S$(products) – ΣS(reactants) = 70.0 – 48.0 **OR** 22(.0) **OR** 0.022 (kJ K^{-1} mol^{-1}) ✓ $T = \frac{6.01}{0.022}$ = 273 (K) **OR** ΔG = 6.01 – 273 x 0.022 ✓ ΔG = 0 **OR** 0 = $\Delta H - T\Delta S$ stated anywhere ✓	3	**FULL ANNOTATIONS MUST BE USED** --- **NO UNITS** required **ALLOW** 273.18 (K) **OR** 273.2 (K) **ASSUME** units are K unless told otherwise **ALLOW** ΔG = 6.01 – 6.006 = +4 x 10^{-3} **ALLOW** 4 x 10^{-3} ~ 0 **ALLOW** 4 x 10^{-3} is very close to zero
			Total	**16**	

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Question			Answer	Marks	Guidance
4	(a)		**Experimental:** ***2 marks*** vary $[S_2O_8^{2-}]$ while keeping $[I^-]$ constant ✓ vary $[I^-]$ while keeping $[S_2O_8^{2-}]$ constant ✓ **Obtaining rate from time** ***1 mark*** Rate $\propto 1/t$ **OR** rate = conc/time ✓ **Rate–concentration relationship – QWC** ***1 mark*** rate–concentration graph gives straight line through origin/0,0 **OR** when concentration doubles, rate doubles **OR** rate is proportional to concentration ✓	4	**FULL ANNOTATIONS MUST BE USED** --- **ALLOW** for 1 mark: 'keep one concentration constant whilst varying the other' **OR** vary the concentration of each reactant in turn, e.g. vary $[S_2O_8^{2-}]$ and then vary $[I^-]$ **ALLOW** rate = $1/t$ **OR** amount/time ***ALLOW*** *expressions communicating* rate $\propto 1/t$ **ALLOW** rate = gradient/tangent of a concentration–time graph **AND** measured at $t = 0$ **ALLOW** 'conc and rate increase by same factor/amount' **OR** 'change in concentration is same as change in rate **ALLOW** 'when concentration doubles, time halves' **IGNORE** constant half-life from conc–time graph *Half life is from continuous method, not in initial rates*
	(b)		$rate = k[I^-][S_2O_8^{2-}]$ **OR** $k = \frac{rate}{[I^-][S_2O_8^{2-}]}$ **OR** $\frac{1.2 \times 10^{-3}}{(8.0 \times 10^{-2}) \times (4.0 \times 10^{-3})}$ ✓ = 3.75 **OR** 3.8 ✓ $dm^3\ mol^{-1}\ s^{-1}$ ✓	3	**Correct numerical answer subsumes previous marking point** **ALLOW** $mol^{-1}\ dm^3\ s^{-1}$ **NO ECF** from incorrect rate equation or k expression

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Question			Answer	Marks	Guidance
	(c)	(i)	**Equation 1:** $S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$ ✓ **Equation 2:** $2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$ ✓	2	**ALLOW** correct multiples **IGNORE** state symbols **ALLOW** 1 mark for **2** correct equations in wrong order: i.e. $2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+}$ $S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$ **ALLOW** ⇌ sign shown instead of arrow as long as equation is shown the 'right way around'
		(ii)	Fe^{3+} could react with I^- ions first ✓	1	**ALLOW** equations in **(i)** could take place in the other order **IGNORE** responses that compare *E* values
			Total	**10**	

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Question			Answer	Marks	Guidance
5	(a)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = 14.6 dm^6 mol^{-2} award 6 marks** **(5 for 14.6 and 1 for units)** **----------** equilibrium amount of CO = 0.114 – 0.052 = 0.062 (mol) ✓ equilibrium amount of H_2 = 0.152 – 2 x 0.052 = 0.048 (mol) ✓ [CO] = 5 x 0.062 = 0.31 (mol dm^{-3}) **AND** [H_2] = 5 x 0.048 = 0.24 (mol dm^{-3}) **AND** [CH_3OH] = 5 x 0.052 = 0.26 (mol dm^{-3}) ✓ (K_c =) $\frac{[CH_3OH]}{[CO]\,[H_2]^2}$ **OR** $\frac{0.26}{0.31 \times 0.24^2}$ ✓ = 14.6 ✓ dm^6 mol^{-2} ✓	6	**FULL ANNOTATIONS MUST BE USED** **----------** **IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. **See list below for marking of answers from common errors** **----------** **ALLOW ECF** from equilibrium amounts Mark is for converting **ALL** 3 amounts into concentrations. For units, **ALLOW** mol^{-2} dm^6 **ALLOW ECF** from previous calculated values **OR** incorrect K_c expression **BUT** final answer **MUST** be to 3 SF (in question) **Common errors for K_c** 364: missing x 5 to calculate concentrations 4 marks + units mark (i.e. just one mark dropped) 3.35: H_2 = 0.100 by not using **2** H_2 4 marks + units mark (i.e. just one mark dropped) 0.79**0:** Use of initial amounts of CO and H_2) (3 marks + units mark) 0.79 Use of initial amounts of CO and H_2 **AND** answer not to 3 SF (2 marks + units mark)

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Question	Answer	Marks	Guidance
(b)		4	**IGNORE** responses in terms of rate **Note**: **ALLOW** suitable alternatives for 'to right' e.g. towards CH_3OH **OR** towards products **OR** in forward direction **OR** increases yield of CH_3OH/products **ALLOW** 'favours the right', as alternative for 'shifts equilibrium to right' ----------
	Pressure: higher pressure shifts (equilibrium position) to the right **AND** right-hand side has fewer (gaseous) moles ✓		**ALLOW** equilibrium shifts to the right **AND** a statement that the concentrations on the top of K_c expression increases less than the bottom
	Temperature: higher temperature shifts (equilibrium position) to left **AND** (forward) reaction is exothermic / ΔH is –ve / gives out heat **OR** reverse reaction is endothermic / ΔH is +ve / takes in heat ✓		
	K_c decreases **AND** (forward) reaction is exothermic ✓		**ALLOW** K_c decreases **AND** reverse reaction is endothermic **Note:** exothermic/endothermic part of **AND** statement may be anywhere within the response
	Comparison Relative effect of pressure and temperature is not known ✓		Pressure and temperature send the equilibrium in opposite directions is **not** sufficient **IGNORE** 'temperature and pressure cancel each other out'
	Total	**10**	

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Question			Answer	Marks	Guidance
6	(a)		**Circuit**: complete circuit with voltmeter and salt bridge linking two half-cells ✓ **Half cells**: Pt **AND** H^+/HCl (solution) **AND** H_2 gas (introduced via enclosed container around Pt) ✓ Fe **AND** Fe^{2+} (solution) ✓ **Conditions**: 1 mol dm^{-3} solutions **AND** 298 K / 25 ºC **AND** 1 atm/100 kPa/101 kPa/1 bar pressure ✓	4	Voltmeter must be shown **AND** salt bridge must be labelled **ALLOW** any correct circuit for a cell **ALL** labels required In H_2 half cell, **DO NOT ALLOW** just 'acid' **ALL** conditions required **ALLOW** if 1 mol dm^{-3}/1M mentioned for just one solution *Look also on diagram in addition to answer lines* **DO NOT ALLOW** 1 mol for concentration
	(b)	(i)	oxygen electrode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ ✓ hydrogen electrode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$ ✓	2	**ALLOW** multiples for each equation State symbols **NOT** required – **IGNORE** even if wrong If oxygen and hydrogen equations are written on the wrong lines **ALLOW** 1 mark if both correct **ALLOW** ⇌ sign shown instead of arrow as long as equation is shown the 'right way around' **ALLOW** one mark if both acid equations are given *i.e.* oxygen electrode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ **AND** hydrogen electrode: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$
		(ii)	$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ ✓	1	**ALLOW** multiples, e.g. $H_2 + ½O_2 \rightarrow H_2O$ **IGNORE** state symbols **DO NOT ALLOW** if H_2O **OR** OH^- **OR** e^- are shown on both sides
		(iii)	1.23 (V) ✓	1	This is the **ONLY** correct answer

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Question	Answer	Marks	Guidance
(c)	A fuel cell reacts a fuel/H_2 with oxygen to produce a voltage/**electrical** energy ✓	1	**ALLOW** a fuel cell requires constant supply of a fuel/H_2 (and oxygen)/reactants **OR** operates continuously as long as a fuel/H_2 (and oxygen) are added **DO NOT ALLOW** storage cells can be recharged (Not all storage cells can be recharged)
(d)	Fossil fuels used to make hydrogen **OR** fossil fuels required to make fuel cell ✓	1	Response requires link between **fossil fuels / carbon-containing compounds** and manufacture of the fuels cell or H_2 i.e. energy required to make H_2 is **not** sufficient
(e)	Correctly calculates amount of Cr = 1.456/52.0 = **0.028(0)** ✓ **NOTE: The remaining marks are ONLY available if a 3:2 molar ratio has been used** **3** mol **X** reacts with **2** mol Cr^{3+} **OR 3** mol **X** ⟶ **2** mol Cr ✓ Correctly calculates amount of **X** = amount of Cr **x 1.5** = 0.028(0) x 1.5 = **0.042(0)** ✓ Correctly calculates Molar mass/A_r of **X** = 1.021/0.042(0) = **24.3** (g mol^{-1}) **AND** **X** identified as Mg ✓	4	**FULL ANNOTATIONS MUST BE USED** --- **ALLOW** equation: $2Cr^{3+} + 3X \longrightarrow 3X^{2+} + 2Cr$ **Note**: 3rd marking point subsumes the 2nd marking point **ALLOW** magnesium **OR** Mg^{2+} Mg with no evidence of how 24.3 had been calculated does **not** score this mark **ALLOW ECF** from incorrect amount of Cr for 2nd, 3rd and 4th marks --- **Common error** 3:2 ratio inverted between 2nd and 3rd marks: 3 marks: 3rd mark ECF: 0.028(0) ÷ 1.5 = 0.0187 (mol) ✓ Molar mass of **X** = 54.7 (g mol^{-1}) **AND X** = Mn ✓
	Total	**14**	

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Question			Answer	Marks	Guidance
7	(a)		$CaCO_3 + 2SO_2 + H_2O \longrightarrow Ca(HSO_3)_2 + CO_2$ ✓	1	**ALLOW** multiples
	(b)	(i)	weak acid: partly dissociates ✓ $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ ✓	2	**ALLOW** ionisation for dissociation $\rightleftharpoons$ sign is required **ALLOW** multiples; state symbols **not** required **DO NOT ALLOW** equation with Ca^{2+} added to each side
		(ii)	$Mg + Ca(HSO_3)_2 \longrightarrow MgSO_3 + CaSO_3 + H_2$ ✓ $Mg + 2H^+ \longrightarrow Mg^{2+} + H_2$ ✓	2	**ALLOW** multiples State symbols **not** required **ALLOW** as products: $MgCa(SO_3)_2 + H_2$ **DO NOT ALLOW** $Mg + Ca(HSO_3)_2 \longrightarrow Mg^{2+} + Ca^{2+} + 2\,SO_3^{2-} + H_2$ **ALLOW** $Mg + 2HSO_3^- \longrightarrow Mg^{2+} + 2\,SO_3^{2-} + H_2$
		(iii)	HSO_3^- can accept a proton/H^+ and donate a proton/H^+ **OR** Base accepts a proton/H^+ **AND** Acid donates a proton/H^+ ✓ $HSO_3^- + OH^- \longrightarrow H_2O + SO_3^{2-}$ ✓ $HSO_3^- + H^+ \longrightarrow H_2O + SO_2$ ✓ **Two correct** equations linked to acid and base behaviour ✓ *This could simply be labels (Acid **AND** base) for each equation,* *i.e.* $HSO_3^- + OH^- \longrightarrow H_2O + SO_3^{2-}$ Acid $HSO_3^- + H^+ \longrightarrow H_2O + SO_2$ Base	4	**ASSUME** 'It' applied to HSO_3^- **ALLOW** equations with $\rightleftharpoons$ **ALLOW** $HSO_3^- + H^+ \longrightarrow H_2SO_3$ **Note**: Final mark can only be awarded if **both** equations are correct

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Question			Answer	Marks	Guidance
	(c)	(i)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF M_r = 122 award first 5 marks** **6th mark is for formula** --- $[H^+] = 10^{-pH} = 10^{-3.52} = 3.02 \times 10^{-4}$ (mol dm^{-3}) ✓ $K_a = \frac{[H^+]\,[A^-]}{[HA]}$ **OR** $\frac{[H^+]^2}{[HA]}$ **OR** $\frac{(3.02\times10^{-4})^2}{[HA]}$ ✓ $[HA] = \frac{(3.02\times10^{-4})^2}{1.51\times10^{-5}}$ ✓ [HA] = 6.04 x 10^{-3} (mol dm^{-3}) ✓ $M = \frac{0.7369}{6.04\times10^{-3}}$ = 122(.0) (g mol^{-1}) ✓ Carboxylic acid is C_6H_5COOH **OR** $C_7H_6O_2$ ✓	6	**FULL ANNOTATIONS MUST BE USED** --- Throughout calculation, **ALLOW** 3 significant figures up to calculator value correctly rounded **ALLOW** 3 SF to calculator value of 3.01995172 x 10^{-4} **ALLOW** any correct equation that shows the relationship between K_a, [H$^+$], [A$^-$], [HA] Correct [HA] expression and calculation subsumes previous marks Using calculator [H$^+$] value, [HA] = 6.039806883 x 10^{-3} Using calculator [HA] value, M_r = 122.0072122 **ALLOW** any feasible formula with a molar mass of 122 containing C, H **AND** at least **two O** atoms e.g. $C_6H_2O_3$; $C_3H_6O_5$ **Note**: a structural formula must contain COOH/CO_2H **ALLOW ECF** for possible formula of HA from an incorrectly calculated molar mass of HA **Note**: the possible formula must be feasible and must contain C, H **AND** at least **two O** atoms **IF** '$[HA]_{eqm}$ = [HA] – [H$^+$]' has been used, M_r = 116 and formula is $C_5H_{11}COOH$ **OR** $C_6H_{12}O_2$ **ALL** marks are available for this answer Calculator unrounded M_r = 116.1972565

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Question			Answer	Marks	Guidance
		(ii)	student is incorrect **AND** acid releases all H^+ ions **OR** more acid dissociates ✓	1	Statement **AND** reason required for the mark **ALLOW** incorrect **AND** equilibrium shifts to right **Note**: The key idea is that more H^+ ions are produced by more dissociation A comment that all the H^+ ions react is just repeating information in the question
			Total	**16**	

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Question			Answer	Marks	Guidance
8	(a)		$(1s^2 2s^2 2p^6)\ 3s^2 3p^6 3d^2$ ✓	1	**ALLOW** $4s^0$: $(1s^2 2s^2 2p^6)\ 3s^2 3p^6 3d^2 4s^0$ **ALLOW** subscripts for superscripts **ALLOW** S, P, D (i.e. upper case)
8	(b)		(Only) 5 electrons in 4s and 3d sub-shells/orbitals ✓	1	**ALLOW** 3d sub-shell is empty **OR** no d electrons left **ALLOW** 6th electron in a 3p sub-shell/orbital **ALLOW** too much attraction on 3p electrons **OR** a lot of energy required to remove 3p electrons **IGNORE** only 5 electrons in outer shell **IGNORE** full outer shell/noble gas electron configuration **IGNORE** no 3d sub-shell **Note**: Key comment about 3d sub-shell being empty **OR** non-removal/greater attraction of 3p electrons
8	(c)	(i)	$KMnO_4$ is purple/pink **AND** V^{n+}/V^{2+} is violet ✓	1	**ALLOW** $KMnO_4$ **AND** V^{n+}/V^{2+} have similar colours **ALLOW** $KMnO_4$ is purple and 'the solution' is violet *Assumption is that 'the solution'* is $V^{2+}(aq)$ **ALLOW** any reasonable description of purple/mauve/violet colours **DO NOT ALLOW** just '$KMnO_4$ is purple/pink' **IGNORE** reference to Mn^{2+} being (pale) pink

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Question			Answer	Marks	Guidance
8	(c)	(ii)	**Marks are for correctly calculated values. Working shows how values have been derived.** $n(KMnO_4) = \frac{2.25\times10^{-2}\times13.2}{1000}$ = **2.97×10^{-4}** (mol) ✓ $n(V) = \frac{0.126}{50.9}$ = **2.48×10^{-3}** (mol) ✓ *Factor of 5:* $\frac{2.48\times10^{-3}}{5}$ = **4.96×10^{-4}** (mol) **OR** 5 x 2.97×10^{-4} = **1.485×10^{-3}** (mol) ✓ ratio $\frac{n(V^{n+})}{n(MnO_4^-)} = \frac{4.96\times10^{-4}}{2.97\times10^{-4}} = \frac{1.67}{1}$ **OR** 1.67 **OR** $\frac{5}{3}$ **OR** 1 mol MnO_4 reacts with 1.67 mol V^{n+} ✓ 5 : 3 ratio seen **AND** n = 2 ✓ Correct equation with all species on both sides cancelled: $5V^{2+}(aq) + 3MnO_4^-(aq) + 3H_2O(l) \longrightarrow 5VO_3^-(aq) + 3Mn^{2+}(aq) + 6H^+(aq)$ $5V^{2+} + 3MnO_4^-$ on left **AND** $5VO_3^- + 3Mn^{2+}$ on right ✓ Complete equation correct ✓	7	**FULL ANNOTATIONS MUST BE USED** --- **ALLOW 2.48 x 10^{-3}** up to calculator value of 2.475442043 x 10^{-3}, correctly rounded **ALLOW 4.95 × 10^{-4}** (mol) from 2.475442043 x 10^{-3} **ALLOW** ratio $\frac{n(V^{n+})}{n(MnO_4^-)} = \frac{2.48\times10^{-3}}{1.485\times10^{-3}} = \frac{1.67}{1}$ **OR** 1.67 **OR** $\frac{5}{3}$ **ALLOW** inverse ratio **DO NOT ALLOW** n = 2 without some justification e.g.: 3 mol MnO_4^- reacts with 5 mol V^{2+}; V changes oxidation number by 3 **OR** 3 electrons transferred to V **IGNORE** state symbols --- ***ALLOW any attempted equation using n = 2, 3 OR 4.*** ***See correct eqn for n=2 and equations on next page*** ---

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Question			Answer	Marks	Guidance
8	(c)	(ii)	*Cont.*		**From V^{4+} :** $5V^{4+}(aq) + MnO_4^-(aq) + 11H_2O(l) \rightarrow 5VO_3^-(aq) + Mn^{2+}(aq) + 22H^+(aq)$ $5V^{4+}$ + MnO_4^- on left **AND** $5VO_3^-$ + Mn^{2+} on right ✓ Complete equation correct ✓ **----------** **From V^{3+} :** $5V^{3+}(aq) + 2MnO_4^-(aq) + 7H_2O(l) \rightarrow 5VO_3^-(aq) + 2Mn^{2+}(aq) + 14H^+(aq)$ ✓✓ $5V^{3+}$ + $2MnO_4^-$ on left **AND** $5VO_3^-$ + $2Mn^{2+}$ on right ✓ Complete equation correct ✓
			Total	**10**	

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RECOGNISING ACHIEVEMENT

Wednesday 13 June 2012 – Morning

A2 GCE CHEMISTRY A

F325 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

F3147506122

F325

Candidate forename		Candidate surname	

Centre number						Candidate number				

INSTRUCTIONS TO CANDIDATES

- The insert will be found in the centre of this document.
- Write your name, centre number and candidate number in the boxes above. Please write clearly and in capital letters.
- Use black ink. Pencil may only be used for graphs and diagrams where they appear.
- Read each question carefully. Make sure that 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 pages at the end of this booklet. The question number(s) must be clearly shown.
- Answer **all** the questions.
- 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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Turn over

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Answer **all** the questions.

1 Lattice enthalpy can be used as a measure of ionic bond strength. Lattice enthalpies can be determined indirectly using Born–Haber cycles.

The table below shows the enthalpy changes that are needed to determine the lattice enthalpy of lithium fluoride, LiF.

enthalpy change	**energy / kJ mol^{-1}**
1st electron affinity of fluorine	–328
1st ionisation energy of lithium	+520
atomisation of fluorine	+79
atomisation of lithium	+159
formation of lithium fluoride	–616

(a) Define the term *lattice enthalpy*.

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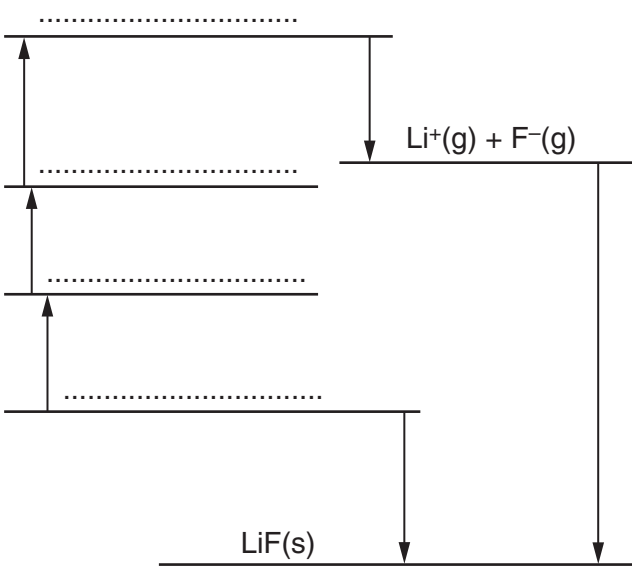
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..... **[2]**

(b) The diagram below shows an incomplete Born–Haber cycle that would allow the lattice enthalpy of lithium fluoride to be determined.

(i) On the four dotted lines, add the species present, including state symbols.



[4]

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(ii) Calculate the lattice enthalpy of lithium fluoride.

lattice enthalpy = ... $kJ\,mol^{-1}$ **[2]**

(c) The change that produces lattice enthalpy is spontaneous but has a negative entropy change.

Why is this change able to take place spontaneously?

.....

.....

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

(d) The lattice enthalpies of sodium fluoride, sodium chloride and magnesium fluoride are shown below.

compound	**lattice enthalpy / $kJ\,mol^{-1}$**
sodium fluoride	–918
sodium chloride	–780
magnesium fluoride	–2957

Explain the differences between these lattice enthalpies.

In your answer, your explanation should show how different factors affect lattice enthalpy.

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

[Total: 12]

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2 A chemist carries out an investigation on the equilibrium system shown below.

$$2CO(g) + 2NO(g) \rightleftharpoons 2CO_2(g) + N_2(g) \qquad \Delta H = -788\,kJ\,mol^{-1}$$

The chemist mixes 0.46 mol of CO with 0.45 mol of NO. The mixture is left to reach equilibrium at constant temperature.

The student analyses the equilibrium mixture and finds that 0.25 mol NO remains. The total volume of the equilibrium mixture is 1.0 dm^3.

(a) (i) Write the K_c expression for this equilibrium.

[1]

(ii) What are the units of this equilibrium constant?

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

(iii) Determine the value of K_c for this equilibrium mixture.

Show all your working.

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

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(iv) What does your value of K_c suggest about the position of equilibrium in this experiment?

.....

.....

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

(b) The chemist increases **both** the temperature and the pressure of the equilibrium mixture. The mixture is left to reach equilibrium again.

(i) What is the effect, if any, on the value of K_c? Explain your answer.

.....

.....

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

(ii) Explain why it is difficult to predict what would happen to the position of equilibrium after these changes in temperature and pressure.

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

[Total: 10]

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3 Butanoic acid, $CH_3(CH_2)_2COOH$, is the 'butter acid', formed when butter turns rancid and tastes sour. A student prepares an aqueous solution of butanoic acid with a concentration of $0.250\,mol\,dm^{-3}$.

The K_a of butanoic acid is $1.51 \times 10^{-5}\,mol\,dm^{-3}$.

(a) (i) Write the expression for the acid dissociation constant of butanoic acid.

[1]

(ii) Calculate the pK_a of butanoic acid.

pK_a = ... **[1]**

(iii) Calculate the pH of the $0.250\,mol\,dm^{-3}$ butanoic acid.

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

pH = ... **[3]**

(b) The student adds aqueous butanoic acid to magnesium.

The student then adds aqueous butanoic acid to aqueous sodium carbonate.

(i) Write the ionic equation for the reaction between aqueous butanoic acid and magnesium.

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

(ii) Write the ionic equation for the reaction between aqueous butanoic acid and aqueous sodium carbonate.

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

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(c) The student adds 50.0 cm^3 of 0.250 $mol\,dm^{-3}$ butanoic acid to 50.0 cm^3 of 0.0500 $mol\,dm^{-3}$ sodium hydroxide. A buffer solution forms.

(i) Explain why a buffer solution forms.

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

(ii) Calculate the pH of the buffer solution.

The K_a of butanoic acid is $1.51 \times 10^{-5}\,mol\,dm^{-3}$.

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

pH = ... **[5]**

(d) The student adds methanoic acid, HCOOH ($K_a = 1.82 \times 10^{-4}\,mol\,dm^{-3}$), to butanoic acid. A reaction takes place to form an equilibrium mixture containing two acid–base pairs.

Complete the equilibrium below and label the conjugate acid–base pairs.

$HCOOH + CH_3(CH_2)_2COOH \rightleftharpoons$ ..... + ...

....

[2]

[Total: 16]

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4 Nitrogen dioxide reacts with ozone as shown below.

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g)$$

(a) The kinetics of the reaction between NO_2 and O_3 was investigated and the following experimental results were obtained.

experiment	$[NO_2(g)]$ / mol dm^{-3}	$[O_3(g)]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.00150	0.00250	4.80×10^{-8}
2	0.00225	0.00250	7.20×10^{-8}
3	0.00225	0.00500	1.44×10^{-7}

(i) Determine the rate equation and rate constant for the reaction of $NO_2(g)$ and $O_3(g)$.

In your answer you should make clear how your conclusions fit with the experimental results.

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..... **[8]**

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(ii) Suggest a possible two-step mechanism for this reaction.

.....

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

(b) The feasibility of the reaction between NO_2 and O_3 is influenced by the enthalpy change and entropy change of the reaction and the temperature.

$$2NO_2(g) + O_3(g) \longrightarrow N_2O_5(g) + O_2(g) \qquad \Delta H = -198\,kJ\,mol^{-1}, \quad \Delta S = -168\,J\,K^{-1}\,mol^{-1}$$

(i) Explain why this reaction has a negative entropy change.

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

(ii) Calculate the value of ΔG, in $kJ\,mol^{-1}$, at 25 °C for the reaction of NO_2 with O_3.

$\Delta G =$ ..... $kJ\,mol^{-1}$ **[3]**

(iii) State and explain how the feasibility of this reaction will change with increasing temperature.

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

[Total: 17]

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5 Iron, copper and platinum are examples of transition elements.

(a) Define the term *transition element*.

Show that iron fits this definition by use of full electron configurations of iron as the element and in its common oxidation states.

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

(b) Describe **one** precipitation reaction and **one** ligand substitution reaction of copper in the +2 oxidation state.

Your answer should include reagents, relevant observations and balanced equations.

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

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(c) Platinum is an extremely unreactive transition element. However, platinum does take part in a redox reaction with '*aqua regia*', a mixture of concentrated hydrochloric and nitric acids. Two products of this reaction are hexachloroplatinic acid, H_2PtCl_6, and nitrogen dioxide, NO_2.

(i) Use oxidation states to show that this is a redox reaction.

.....

.....

.....

.....

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

(ii) Write an equation for the reaction of platinum metal with *aqua regia*.

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

(d) Ammonium hexachloroplatinate, $(NH_4)_2PtCl_6$, is a complex of platinum used in platinum plating. Ammonium hexachloroplatinate contains the hexachloroplatinate ion.

Draw a 3-D diagram to show the shape of a hexachloroplatinate ion.

On your diagram, show

- the charge on the ion
- the value of the bond angle.

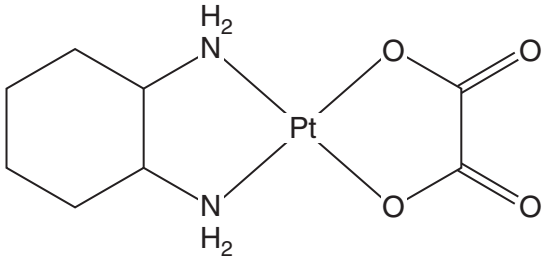
[3]

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(e) Oxaliplatin is a neutral complex of platinum(II) used in cancer treatment.

A molecule of oxaliplatin has a square planar shape about the metal ion with two bidentate ligands. The structure of oxaliplatin is shown below.



(i) What is meant by a *bidentate ligand*?

.....

.....

.....

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

(ii) In the boxes below, show the structures of the two bidentate ligands in oxaliplatin.

[2]

[Total: 21]

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TURN OVER FOR QUESTION 6

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6 Standard electrode potentials for eight redox systems are shown in **Table 6.1**.

You will need to use this information throughout this question.

redox system	half-equation	$E^{\ominus}$/V
1	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
2	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
3	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
4	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
5	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
6	$CO_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons HCOOH(aq)$	–0.22
7	$HCOOH(aq) + 2H^+(aq) + 2e^- \rightleftharpoons HCHO(aq) + H_2O(l)$	+0.06
8	$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.74

Table 6.1

(a) A student sets up a standard cell in the laboratory based on redox systems **2** and **8**. His circuit allows him to measure the standard cell potential.

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

[3]

(ii) Write down the overall cell reaction.

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

(iii) Write down the standard cell potential.

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

(b) Select from **Table 6.1**, the strongest oxidising agent.

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

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(c) Using the redox systems in **Table 6.1**, construct an equation for a reaction between acidified dichromate(VI) ions and methanoic acid, HCOOH.

Rather than using [O] or [H], your equation must show the actual reactants and products.

[2]

(d) A student added some chromium metal to an acidified solution containing copper(II) ions. A reaction took place. The student concluded that 'chromium is more reactive than copper'.

(i) Explain, in terms of their electrode potentials, why 'chromium is more reactive than copper' in this reaction.

.....

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

(ii) When this experiment was carried out, the student observed some bubbles of a gas.

Suggest an explanation for this observation.

.....

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

(e) Methanoic acid, HCOOH, has the common name of 'formic acid'. Direct-Formic Acid Fuel Cells (DFAFCs) are being developed for use in small, portable electronics such as phones and laptop computers.

In this fuel cell, methanoic acid (the fuel) reacts with oxygen to generate a cell potential.

(i) Predict the standard cell potential of a DFAFC.

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

(ii) Suggest **two** advantages of using methanoic acid as the fuel in a fuel cell rather than hydrogen.

.....

.....

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

[Total: 14]

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7 Potassium manganate(VII) can be prepared in the laboratory by a two-step synthesis starting from manganese(IV) oxide.

Step 1

In this step, manganese(IV) oxide is heated strongly with potassium hydroxide and potassium chlorate(V), a powerful oxidising agent.

Manganese(IV) oxide, MnO_2, is oxidised to manganate(VI) ions.

Step 2

Potassium manganate(VI) is separated from the alkaline mixture from **step 1** as a green solid.

In this step, potassium manganate(VI) is heated in water. Manganate(VI) ions disproportionate forming manganate(VII) ions and a precipitate of manganese(IV) oxide.

(a) In **step 1**, a redox reaction takes place.

Add the correct number of electrons to the correct sides of the incomplete oxidation and reduction half-equations shown below.

$$MnO_2 + 4OH^- \rightarrow MnO_4^{2-} + 2H_2O$$

$$3H_2O + ClO_3^- \rightarrow 6OH^- + Cl^-$$

[2]

(b) In **step 2**, an equilibrium is set up.

$$3MnO_4^{2-}(aq) + 2H_2O(l) \rightleftharpoons 2MnO_4^-(aq) + MnO_2(s) + 4OH^-(aq)$$

The equilibrium position can be shifted by bubbling carbon dioxide gas through the mixture.

Suggest, with the aid of an equation, how the equilibrium position shifts.

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

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(c) Aqueous potassium manganate(VII), $KMnO_4$, in acidic conditions can be used in analysis.

A student analyses a sample of sodium sulfite, Na_2SO_3, using the following method.

- The student dissolves 0.720 g of impure sodium sulfite in water.
- The solution is made up to 100.0 cm^3.
- The student titrates 25.0 cm^3 of this solution with 0.0200 mol dm^{-3} $KMnO_4$ under acidic conditions. The volume of $KMnO_4$(aq) required to reach the end-point is 26.2 cm^3.

The equation for the reaction is shown below.

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Determine the percentage purity of the sample of sodium sulfite.

percentage purity = ... % **[5]**

[Total: 10]

END OF QUESTION PAPER

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ADDITIONAL PAGE

If additional space is required, you should use the lined pages below. The question number(s) must be clearly shown.

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GCE

Chemistry A

Advanced GCE

Unit **F325:** Equilibria, Energetics and Elements

Mark Scheme for June 2012

Oxford Cambridge and RSA Examinations

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Annotations available in Scoris.

Annotation	Meaning
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

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Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

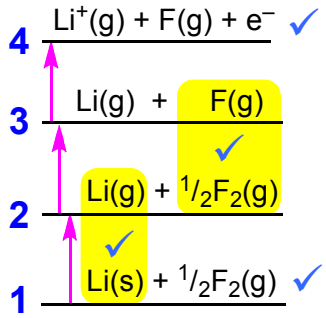
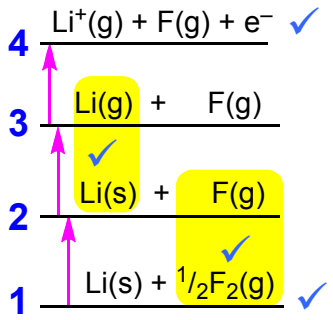
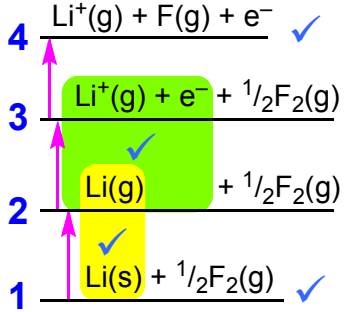
The following questions should be annotated with ticks, crosses, etc. Annotations should be placed to clearly show where they apply within the body of the text (i.e. not in margins)

Question 1(b)(i), (c), (d); **Question 2(a)(iii);** **Question 3c(ii);**
Question 4a(i), (b)(iii); **Question 5(b);** **Question 7(b), (c).**

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Question			Answer	Marks	Guidance
1	(a)		(The enthalpy change that accompanies) the formation of **one mole** of a(n ionic) compound ✓ from its **gaseous ions** ✓ (under standard conditions)	2	**IGNORE** 'Energy needed' **OR** 'energy required' **ALLOW** as alternative for compound: lattice, crystal, substance, solid, product **Note**: 1st mark requires **1 mole** **2nd mark** requires **gaseous ions** **IF** candidate response has '1 mole of gaseous ions', award 2nd mark but **NOT** 1st mark **IGNORE** reference to 'constituent elements' **IGNORE**: $Li^+(g) + F^-(g) \longrightarrow LiF(s)$ *Question asks for a definition, not an equation*

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Question			Answer	Marks	Guidance
1	(b)	(i)	1. Mark **Line 1** first as below (right or wrong) 2. Mark **Line 4** as below (right or wrong) 3. Mark difference in species on **Line 1** and **Line 2** **MUST** match one of the enthalpy changes in the table: atomisation of Li(s) atomisation of ½F_2(g) first ionisation energy of Li(g) 4. Repeat for differences on **Line 2** and **Line 3**		***ANNOTATIONS MUST BE USED*** --- **ALLOW** marks by **ECF** as follows: Follow order at top of Answer column
			 Correct species **and** state symbols required for all marks **IF** an electron has formed, it **MUST** be shown as e^- **OR** e	4	**ALLOW** atomisation of ½F_2(g) before atomisation of Li(s):  **ALLOW** ionisation of Li(g) before atomisation of ½F_2(g):  e^- required for marks involving **Line 3 AND Line 4** **Common errors** **Line 4**: Missing e^- and rest correct 3 marks **Line 1**: **IF** ½F_2(g) is **NOT** shown 2 max [**Line 4** and Li(s) → Li(g)] e.g., for F(g), F(s), F(l), F(aq), F_2(g) **DO NOT ALLOW** F*l* when first seen but credit subsequently

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Question			Answer	Marks	Guidance
1	(b)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –1046 (kJ mol^{-1}) award 2 marks** --- (–616) = (+159) + (+79) + (+520) + (–328) + ΔH_{LE}(LiF) **OR** ΔH_{LE}(LiF) = (–616) –[(+159) + (+79) + (+520) + (–328)] ✓ = –616 – 430 = –1046 (kJ mol^{-1}) ✓	2	**IF** there is an alternative answer, check **the list below for marking of answers from common errors** --- **ALLOW** for **1 mark**: +1046 wrong sign –186 +430 instead of –430 +186 +616 instead of –616 –1006.5 (+79) ΔH_{at}(F) halved to +39.5 –1702 wrong sign for 328 Any other number: **CHECK** for **ECF** from 1st marking point for expressions with **ONE** error only e.g. one transcription error: e.g. +195 instead of +159
	(c)		$\Delta H < T\Delta S$ ***OR*** $\Delta H - T\Delta S < 0$ **OR** ΔH is more negative than $T\Delta S$ **OR** Negative value of ΔH is more significant than negative value of $T\Delta S$ ✓ ——————— **NOTE** **IGNORE** comments about ΔG	1	***ANNOTATIONS MUST BE USED*** **ALLOW** 'exothermic' for negative **ALLOW** a negative lattice energy value **ALLOW** ΔH is negative **AND** magnitude of ΔH > magnitude of $T\Delta S$ **IGNORE ONLY** magnitude of ΔH > magnitude of $T\Delta S$

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Question			Answer	Marks	Guidance
1	(d)		For **FIRST TWO** marking points, assume that the following refer to 'ions', Mg^{2+}, etc. For 'ions', **ALLOW** 'atoms' For Mg^{2+}, Na^+, Cl^- and F^-, **ALLOW** symbols: Mg, Na, Cl and F **ALLOW** names: magnesium, sodium, chlorine, chloride, fluorine, fluoride *i.e.* **ALLOW** Mg has a smaller (atomic) radius For **THIRD** marking point, **IONS** must be used		**DO NOT ALLOW** molecules **ALLOW** F*l* for F
			Comparison of size of anions Chloride ion **OR** Cl^- is larger (than F^-) **OR** Cl^- has smaller charge density (than F^-) ✓ ***Comparison of size AND charge of cations*** Mg^{2+} is smaller (than Na^+) **AND** Mg^{2+} has a greater charge (than Na^+) ✓ ***Comparison of attraction between ions*** F^- has greater attraction for Na^+ / + ions **AND** Mg^{2+} has greater attraction for F^- / – ions ✓ **Quality of Written Communication**: --- Third mark needs to link ionic size and ionic charge with the attraction that results in lattice enthalpy	3	***ANNOTATIONS MUST BE USED*** --- **ORA** F^- is smaller **OR** F^- has a larger charge density ✓ **IGNORE** just Cl^- is large *comparison required* **ORA**: Na^+ is larger **AND** Na^+ has a smaller charge ✓ **IGNORE** just Mg^{2+} is small *comparison required* **ALLOW** 'greater charge density' for 'greater charge' but **NOT** for smaller size ***+ AND – IONS must be used for this mark*** **IGNORE** greater attraction between **ions** in NaF **AND** MgF_2 ***+ AND – ions OR oppositely charged ions are required*** **ASSUME** attraction to be electrostatic unless stated otherwise: e.g. **DO NOT ALLOW** nuclear attraction **ALLOW** pull for attraction **ALLOW** 'attracts with more force' for greater attraction **IGNORE** just 'greater force' (*could be repulsion*) **IGNORE** comparison of bond strength/energy to break bonds **IGNORE** comparisons of numbers of ions **IGNORE** responses in terms of packing
			Total	**12**	

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Question			Answer	Marks	Guidance
2	(a)	(i)	(K_c =) $\frac{[CO_2]^2\,[N_2]}{[CO]^2\,[NO]^2}$ ✓	1	Square brackets required for **ALL** four concentrations
		(ii)	$dm^3\ mol^{-1}$ ✓	1	**ALLOW** $mol^{-1}\ dm^3$

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Question			Answer	Marks	Guidance
2	(a)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 0.95 award **4 marks** --- ***Equilibrium amounts:*** $n(CO) = 0.46 - 0.20 = 0.26$ mol ✓ $n(CO_2) = 0.2(0)$ mol ✓ $n(N_2) = 0.1(0)$ mol ✓ **K_c calculation** **Must** use calculated equilibrium amounts **AND** 0.25 $(K_c =) \frac{0.20^2 \times 0.10}{0.26^2 \times 0.25^2} = 0.95$ (dm^3 mol^{-1}) ✓	4	***ANNOTATIONS MUST BE USED*** **IF** there is an alternative answer, apply **ECF** by checking working for intermediate marks --- **APPLY ECF** from incorrect starting $n(CO)$ By **ECF**, $n(N_2) = n(CO_2)/2$ For **all** parts, **ALLOW** numerical answers from 2 significant figures up to the calculator value **Correct numerical answer with no working scores 4 marks** **ALLOW** calculator value: 0.946745562 down to 0.95 (2SF), correctly rounded, e.g. 0.947 **IGNORE** units, even if incorrect --- **Common errors** 1.89 3 marks use of $n(N_2) = 0.2(0)$ mol $(K_c =) \frac{0.20^2 \times 0.20}{0.26^2 \times 0.25^2} = 1.893491124$ (dm^3 mol^{-1}) ✓ 1.29 3 marks 0.45 and 0.46 swapped over $n(CO) = 0.45 - 0.21 = 0.24$ mol ✓ $n(CO_2) = 0.21$ mol ✓ $n(N_2) = 0.105$ mol ✓ $(K_c =) \frac{0.21^2 \times 0.105}{0.24^2 \times 0.25^2} = 1.28625$ (dm^3 mol^{-1}) ✓ 1.024 3 marks 0.45 used twice $n(CO) = 0.45 - 0.20 = 0.25$ mol ✓ $n(CO_2) = 0.2(0)$ mol ✓ $n(N_2) = 0.1(0)$ mol ✓ $(K_c =) \frac{0.20^2 \times 0.10}{0.25^2 \times 0.25^2} = 1.024$ (dm^3 mol^{-1}) ✓ 1.185 3 marks 0.46 used twice $n(CO) = 0.46 - 0.21 = 0.25$ mol ✓ $n(CO_2) = 0.21$ mol ✓ $n(N_2) = 0.105$ mol ✓ $(K_c =) \frac{0.21^2 \times 0.105}{0.25^2 \times 0.25^2} = 1.185408$ (dm^3 mol^{-1}) ✓

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Question			Answer	Marks	Guidance
2	(a)	(iv)	Mark **ECF** from **(iii)** **IF** K_c from **(iii)** < 1 equilibrium to left/towards reactants **OR** **IF** K_c from **(iii)** > 1 equilibrium to right/towards products ✓	1	**First look at K_c value for (iii) at bottom of cut** **----------** **ALLOW** favours reverse reaction For correct K_c value in **(iii)** of 0.95, **ALSO ALLOW** equilibrium position near to centre ✓
	(b)	**(i)**	K_c has decreased **AND** ΔH is negative **OR** (forward) reaction is exothermic ✓	1	Statement **AND** reason required for mark **ALLOW** for reason: reverse reaction is endothermic
		(ii)	**Effect of *T* and *P* on equilibrium** (increased) temperature shifts equilibrium to left **AND** (increased) pressure shifts equilibrium to right **AND** fewer (gaseous) moles on right-hand side ✓ **Overall effect on equilibrium** Difficult to predict relative contributions of two opposing factors ✓	2	**Reason ONLY** required for pressure Temperature and ΔH had been *required in (i)* **ALLOW** ratio of (gas) moles is 4:3 **ALLOW** opposing effects may not be the same size **ALLOW** effects could cancel each other out **ALLOW** effects oppose one another **DO NOT ALLOW** just 'it is difficult to predict equilibrium position' (*in question*) *For the 2nd mark, we are assessing the idea that we don't know which factor is dominant*
			Total	**10**	

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Question			Answer	Marks	Guidance
3	(a)	(i)	$(K_a =) \frac{[H^+][CH_3(CH_2)_2COO^-]}{[CH_3(CH_2)_2COOH]}$ ✓	1	**ALLOW** $CH_3CH_2CH_2COOH$ **OR** C_3H_7COOH in expression **DO NOT ALLOW** use of HA and A^- in this part. **DO NOT ALLOW**: $\frac{[H^+][CH_3(CH_2)_2COO^-]}{[CH_3(CH_2)_2COOH]} = \frac{[H^+]^2}{[CH_3(CH_2)_2COOH]}$: **CON**
		(ii)	$pK_a = -\log K_a = 4.82$ ✓	1	**ALLOW** 4.82 up to calculator value of 4.821023053 **DO NOT ALLOW** 4.8
		(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 2.71 award **3 marks** --- $[H^+] = \sqrt{[K_a][CH_3(CH_2)_2COOH]}$ **OR** $\sqrt{1.51\times10^{-5}\times0.250}$ ✓ $[H^+] = 1.94 \times 10^{-3}$ (mol dm^{-3}) ✓ $pH = -\log[H^+] = 2.71$ ✓	3	**IF** alternative answer to more or fewer decimal places, check calculator value and working for 1st and 2nd marks --- **ALLOW** use of HA and A^- in this part **Calculator**: $1.942935923 \times 10^{-3}$ **ALLOW** use of calculated K_a value, either calculator value or rounded on script. pH **must** be to 2 decimal places **ALLOW ECF** from incorrectly calculated $[H^+]$ and pH **ONLY** when values for both K_a **AND** $[CH_3CH_2CH_2COOH]$ have been used, i.e. 1.5×10^{-5} **AND** 0.250. e.g.: pH = 5.42 2 marks $-\log(1.51 \times 10^{-5} \times 0.250)$ *No* √ pH = 2.11 2 marks $-\log(\sqrt{\frac{1.51\times10^{-5}}{0.250}})$ pH = 4.22 1 mark $-\log(\frac{1.51\times10^{-5}}{0.250})$ *No* √ **DO NOT ALLOW** just $-\log(1.51 \times 10^{-5}) = 4.82$ **NO MARKS**

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Question			Answer	Marks	Guidance
3	(b)	(i)	$Mg + 2H^+ \longrightarrow Mg^{2+} + H_2$ ✓	1	**IGNORE** state symbols **ALLOW** $Mg + 2\ CH_3(CH_2)_2COOH \longrightarrow 2CH_3(CH_2)_2COO^- + Mg^{2+} + H_2$ **DO NOT ALLOW** on RHS: $(CH_3(CH_2)_2COO^-)_2Mg^{2+}$ ***Ions must be shown separately***
		(ii)	$CO_3^{2-} + 2H^+ \longrightarrow H_2O + CO_2$ ✓	1	**IGNORE** state symbols **ALLOW** $CO_3^{2-} + 2\ CH_3(CH_2)_2COOH \longrightarrow 2\ CH_3(CH_2)_2COO^- + H_2O + CO_2$ **ALLOW** as product H_2CO_3
	(c)	(i)	$CH_3(CH_2)_2COONa$ **OR** $CH_3(CH_2)_2COO^-$ forms **OR** $CH_3(CH_2)_2COOH + OH^- \rightarrow CH_3(CH_2)_2COO^- + H_2O$ ✓ $CH_3(CH_2)_2COOH$ is in excess **OR** acid is in excess **OR** some acid remains ✓	2	**ALLOW names throughout** **ALLOW** '**sodium** salt of **butanoic acid**' **ALLOW** $CH_3(CH_2)_2COOH + NaOH \rightarrow CH_3(CH_2)_2COONa + H_2O$ **DO NOT ALLOW** just 'forms a salt/conjugate base' i.e. identity of product is required

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Question			Answer	Marks	Guidance
3	(c)	(ii)	**Moles (2 marks)** amount $CH_3(CH_2)_2COOH$ = 0.0100 (mol) ✓ amount $CH_3(CH_2)_2COO^-$ = 0.0025 (mol) ✓ **Concentration (1 mark)** $[CH_3(CH_2)_2COOH]$ = 0.100 mol dm^{-3} **AND** $[CH_3(CH_2)_2COO^-]$ = 0.025 mol dm^{-3} ✓ **$[H^+]$ and pH (2 marks)** $[H^+] = 1.51\times10^{-5} \times \frac{0.100}{0.025}$ = 6.04 x 10^{-5} (mol dm^{-3}) ✓ pH = –log 6.04 x 10^{-5} = 4.22 ✓ **pH to 2 DP**	2 1 2	***ANNOTATIONS MUST BE USED*** --- **ALLOW** HA and A^- throughout **Mark** by **ECF** throughout **ONLY** award final 2 marks via a correct pH calculation via $K_a \times \frac{[CH_3(CH_2)_2COOH]}{[CH_3(CH_2)_2COO^-]}$ using data derived from that in the question (i.e. not just made up values)
			ALLOW alternative approach based on Henderson–Hasselbalch equation for final 2 marks $pH = pK_a + \log\frac{0.025}{0.100}$ **OR** $pK_a - \log\frac{0.100}{0.025}$ ✓ pH = 4.82 – 0.60 = 4.22 ✓ **ALLOW** $-\log K_a$ for pK_a		
			TAKE CARE with awarding marks for pH = 4.22 There is a mark for the concentration stage. If this has been omitted, the ratio for the last 2 marks will be 0.0100 and 0.0025. **4 marks max.** **Common errors** **pH = 5.42** As above for 4.22 but with acid/base ratio inverted. Award 4 **OR** 3 marks **Award zero marks for:** 4.12 from no working or random values pH value from K_a square root approach (weak acid pH) pH value from K_w /10^{-14} approach (strong base pH)		**Common errors** **pH = 4.12** use of initial concentrations: 0.250 and 0.050 given in question. **Award last 3 marks for:** 0.250/2 **AND** 0.050/2 = 0.125 **AND** 0.025 ✓ $1.51\times10^{-5} \times \frac{0.125}{0.025}$ = 7.55 x 10^{-5} (mol dm^{-3}) ✓ pH = –log$[H^+]$ = 4.12 ✓ **Award last 2 marks for:** $1.51\times10^{-5} \times \frac{0.250}{0.050}$ = 7.55 x 10^{-5} (mol dm^{-3}) ✓ pH = –log$[H^+]$ = 4.12 ✓ **pH = 5.52** As above for 4.12 but with acid/base ratio inverted. Award 2 **OR** 1 marks as outlined for 4.12 above

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Question			Answer	Marks	Guidance
3	(d)		$HCOOH + CH_3(CH_2)_2COOH \rightleftharpoons HCOO^- + CH_3(CH_2)_2COOH_2^+$ ✓ acid 1 base 2 base 1 acid 2 ✓ **CARE:** Both + and – charges are required for the products in the equilibrium **DO NOT AWARD** the 2nd mark from an equilibrium expression that omits either charge	2	State symbols **NOT** required **ALLOW** 1 **and** 2 labels the other way around. **ALLOW** 'just acid' and 'base' labels throughout if linked by lines so that it is clear what the acid-base pairs are For 1st mark, **DO NOT ALLOW** $COOH^-$ (i.e. H at end rather than start) but within 2nd mark **ALLOW** $COOH^-$ by **ECF** **IF** proton transfer is wrong way around then **ALLOW** 2nd mark for idea of acid–base pairs, i.e. $HCOOH + CH_3(CH_2)_2COOH \rightleftharpoons HCOOH_2^+ + CH_3(CH_2)_2COO^-$ × base 2 acid 1 acid 2 base 1 ✓ For H_2COOH^+ shown with wrong proton transfer, **DO NOT ALLOW** an **ECF** mark for acid–base pairs
			Total	**16**	

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Question			Answer	Marks	Guidance
4	(a)	(i)	***initial rates data:*** **From Experiment 1** to **Experiment 2** **AND** $[NO_2]$ x 1.5, rate x 1.5 ✓ 1st order with respect to NO_2 ✓ **From Experiment 2** to **Experiment 3** **AND** $[O_3]$ is doubled, rate x 2 ✓ 1st order with respect to O_3 ✓ ***rate equation and rate constant:*** *rate* = $k[NO_2]\,[O_3]$ ✓ $k = \frac{rate}{[NO_2][O_3]}$ **OR** $\frac{4.80 \times 10^{-8}}{0.00150 \times 0.00250}$ ✓ = 0.0128 ✓ $dm^3\ mol^{-1}\ s^{-1}$ ✓	8	***ANNOTATIONS MUST BE USED*** **Quality of Written Communication**: --- Changes **MUST** be linked to Experiment numbers **in writing** (*Could be described unambiguously)* **IGNORE** annotations in the table --- For 2nd condition, **ALLOW** 'when $[NO_2]$ increases by half, rate increases by half **NOTE**: Orders may be identified within a rate equation **ALLOW**: working from any of the Experiments : All give the same calculated answer 0.0128 subsumes previous rearrangement mark **ALLOW**: $mol^{-1}\ dm^3\ s^{-1}$ ✓ **DO NOT ALLOW** 0.013 *over-rounding* --- **ALLOW ECF** from inverted *k* expression: $k = \frac{[NO_2][O_3]}{rate}$: *k* = 78.125 ✓ **ALLOW** 3 SF or more **NOTE** units must be from rate equation ✓

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Question			Answer	Marks	Guidance
4	(a)	(ii)	**step 1**: $NO_2 + O_3$ LHS of step one ✓ $\longrightarrow NO_3 + O_2$ **step 2**: $NO_2 + NO_3 \longrightarrow N_2O_5$ rest of equations for step 1 **AND** step 2 ✓ **CHECK** that each equation is balanced **CARE:** **Step 1 AND Step 2** must add up to give overall equation In **Step 2**, **IGNORE** extra species shown on both sides, e.g. $NO_2 + NO_3 + O_2 \longrightarrow N_2O_5 + O_2$ **Step 2** can only gain a mark when **Step 1** is correct	2	State symbols **NOT** required For 'rest of equations', **ALLOW** other combinations that together give the overall equation, *e.g.*: $\longrightarrow NO_5$ $NO_2 + NO_5 \longrightarrow N_2O_5 + O_2$ *e.g.*: $\longrightarrow NO + 2O_2$ $NO + NO_2 + O_2 \longrightarrow N_2O_5$ **DO NOT ALLOW** use of algebraic species, e.g. X
	(b)	(i)	3 **gaseous** moles $\longrightarrow$ 2 **gaseous** moles ✓ Less randomness **OR** becomes more ordered ✓	2	**ALLOW** products have fewer **gaseous** moles **ORA** **ALLOW** 'molecules' instead of 'moles' **ALLOW** fewer ways of distributing energy **OR** fewer degrees of freedom **OR** fewer ways to arrange
		(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = –148 award **3 marks** --- $\Delta G = \Delta H - T\Delta S$ ✓ = –198 – (298 x –168/1000) ✓ = –148 (kJ mol^{-1}) ✓	3	**IF** there is an alternative answer, check calculator value and working for intermediate marks by **ECF** --- 2nd mark subsumes 1st mark for $\Delta G = \Delta H - T\Delta S$ **ALLOW** –148 to calculator value of –147.936 **ALLOW for 2 marks:** 49866 (kJ mol^{-1})*: not converting ΔS from J to kJ (no ÷ 1000)* –193.8 (kJ mol^{-1}) *use of 25 instead of 298*

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Question			Answer	Marks	Guidance
4	(b)	(iii)	**CARE: responses involve changes of negative values** --- **Feasibility with increasing temperature** Reaction becomes less feasible/not feasible **AND** ΔG increases **OR** ΔG becomes less negative **OR** $\Delta G = 0$ **OR** $\Delta G > 0$ **OR** ΔG is positive **OR** ΔG approaches zero ✓ ***IF a candidate makes a correct statement about the link between ΔG and feasibility, **IGNORE** an incorrect ΔH and $T\Delta S$ relationship **IF** there is no ΔG statement, then mark any ΔH and $T\Delta S$ relationship in line with the mark scheme --- **Effect on $T\Delta S$** $T\Delta S$ becomes more negative **OR** $T\Delta S$ decreases **OR** $-T\Delta S$ increases **OR magnitude** of $T\Delta S$ increases ✓ ---	2	***ANNOTATIONS MUST BE USED*** --- As alternative for 'not feasible' **ALLOW 'not** spontaneous' **OR** a comment that implies 'reaction does not take place' **ALLOW for ΔG increases** $\Delta H = T\Delta S$ **OR** $\Delta H > T\Delta S$ **OR** $\Delta H - T\Delta S$ is positive **OR** $T\Delta S$ becomes more significant than ΔH **OR** $T\Delta S$ becomes the same as ΔH **OR** $T\Delta S$ becomes more negative than ΔH **NOTE Last statement will also score 2nd mark** --- **DO NOT ALLOW** $T\Delta S$ increases --- ***APPROACH BASED ON TOTAL ENTROPY:*** **Feasibility with increasing temperature** Reaction becomes less feasible/not feasible **AND** $\Delta S - \Delta H/T$ **OR** ΔS_{total} decreases/ less positive **OR** ΔS outweighs/ is less significant than $\Delta H/T$ ✓ **Effect on $\Delta H/T$** $\Delta H/T$ is less negative **OR** $\Delta H/T$ increases **OR** $-\Delta H/T$ decreases **OR** magnitude of $\Delta H/T$ decreases ✓
			Total	**17**	

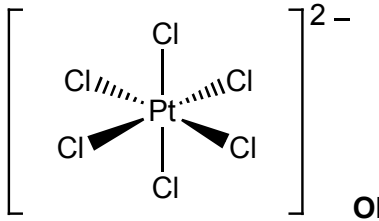
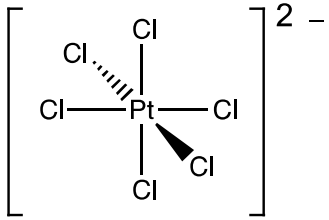
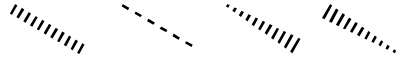
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Question			Answer	Marks	Guidance
5	(a)		(A transition element) has (at least) one **ion** with a partially filled d sub-shell/ d orbital ✓ Fe **AND** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ ✓ Fe(II) / Fe^{2+} **AND** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ ✓ Fe(III) / Fe^{3+} **AND** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ ✓	4	**ALLOW** incomplete for partially filled **DO NOT ALLOW** d shell **ALLOW** 4s before 3d, i.e. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ **IF** candidate has used subscripts **OR** caps **OR** [Ar], **DO NOT ALLOW** when first seen but credit subsequently, i.e. $1s_2 2s_2 2p_6 3s_2 3p_6 3d_6 4s_2$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3D^6$ $[Ar]4s^2 3d^6$ For Fe^{2+} and Fe^{3+}, **ALLOW** $4s^0$ in electron configuration **IGNORE** electron configurations of elements other than Fe
	(b)		**EXAMPLES MUST REFER TO Cu^{2+} FOR ALL MARKS** **PRECIPITATION** **Reagent** NaOH(aq) **OR** KOH(aq) ✓ States not required **Transition metal product AND observation** $Cu(OH)_2$ **AND** blue precipitate/solid ✓ **Correct balanced equation** $Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$ ✓ state symbols **not** required **IF more than one example shown, mark example giving lower mark**	3	***ANNOTATIONS MUST BE USED*** **ALLOW** NaOH in equation if 'reagent' not given in description **ALLOW a small amount** of NH_3/ammonia **DO NOT ALLOW** concentrated NH_3 **DO NOT ALLOW** just OH^- **ALLOW** $Cu(OH)_2(H_2O)_4$ **ALLOW** any shade of blue **ALLOW** (s) as state symbol for ppt (may be in equation) **ALLOW** $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$ For NH_3, also **ALLOW:** $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow Cu(OH)_2(H_2O)_4 + 2NH_4^+$ **ALLOW** full equation, e.g. $CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4$ $CuCl_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaCl$

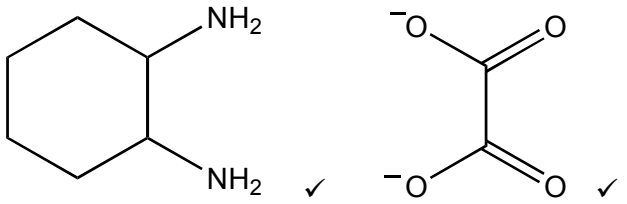
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Question			Answer	Marks	Guidance
5	(b)		**LIGAND SUBSTITUTION – 2 likely** **Reagent** NH_3(aq)/ammonia ✓ State not required **Transition metal product AND observation** $[Cu(NH_3)_4(H_2O)_2]^{2+}$ **AND** deeper/darker blue (solution) ✓ **Correct balanced equation** $[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$ ✓ **OR** ---------- **Reagent** Concentrated HCl **OR** (dilute) HCl(aq) **OR** NaCl(aq) ✓ State not required **Transition metal product AND observation** $[CuCl_4]^{2-}$ **AND** yellow (solution) ✓ **Correct balanced equation** $[Cu(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CuCl_4]^{2-} + 6H_2O$ ✓	3	**IF more than one example shown, mark example giving lower mark** **ALLOW** NH_3 in equation if 'reagent' not given in description **DO NOT ALLOW** precipitate **ALLOW** royal blue, ultramarine blue or any blue colour that is clearly darker than for $[Cu(H_2O)_6]^{2+}$ ✓ ---------- **ALLOW** $CuCl_4^{2-}$ i.e. no brackets **ALLOW** any shades of yellow, e.g. yellow–green **DO NOT ALLOW** precipitate **ALLOW other correct ligand substitutions using same principles for marking as in two examples given**
	(c)	(i)	Pt oxidised from 0 +4 ✓ N reduced from +5 to +4 ✓	2	**ALLOW** 1 mark for Pt from 0 to +4 **AND** N from +5 to +4 i.e. oxidation and reduction not identified or wrong way round **DO NOT ALLOW** Pt is oxidised and N reduced with no evidence **DO NOT ALLOW** responses using other incorrect oxidation numbers **(CON)**

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Question			Answer	Marks	Guidance
5	(c)	(ii)	$Pt + 6HCl + 4HNO_3 \longrightarrow H_2PtCl_6 + 4NO_2 + 4H_2O$ ✓✓	2	**1st mark for ALL species correct and no extras:** i.e: $Pt + HCl + HNO_3 \longrightarrow H_2PtCl_6 + NO_2 + H_2O$ **DO NOT ALLOW** charge on Pt, e.g. Pt^{2+} **2nd mark** for correct balancing **ALLOW** correct multiples
	(d)		 **OR**  **3-D Shape 1 mark** Correct 3-D diagram of Pt surrounded by 6Cl **ONLY** ✓ **Bond angle 1 mark** bond angle of 90° on diagram or stated ✓ **Charge 1 mark** 2– charge shown outside of brackets ✓	3	Must contain 2 'out wedges', 2 'in wedges' and 2 lines in plane of paper **OR** 4 lines, 1 'out wedge' and 1 'in wedge' For bond into paper, **ALLOW**:  **IGNORE** charges on Pt and Cl for this mark The 2 marks for charge **AND** bond angle are **ONLY** available from a diagram showing Pt bonded to 6 Cl **ONLY** **ALLOW ONLY** if diagram has Pt surrounded by 6Cl **ONLY** **BUT** 3-D shape may not be correct **DO NOT ALLOW** if **ANY** charges shown on Pt or Cl within brackets

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Question			Answer	Marks	Guidance
5	(e)	(i)	Donates **two** electron pairs to a **metal** (ion) ✓ forms **two** coordinate bonds ✓	2	**ALLOW** lone pairs for electron pairs **ALLOW** dative (covalent) bond for coordinate bond **ALLOW** 1 mark for a full definition of a ligand (without reference to 2: **i.e.** Donates **an** electron pair to a metal (ion) forming **a** coordinate bond ✓
		(ii)	 ✓ ✓	2	**ALLOW** displayed formulae '– charges' essential in $(COO^-)_2$ structure **DO NOT ALLOW** $–H_2N$
			Total	**21**	

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Question			Answer	Marks	Guidance
6	(a)	(i)	complete circuit with **voltmeter** and **salt bridge** linking two half-cells ✓ Pt electrode in Fe^{3+}/Fe^{2+} half-cell with **same** concentrations ✓ Cr electrode in 1 mol dm^{-3} Cr^{3+} half-cell ✓	3	Salt bridge **MUST** be labelled **ALLOW** Fe^{2+} and Fe^{3+} with concentrations of 1 mol dm^{-3} **ALLOW** 1 M but **DO NOT ALLOW** 1 mol
		(ii)	$Cr + 3Fe^{3+} \longrightarrow Cr^{3+} + 3Fe^{2+}$ ✓	1	**ALLOW** $\rightleftharpoons$ sign **DO NOT ALLOW** if e^- shown uncancelled on both sides, e.g. $Cr + 3Fe^{3+} + 3e^- \longrightarrow Cr^{3+} + 3Fe^{2+} + 3e^-$
		(iii)	1.51 V ✓	1	**IGNORE** sign
	(b)		$Cr_2O_7^{2-}$ **AND** H^+ ✓	1	**ALLOW** acidified dichromate
	(c)		$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3HCOOH(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3CO_2(l)$ ✓✓ State symbols **not** required	2	**1st mark for ALL species correct and no extras:** $Cr_2O_7^{2-}$, H^+, HCOOH, Cr^{3+}, H_2O **AND** CO_2 **NOTE**: H^+ may be shown on both sides **ALLOW** $\rightleftharpoons$ sign **2nd mark** for correct balancing with H^+ cancelled down
	(d)	(i)	$E^{\ominus}$ for chromium (redox system) is more negative/lower/less (than copper redox system) **ORA** ✓ chromium system shifts to the left / $Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$ **AND** copper system shifts to the right / $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ ✓	2	**ALLOW** E_{cell} is +1.08 V (sign required) **ALLOW** Cr loses electrons more readily/more easily oxidised **OR** Cr is a stronger reducing agent **OR** Cu loses electrons less readily **OR** Cu is a weaker reducing agent

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Question			Answer	Marks	Guidance
6	(d)	(ii)	Cr reacts with H^+ ions/acid to form H_2 gas ✓	1	**ALLOW** equation: $2Cr + 6H^+ \longrightarrow 2Cr^{3+} + 3H_2$ (**ALLOW** multiples) **DO NOT ALLOW** just 'hydrogen forms', i.e. Cr, H^+/acid **AND** H_2 must **all** be included for the mark
	(e)	(i)	1.45 V ✓	1	**IGNORE** sign
		(ii)	**2 marks**, ✓ ✓, for **two** points from the following list: **1.** Methanoic acid is a liquid **AND** easier to store/transport **OR** hydrogen is a gas **AND** harder to store/transport **OR** hydrogen as a liquid is stored under pressure **2.** Hydrogen is explosive/more flammable **3.** HCOOH gives a greater cell potential/voltage **4**. HCOOH has more public/political acceptance than hydrogen as a fuel	2	**ASSUME** 'it' refers to HCOOH **DO NOT ALLOW** 'produces no CO_2' **IGNORE** comments about biomass and renewable *HCOOH and H_2 are **both** manufactured from natural gas*
			Total	**14**	

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Question			Answer	Marks	Guidance
7	(a)		$MnO_2 + 4OH^- \longrightarrow MnO_4^{2-} + 2H_2O$ **+ 2e⁻** ✓ $3H_2O + ClO_3^-$ **+ 6e⁻** ✓ $\longrightarrow 6OH^- + Cl^-$	2	**ALLOW** 'e': i.e. – sign not required
	(b)		**Role of CO_2** CO_2 reacts with H_2O forming an acid **OR** carbonic acid/H_2CO_3 forms **OR** CO_2 is acidic ✓ **Equation involving OH^-** $H_2CO_3 + OH^- \longrightarrow H_2O + HCO_3^-$ **OR** $H_2CO_3 + 2OH^- \longrightarrow 2H_2O + CO_3^{2-}$ **OR** $CO_2 + OH^- \longrightarrow CO_3^{2-} + H^+$ **OR** $CO_2 + OH^- \longrightarrow HCO_3^-$ **OR** $CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O$ **OR** $H^+ + OH^- \longrightarrow H_2O$ ✓ **Effect on equilibrium with reason** equilibrium shifts to right **AND** to restore OH^- ✓	3	***ANNOTATIONS MUST BE USED*** --- **ALLOW** equation: $CO_2 + H_2O \longrightarrow H_2CO_3$ **OR** $CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$ **OR** $CO_2 + H_2O \longrightarrow 2H^+ + CO_3^{2-}$ **ALLOW** for 'restores OH^-' the following: 'makes more OH^-', 'OH^- has been used up' **DO NOT ALLOW** just 'equilibrium shifts to right'

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Question			Answer	Marks	Guidance
7	(c)		**FOLLOW through stages to mark** --- **Moles in titration** $n(KMnO_4) = 0.0200 \times \frac{26.2}{1000} = 5.24 \times 10^{-4}$ mol ✓ $n(SO_3^{2-}) = 1.31 \times 10^{-3}$ mol ✓ **Scaling** $n(SO_3^{2-})$ in original 100 cm^3 $= 4 \times 1.31 \times 10^{-3} = 5.24 \times 10^{-3}$ mol ✓ **Mass** Mass of Na_2SO_3 in sample $= 126.1 \times 5.24 \times 10^{-3}$ g = 0.660764 g ✓ **Percentage** % $Na_2SO_3 = \frac{0.660764}{0.720} \times 100 = 91.8\%$ ✓	5	***ANNOTATIONS MUST BE USED*** ***AT LEAST 3 SF for each step*** --- **ECF** 2.5 x answer above **ECF** 4 x answer above **ECF** 126.1 x answer above **ALLOW** 0.661 g up to calculator value **ECF** $\frac{\text{calculated mass above}}{0.720} \times 100$ **ALLOW** 91.8% (1 DP) up to calculator value of 91.77277778 i.e. **DO NOT ALLOW** 92%
			ALLOW alternative approach based on theoretical content of Na_2SO_3 for last 2 marks **Theoretical amount, in moles, of Na_2SO_3 in sample** $n(Na_2SO_3) = \frac{0.720}{126.1} = 5.71 \times 10^{-3}$ mol ✓ **Percentage** % $Na_2SO_3 = \frac{5.24 \times 10^{-3}}{5.71 \times 10^{-3}} \times 100 = 91.8\%$ ✓		**COMMON ERRORS**: 36.8(1)% 4 marks no 2.5 factor 22.9(4)% 4 marks no scaling by 4 9.18% 3 marks no 2.5 and no x 4 Watch for random ECF %s for % from incorrect $M(Na_2SO_3)$, e.g. use of $M(SO_3^{2-})$ = 80.1 giving 58.3%
			Total	**10**	

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RECOGNISING ACHIEVEMENT

Wednesday 1 February 2012 – Morning

A2 GCE CHEMISTRY A

F325 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

F325

F3144801121

Candidate forename		Candidate surname	

Centre number						Candidate number				

INSTRUCTIONS TO CANDIDATES

- The Insert will be found in the centre of 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 pages 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 **24** pages. Any blank pages are indicated.

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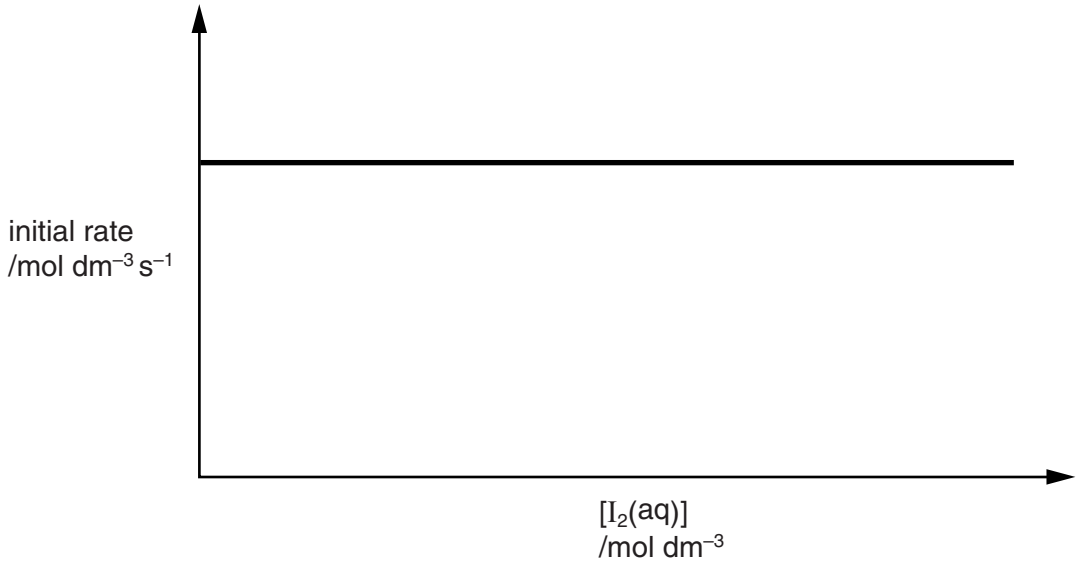
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Answer **all** the questions.

1 A student investigates the reaction between iodine, I_2, and propanone, $(CH_3)_2CO$, in the presence of aqueous hydrochloric acid, HC*l*(aq).

The results of the investigation are shown below.

Rate–concentration graph



Results of initial rates experiments

experiment	[$(CH_3)_2CO$(aq)] / mol dm^{-3}	[HC*l*(aq)] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.50×10^{-3}	2.00×10^{-2}	2.10×10^{-9}
2	3.00×10^{-3}	2.00×10^{-2}	4.20×10^{-9}
3	3.00×10^{-3}	5.00×10^{-2}	1.05×10^{-8}

(a) Determine the orders with respect to I_2, $(CH_3)_2CO$ and HC*l*, the rate equation and the rate constant for the reaction.

Explain all of your reasoning.

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..... **[9]**

(b) The student then investigates the reaction of hydrogen, H_2, and iodine monochloride, ICl.

The equation for this reaction is shown below.

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

The rate equation for this reaction is shown below.

$$\text{rate} = k[H_2(g)]\,[ICl(g)]$$

Predict a possible two-step mechanism for this reaction. The first step should be the rate-determining step.

step 1 .....

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

[Total: 11]

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2 Lattice enthalpies can be calculated indirectly using Born–Haber cycles.

Table 2.1 shows enthalpy changes needed to calculate the lattice enthalpy of sodium oxide, Na_2O.

letter	enthalpy change	energy /kJ mol^{-1}
A	1st electron affinity of oxygen	–141
B	2nd electron affinity of oxygen	+790
C	1st ionisation energy of sodium	+496
D	atomisation of oxygen	+249
E	atomisation of sodium	+108
F	formation of sodium oxide	–414
G	lattice enthalpy of sodium oxide	

Table 2.1

(a) Define the term *lattice enthalpy*.

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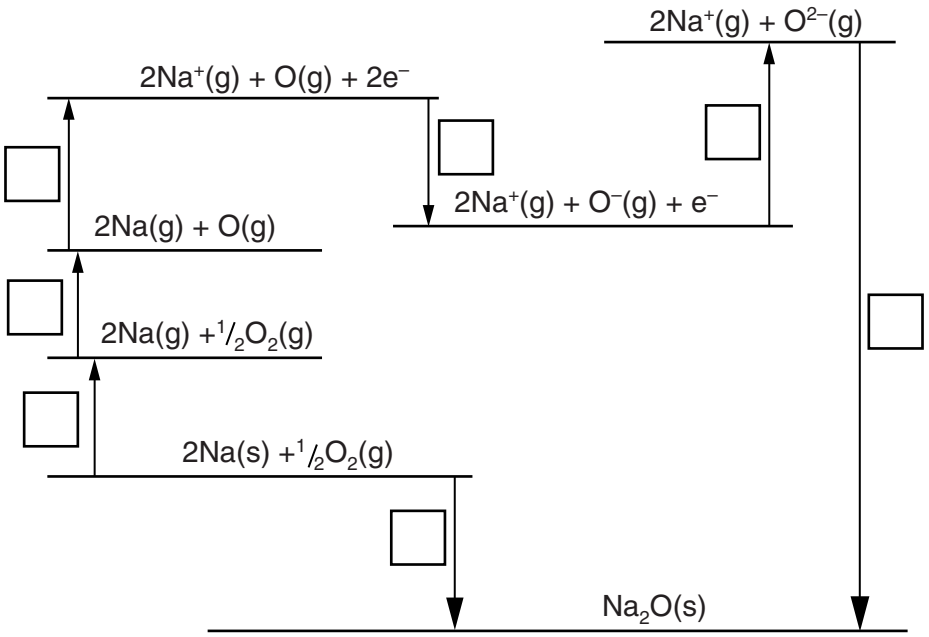
..... **[2]**

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(b) The Born–Haber cycle below links the lattice enthalpy of sodium oxide with its enthalpy change of formation.

(i) On the Born–Haber cycle, write the correct letter from **Table 2.1** in each box.



[3]

(ii) Calculate the lattice enthalpy of sodium oxide, **G**.

answer = ... kJ mol^{-1} **[2]**

(c) Explain why it is difficult to predict whether the lattice enthalpy of magnesium sulfide would be more or less exothermic than the lattice enthalpy of sodium oxide.

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

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(d) A student wanted to determine the lattice enthalpy of sodium carbonate, Na_2CO_3. Unfortunately this is very difficult to do using a similar Born–Haber cycle to that used for sodium oxide in **(b)**.

(i) Suggest why this is very difficult.

.....

.....

.....

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

(ii) The student thought that he could determine the lattice enthalpy of Na_2CO_3 using a Born–Haber cycle that links lattice enthalpy with enthalpy change of solution.
The enthalpy change of solution of Na_2CO_3 is exothermic.

- Sketch this Born–Haber cycle,
- Explain how the lattice enthalpy of Na_2CO_3 could be calculated from the enthalpy changes in the cycle.

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

[Total: 14]

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3 Cobalt is a transition element. Solid compounds of cobalt are often complexes and in solution, complex ions are formed.

(a) In its complexes, the common oxidation numbers of cobalt are +2 and +3.

Complete the electron configurations of cobalt as the element and in the +3 oxidation state:

cobalt as the element: $1s^2\ 2s^2\ 2p^6$ .....

cobalt in the +3 oxidation state: $1s^2\ 2s^2\ 2p^6$ ..... **[2]**

(b) State **one** property of cobalt(II) and cobalt(III), other than their ability to form complex ions, which is typical of ions of a transition element.

.....

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

(c) Complex ions contain ligands.

State the meaning of the term *ligand*.

.....

.....

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

(d) Aqueous cobalt(II) sulfate, $CoSO_4(aq)$, takes part in the following reactions.

For each reaction, state the formula of the transition element species formed and the type of reaction taking place.

(i) Aqueous cobalt(II) sulfate, $CoSO_4(aq)$, reacts with aqueous sodium hydroxide.

transition element species formed: .....

type of reaction: ..... **[2]**

(ii) Aqueous cobalt(II) sulfate, $CoSO_4(aq)$, reacts with concentrated hydrochloric acid.

transition element species formed: .....

type of reaction: ..... **[2]**

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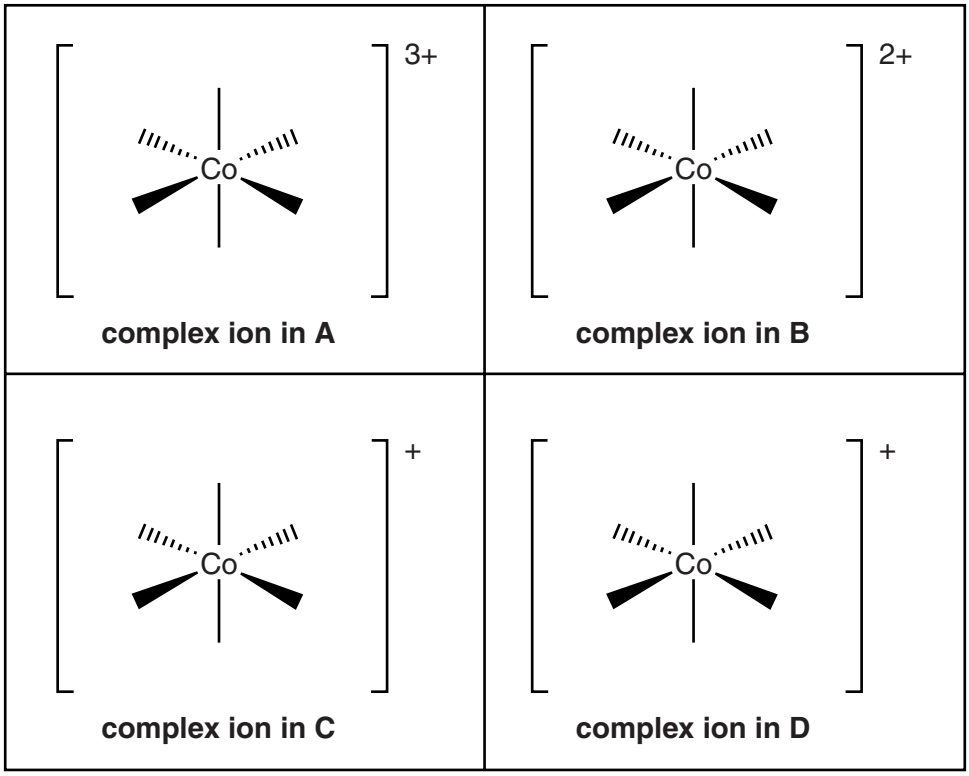
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(e) Cobalt(III) chloride, $CoCl_3$, reacts with ammonia to form a range of complexes. These complexes contain different amounts of ammonia. Information about these complexes is summarised below.

The complex ions **C** and **D** are stereoisomers.

complex	formula	formula of complex
A	$CoCl_3(NH_3)_6$	$[Co(NH_3)_6]^{3+}\ 3Cl^-$
B	$CoCl_3(NH_3)_5$	$[Co(NH_3)_5Cl]^{2+}\ 2Cl^-$
C	$CoCl_3(NH_3)_4$	$[Co(NH_3)_4Cl_2]^{+}\ Cl^-$
D	$CoCl_3(NH_3)_4$	$[Co(NH_3)_4Cl_2]^{+}\ Cl^-$

(i) Complete the diagrams below to suggest possible structures for the complex ion in complexes **A** to **D**.



[4]

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(ii) Chemists provided evidence for the formulae of these complexes from their reactions with aqueous silver nitrate. Aqueous silver nitrate reacts with aqueous halide ions in a precipitation reaction.

An excess of silver nitrate solution was reacted with 0.0100 mol of one of the complexes **A** to **D**. 2.868 g of a precipitate was formed.

Determine which complex was reacted.



In your answer you should explain how the result of the experiment would allow the formula of the complex to be identified.

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

[Total: 15]

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4 This question looks at acids, bases and buffer solutions.

(a) Nitric acid, HNO_3, is a strong Brønsted–Lowry acid.
Nitrous acid, HNO_2, is a weak Brønsted–Lowry acid with a K_a value of 4.43×10^{-4} mol dm^{-3}.

(i) What is the difference between a strong acid and a weak acid?

.....

.....

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

(ii) What is the expression for the acid dissociation constant, K_a, of nitrous acid, HNO_2?

[1]

(iii) Calculate the pH of 0.375 mol dm^{-3} nitrous acid, HNO_2.

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

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

(iv) A student suggests that an acid–base equilibrium is set up when nitric acid is mixed with nitrous acid.

Complete the equation for the equilibrium that would be set up and label the conjugate acid–base pairs.

HNO_3 + HNO_2 $\rightleftharpoons$ ..... + ...

....

[2]

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(b) Calcium hydroxide, $Ca(OH)_2$, is a strong Brønsted–Lowry base.

(i) Explain what is meant by the term *Brønsted–Lowry base*.

.....

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

(ii) Calculate the pH of 0.0400 mol dm^{-3} $Ca(OH)_2$.

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

pH = ... **[3]**

(c) Aqueous calcium hydroxide is added to nitrous acid, HNO_2.

Write the overall equation and the ionic equation for the reaction that takes place.

overall: .....

ionic: ..... **[2]**

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(d) Carbonic acid, H_2CO_3, is a weak Brønsted–Lowry acid formed when carbon dioxide dissolves in water. Healthy blood is buffered to a pH of 7.40. The most important buffer solution in blood is a mixture of carbonic acid and hydrogencarbonate ions, HCO_3^-.

(i) Explain how the carbonic acid–hydrogencarbonate mixture acts as a buffer in the control of blood pH.

In your answer you should explain how equilibrium allows the buffer solution to control the pH.

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.... **[5]**

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(ii) Healthy blood at a pH of 7.40 has a hydrogencarbonate : carbonic acid ratio of 10.5 : 1. A patient is admitted to hospital. The patient's blood pH is measured as 7.20.

Calculate the hydrogencarbonate : carbonic acid ratio in the patient's blood.

[5]

[Total: 22]

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

(a) A student carries out an investigation based on the redox systems shown in **Table 5.1** below.

	redox system	$E^{\ominus}$/V
1	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.25
2	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
3	$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.74

Table 5.1

The student sets up two standard cells to measure two standard cell potentials.

- **Cell A** is based on redox systems **1** and **2**.
- **Cell B** is based on redox systems **1** and **3**.

(i) Draw a labelled diagram to show how the student could have set up **Cell A**, based on redox systems **1** and **2**, to measure the standard cell potential.

[3]

(ii) For each standard cell below,

- what would be the standard cell potential?
- what would be the sign of the Ni electrode?

Cell A based on redox system **1** and **2**:

standard cell potential = ... V

sign of Ni electrode, + or – = ...

Cell B based on redox system **1** and **3**:

standard cell potential = ... V

sign of Ni electrode, + or – = ...

[2]

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(b) The student left each cell in **(a)** connected for a length of time.

For each cell, the student weighed the nickel electrode before connecting the cell and after the cell had been disconnected.

The student made the following observations.

- In **Cell A**, the nickel electrode lost mass.
- In **Cell B**, the nickel electrode gained mass.
- In **both** cells, the measured cell potential slowly changed.

Explain these observations. Include equations in your answer.

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

(c) Nickel metal hydride cells (NiMH cells) are being developed for possible use in cars.
In a NiMH cell, an alloy is used to absorb hydrogen as a metal hydride. For simplicity, the alloy can be represented as M and the metal hydride as MH.

The overall cell reaction in a NiMH cell is shown below.

$$MH + NiO(OH) \longrightarrow M + Ni(OH)_2$$

The half-equation at one electrode is shown below.

$$NiO(OH) + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$$

(i) Deduce the half-equation at the other electrode.

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

(ii) State a method, other than absorption, that is being developed to store hydrogen for possible use as a fuel in cars.

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

[Total: 10]

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6 Free energy changes can be used to predict the feasibility of processes.

(a) Write down the equation that links the free energy change with the enthalpy change and temperature.

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

(b) You are provided with equations for five processes.

For each process, predict the sign of ΔS.

process	sign of ΔS
$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$	
$NaCl(s) + (aq) \rightarrow NaCl(aq)$	
$H_2O(l) \rightarrow H_2O(s)$	
$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$	
$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 \bullet 5H_2O(s)$	

[2]

(c) Ammonia can be oxidised as shown in the equation below.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Standard entropies are given in the table below.

substance	$NH_3(g)$	$O_2(g)$	$NO(g)$	$H_2O(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	192	205	211	189

Calculate the standard entropy change, in J K^{-1} mol^{-1}, for this oxidation of ammonia.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} **[2]**

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(d) The exothermic reaction below occurs spontaneously at low temperatures but does **not** occur at very high temperatures.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

Explain why.

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.....

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

(e) An ore of iron contains iron(III) oxide, Fe_2O_3.
Iron is extracted from this ore by heating with carbon.
The equation below shows one of the reactions which takes place.

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$$

$\Delta S = +543\,J\,K^{-1}\,mol^{-1}$ and $\Delta H = +493\,kJ\,mol^{-1}$

Calculate the minimum temperature at which this reaction becomes feasible.

Show **all** your working.

minimum temperature = ... **[3]**

[Total: 10]

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7 Dinitrogen tetroxide, $N_2O_4(g)$, and nitrogen dioxide, $NO_2(g)$, coexist in the following equilibrium.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57\,kJ\,mol^{-1}$$

A chemist adds 4.00 mol NO_2 to a container with a volume of 2.00 dm^3. The container is sealed, heated to a constant temperature and allowed to reach equilibrium.

The equilibrium mixture contains 3.20 mol NO_2.

(a) Calculate the value for K_c under these conditions.

[5]

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(b) The experiment is repeated but the pressure in the container is doubled.

Explain in terms of K_c the effect on the concentrations of NO_2 and N_2O_4 when the mixture has reached equilibrium.

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

[Total: 8]

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8 Haematite is the main ore of iron. The percentage of iron in a sample of haematite can be determined using the method below.

Method

Stage 1. An excess of concentrated hydrochloric acid is added to a 3.25 g sample of haematite. The iron(III) oxide in the haematite reacts to form a solution containing Fe^{3+} ions.

Stage 2. An excess of aqueous tin(II) chloride is added. Sn^{2+} reduces the Fe^{3+} present to Fe^{2+}. Excess Sn^{2+} is removed.

Stage 3. The solution is diluted and made up to 250.0 cm^3 in a volumetric flask.

Stage 4. A 25.0 cm^3 sample of this solution is pipetted into a conical flask.

Stage 5. The solution in the conical flask is titrated with 0.0200 mol dm^{-3} aqueous potassium dichromate(VI), $K_2Cr_2O_7$.
The Fe^{2+} ions are oxidised to Fe^{3+} ions.

Stage 6. Stages 4 and **5** are repeated to obtain an average titre of 26.5 cm^3.

You are provided with the following electrode potentials.

You may need to use this information throughout this question.

$$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq) \qquad E^{\ominus} = +0.15\,V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^{\ominus} = +0.77\,V$$

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\ominus} = +1.33\,V$$

$$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^{\ominus} = +1.36\,V$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^{\ominus} = +1.51\,V$$

(a) Write an equation for the reaction between iron(III) oxide and concentrated hydrochloric acid, occurring in **Stage 1**.

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

(b) Write equations for the reactions involving iron ions in **Stages 2** and **5**.

Stage 2 .....

Stage 5 ..... **[2]**

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(c) Calculate the percentage by mass of iron in the haematite ore.

percentage iron = ... % **[5]**

(d) Aqueous potassium manganate(VII), $KMnO_4(aq)$, is **not** suitable for titrating the solution in this method. Aqueous potassium dichromate(VI), $K_2Cr_2O_7(aq)$, is used instead.

Suggest and explain why potassium dichromate(VI), $K_2Cr_2O_7$, is suitable for this titration whereas potassium manganate(VII), $KMnO_4$, is not suitable.

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.....

.....

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

[Total: 10]

END OF QUESTION PAPER

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ADDITIONAL PAGE

If additional space is required, you should use the lined pages below. The question number(s) must be clearly shown.

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ADDITIONAL PAGE

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ADDITIONAL PAGE

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RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

Unit **F325:** Equilibria, Energetics and Elements

Mark Scheme for January 2012

Oxford Cambridge and RSA Examinations

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Annotations available in Scoris.

Annotation	Meaning
	Benefit of doubt given
	Contradiction
	Incorrect response
	Error carried forward
	Ignore
	Not answered question
	Benefit of doubt not given
	Power of 10 error
	Omission mark
	Rounding error
	Error in number of significant figures
	Correct response

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Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

Annotation	Meaning
DO NOT ALLOW	Answers which are not worthy of credit
IGNORE	Statements which are irrelevant
ALLOW	Answers that can be accepted
( )	Words which are not essential to gain credit
__	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA	Or reverse argument

12. The following questions should be annotated with ticks, crosses, etc. Annotations should be placed to clearly show where they apply within the body of the text (i.e. not in margins)

Question 1(a); Question 2(c), 2d(ii); Question 3e(i); Question 4d(i), 4d(ii); Question 6d; Question 7(a); Question 8(c)

All the Additional Pages in the examination script must be checked to see if any candidates include any answers.

- When you open question **1(a)** you will see a view of page 22, one of the Additional Pages.
- If the page is blank then, using the marking mode, annotate the page with an omission mark, ^.
- Scroll down to page 23 and annotate with a ^ if the page is blank.
- Scroll down to page 24 and annotate with a ^ if the page is blank.

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- If pages 22, 23 or 24 are not blank then use the paper clip icon to link the pages to the correct questions.
- You may need to contact your Team Leader if you do not know how to do this.

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Question			Expected answers	Marks	Additional guidance
1	a		***graph:*** Rate does not change with concentration **AND** zero-order with respect to I_2 ✓ ***initial rates data:*** Mark independently When $[(CH_3)_2CO]$ × 2, rate × 2 (2^1) ✓ 1st order with respect to $(CH_3)_2CO$ ✓ When [HCl] x 2.5, rate × 2.5 ✓ 1st order with respect to HCl ✓		***ANNOTATIONS MUST BE USED*** **ALLOW** (straight) line with zero gradient **AND** zero-order **ALLOW** horizontal line **AND** zero-order **IGNORE** just 'constant line' **OR** just 'straight line' *also fits 1st order* ***CARE** with comparisons in opposite direction* **ALLOW** $[(CH_3)_2CO]$ × 0.5, rate × 0.5 (0.5^1) **ALLOW** [HCl] × 0.4, rate × 0.4 (0.4^1) **ALLOW** H^+ for HCl **CARE:** Comparison of **Experiments 1** and **3** may be valid despite **BOTH** concentrations changing
			Rate equation and rate constant: rate = $k[(CH_3)_2CO(aq)]\,[HCl(aq)]$ ✓ $k = \dfrac{rate}{[(CH_3)_2CO(aq)]\,[HCl(aq)]}$ **OR** $\dfrac{2.10 \times 10^{-9}}{(1.50 \times 10^{-3}) \times (2.00 \times 10^{-2})}$ ✓ = $7(.00) \times 10^{-5}$ **OR** $0.00007(00)$ ✓ units: $dm^3\ mol^{-1}\ s^{-1}$ ✓	**9**	**ALLOW ECF** from incorrect orders In rate equation, square brackets **are required** rate = $k[(CH_3)_2CO(aq)][HCl(aq)][I_2(aq)]^0$ **ALLOW** H^+ for HCl **IGNORE** state symbols, even if wrong **ALLOW ECF** for units 'correct' for incorrect expression used to calculate *k, e.g. upside down or wrong orders* $\dfrac{[(CH_3)_2CO(aq)]\,[H^+(aq)]}{rate}$ × units: mol s dm^{-3} ✓

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Question			Expected answers	Marks	Additional guidance
1	b		**step 1**: $H_2(g)$ + ICl(g) $\longrightarrow$ LHS of step 1 ✓ $\longrightarrow$ HCl(g) + HI(g) **step 2**: HI(g) + ICl(g) $\longrightarrow$ HCl(g) + $I_2(g)$ products of step 1 **AND** step 2 ✓	2	State symbols **NOT** required **2nd mark** can **ONLY** be awarded provided that • **1st mark** has been awarded • **step 1 AND step 2** add up to the overall equation. e.g. **ALLOW** $\longrightarrow$ $H_2ICl(g)$ **step 2**: $H_2ICl(g)$ + ICl(g) $\longrightarrow$ 2HCl(g) + $I_2(g)$ In **step 2**, **ALLOW** inclusion of extra species on **both** sides of the equation **only** if they cancel, e.g. HI(g) + HCl(g) + ICl(g) $\longrightarrow$ 2HCl(g) + $I_2(g)$
			Total	**11**	

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Question			Expected answers	Marks	Additional guidance
2	a		(The enthalpy change that accompanies) the formation of **one mole** of a(n ionic) compound ✓ from its **gaseous ions** ✓ (under standard conditions)	2	**IGNORE** 'Energy needed' **OR** 'energy required' **ALLOW** as alternative for compound: lattice, crystal, substance, solid, product **Note**: 1st mark requires **1 mole** **2nd mark** requires **gaseous ions** **IF** candidate response has '1 mole of gaseous ions', award 2nd mark but **NOT** 1st mark **IGNORE** reference to 'constituent elements' **IGNORE**: $2Na^+(g) + O^{2-}(g) \longrightarrow Na_2O(s)$ *Question asks for a definition, not an equation*
	b	i	**C** (or 2**C**) **A** **B** **D** **G** **E** (or 2**E**) **F** All seven correct ✓✓✓ Five **OR** six correct ✓✓ Three **OR** four correct ✓	3	**ALLOW** **496 (OR** 992**)** **–141** **790** **249** **G OR** **Lattice enthalpy/LE** [**OR** answer to **(ii)**] **108** (**OR** 216) **–414**
		ii	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –2520 (kJ mol^{-1}) award 2 marks** --- $-414 = (2 \times 108) + 249 + (2 \times 496) + (-141) + 790) + \Delta H_{LE}$ **OR** $\Delta H_{LE} = -414 - [(2 \times 108) + 249 + (2 \times 496) + (-141) + 790]$ ✓ $= -414 - 2106 =$ **–2520** (kJ mol^{-1}) ✓	2	**IF** there is an alternative answer, check **the list below for marking of answers from common errors** --- **ALLOW** for **1 mark**: –1692 wrong sign for 414 –1916 2 × 108 and 2 × 496 not used for Na^+ –2412 2 × 108 not used for Na^+ –2024 2 × 496 not used for Na^+ +2520 wrong sign for final answer –2802 sign changed for 1st electron affinity of oxygen –2395.5 atomisation of oxygen halved

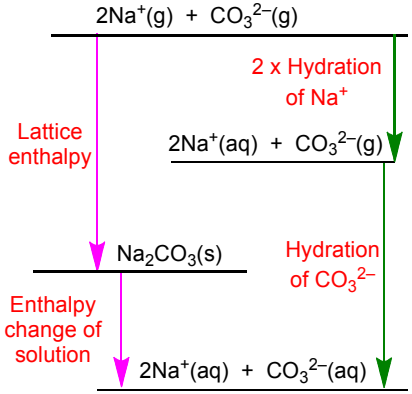
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Question			Expected answers	Marks	Additional guidance
					Any other number: **CHECK** for **ECF** from 1st marking point for expressions with **ONE** error only
2	**c**		**ALLOW** reverse argument throughout (**ORA**)		***ANNOTATIONS MUST BE USED*** **NOTE**: For **ALL** marking points, assume that the following refer to 'ions', Mg^{2+}, etc. For 'ions', **ALLOW** 'atoms' For Mg^{2+}, Na^{+}, O^{2-} and S^{2-}, **ALLOW** symbols: Mg, Na, O and S **ALLOW** names: magnesium, sodium, oxygen, oxide, sulfur, sulfide **BUT DO NOT ALLOW** molecules *i.e.* **ALLOW** Mg has a smaller (atomic) radius **IGNORE** idea of close packing of ions
			Comparison of size AND charge of cations Mg^{2+} is smaller **AND** Mg^{2+} has a greater charge **OR** Mg^{2+} has **a** greater charge density ✓		**ORA**: Na^{+} is larger **AND** Na^{+} has a smaller charge **OR** Na^{+} has a smaller charge density ✓ **IGNORE** just Mg^{2+} is small *comparison required*
			Comparison of size of anions S^{2-} is larger **OR** S^{2-} has a smaller charge density ✓		**ORA** O^{2-} is smaller **OR** O^{2-} has a larger charge density ✓ **IGNORE** just S^{2-} is large *comparison required*
			Comparison of attraction of a cation and an anion Mg^{2+} has stronger attraction **OR** Na^{+} has weaker attraction **AND** S^{2-} has weaker attraction **OR** O^{2-} has stronger attraction ✓	**3**	**ALLOW** pull for attraction **ALLOW** 'attracts with more force' for greater attraction **BUT** … **IGNORE** just 'greater force' (*could be repulsion*) **OR** comparison of bond strength/energy to break bonds **IGNORE** comparisons of numbers of ions

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Question			Expected answers	Marks	Additional guidance
	d	i	Cycle needs **formation** of CO_3^{2-} ions (from C and O) ✓ *i.e. **NOT** breaking up of CO_3^{2-} ion*	1	**ALLOW** carbonate ion contains C and O **ALLOW** carbonate ion contains 2 elements **IGNORE** sodium carbonate contains 3 elements **IGNORE** carbonate ion has covalent bonds
2	d	ii	See also **Appendix 1** at end of mark scheme **Mark allocation** **1 –** $2Na^+(g)$ + $CO_3^{2-}(g)$ on a top line **AND** $Na_2CO_3(s)$ on a lower line **AND** 'Lattice enthalpy' label (as below) links the lines ✓ **2 –** $2Na^+(g)$ + $CO_3^{2-}(g)$ on a top line **AND** $2Na^+(aq)$ + $CO_3^{2-}(g)$ on a middle line **AND** $2Na^+(aq)$ + $CO_3^{2-}(aq)$ on a lower line **AND** 'ΔH hydration' labels (as below) link the lines ✓ **NOTE:** For hydration labels, see diagram below **2** x hydration of Na^+ **OR** hydration of **2** x Na^+ is **required** **3 –** ΔH solution' label **BELOW** $Na_2CO_3(s)$ **AND ALL** arrows in correct directions ✓	3	***ANNOTATIONS MUST BE USED*** **MARK AS FOLLOWS** **1.** Mark the cycle **2. IF** there is **no cycle**, mark the equation below --- **State symbols** are required for **ALL** species **IGNORE** direction of any arrows until **MARK 3** **ALLOW** $Na_2CO_3(aq)$ on a lower line as an alternative for $2Na^+(aq)$ + $CO_3^{2-}(aq)$ **ALLOW** CO_3^{2-} hydrated first: i.e. $2Na^+(g)$ + $CO_3^{2-}(aq)$ on middle line **ALLOW** two hydration stages combined i.e. $2Na^+(g)$ + $CO_3^{2-}(g)$ on a top line **AND** $2Na^+(aq)$ + $CO_3^{2-}(aq)$ on a lower line **AND BOTH** 'Hydration' labels link the lines ✓ **IF** cycle shown using $NaCO_3$, Na^+ and CO_3^- **ALLOW ECF** for third marking point only **NOTE: DO NOT ALLOW ECF** from any other species **For simple energy cycles** a maximum of 2 marks only can be awarded **–** See **APPENDIX 1** --- **For an equation,** only **1 mark** can be awarded Lattice enthalpy = $-\Delta H$(solution) Na_2CO_3 + [2 x ΔH(hydration) Na^+] + ΔH(hydration) CO_3^{2-}

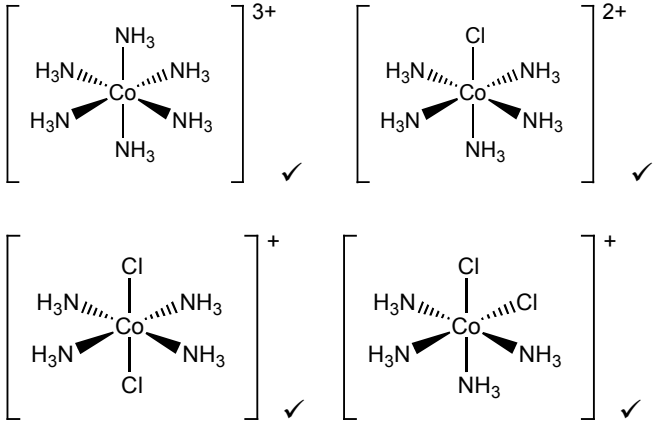
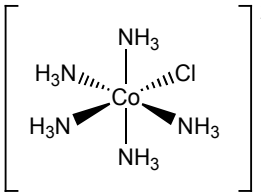
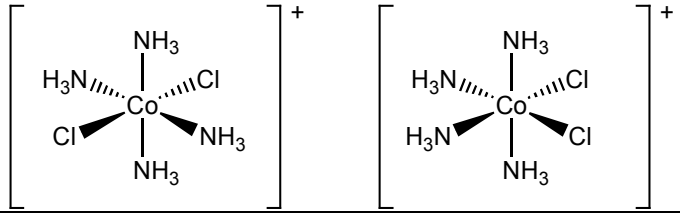
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Question	Expected answers	Marks	Additional guidance
			**OR** Lattice enthalpy + ΔH(solution) Na_2CO_3 = 2 x ΔH(hydration) Na^+ + ΔH(hydration) CO_3^{2-} ✓ **IGNORE** state symbols for equation approach
	Total	**14**	

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Question			Expected answers	Marks	Additional guidance
3	a		Co: $(1s^2 2s^2 2p^6)3s^2 3p^6 3d^7 4s^2$ ✓ Co^{3+}: $(1s^2 2s^2 2p^6)3s^2 3p^6 3d^6$ ✓	2	**ALLOW** $(1s^2 2s^2 2p^6)3s^2 3p^6 4s^2 3d^7$ (i.e. 4s before 3d) **ALLOW** upper case D, etc. and subscripts, e.g. $[Ar]4S_2 3D_7$ If included, **ALLOW** $4s^0$
	b		catalyst **OR** coloured ✓	1	**IGNORE** forms different oxidation states
	c		Donates an electron/lone pair to a metal ion **OR** forms a coordinate bond to a metal ion ✓	1	**ALLOW** donates an electron pair/lone pair to a metal/transition element **ALLOW** dative (covalent) bond for coordinate bond
	d	i	$Co(OH)_2$ ✓ precipitation ✓	2	Mark independently **ALLOW** $Co(OH)_2(H_2O)_4$ **ALLOW** precipitate (reaction)
		ii	$CoCl_4^{2-}$ ✓ ligand substitution ✓	2	Mark independently **ALLOW** ligand exchange **DO NOT ALLOW** just substitution

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Question			Expected answers	Marks	Additional guidance
3	e	i		4	***ANNOTATIONS MUST BE USED*** **CARE**: Cl can be on any position, e.g. for **B**  complex ions in **C** and **D** can be other way around In one complex ion, the 2 Cls must be opposite one another In the other complex ion, the 2 Cls must be next to one another **CARE**: Cl atoms can be on any position, e.g. for **C** and **D** 

Marking sequence **See also Appendix 2 for examples**

1. Mark any correct complex ions first
Do **not** look at these complex ions again

2. Mark with crosses any complex ions with incorrect ligands. This could include Cl in complex **A**, and NH_3Cl and $NH_3^+Cl^-$, but **NOT** NH_3------ connectivity on the **LEFT** only and **NOT** Cl^- and **NOT** just NH_3^+
Do **not** look at these complex ions again

3. In the remaining complex ions, identify errors in ligands (See Appendix 2): e.g.

- NH_3 ligands bonded to an H on the **LEFT** only: NH_3----- *(connectivity error)*
- Cl^-
- NH_3^+

Mark these complex ions to maximise errors but treat any incorrectly bonded NH_3, Cl^- and NH_3 as **ECF**

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Question			Expected answers	Marks	Additional guidance
			SEE APPENDIX 2 FOR EXAMPLES		
3	**e**	**ii**	143.4 **OR** 107.9 + 35.5 (g mol^{-1}) used *i.e. molar mass AgCl* **OR** amount of AgCl = 0.02(000) mol ✓ **Ratio** ratio complex : **Cl^-** = 1 : 2 **OR** 0.01 : 0.02 ✓ **Identification – available from 1 : 2 ratio OR 2Cl^-** Therefore the complex is **B** ✓	**3**	**DO NOT ALLOW** $AgCl_2$ **DO NOT ALLOW** $\frac{2.868}{0.01}$ *0.01 linked to AgCl, not complex* **ALLOW** this mark **ONLY** for evidence of Cl^- ***Quality of Written Communication*** Identification as **B** is dependent on correct 1 : 2 ratio **OR 2**Cl^- for this mark
			Total	**15**	

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Question			Expected answers	Marks	Additional guidance
4	a	i	A strong acid completely dissociates **AND** a weak acid partially dissociates ✓	1	**ALLOW** ionises for dissociates
		ii	$(K_a =) \frac{[H^+]\,[NO_2^-]}{[HNO_2]}$ ✓	1	**DO NOT ALLOW** $\frac{[H^+]^2}{[HNO_2]}$ Square brackets **are required**
		iii	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 1.89 award **2 marks** **IF** answer = 1.9 award **1 mark** --- pH = –log 0.0129 = **1.89** ✓✓ **OR** pH = –log 0.0129 = **1.9** ✓ ***not*** *two decimal places*	2	**IF** there is an alternative answer to more decimal places, check calculator value --- **Working to get to 0.0129 (mol dm^{-3})** **Not required and no credit** $[H^+] = \sqrt{K_a \times [HNO_2]} = \sqrt{4.43 \times 10^{-4} \times 0.375}$ **ALLOW 1 mark** for an answer with more than 2 decimal places that rounds back to 1.89
		iv	$HNO_3 + HNO_2 \rightleftharpoons NO_3^- + H_2NO_2^+$ ✓ Acid 1 Base 2 Base 1 Acid 2 ✓	2	State symbols **NOT** required **ALLOW** 1 **AND** 2 labels the other way around. **ALLOW** 'just acid' and 'base' labels if linked by lines so that it is clear what the acid–base pairs are **IF** proton transfer is wrong way around **ALLOW** 2nd mark for idea of acid–base pairs, *i.e.* $HNO_3 + HNO_2 \rightleftharpoons H_2NO_3^+ + NO_2^-$ × Base 2 Acid 1 Acid 2 Base 1 ✓ **NOTE** For the 2nd marking point (acid–base pairs), this is the **ONLY** acceptable **ECF**

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Question			Expected answers	Marks	Additional guidance
					*i.e., **NO ECF** from impossible chemistry*
4	**b**	**i**	Proton acceptor ✓	**1**	**ALLOW** H^+ acceptor
		ii	**Marks are for correctly calculated values.** **Working shows how values have been derived.** $[OH^-] = 2 \times 0.04(00) = 0.08(00)$ (mol dm^{-3}) ✓ $[H^+] = \frac{1.00 \times 10^{-14}}{0.08(00)}$ **OR** 1.25×10^{-13} (mol dm^{-3}) ✓ pH = –log 1.25×10^{-13} = **12.90** ✓ --- **pOH variation (also worth 3 marks)** $[OH^-] = 2 \times 0.04(00) = 0.08(00)$ (mol dm^{-3}) ✓ pOH –log 0.08(00) = 1.10 ✓ pH = 14.00 – 1.10 = 12.90 ✓	**3**	**ALLOW** by **ECF** $\frac{1.00 \times 10^{-14}}{\text{calculated value of } [OH^-]}$ **DO NOT ALLOW** 12.9 *not **two** decimal places* --- **COMMON ERRORS** 12.60 ✓✓ *no × 2 for $[OH^-]$* 12.6 ✓ *no × 2 for $[OH^-]$ **AND** 1 DP only* 12.30 ✓✓ *÷ 2 $[OH^-]$* 12.3 ✓ *÷ 2 $[OH^-]$ **AND** 1 DP only* 1.40 **NO** marks
	c		$Ca(OH)_2 + 2HNO_2 \rightarrow Ca(NO_2)_2 + 2H_2O$ ✓ $H^+ + OH^- \longrightarrow H_2O$ ✓	**2**	**ALLOW**: $2H^+ + 2OH^- \rightarrow 2H_2O$

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Question			Expected answers	Marks	Additional guidance
4	d	i	**Equilibrium** $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ ✓		***ANNOTATIONS MUST BE USED*** **Equilibrium sign is required** **IGNORE** $HA \rightleftharpoons H^+ + A^-$ **DO NOT ALLOW** $H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$ **DO NOT ALLOW** $NaHCO_3 \rightleftharpoons Na^+ + HCO_3^-$ **IGNORE** $H_2O + CO_2 \rightleftharpoons H_2CO_3$
			Action of buffer **Added alkali** H_2CO_3 reacts with added alkali **OR** $H_2CO_3 + OH^- \rightarrow$ **OR** added alkali reacts with H^+ **OR** $H^+ + OH^- \rightarrow$ ✓ Equilibrium $\rightarrow$ right **OR** equilibrium shifts forming H^+ **OR** HCO_3^- ✓		**IF** $HA \rightleftharpoons H^+ + A^-$ **OR** $H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$ have been used above: **ALLOW** all marks that meet marking alternatives as written **NOTE** The 1st '**added acid**' mark **cannot** then be accessed Equilibrium responses **must** refer back to a written equilibrium **BUT IF** $H_2CO_3 \rightarrow H^+ + HCO_3^-$ shown above, assume that any equilibrium comments apply to the correct equilibrium **IF** more than one equilibrium shown, it **must** be clear which equilibrium is being referred to **ALLOW** added alkali reacts with weak acid ***Quality of Written Communication*** Mark is for linking the action of the buffer in controlling added alkali and hence pH

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Question			Expected answers	Marks	Additional guidance
			Added acid HCO_3^- reacts with added acid ✓ Equilibrium → left **OR** equilibrium shifts forming H_2CO_3 ✓	**5**	**HCO_3^- is required** for this mark **BUT** … **ALLOW** added acid reacts with conjugate base **ONLY** if HCO_3^- is present in equilibrium with H_2CO_3 **DO NOT ALLOW** salt reacts with added acid
4	**d**	**ii**	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **6.6 : 1 OR 1 : 0.15** **CHECK** ratio is HCO_3^- : H_2CO_3 and award **5 marks.** **IF** answer = **0.15 : 1** , **CHECK** ratio is H_2CO_3 : HCO_3^- and award **4 marks** --- In blood at pH 7.40, $[H^+] = 10^{-pH} = 10^{-7.40} = 3.98 \times 10^{-8}$ (mol dm^{-3}) ✓ $K_a = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = \frac{3.98 \times 10^{-8} \times 10.5}{1}$ **OR** $K_a = 4.18 \times 10^{-7}$ (mol dm^{-3}) ✓ In blood at pH 7.20, $[H^+] = 10^{-pH} = 10^{-7.20} = 6.31 \times 10^{-8}$ (mol dm^{-3}) ✓ $\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_a}{[H^+]}$ **OR** $\frac{4.18 \times 10^{-7}}{6.31 \times 10^{-8}}$ ✓ $= \frac{6.6}{1}$ **OR** 6.6 : 1 ✓ (up to calc. value, see below) **ALLOW** any answer with > 1 decimal place that rounds back to 6.62 **OR** 6.63	**5**	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- ***ANNOTATIONS MUST BE USED*** **FOR ALTERNATIVE** using Henderson–Hasselbalch equation below --- **ALLOW** 3.98×10^{-8} up to calculator value of $3.981071706 \times 10^{-8}$ correctly rounded **ALLOW** 6.31×10^{-8} up to calculator value of $6.309573445 \times 10^{-8}$ correctly rounded --- **Common errors** 0.15 : 1 ✓✓✓✓ *Inverse ratio of H_2CO_3 : HCO_3^-* 16.6 : 1 **OR** 0.06 : 1 ✓✓✓✓ *10.5/1 swapped over in 2nd mark giving K_a value of 3.79 x 10^{-9}* ***ALLOW*** *answer with > 1 decimal place that rounds back to 16.64* ***OR*** *16.65*
			ALTERNATIVE approach for concentrations using Henderson–Hasselbalch equation ***(5 marks)*** $pH = pK_a + \log\frac{[HCO_3^-]}{[H_2CO_3]}$ **OR** $-\log K_a + \log\frac{[HCO_3^-]}{[H_2CO_3]}$ ✓ $pK_a = pH - \log\frac{[HCO_3^-]}{[H_2CO_3]} = 7.40 - \log\frac{10.5}{1} = 6.38$ ✓ (subsumes previous mark) Calculator: 6.378810701		

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Question			Expected answers	Marks	Additional guidance
			At pH = 7.20, $\log \frac{[HCO_3^-]}{[H_2CO_3]}$ = pH – pK_a = 7.20 – 6.38 = 0.82 ✓ (subsumes previous mark) $\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{0.82}$ ✓ = $\frac{6.6}{1}$ **OR** 6.6 : 1 ✓		
			Total	**22**	

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Question			Expected answers	Marks	Additional guidance
5	a	i	Complete circuit with electrodes to voltmeter **AND** salt bridge between solutions ✓ Fe^{3+}/Fe^{2+} half-cell with Pt electrode **AND** 1 mol dm^{-3}/ 1 M Fe^{2+} and 1 mol dm^{-3}/ 1 M Fe^{3+} ✓ Ni electrode in (1 mol dm^{-3}) Ni^{2+} half-cell ✓	3	circuit shown **must** be complete, *i.e. must be capable of working* salt bridge **must** be labelled. electrodes **AND** salt bridge **must** dip into/touch both solutions **ALLOW** cells drawn either way around **ALLOW** Fe^{3+}/Fe^{2+} 1 mol dm^{-3} / 1 M /1 molar **ALLOW BOTH** solutions same concentration/equimolar **DO NOT ALLOW** 1 mol **OR** 1 dm^{-3} **IGNORE** any temperature or pressure, even if wrong
		ii	1.02 V **AND** – sign ✓ 0.49 V **AND** + sign ✓	2	**IGNORE** any sign **BEFORE** cell potential **ALLOW 1 mark** for correct values **AND** signs **BOTH** the wrong way round: *i.e.*1.02 V **AND** + sign **AND** 0.49 V **AND** – sign
	b		**Cell A** (based on **1** and **2**) $Ni + 2Fe^{3+} \longrightarrow Ni^{2+} + 2Fe^{2+}$ ✓ **Cell B** (based on **1** and **3**) $2Cr + 3Ni^{2+} \longrightarrow 2Cr^{3+} + 3Ni$ ✓ **concentrations** (of the ions in each cell) change **OR** **concentrations** are not standard ✓	3	In equations, **ALLOW** equilibrium sign, ⇌ instead of → **Equations are required** for the first two marking points **ALLOW** $Ni \longrightarrow Ni^{2+} + 2e^-$ **ALLOW** $Ni^{2+} + 2e^- \longrightarrow Ni$ **ALLOW** any statement that a **concentration** is changing **IGNORE** 'non-standard conditions'
	c	i	$MH + OH^- \longrightarrow M + H_2O + e^-$ ✓	1	**ALLOW** $MH \longrightarrow M + H^+ + e^-$
		ii	adsorbed (on a solid) **OR** on the surface (of a solid) **OR** as a liquid under pressure ✓	1	**DO NOT ALLOW** adsorbed **into** the solid ***CON*** **DO NOT ALLOW** just 'as a liquid'
			Total	10	

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Question			Expected answers	Marks	Additional guidance
6	a		$\Delta G = \Delta H - T\Delta S$ ✓	1	
	b		process — sign $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$ **−** $NaCl(s) + (aq) \longrightarrow NaCl(aq)$ **+** $H_2O(l) \longrightarrow H_2O(s)$ **−** $Mg(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2(g)$ **+** $CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4{\bullet}5H_2O(s)$ **−** **All 5 correct ⟶ 2 marks** ✓✓ **4 correct ⟶ 1 mark** ✓	2	
	c		$\Delta S = (4 \times 211 + 6 \times 189) - (4 \times 192 + 5 \times 205)$ ✓ $\Delta S = (+)185$ (J K^{-1} mol^{-1}) ✓	2	**ALLOW ECF** from working line above from a single error --- **COMMON ERRORS** (+)3 (J K^{-1} mol^{-1}) ✓ (211 + 189) – (192 + 205) – 185 (J K^{-1} mol^{-1}) ✓ *incorrect sign*
	d		With increasing temperature $T\Delta S$ is more negative **OR** $T\Delta S$ decreases **OR** $-T\Delta S$ increases **OR** $\lvert T\Delta S\rvert$ increases **OR magnitude** of $T\Delta S$ increases ✓ At high temperature $T\Delta S$ is more negative that ΔH **OR** at high T, $T\Delta S$ outweighs/is more significant than ΔH **OR** At low temperature $\Delta H - T\Delta S < 0$ **OR** At high temperature $\Delta H - T\Delta S > 0$ ✓	2	***ANNOTATIONS MUST BE USED*** **DO NOT ALLOW** just $T\Delta S$ increases **DO NOT ALLOW** At high T, '$-T\Delta S$ is greater (than ΔH)' ***APPROACH BASED ON TOTAL ENTROPY:*** With increasing temperature $\Delta H/T$ is less negative **OR** $\Delta H/T$ increases **OR** $-\Delta H/T$ decreases **OR** $\lvert\Delta H/T\rvert$ decreases **OR** magnitude of $\Delta H/T$ decreases ✓ **ALLOW** at high temperatures $\Delta S - \Delta H/T < 0$

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Question			Expected answers	Marks	Additional guidance
					OR ΔS is more negative than $\Delta H/T$ **OR** ΔS outweighs/ is more significant than $\Delta H/T$
6	**e**		(For feasibility,) $\Delta G < 0$ **OR** $\Delta G = 0$ **OR** $0 < \Delta H - T\Delta S$ **OR** $0 = \Delta H - T\Delta S$ **OR** 0 = 493 – T x 543/1000 ✓ $T = \frac{\Delta H}{\Delta S}$ = 493 x 1000/543 ✓ = 908 K ✓ Units of temperature are **required**	**3**	**ALLOW** total entropy statement: ΔS(total) = 0 **OR** ΔS(total) >0 **ALLOW** 0 = 493 – T × 543 ✓ *i.e.* This *mark focuses on* ΔG ***OR*** $\Delta H - T\Delta S$ *being = 0 and* ***NOT*** *on conversion of* ΔS *value into kJ* K^{-1} mol^{-1} **Mark temperature given on answer line** **ALLOW** 3 SF up to calculator value 907.9189687 correctly rounded, e.g. 907.9, 907.92 **ALLOW** temperature in ºC: i.e. **ALLOW** by subtraction of 273: 635, 634.9, 634.91 ^{o}C **ALLOW** by subtraction of 273.15: 635, 634.8, 634.77 ^{o}C up to calculator value correctly rounded **ALLOW** C for ºC; ºK for K **IF** ΔS has not been converted to kJ, **DO NOT ALLOW** 2nd mark **BUT** … **ALLOW** calculated answer = 493/543 = 0.91 K (calculator: 0.907918968) ***ALLOW 2 marks only for absence of one of the statements required for 1st marking point***
			Total	**10**	

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Question			Expected answers	Marks	Additional guidance
7	a		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** numerical value = 7.81×10^{-2} **OR** 0.0781 **AND** $[N_2O_4]$ = 0.2(00 mol dm^{-3} **AND** $[NO_2]$ =1.6(0), award 4 calculation marks and check for the mark for correct units --- **Equilibrium amount of N_2O_4** 0.400 mol N_2O_4 ✓ **Equilibrium concentrations** $[N_2O_4]$ = 0.200 mol dm^{-3} **AND** $[NO_2]$ = 1.60 mol dm^{-3} ✓ **K_c expression** $K_c = \frac{[N_2O_4]}{[NO_2]^2}$ (Square brackets **essential**) **OR** $\frac{0.200}{1.60^2}$ ✓ **Calculation** = 7.81×10^{-2} ✓ **Units** $dm^3\ mol^{-1}$ ✓	**5**	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- ***ANNOTATIONS MUST BE USED*** --- **ALLOW ECF** for equilibrium amounts ÷ 2 **ALLOW** 3 SF up to calculator value of 0.078125 correctly rounded **ALLOW ECF** using calculated equilibrium concentrations For units, **ALLOW** $mol^{-1}\ dm^3$ **ALLOW ECF** from incorrect K_c expression
			Common errors for 4 calculation marks **– Remember there is another mark for units** 7.81×10^{-2} from wrong concs ✓✓ + units — *look for $[N_2O_4]$ = 0.8 **AND** $[NO_2]$ = 3.2* 0.03906 ✓ ✓✓ + units — *no conversion of both moles to concentration* 0.01953 ✓✓✓ + units — *no conversion of NO_2 moles to concentration* 0.3125 ✓✓✓ + units — *moles of N_2O_4 taken as 3.2/2* 12.8 ✓✓✓ + units: mol dm^{-3} — *K_c expression upside down* 0.125 ✓✓✓ + units; **none** — *$[NO_2]$ instead of $[NO_2]^2$* ***'No units' MUST be stated*** **0.15625 MARK BY ECF as there are many different routes to this answer**		

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Question			Expected answers	Marks	Additional guidance
7	b		***Each marking point is independent***		
			Effect on K_c K_c does not change (with pressure) ✓		**ALLOW** K_c **only** changes with temperature **IGNORE** K_c changes with temperature
			Comparison of conc terms after increase in pressure $[NO_2]^2$ increases more than $[N_2O_4]$ **OR** concentration (term) on bottom (of K_c) increases more that concentration (term) on top (of K_c) ✓		**ALLOW** $\frac{[N_2O_4]}{[NO_2]^2} < K_c$ **OR** $\frac{[N_2O_4]}{[NO_2]^2}$ decreases **IGNORE** K_c decreases
			Changes in concentrations linked to K_c (amount /concentration of) N_2O_4 increases **AND** (amount /concentration of) NO_2 decreases **AND** to maintain/restore ***K_c*** ✓	**3**	**ALLOW** top of K_c expression increases and bottom decreases until K_c is reached **ALLOW** equilibrium shifts to right to maintain/restore K_c **IGNORE** just 'restores equilibrium' ***K_c* IS REQUIRED** **IGNORE** just 'equilibrium shifts to right **IGNORE** le Chatelier response: 'equilibrium shifts to right' because there are fewer moles of gas on right-hand side
			Total	**8**	

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Question			Expected answers	Marks	Additional guidance
8	a		$Fe_2O_3 + 6H^+ \longrightarrow 2Fe^{3+} + 3H_2O$ ✓	1	**ALLOW** $Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$ **OR** $Fe_2O_3 + 6HCl \longrightarrow 2Fe^{3+} + 6Cl^- + 3H_2O$ **ALLOW** correct multiples **IGNORE** state symbols **DO NOT ALLOW** Fe_2Cl_6 as a product
	b		$Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$ ✓ $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$ ✓	2	**IGNORE** state symbols **ALLOW** overall equations: $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$ $6FeCl_2 + K_2Cr_2O_7 + 14HCl \rightarrow 6FeCl_3 + 2CrCl_3 + 2KCl + 7H_2O$ **ALLOW** correct multiples

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Question			Expected answers	Marks	Additional guidance
8	c		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 54.6%, award **5 marks** --- **Amount Fe^{2+} in 250 cm^3 solution – 3 marks** amount $Cr_2O_7^{2-}$ used = $0.0200 \times \frac{26.5}{1000}$ $= 5.30 \times 10^{-4}$ (mol) ✓ amount Fe^{2+} = **6** × 5.30 x 10^{-4} $= 3.18 \times 10^{-3}$ mol ✓ amount Fe^{2+} in original 250 cm^3 = **10** × 3.18 x 10^{-3} $= 3.18 \times 10^{-2}$ (mol) ✓		***ANNOTATIONS MUST BE USED*** **IF** there is an alternative answer, 1st check common errors below. Then see if there is any **ECF** credit possible using working below --- **Working must be to at least 3 SF throughout** **BUT** ignore trailing zeroes, *i.e.* for 0.490 allow 0.49 **ALLOW ECF** from different Fe^{2+} ratio in equation from **8(b)** **BUT** still **ALLOW** 6 : 1 even from different ratio in equation If no equation use actual 6 : 1 ratio **DO NOT AWARD** 'ratio mark' at all for use of 1 : 1 ratio – *makes problem easier* **ECF** 10 × answer above
			% Fe in ore – 2 marks mass of Fe in ore = $55.8 \times 3.18 \times 10^{-2}$ g = 1.77444 g ✓		**ECF** 55.8 × answer above **IF** answer above has **not** been used **AND** × 55.8, **DO NOT ALLOW** this mark but do **ALLOW** final % **IF** answer above **AND** 55.8 are **BOTH not** used, then **DO NOT ALLOW ANY** further marks
			percentage Fe in ore = $\frac{1.77444}{3.25} \times 100$ = 54.6% ✓	**5**	**ECF** $\frac{\text{answer above}}{3.25} \times 100$ **ALLOW** 54.5% (from 1.77 g) **AND** any answer with > 1 decimal place that rounds back to 54.5 **OR** 54.6
					COMMON ERRORS 5.46 ✓✓✓✓ × *10 omitted* 51.5 ✓✓✓✓ *titre taken as 25.0* 156.2 ✓✓✓✓ × *159.6 instead of 55.8* 15.62 ✓✓✓ × *159.6 and* × *10 omitted* 45.5 ✓✓✓✓ *5 : 1 ratio* 1.52 ✓✓✓✓ ÷ 6 instead of × 6

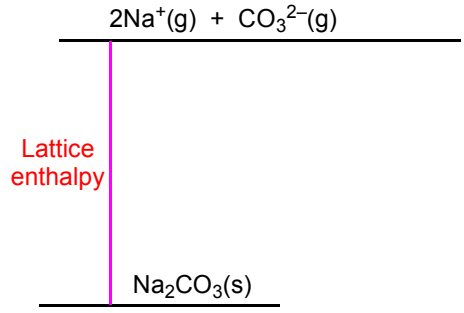
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Question			Expected answers	Marks	Additional guidance
8	d		$E^{\ominus}$ for MnO_4^- is more positive/greater than Cl_2 **OR** $E^{\ominus}$ for $Cr_2O_7^{2-}$ is less positive/smaller than Cl_2 ✓ MnO_4^- reacts with Cl^- **OR** HCl (forming Cl_2 gas) **OR** $Cr_2O_7^{2-}$ does **not** react with Cl^- ions ✓	**2**	**ORA:** $E^{\ominus}$ for Cl_2 is less positive/smaller than MnO_4^- **OR** $E^{\ominus}$ for Cl_2 is more positive/greater than $Cr_2O_7^{2-}$
			Total	**10**	

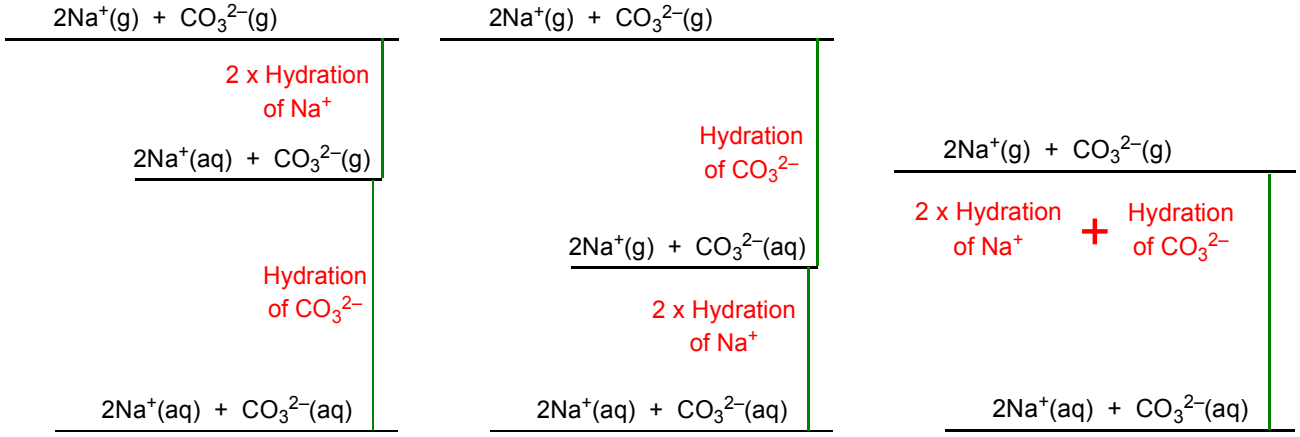
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APPENDIX 1

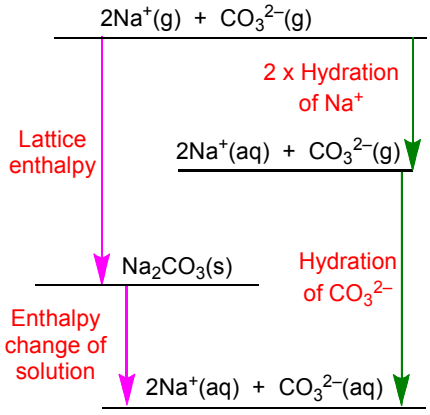
MARK 1



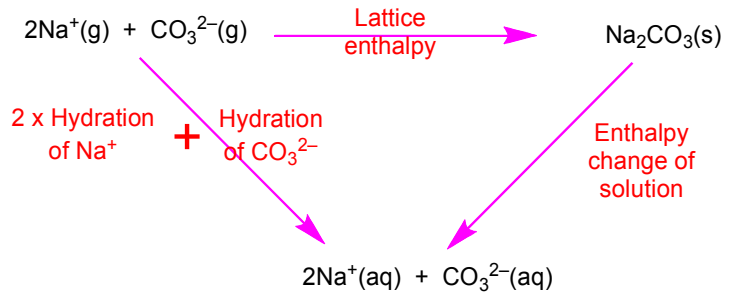
MARK 2



MARK 3



A simple energy cycle can be awarded 2 marks only

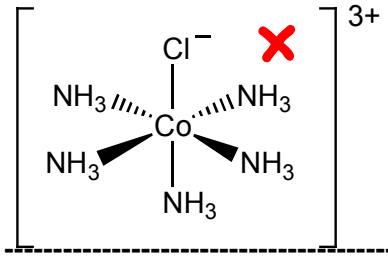


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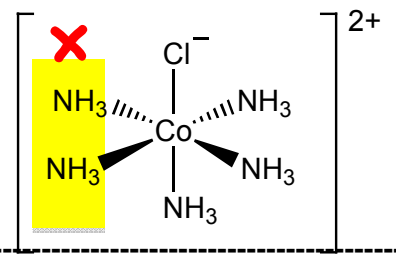
Mark 1 All species, state symbols and labels
Mark 2 Arrows added in correct directions

APPENDIX 2

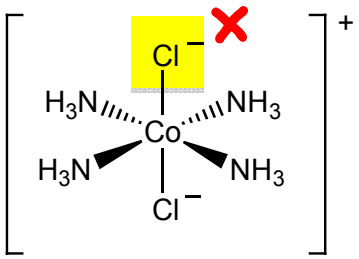
Example 1



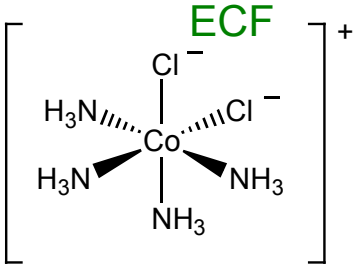
---- **A**



B



C



D

No complex ions are correct

A is wrong because a wrong ligand has been attached. This would have been wrong even if Cl had been attached so the Cl^- charge is ignored at this stage

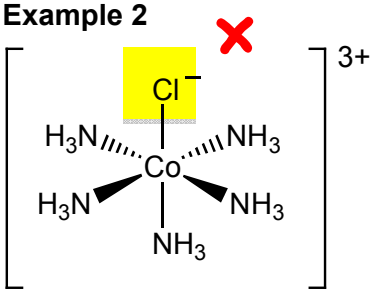
B has connectivity **and** Cl^- errors

C and **D** have Cl^- errors

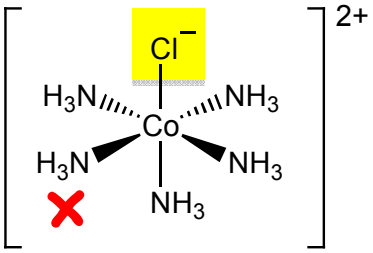
In **B**, either connectivity **OR** Cl^- could have been penalised Choose which to penalise based on maximising identification of errors

If Cl^- had been penalised in **B**, then **C** would have been marked correctly by **ECF**.
But the candidate has clearly made 2 mistakes across **B** and **C** so NH_3 connectivity had been penalised in **B**

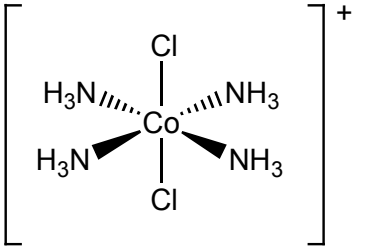
Example 2



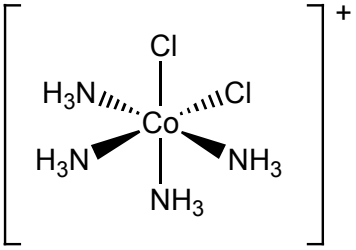
A



B



C



D

C and **D** are correct and they have been marked correct

A is wrong because a wrong ligand has been attached. This would have been wrong even if Cl had been attached so the Cl^- charge is ignored at this stage

In **B**, the only error is Cl^-
A also had Cl^-but the charge had been ignored as Cl was incorrect anyway
B is therefore marked wrong

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RECOGNISING ACHIEVEMENT

ADVANCED GCE

CHEMISTRY A

Equilibria, Energetics and Elements

F325

Candidates answer on the question paper.

OCR Supplied Materials:
- *Data Sheet for Chemistry A* (inserted)

Other Materials Required:
- Scientific calculator

Wednesday 15 June 2011
Afternoon

Duration: 1 hour 45 minutes

F3186060611

F325

Candidate forename		Candidate surname	

Centre number						Candidate number				

INSTRUCTIONS TO CANDIDATES

- The insert will be found in the centre of this document.
- Write your name, centre number and candidate number in the boxes above. Please write clearly and in capital letters.
- Use black ink. Pencil may only be used for graphs and diagrams where they appear.
- Read each question carefully. Make sure that you know what you have to do before starting your answer.
- Write your answer to each question in the space provided. Additional paper may be used if necessary but you must clearly show your candidate number, centre number and question number(s).
- Answer **all** the questions.
- 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 **24** pages. Any blank pages are indicated.

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Answer **all** the questions.

1 Born–Haber cycles provide a model that chemists use to determine unknown enthalpy changes from known enthalpy changes. In this question, you will use a Born–Haber cycle to determine an enthalpy change of hydration.

(a) Magnesium chloride has a lattice enthalpy of –2493 kJ mol^{-1}.

Define in words the term *lattice enthalpy*.

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

(b) The table below shows the enthalpy changes that are needed to determine the enthalpy change of hydration of magnesium ions.

enthalpy change	**energy/kJ mol^{-1}**
lattice enthalpy of magnesium chloride	–2493
enthalpy change of solution of magnesium chloride	–154
enthalpy change of hydration of chloride ions	–363

(i) Why is the enthalpy change of hydration of chloride ions exothermic?

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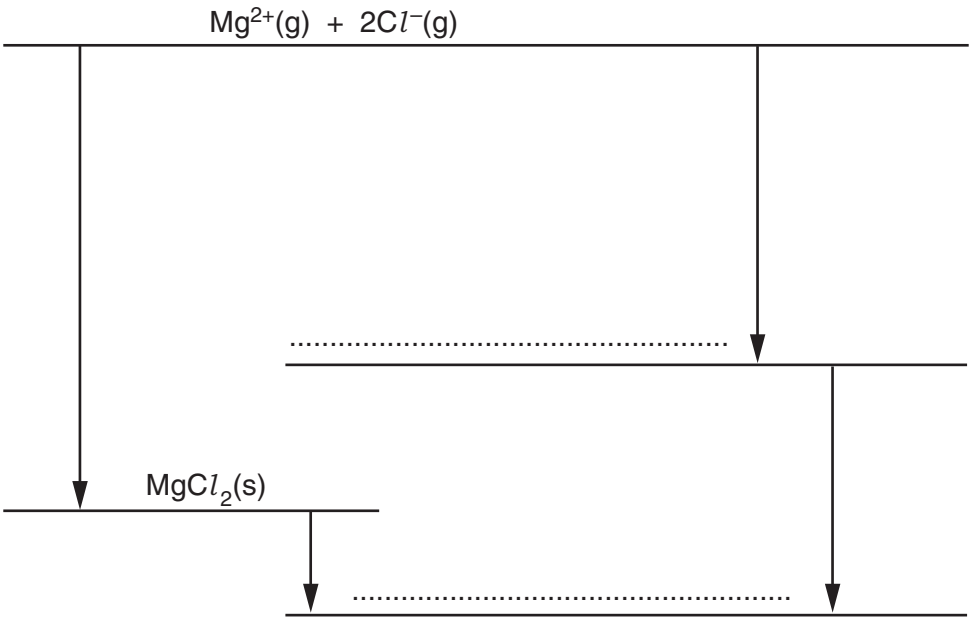
..... **[1]**

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(ii) In this part, you will use the Born–Haber cycle to determine the enthalpy change of hydration of magnesium ions.

On the two dotted lines, add the species present, including state symbols.



[2]

(iii) Calculate the enthalpy change of hydration of magnesium ions.

answer = ... $kJ\,mol^{-1}$ **[2]**

(c) The enthalpy change of hydration of magnesium ions is more exothermic than the enthalpy change of hydration of calcium ions.

Explain why.

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

[Total: 9]

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2 Nitric acid, HNO_3, is manufactured in large quantities. The main use of nitric acid is in the manufacture of fertilisers.

In its industrial preparation, nitric acid is produced in three main stages.

Stage 1
Ammonia is heated with oxygen in the air to form nitrogen monoxide, NO.

Stage 2
The hot nitrogen monoxide gas is then mixed with air and cooled under pressure. Nitrogen dioxide, NO_2, forms in a reversible reaction.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = -115 \text{ kJ mol}^{-1}$$

Stage 3
The nitrogen dioxide is reacted with water in a series of reactions to form nitric acid, HNO_3. The first of these reactions forms a mixture of nitric acid, HNO_3, and nitrous acid, HNO_2.

(a) In **Stage 2**, explain why the equilibrium mixture is both cooled **and** put under pressure.

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

(b) Construct an equation for

- the reaction that takes place in **Stage 1**
- the first reaction that takes place in **Stage 3**.

Stage 1: .....

Stage 3: ..... **[2]**

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(c) An industrial chemist carries out some research into the $NO/O_2/NO_2$ equilibrium used in **Stage 2** of the manufacture of nitric acid.

- The chemist mixes together 0.80 mol NO(g) and 0.70 mol of O_2(g) in a container with a volume of 2.0 dm^3.
- The chemist heats the mixture and allows it to stand at constant temperature to reach equilibrium.
  The container is kept under pressure so that the total volume is maintained at 2.0 dm^3.
- At equilibrium, 75% of the NO has reacted.

(i) Write an expression for K_c for this equilibrium.

[1]

(ii) Calculate the equilibrium constant, K_c, including units, for this equilibrium.

K_c = ... units ..... **[5]**

[Total: 11]

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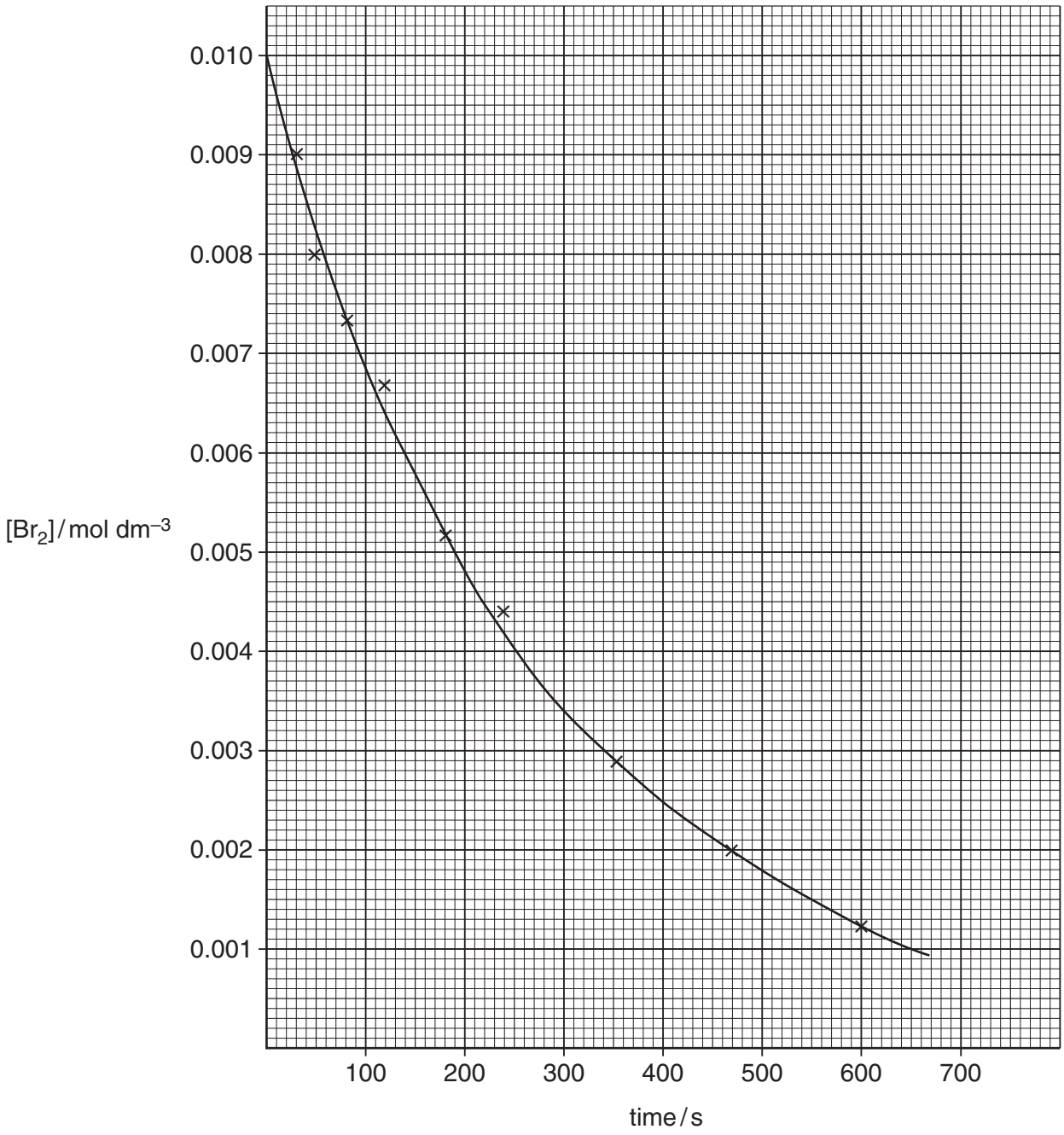
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3 In aqueous solution, methanoic acid, HCOOH, reacts with bromine, Br_2.

$$HCOOH(aq) + Br_2(aq) \longrightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$

A student carried out an investigation on the rate of this reaction. The student used a large excess of methanoic acid which ensured that its concentration was effectively constant throughout. During the reaction, bromine is used up and its orange colour becomes less intense. The intensity of the bromine colour can be measured with a colorimeter to give the bromine concentration.

The graph below was plotted from the experimental results.



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In this investigation, a large excess of methanoic acid was used. Under these conditions, the reaction is effectively zero-order with respect to methanoic acid.

- Using the graph, determine the order of reaction with respect to bromine.
- Using the graph, determine the initial rate of the reaction.
- Calculate the rate constant, *k*, for the reaction between methanoic acid and bromine under these conditions.

In your answer you should make clear how your conclusions fit with the experimental results, including working shown on the graph and units where appropriate.

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..... **[9]**

[Total: 9]

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4 Chemists and biochemists use pK_a values to compare the strengths of different acids. pK_a is a more convenient way of comparing acid strengths than K_a values.

pK_a values of several naturally occurring Brønsted–Lowry acids are shown in **Table 4.1** below.

common name and source	systematic name	structural formula	pK_a (at 25 °C)
benzoic acid (from bark resin)	benzenecarboxylic acid	C_6H_5COOH	4.19
acetic acid (from vinegar)	ethanoic acid	CH_3COOH	4.76
pyruvic acid (formed during metabolism)	2-oxopropanoic acid	$CH_3COCOOH$	2.39
lactic acid (from milk)	2-hydroxypropanoic acid	$CH_3CHOHCOOH$	3.86

Table 4.1

(a) (i) What is meant by the term *Brønsted–Lowry acid*?

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

(ii) What is meant by the *strength* of an acid?

In your answer, include an equation for one of the acids in **Table 4.1**.

.....

.....

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

(iii) Place the four acids in **Table 4.1** in order of increasing strength.

weakest acid .....

.....

.....

↓

strongest acid ..... **[1]**

(iv) Aqueous benzoic acid was mixed with aqueous lactic acid. An equilibrium mixture was formed containing conjugate acid–base pairs.

Complete the equilibrium below to show the components in the equilibrium mixture.

$C_6H_5COOH + CH_3CHOHCOOH \rightleftharpoons$ ..... + ... **[1]**

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(b) Aqueous pyruvic acid was reacted with an aqueous solution of calcium hydroxide.

(i) Write an equation for this reaction.

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

(ii) Write an ionic equation for this reaction.

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

(c) The pH of an acid solution can be calculated from its pK_a value.

Calculate the pH of a 0.0150 mol dm^{-3} solution of pyruvic acid at 25 °C.

Show **all** your working.
Give the pH to **two** decimal places.

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

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(d) Oxalic acid (ethanedioic acid), $C_2H_2O_4$, is present in the leaves of rhubarb plants. Oxalic acid has two dissociations with $pK_a = 1.23$ and $pK_a = 4.19$.

(i) Draw the structure of oxalic acid.

[1]

(ii) Predict the equations that give rise to each dissociation.

$pK_a = 1.23$

$pK_a = 4.19$

[2]

(e) The 'magic tang' in many sweets is obtained by use of acid buffers. A sweet manufacturer carried out tasting tests with consumers and identified the acid taste that gives the 'magic tang' to a sweet.

The manufacturer was convinced that the 'magic tang' would give the company a competitive edge and he asked the company's chemists to identify the chemicals needed to generate the required taste. The chemists' findings would be a key factor in the success of the sweets.

The team of chemists identified that a pH of 3.55 was required and they worked to develop a buffer at this pH.

The chemists decided to use one of the acids in **Table 4.1** (page 8) and a salt of the acid to prepare this buffer.

- Deduce the chemicals required by the chemists to prepare this buffer.
- Calculate the relative concentrations of the acid and its salt needed by the chemist to make this buffer.
- Comment on the validity of the prediction that the pH of the sweet would give the sweets the 'magic tang'.

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[6]

[Total: 20]

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5 Chemists use three energy terms, enthalpy, entropy and free energy, to help them make predictions about whether reactions may take place.

(a) The table below shows five processes. Each process has either an increase in entropy or a decrease in entropy.

For each process, tick (✓) the appropriate box.

process		increase in entropy	decrease in entropy
A	$C_2H_5OH(l) \longrightarrow C_2H_5OH(g)$		
B	$C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$		
C	$NH_4Cl(s) + aq \longrightarrow NH_4Cl(aq)$		
D	$4Na(s) + O_2(g) \longrightarrow 2Na_2O(s)$		
E	$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$		

[2]

(b) At 1 atm (101 kPa) pressure, ice melts into water at 0 °C.

Complete the table below using the symbols '+', '–' or '0' to show the sign of ΔH and ΔS for the melting of ice at 0 °C and 1 atm.

For each sign, explain your reasoning.

energy change	sign +, – or 0	reasoning
ΔH		
ΔS		

[2]

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(c) Much of the hydrogen required by industry is produced by reacting natural gas with steam:

$$CH_4(g) + H_2O(g) \longrightarrow 3H_2(g) + CO(g)$$

Standard entropies are given in the table below.

substance	$CH_4(g)$	$H_2O(g)$	$H_2(g)$	$CO(g)$
$S^{\ominus}$ **/ J K^{-1} mol^{-1}**	186	189	131	198

(i) Calculate the standard entropy change, in J K^{-1} mol^{-1}, for this reaction of natural gas with steam.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} **[2]**

(ii) State **two** large-scale uses for the hydrogen produced.

1. .....

2. ..... **[1]**

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(d) Ammonium chloride, NH_4Cl, can dissociate to form ammonia, NH_3, and hydrogen chloride, HCl.

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$$

At 298 K, $\Delta H = +176\,kJ\,mol^{-1}$ and $\Delta G = +91.2\,kJ\,mol^{-1}$.

- Calculate ΔG for this reaction at 1000 K.
- Hence show whether this reaction takes place spontaneously at 1000 K.

Show **all** your working.

ΔG = ... $kJ\,mol^{-1}$ **[4]**

[Total: 11]

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TURN OVER FOR QUESTIONS 6, 7 AND 8

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6 Nickel is a typical transition element in the d-block of the Periodic Table. Many nickel ions are able to interact with ligands to form complex ions, such as $[Ni(H_2O)_6]^{2+}$.

(a) Using the information about nickel above, explain the meaning of the terms *d-block element*, *transition element*, *ligand* and *complex ion*.

Include electron structures and diagrams in your answer.

..... **[7]**

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(b) A student dissolves nickel(II) sulfate in water. A green solution forms containing the complex ion $[Ni(H_2O)_6]^{2+}$.

The student then reacts separate portions of the green solution of nickel(II) sulfate as outlined below.

- Concentrated hydrochloric acid is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a lime-green colour and contains the four-coordinate complex ion **A**.
- Aqueous sodium hydroxide is added to the green solution of nickel(II) sulfate. A pale-green precipitate **B** forms.
- Concentrated aqueous ammonia is added to the green solution of nickel(II) sulfate until there is no further change. The solution turns a violet colour and contains the complex ion **C**.
  C has a molar mass of $160.7\,g\,mol^{-1}$.

(i) Draw a 3-D diagram for the $[Ni(H_2O)_6]^{2+}$ ion.
Show a value for the bond angles on your diagram.

[2]

(ii) Suggest the formulae of **A** and **B**.

A .....

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

(iii) Deduce the formula of **C**.

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

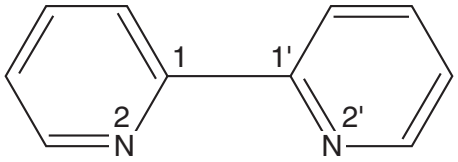
(iv) Write an equation for the formation of **C** from $[Ni(H_2O)_6]^{2+}$.

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

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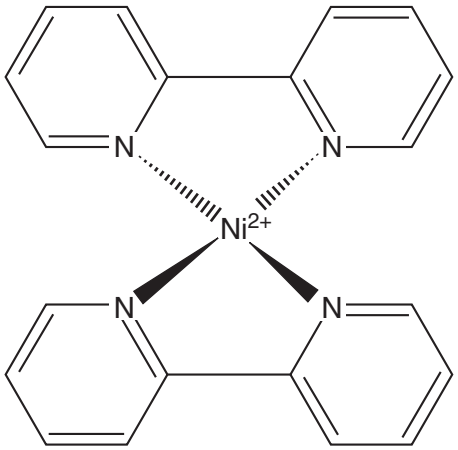
(c) 2,2'-Bipyridine (or 'bipy') is a bidentate ligand that forms complexes with many transition metals. The structure of 2,2'-bipyridine is shown below.



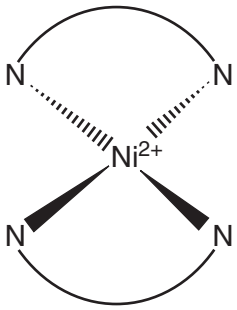
2,2'-bipyridine

In the naming of bipyridines, the numbering starts at the carbon atom that links to the other ring.

2,2'-Bipyridine forms a complex, $[Ni(bipy)_2]^{2+}$. The structure of $[Ni(bipy)_2]^{2+}$ is shown in **Fig 6.1** below.



structure



simplified diagram

$[Ni(bipy)_2]^{2+}$

Fig 6.1

(i) What is the molecular formula of 2,2'-bipyridine?

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

(ii) What is the coordination number of the $[Ni(bipy)_2]^{2+}$ complex ion?

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

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(iii) 2,2'-Bipyridine forms a complex with the transition metal ruthenium with the formula $[Ru(bipy)_3]^{2+}$. This complex exists as two stereoisomers.

Draw 3-D diagrams to predict the structures for these stereoisomers of $[Ru(bipy)_3]^{2+}$. You can represent the 2,2'-bipyridine ligands as in the simplified diagram for $[Ni(bipy)_2]^{2+}$ in **Fig 6.1**.

[2]

(iv) 4,4'-Bipyridine (4,4'-bipy) can also form complexes with transition metal ions. Because of its structure, 4,4'-bipyridine can bridge between metal ions to form 'coordination polymers'. For example, nickel(II) can form a coordination polymer with 4,4'-bipyridine containing $\{[Ni(H_2O)_4(4,4'\text{-bipy})]^{2+}\}_n$ chains.

Draw a 3-D diagram to predict the repeat unit in this coordination polymer of nickel(II). Your diagram should show the complete structure of 4,4'-bipyridine and all coordinate bonds.

[3]

[Total: 21]

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7 Nickel–cadmium cells (NiCd cells) have been extensively used as rechargeable storage cells. NiCd cells have been a popular choice for many electrical and electronic applications because they are very durable, reliable, easy-to-use and economical.

The electrolyte in NiCd cells is aqueous KOH. The standard electrode potentials for the redox systems that take place in NiCd cells are shown below.

$$Cd(OH)_2 + 2e^- \rightleftharpoons Cd + 2OH^- \qquad E^\ominus = -0.80\,V$$
$$NiO(OH) + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^- \qquad E^\ominus = +0.45\,V$$

(a) Define the term *standard electrode potential*, including all standard conditions in your answer.

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

(b) What is the standard cell potential of a NiCd cell?

answer = ... V **[1]**

(c) When a NiCd cell is being used for electrical energy, it is being discharged.

(i) Construct the overall cell reaction that takes place during discharge of a NiCd cell.

.....

.....

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

(ii) Using oxidation numbers, show the species that have been oxidised and reduced during discharge of a NiCd cell.

oxidation .....

.....

reduction .....

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

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(d) NiCd cells are recharged using a battery charger.

(i) Suggest the reactions that take place in the NiCd cell during the recharging process.

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

(ii) As the cell approaches full charge, the aqueous KOH electrolyte starts to decompose, forming hydrogen gas at one electrode and oxygen gas at the other electrode.

Predict half-equations that might take place at each electrode for the decomposition of the electrolyte to form hydrogen and oxygen.

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

[Total: 10]

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8 Brass is an alloy which contains copper.
The percentage of copper in brass can be determined using the steps below.

Step 1 2.80 g of brass is reacted with an excess of concentrated nitric acid, HNO_3.
The half-equations taking place are shown below.

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$
$$2HNO_3(l) + e^- \longrightarrow NO_3^-(aq) + NO_2(g) + H_2O(l)$$

Step 2 Excess aqueous sodium carbonate is added to neutralise any acid. The mixture effervesces and a precipitate forms.

Step 3 The precipitate is reacted with ethanoic acid to form a solution which is made up to 250 cm^3 with water.

Step 4 A 25.0 cm^3 sample of the solution is pipetted into a conical flask and an excess of aqueous potassium iodide is added.
A precipitate of copper(I) iodide and a solution of iodine, $I_2(aq)$, forms.

Step 5 The resulting mixture is titrated with 0.100 mol dm^{-3} sodium thiosulfate to estimate the iodine present:

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

Step 6 **Steps 4** and **5** are repeated to obtain an average titre of 29.8 cm^3.

- For **steps 1**, **2** and **4**, write ionic equations, including state symbols, for the reactions taking place.
- Determine the percentage, by mass, of copper in the brass.
  Give your answer to **one** decimal place.

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[Total: 9]

END OF QUESTION PAPER

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GCE

Chemistry A

Advanced GCE

Unit **F325:** Equilibria, Energetics and Elements

Mark Scheme for June 2011

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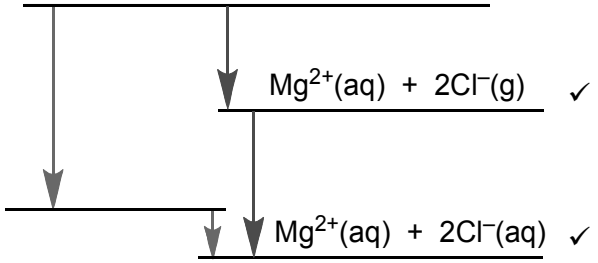
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Question			Answer	Mark	Guidance
1	(a)		(The enthalpy change that accompanies) the formation of **one mole** of a(n ionic) compound ✓ from its **gaseous ions** ✓ (under standard conditions)	2	**IGNORE** 'Energy needed' **OR** 'energy required' **ALLOW** as alternative for compound: lattice, crystal, substance, solid **Note**: 1st mark requires **1 mole** **2nd mark** requires **gaseous ions** **IF** candidate response has '1 mole of gaseous ions', award 2nd mark but **NOT** 1st mark **IGNORE**: $Mg^{2+}(g) + 2Cl^{-}(g) \longrightarrow MgCl_2(s)$ (question asks for words)
	(b)	(i)	Hydration involves bond forming **OR** bonds are made ✓	1	**ALLOW** statement of **any type of bond** being formed **ALLOW** (chloride) ions attract water (molecules) **ALLOW** a response in terms of **hydrogen bonds** breaking **AND** bond making **DO NOT ALLOW** response stating that energy is required **DO NOT ALLOW** response that refers to ions in H_2O, eg H^+
		(ii)		2	Correct species **AND** state symbols required for both marks Mark each marking point independently **ALLOW** response on upper line: $Mg^{2+}(g) + 2Cl^{-}(aq)$ (ie Cl^- hydrated before Mg^{2+}) **ALLOW** $MgCl_2(aq)$

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Question			Answer	Mark	Guidance
1	(b)	(iii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF answer = –1921 (kJ mol^{-1}) award 2 marks** --- (–2493) + (–154) = (2 x –363) + $\Delta H_{hyd}(Mg^{2+})$ ✓ $\Delta H_{hyd}(Mg^{2+})$ = (–2493) + (–154) – (2 x –363) = –1921 (kJ mol^{-1}) ✓	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below. **See list below for marking of answers from common errors** --- **ALLOW** for **1 mark**: –2284 use of Cl^- rather than 2 x Cl^- (+)1921 signs all reversed **OR** lack of 2 for 363 –1613 sign wrong for 154 (+)3065 sign wrong for 2493 –3373 sign wrong for 2 x 363
	(c)		Magnesium ion **OR** Mg^{2+} is smaller **OR** Mg^{2+} has greater charge density ✓ Mg^{2+} has a stronger attraction to H_2O **OR** Mg^{2+} has a stronger bonding with H_2O ✓	2	**ORA:** Calcium ion **OR** Ca^{2+} is larger **OR** Ca^{2+} has smaller charge density **IGNORE** idea of close packing of ions **IGNORE** 'atomic' and 'atoms' and assume that Mg or Ca refer to ions, ie **ALLOW** Mg has a smaller (atomic) radius **ALLOW** Mg has a stronger attraction to H_2O **ORA:** e.g. Ca^{2+} has less attraction to H_2O **DO NOT ALLOW** Mg **atoms** have a stronger attraction to H_2O **DO NOT ALLOW** stronger attraction/bonding between ions **Note:** Response must refer to attraction/bonding with H_2O or this must be implied from the whole response
			Total	9	

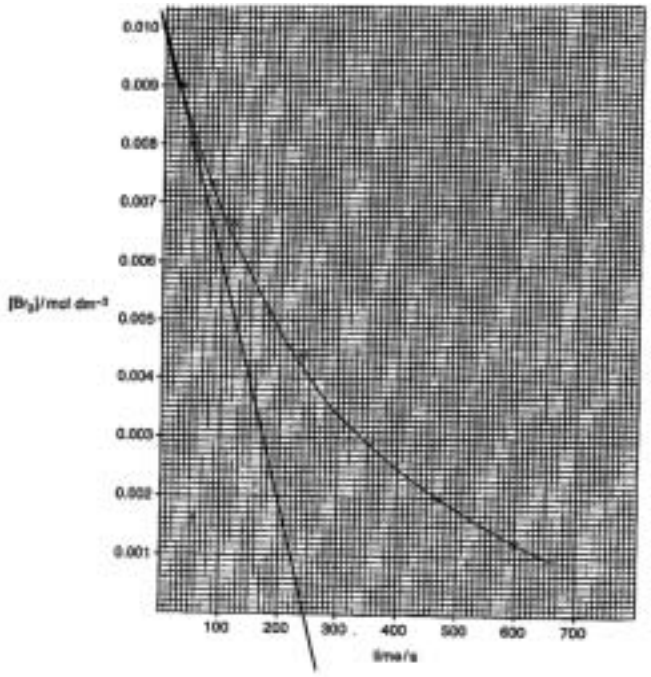
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Question			Answer	Mark	Guidance
2	(a)		**Temperature**: (Forward) reaction is exothermic **OR** gives out heat **OR** reverse reaction is endothermic **OR** takes in heat ✓ **Pressure**: Right-hand side has fewer number of (gaseous) moles ✓ **ORA** **Equilibrium** Lower temperature/cooling **AND** increasing pressure shifts (equilibrium position) to the right ✓	3	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** K_c increases at lower temperatures **3rd mark** is for stating that **BOTH** low temperature and high pressure shift equilibrium to the right (Could be separate statements) **Note: ALLOW** suitable alternatives for 'to right', e.g.: towards NO_2 **OR** towards products **OR** in forward direction **OR** increases yield of NO_2/products **ALLOW** 'favours the right', as alternative for 'shifts equilibrium to right' **IGNORE** responses in terms of rate
	(b)		$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$ ✓ $2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$ ✓	2	**ALLOW** multiples, e.g. $2NH_3 + 2½O_2 \longrightarrow 2NO + 3H_2O$ **ALLOW** $\rightleftharpoons$ **OR** $\rightarrow$ in equations
	(c)	(i)	$(K_c =) \dfrac{[NO_2]^2}{[NO]^2\,[O_2]}$ ✓	1	Square brackets are **essential**

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Question			Answer	Mark	Guidance
2	(c)	(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 45 dm^3 mol^{-1}, award **5 marks** **IF** answer = 45 with incorrect units, award **4 marks** --- **Equilibrium moles** 0.60 mol NO_2 ✓ 0.20 mol NO **AND** 0.40 mol O_2 ✓ **Equilibrium concentrations (equilibrium moles ÷ 2)** $[NO_2]$ = 0.30 mol dm^{-3} **AND** [NO] = 0.10 mol dm^{-3} **AND** $[O_2]$ = 0.20 mol dm^{-3} ✓ **Calculation of K_c and units** $K_c = \frac{0.30^2}{0.10^2 \times 0.20}$ = 45 ✓ dm^3 mol^{-1} ✓	**5**	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW ECF** throughout ***Alternative route if concs NO and O_2 calculated at start:*** **initial concentrations:** 0.40 mol dm^{-3} NO **AND** 0.35 mol dm^{-3} O_2 ✓ **Equilibrium concentrations:** $[NO_2]$ = 0.30 mol dm^{-3} ✓ [NO] = 0.10 mol dm^{-3} **AND** $[O_2]$ = 0.20 mol dm^{-3} ✓ For units, **ALLOW** mol^{-1} dm^3 **ALLOW ECF** using any incorrect values for **concentrations OR moles** of NO, O_2 AND NO_2 For **ECF**, **ALLOW** 2 significant figures up to calculator value correctly rounded **ALLOW ECF** from incorrect K_c expression for both calculation and units **Common ECFs worth less than 5 marks:** **22.5** not ÷2 3 marks + unit mark **1.61** 0.6 for NO_2 but 0.8 for NO and 0.7 for O_2 No mark for moles NO and O_2 3 marks + unit mark **0.804** As above but also no ÷2 No mark for moles NO and O_2 **AND** ÷2 2 marks + unit mark
			Total	**11**	

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Question			Answer	Mark	Guidance
3			Evidence of at least two half-lives measured on graph **OR** within text (would need evidence of two half-lives) ✓ Any half-life value stated in range 180–220 s **OR** constant half-life ✓ 1st order ✓ **Note**: This is only correct response for order (ie no **ECF**). If not stated separately, this mark can be awarded from a rate equation, e.g. *rate* = $k[Br_2]^1$ **OR** *rate* = $k[Br_2]$ Evidence of tangent on graph drawn to line at t = 0 s ✓ e.g.  	4	**ANNOTATE ALL Q3 WITH TICKS AND CROSSES, etc** **MARK ON GRAPH OR IN TEXT** **LOOK FOR STATEMENT ON GRAPH OR WITHIN TEXT** **ALLOW** almost constant half-life --- **Note:** Response may use an alternative approach from half-life for the 1st two marks based on gradients of tangents**:** **1st mark** would be awarded for evidence of two tangents drawn on graph **2nd mark** would be awarded for stating that ratio of concentrations = ratio of rates, e.g. gradient of tangent at 0.010 mol dm^{-3} has twice the value of gradient of tangent at 0.005 mol dm^{-3} --- **MARK TANGENTS ON GRAPH** **ALLOW** some leeway but tangent must coincide with part of curve that is 'straight' (ie between $[Br_2]$ = 0.010–0.009 and **MUST NOT** cross the curve

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Question	Answer	Mark	Guidance
3	$rate = \frac{0.010}{250} = 0.000040$ **OR** 4.0×10^{-5} ✓ units: mol dm^{-3} s^{-1} ✓	2	**ALLOW** values from 1 SF (0.00004 **OR** 4×10^{-5}) up to calculator value, correctly rounded **ALLOW** range ~ $\frac{0.010}{160}$ to $\frac{0.010}{300}$: i.e. **ALLOW** a calculated gradient in the range $6 \times 10^{-5} - 3 \times 10^{-5}$ from a tangent drawn at $t = 0$ **IF** tangent is drawn on graph at a different time or incorrectly (e.g. crossing curve), then mark rate calculation by **ECF** using the gradient of the tangent drawn by the candidate (*ie* not the range above). **IF** no tangent is drawn **ALLOW** a value in the range above **ONLY** Credit **only** attempts at tangents, not just a random straight line **IGNORE** a '– sign'
	$rate = k[Br_2]$ **OR** $k = \frac{rate}{[Br_2]}$ ✓ k = calculated result from $\frac{\text{calculated value for rate}}{0.010}$ ✓ units: s^{-1} ✓	3	**DO NOT ALLOW** $rate = k[Br]$, *ie* Br instead of Br_2 **DO NOT ALLOW** just $k[Br_2]$, *ie* '*rate* =' **OR** '*r* =' must be present **Calculation of *k* is from candidate's calculated initial rate** From 0.00004, $k = \frac{0.000040}{0.010} = 4 \times 10^{-3}$ s **Note:** **IF** order with respect to Br_2 has been shown as 2nd order, then mark this part by **ECF,** e.g. if Br_2 shown to be 2nd order, rate = $k[Br_2]^2$ k = calculated result from $\frac{\text{calculated value for rate}}{0.010^2}$ **units**: dm^3 mol^{-1} s^{-1} **OR** mol^{-1} dm^3 s^{-1} **Note:** Units mark must correspond to the candidate's stated rate equation, **NOT** an incorrectly rearranged *k* expression
	Total	9	

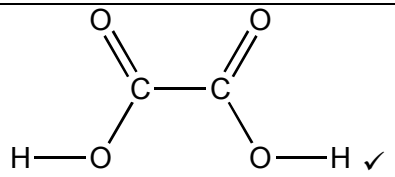
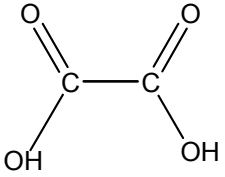
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Question			Answer	Mark	Guidance
4	(a)	(i)	proton donor ✓	1	**ALLOW** H^+ donor
		(ii)	(the proportion of) dissociation ✓ Correct equation for **any** of the four acids: $C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$ **OR** $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ **OR** $CH_3COCOOH \rightleftharpoons H^+ + CH_3COCOO^-$ **OR** $CH_3CHOHCOOH \rightleftharpoons H^+ + CH_3CHOHCOO^-$ ✓	2	**ALLOW** a weak acid partly dissociates **ALLOW** a strong acid totally dissociates **ALLOW** ionisation for dissociation **ALLOW** the ability to donate a proton Equilibrium sign **required** **ALLOW** equilibria involving H_2O and H_3O^+ e.g. $C_6H_5COOH + H_2O \rightleftharpoons H_3O^+ + C_6H_5COO^-$, etc **DO NOT ALLOW** $HA \rightleftharpoons H^+ + A^-$
		(iii)	weakest: CH_3COOH acetic acid C_6H_5COOH benzoic acid $CH_3CHOHCOOH$ lactic acid strongest: $CH_3COCOOH$ ✓ pyruvic acid	1	**ALLOW** correct order using **any** identifier from the table, *ie*, common name, systematic name, structural formula **OR** pK_a value
		(iv)	$C_6H_5COOH_2^+ + CH_3CHOHCOO^-$ ✓	1	**BOTH** products **AND** correct charges required for mark Mark **ECF** from incorrect order in **(iii)** See response from **(iii)** below response to **(iv)**

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Question			Answer	Mark	Guidance
4	(b)	(i)	$2CH_3COCOOH + Ca(OH)_2 \rightarrow (CH_3COCOO)_2Ca + 2H_2O$ ✓ **Note:** pyruvic acid must have been used here and formula of pyruvic acid and pyruvate **must** be correct	1	All species **AND** balancing required for the mark **ALLOW** $(CH_3COCOO^-)_2Ca^{2+}$ **ALLOW** equation showing $2CH_3COCOO^- + Ca^{2+}$ **IF** charges shown, charges **must** balance, e.g. **DO NOT ALLOW** $(CH_3COCOO^-)_2Ca$ **IGNORE** state symbols if shown **ALLOW** multiples **ALLOW** equilibrium sign
		(ii)	$H^+ + OH^- \longrightarrow H_2O$	1	**ALLOW** multiples but **not** same species on both sides **ALLOW** equilibrium sign **IGNORE** state symbols if shown **ALLOW** $H_3O^+ + OH^- \longrightarrow 2H_2O$ **ALLOW** $CH_3COCOOH + OH^- \longrightarrow CH_3COCOO^- + H_2O$
	(c)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 2.11, award **4 marks** --- $K_a = 10^{-pKa}$ $= 10^{-2.39}$ **OR** 0.00407 ✓ $K_a = \frac{[H^+]\,[CH_3COCOO^-]}{[CH_3COCOOH]}$ (**ALLOW** use of HA,H^+ and A^-) **OR** $[H^+] = \sqrt{(K_a \times [HA])}$ **OR** $[H^+] = \sqrt{0.00407 \times 0.0150}$ ✓ (subsumes 1st marking point) $[H^+] =$ 0.00782 (mol dm^{-3}) ✓ pH = –log 0.00782 = **2.11** ✓	4	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **IF ECF, ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 0.0041 to calculator value: 0.004073802 **IF** the pK_a of a different weak acid has been used use **ECF** from 2nd marking point **ALLOW** 0.0078 to calculator value (depending on previous rounding) **ALLOW ONLY 2.11** **(This is to take into account poor previous rounding)** **IF** candidate has used 0.0150 mol dm^{-3} (*ie* assumes strong acid) **ALLOW** final mark **ONLY** by **ECF** for a pH of 1.82 **IF** no square root used, pH = 4.21 3 marks

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Question			Answer	Mark	Guidance
4	(d)	(i)	 ✓	1	**ALLOW** correct structural **OR** displayed **OR** skeletal formula **OR** recognisable mixture of formulae **DO NOT ALLOW** molecular formula but **ALLOW** $(COOH)_2$ **OR** $(CO_2H)_2$  **ALLOW** OH **BUT not** O–H–C
		(ii)	$C_2H_2O_4 \rightleftharpoons H^+ + C_2HO_4^-$ ✓ $C_2HO_4^- \rightleftharpoons H^+ + C_2O_4^{2-}$ ✓	2	**ALLOW** in **either** order **ALLOW** arrow instead of equilibrium sign **ALLOW** molecular formulae for this part **ALLOW** equilibria involving H_2O and H_3O^+ **ALLOW** equations using structures

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Question			Answer	Mark	Guidance
4	(e)		***Chemicals (1 mark)*** lactic acid / $CH_3CHOHCOOH$ **AND** (sodium) lactate / $CH_3CHOHCOO^-$ (Na^+) ✓ ***Concentrations (4 marks)*** **EITHER** $[H^+(aq)]$ = $10^{-3.55}$ **OR** 2.8 x 10^{-4} **OR** 2.82 x 10^{-4} (mol dm^{-3})✓ *separate marking point* K_a = $10^{-3.86}$ **OR** 1.4 x 10^{-4} **OR** 1.38 x 10^{-4} (mol dm^{-3}) ✓ *separate marking point* $\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}$ **OR** $\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$ ✓ $\frac{[HA]}{[A^-]} = \frac{2.8\times10^{-4}}{1.4\times10^{-4}}$ **OR** $\frac{2}{1}$ **OR** 2 **OR** $\frac{[A^-]}{[HA]} = \frac{0.5}{1}$ **OR** 0.5✓ This marking point subsumes previous marking point **ONLY** ***Comment (1 mark)*** Magic tang/taste could come from other chemicals/substances in the sweet **OR** The buffer would have the same taste/tang as the magic tang ✓	**6**	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** any lactate salt **ALLOW** lactic acid **AND** NaOH **OR** lactic acid **AND** OH^- --- **FOR ALTERNATIVE** using Henderson–Hasselbalch equation, **SEE PAGE 11** --- If another weak acid has been selected and salt has been selected, allow **ECF** for remainder of question **SEE PAGE 12** --- **ALLOW** 2.8 x 10^{-4} up to calculator value of 2.81838 x 10^{-4} **ALLOW** 0.00028, etc **ALLOW** 1.4 x 10^{-4} up to calculator value of 1.38038 x 10^{-4} **ALLOW** 0.00014, etc **ALLOW** use of $CH_3CHOHCOOH$ **AND** $CH_3CHOHCOO^-(Na^+)$ **ALLOW** use of acid **AND** salt **ALLOW** value from $\frac{\text{calculated value of } [H^+]}{\text{calculated value of } K_a}$ **ALLOW** 2SF up to calculator value of 2.041742129 correctly rounded but **ALLOW** 2 if 2.8 x 10^{-4} and 1.4 x 10^{-4} used **ALLOW** 2 mol dm^{-3} HA **AND** 1 mol dm^{-3} A^- **OR** any concentration ratio of 2(acid) : 1(salt) **ALLOW** 2SF up to calculator value of 0.489778819 correctly rounded but **ALLOW** 0.5 if 2.8 x 10^{-4} and 1.4 x 10^{-4} used

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Question	Answer	Mark	Guidance
	ALTERNATIVE approach for concentrations using Henderson–Hasselbalch equation ***(4 marks)***		**ALLOW** use of $CH_3CHOHCOOH$ **AND** $CH_3CHOHCOO^-(Na^+)$ **ALLOW** use of acid **AND** salt
	$pH = pK_a + \log\frac{[A^-]}{[HA]}$ **OR** $-\log K_a + \log\frac{[A^-]}{[HA]}$ ✓		**ALLOW** $pH = pK_a - \log\frac{[HA]}{[A^-]}$ **OR** $-\log K_a - \log\frac{[HA]}{[A^-]}$
	$\log\frac{[A^-]}{[HA]} = 3.55 - 3.86$ ✓ (subsumes previous mark)		**ALLOW** $\log\frac{[HA]}{[A^-]} = 3.86 - 3.55$ (subsumes previous mark)
	$\log\frac{[A^-]}{[HA]} = -0.31$ ✓ (subsumes previous mark)		**ALLOW** $\log\frac{[HA]}{[A^-]} = 0.31$ (subsumes previous mark)
	$\frac{[A^-]}{[HA]} = 10^{-0.31} = \frac{0.490}{1}$ **OR** 0.490 ✓		**ALLOW** $\frac{[HA]}{[A^-]} = 10^{0.31} = \frac{2.04}{1}$ **OR** $\frac{2}{1}$ **OR** 2 For $\frac{[A^-]}{[HA]}$, **ALLOW** 2 SF up to calculator value of 0.48978819 For $\frac{[HA]}{[A^-]}$, **ALLOW** 2 SF up to calculator value of 2.041737945 but **ALLOW** 2 if $10^{-0.31}$ used

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<table>
<tr><th colspan="3">Question</th><th>Answer</th><th>Mark</th><th>Guidance</th></tr>
<tr><td>4</td><td>(e)</td><td></td><td colspan="3">
SUMMARY OF 4(e) MARKING POINTS FOR EACH POSSIBLE ACID CHOSEN
FIRST, CHECK THE ANSWER ON ANSWER LINE: IF answer is correct for weak acid chosen, award MP2–MP5
IF there is an alternative answer, check to see if there is any ECF credit possible using working below
<table>
<tr><th></th><th>lactic</th><th>pyruvic</th><th>acetic</th><th>benzoic</th></tr>
<tr><td>pK_a</td><td>3.86</td><td>2.39</td><td>4.76</td><td>4.19</td></tr>
<tr><td>MP1</td><td>lactic AND lactate
OR lactic acid AND OH^-</td><td>No mark</td><td>No mark</td><td>No mark</td></tr>
<tr><td>MP2: $[H^+]$</td><td colspan="4">$10^{-3.55}$ OR 2.82×10^{-4} (calc: 2.81838×10^{-4})</td></tr>
<tr><td>MP3: K_a
calc:</td><td>$10^{-3.86}$ OR 1.38×10^{-4}
$1.380384265 \times 10^{-4}$</td><td>$10^{-2.39}$ OR 4.07×10^{-3}
$4.073802778 \times 10^{-3}$</td><td>$10^{-4.76}$ OR 1.74×10^{-5}
$1.737800829 \times 10^{-5}$</td><td>$10^{-4.19}$ OR 6.46×10^{-5}
$6.45654229 \times 10^{-5}$</td></tr>
<tr><td>MP4: ratio expression</td><td colspan="4">$\frac{[HA]}{[A^-]} = \frac{[H^+]}{K_a}$ OR $\frac{[A^-]}{[HA]} = \frac{K_a}{[H^+]}$</td></tr>
<tr><td>MP5: $\frac{[HA]}{[A^-]}$
calc:</td><td>$\frac{2.82\times10^{-4}}{1.38\times10^{-4}}$ OR 2.04
2.041737945</td><td>$\frac{2.82\times10^{-4}}{4.07\times10^{-3}}$ OR 0.0693
calc: 0.069183097</td><td>$\frac{2.82\times10^{-4}}{1.74\times10^{-5}}$ OR 16.2
calc: 16.21810097</td><td>$\frac{2.82\times10^{-4}}{6.46\times10^{-5}}$ OR 4.37
calc: 4.365158322</td></tr>
<tr><td>OR $\frac{[A^-]}{[HA]}$
calc:</td><td>$\frac{1.38\times10^{-4}}{2.82\times10^{-4}}$ OR 0.489
0.489778819</td><td>$\frac{4.07\times10^{-3}}{2.82\times10^{-4}}$ OR 14.4
14.45439771</td><td>$\frac{1.74\times10^{-5}}{2.82\times10^{-4}}$ OR 0.0617
0.0616595</td><td>$\frac{6.46\times10^{-5}}{2.82\times10^{-4}}$ OR 0.229
0.229086765</td></tr>
</table>
TAKE CARE: Calc values are completely unrounded and may differ between brands of calculator
Use actual candidate values at each stage using rounding to 2 or more SF.
MP5: calculated using 3 SF from MP2 and MP3
calc values for MP5 are completely unrounded (using calculator values from MP2 and MP3)
Be slightly flexible as candidates may have written down rounded values but carried on with calculator values
– This approach is ACCEPTABLE
</td></tr>
<tr><td></td><td></td><td></td><td>Total</td><td>20</td><td></td></tr>
</table>

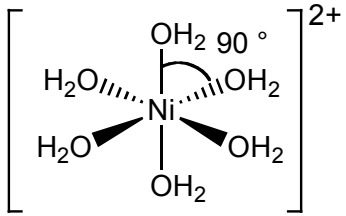
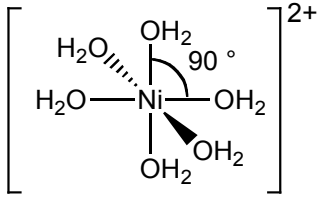
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Question			Answer	Mark	Guidance
5	(a)		**process** **increase** **decrease** $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$ ✓ $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$ ✓ $NH_4Cl(s) + aq \rightarrow NH_4Cl(aq)$ ✓ $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$ ✓ $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$ ✓ **All 5 correct ⟶ 2 marks** **4 correct ⟶ 1 mark**	**2**	
	(b)		ΔH: + **AND** bonds broken ✓ ΔS: + **AND** more random/more disorder/more ways of arranging energy ✓	**2**	**Sign and reason required for each mark** **ALLOW** forces of attraction/hydrogen bonds are overcome **DO NOT ALLOW** response in terms of bonds breaking **AND** bond making (for melting bonds are just broken) **DO NOT ALLOW** responses implying that bonds within H_2O molecules are broken **IGNORE** comments related to ΔG **IGNORE** comments related to ΔG
	(c)	**(i)**	$\Delta S = (3 \times 131 + 198) - (186 + 189)$ ✓ ΔS = (+)216 (J K^{-1} mol^{-1}) ✓	**2**	**ALLOW** 1 mark for –216 (wrong sign) **ALLOW** 1 mark for –46 (131 instead of 3 x 131) **ALLOW** 1 mark for 594 (sign of 189)

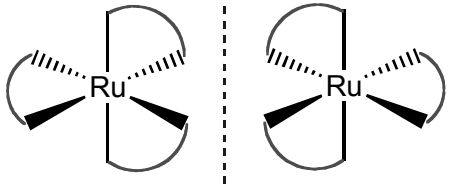
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Question			Answer	Mark	Guidance
5	(c)	(ii)	Two from points below: 1. fuel **OR** fuel cells 2. manufacture of margarine **OR** hydrogenation of alkenes/unsaturated fats 3. manufacture of ammonia **OR** 'Haber process' ✓ 4. manufacture of HCl/hydrochloric acid 5. reduction of metal ores/metal oxides	1	**2 uses for one mark** **IGNORE** hydrogenation of margarine
	(d)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = –109, award first **3 marks** for calculation --- At 298 K, 91.2 = 176 – $T\Delta S$ ✓ ΔS (= $\frac{176-91.2}{298}$) = 0.285 (kJ K^{-1} mol^{-1}) **OR** ΔS (= $\frac{176000-91200}{298}$) = 285 (J K^{-1} mol^{-1}) ✓ *subsumes 1st marking point* At 1000 K, ΔG = 176 – 1000 x 0.285 = –109 (kJ mol^{-1}) ✓ Reaction **does** take place (spontaneously) because ΔG < 0 **OR** ΔG is -ve ✓ **Note**: If no value of ΔG, this mark **cannot** be awarded.	4	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 0.285 (3 SF) up to calculator value of 0.284563758 **ALLOW** 285 (3 SF) up to calculator value of 284.563758 **ALLOW** –109 up to calculator value correctly rounded, i.e. –108.6, –108.56, etc **ALLOW ECF** from incorrect ΔS, *ie* calculated value of ΔG from ΔG = 176 – 1000 x calculated value of ΔS Answer and reason **BOTH** needed for mark **ALLOW** reaction is feasible for 'reaction does take place' **Note**: If candidate has a + ΔG value, mark **ECF**, ie reaction does not take place because ΔG > 0 **OR** ΔG is +ve
			Total	**11**	

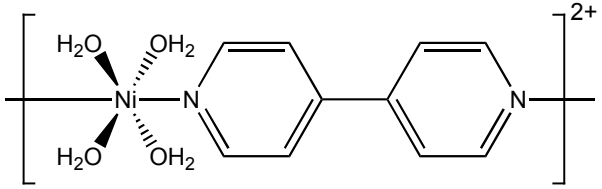
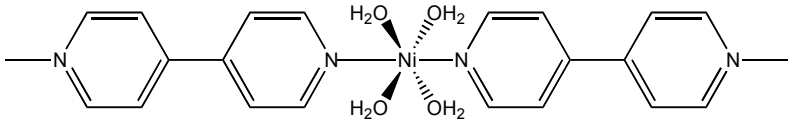
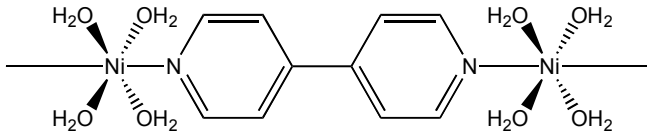
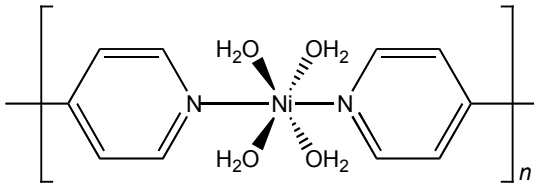
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Question			Answer	Mark	Guidance
6	(a)		Ni $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$ ✓ d block: (Ni:) 'd' is **highest energy** sub-shell/orbital ✓ Ni^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$ ✓ Transition element: has **an ion** with an incomplete/partially-filled d **sub-shell/orbital** ✓ --- A ligand donates an electron pair to Ni^{2+} **OR** metal ion **OR** metal ✓ A complex ion is an ion bonded to ligand(s)/surrounded by ligands ✓ Coordinate bond/dative covalent mentioned at least once in the right context ✓	4 3	**ANNOTATE WITH TICKS AND CROSSES, etc** **Note:** Examples must be for Ni, not other d block elements **ALLOW** 4s before 3d, ie $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$ **ALLOW** $[Ar]4s^2 3d^8$ **OR** $[Ar]3d^8 4s^2$ **ALLOW** upper case D, etc and subscripts, e.g. $[Ar]4S_2 3D_8$ **DO NOT ALLOW** highest energy shell is 'd' **OR** 'd is the outer sub-shell' (4s as well) **ALLOW** $[Ar]3d^8$ **ALLOW** electron configurations with $4s^0$ **ALLOW** for example Ni^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ **OR** $[Ar]3d^7$ ***No other Ni ions are acceptable*** **ALLOW** lone pair forms a coordinate bond to Ni^{2+} (which will also collect the coordinate bond mark) **ALLOW** diagram of $[Ni(H_2O)_6]^{2+}$ complex ion for 2nd marking point
	(b)	(i)	 3D diagram ✓ 90º bond angle ✓	2	Must contain 2 'out wedges', 2 'in wedges' and 2 lines in plane of paper **OR** 4 lines, 1 'out wedge' and 1 'in wedge':  **ALLOW** dotted line **OR** unfilled wedge as alternatives for dotted wedge Accept bonds to H_2O (does not need to go to 'O') Accept 90 ° written by diagram. Charge **NOT** needed. Square brackets **NOT** needed

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Question			Answer	Mark	Guidance
6	(b)	(ii)	**A:** $NiCl_4^{2-}$ ✓ **B**: $Ni(OH)_2$ ✓	2	**ALLOW** $[NiCl_4]^{2-}$ **DO NOT ALLOW** $Ni(Cl^-)_4^{2-}$ **ALLOW** $Ni(OH)_2(H_2O)_4$ **OR** $[Ni(OH)_2(H_2O)_4]$
		(iii)	**C**: $[Ni(NH_3)_6]^{2+}$ ✓	1	**Square** brackets essential 2+ charge must be outside square brackets **ALLOW** $[Ni(OH)_6]^{4-}$
		(iv)	$[Ni(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$ ✓ ✓	2	**1 mark for each side of equation** **ALLOW** equilibrium sign **ALLOW ECF** from **(iii)** for the following: $[Ni(NH_3)_4]^{2+}$ (wrong number of NH_3) **Any** 6 coordinate Ni^{2+} complex with NH_3 and H_2O ligands, e.g. $[Ni(NH_3)_4(H_2O)_2]^{2+}$, $[Ni(NH_3)_5(H_2O)]^{2+}$, etc **ALLOW** from $[Ni(OH)_6]^{4-}$, $[Ni(H_2O)_6]^{2+} + 6OH^- \longrightarrow [Ni(OH)_6]^{4-} + 6H_2O$ **OR** $[Ni(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Ni(OH)_6]^{4-} + 6NH_4^+$
	(c)	(i)	$C_{10}H_8N_2$ ✓	1	**ALLOW** atoms in any order
		(ii)	4 ✓	1	
		(iii)	 ✓ ✓ One mark for each structure *2nd structure must be correct mirror image of 1st structure*	2	Charge and N atom labels **NOT** needed **ALLOW** any attempt to show bipy. Bottom line is the diagram on the left. 1 mark for 3D diagram with ligands attached for ONE stereoisomer. Must contain 2 out wedges, 2 in wedges and 2 lines in plane of paper: **ALLOW** structures with Ni in centre

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Question			Answer	Mark	Guidance
6	(c)	(iv)	**3 marks available** **1st mark** Correct 4,4'-bipy structure shown separately or within attempted structure with Ni^{2+} ✓ **2 marks** The remaining 2 marks are available for a section of the polymer with repeat unit identified as follows: **IF** Ni is bonded to 4 H_2Os (bond to O) with a bond to N end **of two** 4,4'-bipy structure **OR** **IF each N of** 4,4'-bipy is bonded to a Ni bonded to 4 H_2Os (bond to O), award 1 mark ✓ **IF** correct repeat unit is shown, award 2 marks ✓✓ 	3	**ALLOW** aromatic rings   Charge **NOT** needed. Square brackets **NOT** needed Bonds around Ni do **NOT** need to be shown 3D Accept bonds to H_2O (does **NOT** need to go to 'O') **ALLOW** the following structure for repeat unit for all 2nd and 3rd marks: 
			Total	**21**	

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Question			Answer	Mark	Guidance
7	(a)		**Definition** The e.m.f. (of a half-cell) compared with a standard hydrogen half-cell/standard hydrogen electrode ✓ **Standard conditions** Temperature of 298 K / 25ºC **AND** (solution) concentrations of 1 mol dm^{-3} **AND** pressure of 101 kPa **OR** 100 kPa ✓	**2**	**ALLOW** voltage **OR** potential difference **OR** p.d. **OR** electrode potential **OR** reduction potential **OR** redox potential as alternative for e.m.f. **IGNORE** S.H.E. (as abbreviation for standard hydrogen electrode) **ALLOW** 1 atmosphere/1 atm **OR** 10^5 Pa **OR** 1 bar
	(b)		1.25 (V) ✓	**1**	**IGNORE** any sign
	(c)	(i)	$Cd + 2NiO(OH) + 2H_2O \longrightarrow Cd(OH)_2 + 2Ni(OH)_2$ LHS: correct species and correctly balanced ✓ RHS: correct species and correctly balanced ✓	**2**	**2 marks for correct equation** **ALLOW** NiOOH OR NiO_2H **ALLOW** ⇌ sign for equation (*ie* assume reaction goes from left to right) **ALLOW** 1 mark for correctly balanced equation with e^- and/or OH^- shown e.g.: $Cd + 2NiO(OH) + 2H_2O + 2OH^- + 2e^- \longrightarrow Cd(OH)_2 + 2Ni(OH)_2 + 2OH^- + 2e^-$ **ALLOW** 1 mark for balanced correct reverse equation with OH^- **AND** e^- cancelled: $Cd(OH)_2 + 2Ni(OH)_2 \longrightarrow Cd + 2NiO(OH) + 2H_2O$
		(ii)	oxidation: Cd from 0 to +2 ✓ '+' sign **not** required reduction: Ni from +3 to +2 ✓'+' sign **not** required	**2**	**ALLOW** $Cd^0 \rightarrow Cd^{2+}$ (shows 0 and 2+) **ALLOW** $Ni^{3+} \rightarrow Ni^{2+}$ (shows 3+ and 2+) **ALLOW ECF** from **(c)(i)** equation written 'wrong way around'.
	(d)	(i)	reverse reactions to charging **OR** $Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$ $Ni(OH)_2 + OH^- \longrightarrow NiO(OH) + H_2O + e^-$ **OR** reaction that is reverse to reaction given in **c(i):** $Cd(OH)_2 + 2Ni(OH)_2 \longrightarrow Cd + 2NiO(OH) + 2H_2O$ ✓	**1**	If half-equations are given, then **BOTH** equations required **ALLOW** ⇌ sign for equation (*ie* assume reaction goes from left to right)

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Question			Answer	Mark	Guidance
7	(d)	(ii)	$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$ ✓ $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ ✓	2	**ALLOW** multiples; **ALLOW** ⇌ sign for each equation **Note**: These are the **only** correct responses
			Total	10	

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Question			Answer	Mark	Guidance
8			**step 1** $Cu + 4HNO_3 \longrightarrow Cu^{2+} + 2NO_3^- + 2NO_2 + 2H_2O$ **OR** $Cu + 2H^+ + 2HNO_3 \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$ **OR** $Cu + 4H^+ + 2NO_3^- \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$ ✓ **step 2** **2 equations with 1 mark for each** $Cu^{2+} + CO_3^{2-} \longrightarrow CuCO_3$ ✓ $2H^+ + CO_3^{2-} \longrightarrow H_2O + CO_2$ ✓ **step 4** $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$ ✓	4	**ANNOTATE ALL Q8 WITH TICKS AND CROSSES, etc** **ALLOW** multiples throughout **IGNORE** state symbols throughout **ALLOW** $Cu(NO_3)_2$ for $Cu^{2+} + 2NO_3^-$ **AWARD 2 MARKS for a combined equation:** $Cu^{2+} + 2H^+ + 2CO_3^{2-} \longrightarrow CuCO_3 + H_2O + CO_2$ ✓✓ **DO NOT ALLOW** $2H^+ + CO_3^{2-} \longrightarrow H_2CO_3$ **ALLOW** $2Cu^{2+} + 4KI \longrightarrow 2CuI + I_2 + 4K^+$ **ALLOW** $Cu^{2+} + I^- \longrightarrow Cu^+ + ½I_2$

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Question	Answer	Mark	Guidance
8	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 67.6%, award **5 marks.** **Ignore any attempted equation in step 4** **IF** answer = **33.8% AND IF** Cu^{2+}/I_2 in **step 4** equation shown with 1:1 molar ratio, award 5 marks for **ECF** --- amount $S_2O_3^{2-}$ used = 0.100 x $\frac{29.8}{1000}$ = 2.98 x 10^{-3} mol ✓ amount I_2 = 1.49 x 10^{-3} mol **OR** amount Cu^{2+} = 2.98 x 10^{-3} mol ✓ amount Cu^{2+} in original 250 cm^3 = **10 x** 2.98 x 10^{-3} = 2.98 x 10^{-2} mol ✓ Mass of Cu/Cu^{2+} in brass = 63.5 x 2.98 x 10^{-2} g = 1.8923 g ✓ percentage Cu in brass = $\frac{1.8923}{2.80} \times 100$ = 67.6% ✓ **MUST** be to **one** decimal place (in the question)	**5**	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **Working must be to 3 SF throughout until final % mark** BUT ignore trailing zeroes, ie for 0.490 allow 0.49 **ECF** answer above **ECF** 10 x answer above **ECF** 63.5 x answer above **ALLOW** 1.88 g **ECF** $\frac{\text{answer above}}{2.80} \times 100$ Answer **must** be to one decimal place **ALLOW** % Cu = 67.5 % **IF** mass of Cu has been rounded to 1.89 g in previous step **Common ECFs:** **6.76%** x10 missing 3/5 marks for calculation 2 d.p. MS states 1 d.p. **33.8%** **IF** Cu^{2+}/I_2 in **step 4** equation with 2:1 ratio **OR** not attempted, response, 4/5 marks for calculation (moles Cu^{2+} incorrect)
	Total	**9**	

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OCR
RECOGNISING ACHIEVEMENT

ADVANCED GCE

CHEMISTRY A

Equilibria, Energetics and Elements

F325

OCE/23216

Candidates answer on the question paper.

OCR Supplied Materials:
- *Data Sheet for Chemistry A* (inserted)

Other Materials Required:
- Scientific calculator

Monday 31 January 2011
Morning

Duration: 1 hour 45 minutes

F325

Candidate forename		Candidate surname	

Centre number						Candidate number				

INSTRUCTIONS TO CANDIDATES

- The insert will be found in the centre of this document.
- Write your name, centre number and candidate number in the boxes above. Please write clearly and in capital letters.
- Use black ink. Pencil may be used for graphs and diagrams only.
- 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 pages at the end of this booklet. The question number(s) must be clearly shown.
- Answer **all** the questions.
- 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 **24** pages. Any blank pages are indicated.

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Answer **all** the questions.

1 Hydrogen, H_2, reacts with nitrogen monoxide, NO, as shown in the equation below.

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

A chemist carries out a series of experiments and determines the rate equation for this reaction:

$$\text{rate} = k[H_2(g)][NO(g)]^2$$

(a) In one of the experiments, the chemist reacts together:

- 1.2×10^{-2} mol dm^{-3} $H_2(g)$
- 6.0×10^{-3} mol dm^{-3} NO(g)

The initial rate of this reaction is 3.6×10^{-2} mol dm^{-3} s^{-1}.

Calculate the rate constant, *k*, for this reaction. State the units, if any.

k = ... units ..... **[3]**

(b) Predict what would happen to the initial rate of reaction for the following changes in concentrations.

(i) The concentration of $H_2(g)$ is doubled.

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

(ii) The concentration of NO(g) is halved.

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

(iii) The concentrations of $H_2(g)$ and NO(g) are **both** increased by four times.

.....

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

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(c) The chemist carries out the reaction between hydrogen and nitrogen monoxide at a higher pressure.

(i) Explain, with a reason, what happens to the initial rate of reaction.

.....

.....

.....

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

(ii) State what happens to the rate constant.

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

(d) This overall reaction between hydrogen and nitrogen monoxide takes place by a two-step mechanism. The first step is much slower than the second step.

Suggest a possible two-step mechanism for the overall reaction.

step 1: .....

step 2: ..... **[2]**

[Total: 10]

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2 Iron and platinum are transition elements. They both form ions that combine with ligands to form complex ions. Some of these complexes are important in biological systems.

(a) Complete the electron structures of:

an atom of Fe: $1s^2 2s^2 2p^6$ .....

an ion of Fe^{2+}: $1s^2 2s^2 2p^6$ ..... **[2]**

(b) State **one** property of Fe^{2+}, other than the ability to form complex ions, which is typical of an ion of a transition element.

.....

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

(c) Aqueous iron(II) sulfate takes part in redox reactions.

Using oxidation numbers, show that both reduction and oxidation have taken place in the redox reaction of aqueous iron(II) sulfate shown below.

$$6FeSO_4 + 7H_2SO_4 + Na_2Cr_2O_7 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O$$

.....

.....

.....

.....

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

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(d) Hexaaquairon(II) ions, $[Fe(H_2O)_6]^{2+}$, take part in a ligand substitution reaction with ammonia.

$$[Fe(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Fe(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

Write an expression for the stability constant, K_{stab}, for this equilibrium.

[2]

(e) Haemoglobin is a complex of iron(II).

(i) Explain how ligand substitutions allow haemoglobin to transport oxygen in the blood.

.....

.....

.....

.....

.....

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

(ii) In the presence of carbon monoxide, less oxygen is transported in the blood.

In terms of stability constants, suggest why.

.....

.....

.....

.....

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

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(f) Platin, $Pt(NH_3)_2Cl_2$, is a complex of platinum(II) that has two stereoisomers. One of these stereoisomers is used in medicine.

(i) Platin is a neutral complex.

Explain why platin is neutral.

.....

.....

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

(ii) Draw diagrams of the two stereoisomers of platin and describe its bonding.

.....

.....

.....

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

(iii) Describe the action of platin in the treatment of cancer patients.

.....

.....

.....

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

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(g) The use of platin in medicine can cause unpleasant side effects for patients.

In the search for alternatives, chemists often start with the current drug and modify its properties by chemically changing some of the groups.

A recent discovery is a drug called carboplatin. The structure of carboplatin is similar to platin except that a single 1,1-cyclobutanedicarboxylate ion replaces the two chloride ligands in the structure of platin.

Draw the structures of,

- the 1,1-cyclobutanedicarboxylate ion
- carboplatin.

1,1-cyclobutanedicarboxylate ion

carboplatin

[2]

[Total: 18]

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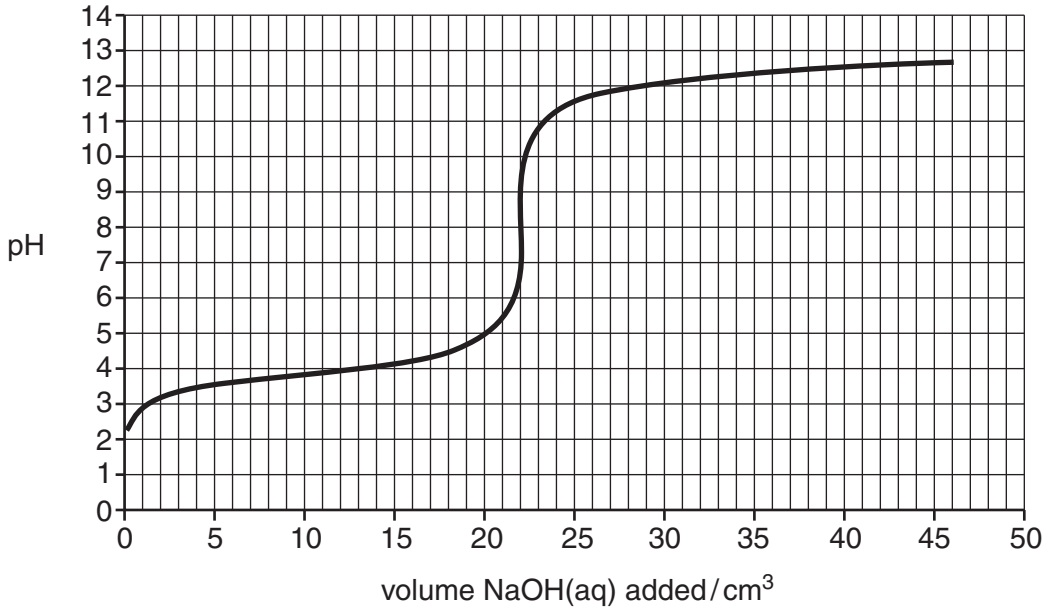
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3 Glycolic acid, $HOCH_2COOH$, and thioglycolic acid, $HSCH_2COOH$, are weak acids.

(a) Glycolic acid reacts with bases, such as aqueous sodium hydroxide, NaOH(aq), to form salts.

A student pipetted 25.0 cm^3 of 0.125 mol dm^{-3} glycolic acid into a conical flask. The student added NaOH(aq) from a burette. A pH meter and data logger were used to measure continuously the pH of the contents of the conical flask.

The pH curve that the student obtained is shown below.



1 mol of glycolic acid reacts with 1 mol of sodium hydroxide.

(i) Write the equation for the reaction that takes place in the titration.

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

(ii) Determine the concentration, in mol dm^{-3}, of the NaOH.

concentration of NaOH = ... mol dm^{-3} **[2]**

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(iii) The student decided to carry out this titration using an acid–base indicator.

What important factor does the student need to consider when deciding on the most suitable indicator to use for this titration?

.....

.....

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

(b) The 0.125 mol dm^{-3} glycolic acid had a pH of 2.37.

(i) What is the expression for the acid dissociation constant, K_a, of glycolic acid?

[1]

(ii) Calculate K_a for glycolic acid.

K_a = ... units ..... **[3]**

(iii) Calculate the percentage molar dissociation of the glycolic acid.

percentage dissociation = ... % **[1]**

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(c) A buffer of glycolic acid and ammonium glycolate is used in a facial cleanser.

Explain, using equations,

- how a solution containing glycolic acid and glycolate ions can act as a buffer
- how this buffer could be prepared from ammonia and glycolic acid.

In your answer you should explain how the equilibrium system allows the buffer solution to control the pH.

[7]

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(d) Ammonium thioglycolate, $HSCH_2COONH_4$, is the ammonium salt of thioglycolic acid, $HSCH_2COOH$.

When ammonium thioglycolate is dissolved in water, an acid–base equilibrium is set up. The equilibrium lies well to the left-hand side.

$$HSCH_2COO^-(aq) \quad + \quad NH_4^+(aq) \quad \rightleftharpoons \quad HSCH_2COOH(aq) \quad + \quad NH_3(aq)$$

…… …… …… ……

In the spaces above,

- label one conjugate acid–base pair as '**Acid 1**' and '**Base 1**'
- label the other conjugate acid–base pair as '**Acid 2**' and '**Base 2**'. **[2]**

(e) Ammonium thioglycolate is used by hairdressers to perm hair.

Hair is a protein and its shape is largely the result of cross-linked disulfide bonds, –S–S–. The formula of the protein in hair can be represented as R–S–S–R.

Perming of hair involves two stages.

Stage 1

- Hair is first wound around curlers and a solution of ammonium thioglycolate is applied to the hair.
- In this process, each disulfide bond is broken by two thioglycolate ions to form two molecules containing thiol groups, –S–H, and one other product.

Stage 2

- After 15–30 minutes, the hair is rinsed with a weak solution of hydrogen peroxide, H_2O_2.
- The hydrogen peroxide reforms disulfide bonds that lock the hair in the shape of the curlers. The hair is now 'permed'.

Suggest equations for the two processes that take place during perming.
In your equations, use R–S–S–R to represent the protein in hair.

Stage 1

Stage 2

[2]

[Total: 20]

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4 Redox reactions are used to generate electrical energy from electrochemical cells.

(a) **Table 4.1** shows three redox systems, and their standard redox potentials.

redox system	$E^{\ominus}$/V
$Cu^{+}(aq) + e^{-} \rightleftharpoons Cu(s)$	+0.52
$Cr^{3+}(aq) + 3e^{-} \rightleftharpoons Cr(s)$	–0.74
$Sn^{4+}(aq) + 2e^{-} \rightleftharpoons Sn^{2+}(aq)$	+0.15

Table 4.1

(i) Draw a labelled diagram to show how the standard electrode potential of a Sn^{4+}/Sn^{2+} redox system could be measured.

[3]

(ii) Using the information in **Table 4.1**, write equations for the reactions that are feasible.

Suggest **two** reasons why these reactions may **not** actually take place.

.....

.....

.....

.....

.....

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.....

.....

..... **[5]**

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(b) Modern fuel cells are being developed as an alternative to the direct use of fossil fuels. The 'fuel' can be hydrogen but many other substances are being considered.
In a methanol fuel cell, the overall reaction is the combustion of methanol.

As with all fuel cells, the fuel (methanol) is supplied at one electrode and the oxidant (oxygen) at the other electrode.

Oxygen reacts at the negative electrode of a methanol fuel cell:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

(i) Write an equation for the complete combustion of methanol.

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

(ii) Deduce the half-equation for the reaction that takes place at the positive electrode in a methanol fuel cell.

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

(iii) State **two** advantages of vehicles using fuel cells compared with the combustion of conventional fossil fuels.

.....

.....

.....

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

(iv) Suggest **one** advantage of using methanol, rather than hydrogen, in a fuel cell for vehicles. Justify your answer.

.....

.....

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

[Total: 13]

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5 Entropy changes are an important factor in determining the feasibility of reactions.

(a) You are provided with equations for four processes.

A $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
B $H_2O(l) \longrightarrow H_2O(g)$
C $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$
D $2C(s) + O_2(g) \longrightarrow 2CO(g)$

For each process, explain why ΔS has the sign shown below.

A: sign of ΔS: negative

reason for sign: .....

.....

B: sign of ΔS: positive

reason for sign: .....

.....

C: sign of ΔS: negative

reason for sign: .....

.....

D: sign of ΔS: positive

reason for sign: .....

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

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(b) Calcium oxide, CaO, is used to make cement. Calcium oxide is manufactured by the thermal decomposition of calcium carbonate.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \Delta H = +178\,kJ\,mol^{-1}$$

Standard entropies of $CaCO_3(s)$, $CaO(s)$ and $CO_2(g)$ are given in the table below.

substance	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
S **/ J K^{-1}mol^{-1}**	89	40	214

- Using the information in the table, show that the entropy change, ΔS, for the decomposition of calcium carbonate is $0.165\,kJ\,K^{-1}\,mol^{-1}$.
- Show that calcium carbonate is stable at room temperature (25 °C).
- Calculate the minimum temperature needed to decompose calcium carbonate.

Show all your working.

[7]

[Total: 11]

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6 The dissociation of water is a reversible reaction.

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

The ionic product of water, K_w, measures the extent of dissociation of water.

K_w varies with temperature. Therefore, it is always important to quote the temperature at which measurements are being taken.

Fig. 6.1 shows the variation of K_w between 0 °C and 60 °C.

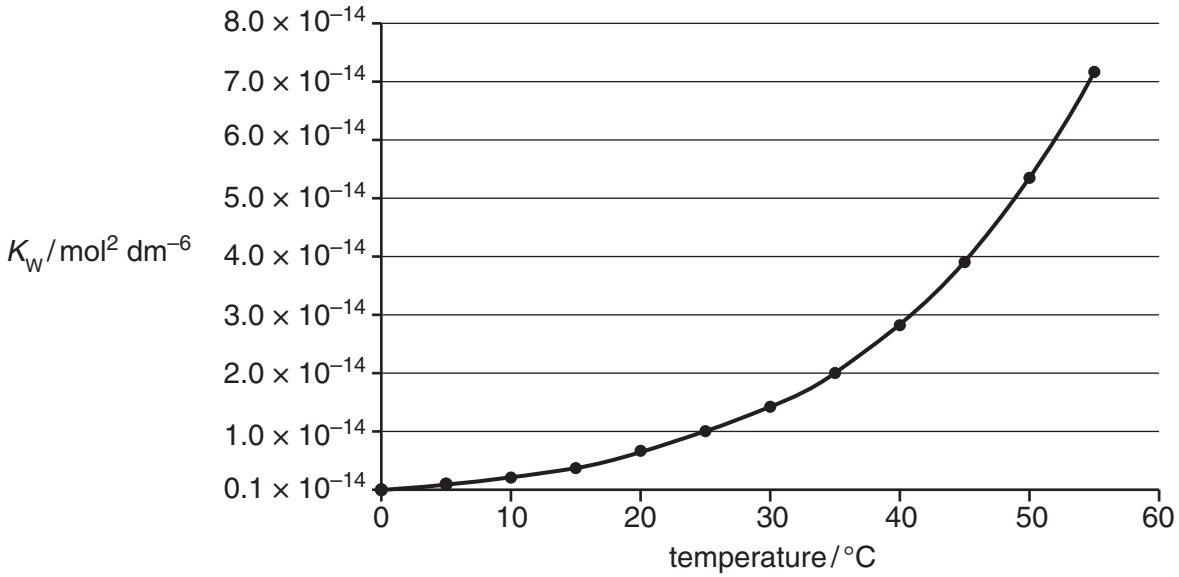


Fig. 6.1

(a) (i) Write the expression for K_w.

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

(ii) Calculate the $OH^-(aq)$ concentration in an aqueous solution of hydrochloric acid with a pH of 4.37 at 25 °C.

Give your answer to **two** significant figures.

OH^- concentration = ... mol dm^{-3} **[2]**

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(b) (i) Using **Fig. 6.1**, explain whether the dissociation of water is an exothermic or endothermic process.

.....

.....

.....

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

(ii) Determine the pH of pure water at body temperature, 37 °C.

pH = ... **[3]**

(iii) Many experimental measurements use published data, such as K_w, measured at 25 °C. Often these measurements have been taken at different temperatures, especially in experimental work carried out at body temperature.

What is the consequence of this for published scientific work?

.....

.....

.....

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

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(c) The reverse reaction of the dissociation of water is called neutralisation.

Plan an experiment that a student could carry out to measure the enthalpy change of neutralisation.

In your answer you should explain how the enthalpy change of neutralisation could be calculated from the experimental results.

[6]

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(d) When dissolved in water, the enthalpy change of solution of the salt potassium fluoride, KF, is $-15\,kJ\,mol^{-1}$.

The salt rubidium fluoride, RbF, has an enthalpy change of solution in water of $-24\,kJ\,mol^{-1}$.

Suggest reasons for the difference between the enthalpy changes of solution of KF and RbF.

.....

.....

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.....

.....

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

(e) A student hurt his ankle whilst playing football. The physiotherapist applied a cold pack to soothe the pain.

The cold pack is made of two separated compartments, one containing ammonium nitrate crystals, NH_4NO_3, the other containing water. The pack is activated by breaking the barrier between the two compartments. The crystals dissolve spontaneously in the water causing the temperature of the pack to drop.

Explain why ammonium nitrate in the cold pack dissolves spontaneously in water even though this process is endothermic.

.....

.....

.....

.....

.....

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

[Total: 20]

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7 The Dissolved Oxygen Concentration (DOC) in rivers and lakes is important for aquatic life. If the DOC falls below 5 mg dm^{-3}, most species of fish cannot survive.

Environmental chemists can determine the DOC in water using the procedure below.

- A sample of river water is shaken with aqueous Mn^{2+} and aqueous alkali.
  The dissolved oxygen oxidises the Mn^{2+} to Mn^{3+}, forming a pale brown precipitate of $Mn(OH)_3$.

$$O_2(aq) + 4Mn^{2+}(aq) + 8OH^-(aq) + 2H_2O(l) \longrightarrow 4Mn(OH)_3(s)$$

- The $Mn(OH)_3$ precipitate is then reacted with an excess of aqueous potassium iodide, which is oxidised to iodine, I_2.

$$2Mn(OH)_3(s) + 2I^-(aq) \longrightarrow I_2(aq) + 2Mn(OH)_2(s) + 2OH^-(aq)$$

- The iodine formed is then determined by titration with aqueous sodium thiosulfate, $Na_2S_2O_3(aq)$.

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

A 25.0 cm^3 sample of river water was analysed using the procedure above.

The titration required 24.6 cm^3 of 0.00100 mol dm^{-3} $Na_2S_2O_3(aq)$.

(a) (i) Calculate the DOC of the sample of river water, in mg dm^{-3}.

DOC = ... mg dm^{-3} **[4]**

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(ii) Comment on whether there is enough dissolved oxygen in the river water for fish to survive.

.....

.....

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

(b) The presence of nitrate(III) ions, NO_2^-, interferes with this method because NO_2^- ions can also oxidise iodide ions to iodine.

During the reaction, a colourless gas is produced with a molar mass of $30\,g\,mol^{-1}$.

(i) Predict the formula of the colourless gas.

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

(ii) Write an equation for the oxidation of aqueous iodide ions by aqueous nitrate(III) ions. Hydroxide ions are produced in this reaction.

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

[Total: 8]

END OF QUESTION PAPER

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ADDITIONAL PAGE

If additional space is required, you should use the lined pages below. The question number(s) must be clearly shown.

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RECOGNISING ACHIEVEMENT

GCE

Chemistry A

Advanced GCE

Unit **F325:** Equilibria, Energetics and Elements

Mark Scheme for January 2011

Oxford Cambridge and RSA Examinations

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Question			Answer	Mark	Guidance
1	(a)		**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 8.3×10^4 **OR** 83333 award **2 marks** **THEN IF** units are **dm^6 mol^{-2} s^{-1}**, award 1 further mark		
			$k = \frac{rate}{[H_2(g)]\,[NO(g)]^2}$ **OR** $\frac{3.6 \times 10^{-2}}{(1.2 \times 10^{-2}) \times (6.0 \times 10^{-3})^2}$ ✓		
			= 8.3×10^4 **OR** 83000 **OR** 83333 ✓	2	**ALLOW** 2 SF up to calculator value of 8.33333333×10^4 correctly rounded **ALLOW ECF** for calculated answer from incorrectly rearranged *k* expression but **not** for units (Marked independently see below)
			units: $dm^6\ mol^{-2}\ s^{-1}$ ✓	1	**ALLOW** dm^6, mol^{-2} and s^{-1} in any order, ***eg*** $mol^{-2}\ dm^6\ s^{-1}$ **DO NOT ALLOW** other units (Rate equation supplied on paper – **not** derived from data)
	(b)	**(i)**	*effect on rate* × 2 ✓	1	**ALLOW** 'doubles' **OR** *rate* = 7.2 x 10^{-2} (mol dm^{-3} s^{-1})
		(ii)	*effect on rate* × ¼ **OR** x 0.25 ✓	1	**ALLOW** 'a quarter' **OR** decrease by ¼ **OR** decrease by 0.25 **OR** rate decreases by 4 **OR** decrease by 75% **OR** *rate* = 0.9 × 10^{-2} (mol dm^{-3} s^{-1}) **DO NOT ALLOW** just 0.5^2 of rate **OR** rate decreases by 2^2
		(iii)	*effect on rate* × 64 ✓	1	**ALLOW** *rate* = 2.3(04) (mol dm^{-3} s^{-1}) **DO NOT ALLOW** just 'increases by 4 and then by 16 / 4^2 **OR** increases by 4^3

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Question			Answer	Mark	Guidance
1	(c)	(i)	(initial) rate increases **AND** more frequent collisions **OR** more collisions **per second/time** ✓	1	**BOTH** points required for mark **ALLOW** rate increases **AND** concentration increases For concentration increases, **ALLOW** particles closer together **OR** less space between particles **DO NOT ALLOW** just more collisions **OR** collisions more likely
		(ii)	rate constant does not change ✓	1	
	(d)		step 1: $H_2(g) + 2\,NO(g) \longrightarrow N_2O(g) + H_2O(g)$ LHS of step one ✓ step 2: $H_2(g) + N_2O(g) \longrightarrow N_2(g) + H_2O(g)$ rest of equations for step 1 **AND** step 2 ✓	2	State symbols **NOT** required For 'rest of equations', This mark can **only** be awarded if 1st mark can be awarded **ALLOW** other combinations of **two** steps that together give the overall equation (shown above part in scoris window), *eg* step 1: $\longrightarrow N_2(g) + ½\,O_2(g) + H_2O(g)$ step 2: $H_2(g) + ½\,O_2(g) \longrightarrow H_2O(g)$ step 1: $\longrightarrow H_2O_2(g) + N_2(g)$ step 2: $H_2(g) + H_2O_2(g) \longrightarrow 2H_2O(l)$ There may be others with species, such as $H_2N_2O_2$ and HNO. Provided the two steps add up to give the overall equation **AND** charges balance, the 2nd mark can be awarded
			Total	**10**	

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Question			Answer	Mark	Guidance
2	(a)		Fe: $(1s^2 2s^2 2p^6)3s^2 3p^6 3d^6 4s^2$ ✓ Fe^{2+}: $(1s^2 2s^2 2p^6)3s^2 3p^6 3d^6$ ✓	2	**ALLOW** 4s before 3d, i.e. $(1s^2 2s^2 2p^6)3s^2 3p^6 4s^2 3d^6$ **ALLOW** $4s^0$ **ALLOW** subscripts **IGNORE** $1s^2 2s^2 2p^6$ is written out a second time
	(b)		coloured (compound/complex/precipitate/ions) **OR** catalyst ✓	1	**IGNORE** 'variable oxidation states' **….** but **ALLOW** the idea that Fe^{2+} can react to form an **ion** with a different charge/oxidation state. '**ion**' is essential: 'atom' or 'metal' is **not** sufficient **IGNORE** partially filled d sub-shell/d orbital (question refers to property of Fe^{2+})
	(c)		Fe oxidised from +2 to +3 ✓ Cr reduced from +6 to +3 ✓	2	**CHECK** and credit oxidation numbers on equation **ALLOW** Fe^{2+} oxidised to Fe^{3+} **ALLOW** Cr^{6+} reduced to Cr^{3+} **ALLOW** + sign after number in oxidation number, *ie* 2+, etc **ALLOW** 1 mark only if oxidation numbers given with no identification of which species has been oxidised or reduced, *ie* Fe goes from +2 to +3 **AND** Cr goes from +6 to +3 Fe reduced from +2 to +3 **AND** Cr oxidised from +6 to +3 (*oxidation and reduction the wrong way around*) **DO NOT ALLOW** just 'Fe is oxidised **and** Cr reduced' **IGNORE** other oxidations numbers (even if wrong) **IGNORE** any references to electrons

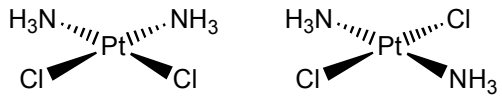
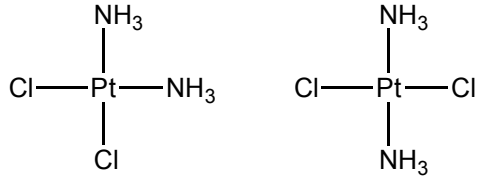
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Question			Answer	Mark	Guidance
2	(d)		(K_{stab} =) $\dfrac{\left[[Fe(NH_3)_6]^{2+}\right]}{\left[[Fe(H_2O)_6]^{2+}\right]\left[NH_3\right]^6}$ On **top**, **ONLY** $[Fe(NH_3)_6]^{2+}$ shown **AND** on bottom, $[Fe(H_2O)_6]^{2+}$ **AND** $[NH_3]^6$ shown ✓ correct use of square brackets and double square brackets in expression ✓	2	**IGNORE** state symbols **ALLOW** 1 mark if complete expression with correct use of double brackets is shown but upside down **DO NOT ALLOW** round brackets for concentrations and complex ions **ALLOW for 1 mark** (K_{stab} =) $\dfrac{\left[[Fe(NH_3)_6]^{2+}\right]\left[H_2O\right]^6}{\left[[Fe(H_2O)_6]^{2+}\right]\left[NH_3\right]^6}$
	(e)	(i)	O_2/oxygen bonds to Fe^{2+}/Fe(II)/Fe ✓ When required, O_2 substituted **OR** O_2 released ✓	2	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** O_2 binds to Fe^{2+} **OR** O_2 donates electron pair to Fe^{2+} **ALLOW** O_2 bonds to metal ion/metal **DO NOT ALLOW** just O_2 bonds to haemoglobin **OR** O_2 bonds to complex **ALLOW** bond breaks between O_2 and Fe^{2+} when O_2 required **OR** O_2 replaces H_2O **OR** vice versa **ALLOW** O_2 replaces CO_2 **OR** vice versa **ALLOW** O_2 replaces a ligand **OR** vice versa **IGNORE** just 'by ligand substitution' (in the question)

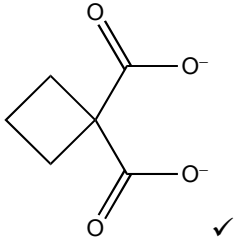
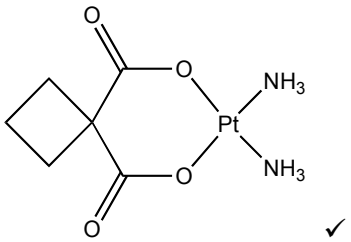
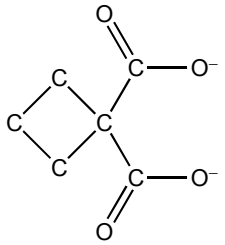
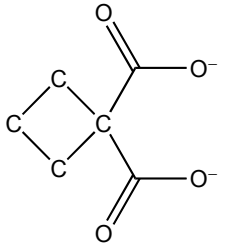
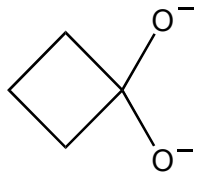
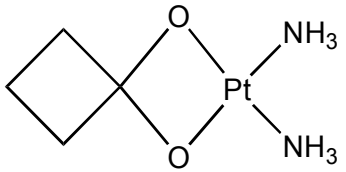
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Question			Answer	Mark	Guidance
2	(e)	(ii)	(For complex) with CO, stability constant is greater (than with complex in O_2) **OR** with CO, stability constant is high ✓ (Coordinate) bond with CO is stronger (than O_2) **OR** bond with CO is strong ✓	2	**ANNOTATE WITH TICKS AND CROSSES, etc** **Comparison** of CO and O_2 is **NOT** required **ALLOW** stability constant with/of CO is greater **IGNORE** (complex with) CO is more stable **ALLOW** bond with CO is less likely to break **OR** bond with CO more likely to form **OR** 'CO cannot be removed' **OR** idea that attachment of CO is irreversible **OR** CO is a stronger ligand (than O_2) **OR** CO has greater affinity for ion/metal/haemoglobin (than O_2) **IGNORE** CO bonds more easily
	(f)	(i)	Pt^{2+}/Pt is +2/2+, 2 x Cl^- –2 ✓	1	**DO NOT ALLOW** response in terms of Cl_2 rather than Cl^- **DO NOT ALLOW** 'charges cancel' without the charges involved being stated

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Question			Answer	Mark	Guidance
2	(f)	(ii)	 **OR**  ✓✓ For each structure Ligand donates an electron pair to metal (ion)/Pt^{2+}/Pt **OR** forms a coordinate bond to the metal (ion)/Pt^{2+}/Pt ✓	3	**IGNORE** any charge, ie Pt^{2+} **OR** Cl^-, even if wrong **IGNORE** any angle, even if wrong **ACCEPT** bonds to H_3N (does not need to go to 'N') Assume that a solid line is in plane of paper Each structure **must** contain 2 'out wedges' **AND** 2 'in wedges' or **dotted** lines **OR** 4 **solid** lines at right angles (all in plane of paper) **DO NOT ALLOW any** structure that cannot be in one plane **DO NOT ALLOW any** structure with Cl_2 as a ligand **DO NOT** apply **ECF** from one structure to the other **ALLOW** coordinate bonds shown on diagrams provide that they start from a lone pair **ALLOW** 'dative covalent bond' or 'dative bond' as alternative for 'coordinate bond **IGNORE** *cis* and *trans* labels (even if incorrect) **IGNORE** incorrect connectivity to NH_3, ie **ALLOW** NH_3—
		(iii)	platin binds to DNA (of cancer cells) **OR** platin stops (cancer) cells dividing/replicating ✓	1	

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Question	Answer	Mark	Guidance
2 (g)	**1,1-cyclobutanedicarboxylate ion**  ✓ **Correct charge required** **(could also be 2– outside square brackets)** **carboplatin** (*cis* isomer shown below)  ✓	2	Must show cyclobutane ring with both COO^- groups bonded to same carbon **ALLOW** COO^- **OR** CO_2^- for each carboxylate ion **ALLOW** structures showing CH_2 or C atoms provided it is clear that C skeleton is shown, **Note**: H atoms are not required if C atoms shown, *ie*   **DO NOT ALLOW** circle inside cyclobutane ring Two bonds from Pt to O atoms Any bonds from ligand **MUST** come from O **OR** from atom with lone pair **IGNORE** any charge shown **Note**: H atoms are not required if C atoms shown, (see ion in 1st structure) **ALLOW ECF** from 1st structure provided that the attached atoms are capable of forming coordinate bonds (*ie* they contain a lone pair of electrons) ***Example*** if 1st structure is as below, then **ALLOW** 1 mark **ECF**   **X** **ECF ✓**
	Total	**18**	

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Question			Answer	Mark	Guidance
3	(a)	(i)	$HOCH_2COOH + NaOH \rightarrow HOCH_2COONa + H_2O$ ✓	1	**ALLOW:** $HOCH_2COOH + OH^- \rightarrow HOCH_2COO^- + H_2O$ **ALLOW:** $H^+ + OH^- \rightarrow H_2O$ **DO NOT ALLOW** molecular formulae (cannot see which OH has reacted)
		(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **0.142** (mol dm^{-3}), award **2 marks** --- amount of $HOCH_2COOH = 0.125 \times \frac{25.0}{1000}$ = 0.003125 (mol) ✓ concentration NaOH = $0.003125 \times \frac{1000}{22.00}$ = 0.142 (mol dm^{-3}) ✓ ---	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below --- **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 3.125×10^{-3} mol **ALLOW ECF**: answer above $\times \frac{1000}{22.00}$ **ALLOW** 2 SF: 0.14 to calculator value: 0.142045454 --- If candidate has written in **(a)(i)**: $HOCH_2COOH$ + **2**NaOH, mark by **ECF**: concentration NaOH = **2** $\times$ 0.003125 $\times \frac{1000}{22.00}$ = 0.284 (mol dm^{-3})
		(iii)	Vertical section matches the (pH) range (of the indicator) **OR** colour change (of the indicator) **OR** end point (of the indicator) ✓	1	**ALLOW** stated pH range for vertical section at about 7–10, 6–10, etc ie **ALLOW** 'pH range must be about 7–10' **ALLOW** 'pH changes rapidly' for vertical section **ALLOW** 'equivalence point' for vertical section, *ie* **ALLOW** equivalence point matches the (pH) range, *etc* **DO NOT ALLOW** just 'end point matches (pH) range' **DO NOT ALLOW** just 'indicator matches vertical section' Response **must** link either the pH range or colour change or end point with the vertical section / pH range ~ 7–10

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Question			Answer	Mark	Guidance
3	(b)	(i)	$(K_a =)\ \dfrac{[H^+][HOCH_2COO^-]}{[HOCH_2COOH]}$ ✓	1	**IGNORE** state symbols **IGNORE** $\dfrac{[H^+]^2}{[HOCH_2COOH]}$ in **(i)** but **ALLOW** in **(ii)**
		(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **1.46 x 10^{-4}**, award **2 marks** **THEN IF** units are **mol dm^{-3}**, award 1 **further mark** --- $[H^+] = 10^{-2.37} = 0.00427$ (mol dm^{-3}) ✓ $K_a = \dfrac{0.00427^2}{0.125} = 1.46 \times 10^{-4}$ ✓ units: mol dm^{-3} ✓	2 1	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below **UNITS** can be credited with no numerical answer --- **ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 4.27 x 10^{-3} (mol) **ALLOW** 2 SF: 0.0043 up to 0.004265795188 (calc value) **IF** candidate has rounded to 0.00427 (mol dm^{-3}) in 1st response, credit **EITHER** 2 SF: 1.5 x 10^{-4} up to 1.458632 × 10^{-4} (from 0.00427) **OR** 2 SF: 1.5 x 10^{-4} up to 1.455760687 × 10^{-4} (from unrounded calculator value of 0.004265795188) **ALLOW** calculation based on equilibrium conc of glycolic acid as 0.125 – $[H^+]$: Using $[H^+] = 0.00427$, $K_a = \dfrac{0.00427^2}{0.125 - 0.00427} = 1.51 \times 10^{-4}$ For **UNITS** this is the **ONLY** correct answer
		(iii)	% dissociation = $\dfrac{0.00427}{0.125} \times 100 = 3.4$ (%) ✓ Assume working from **EITHER** from a rounded $[H^+]$ **OR** unrounded calculator value of **b(ii)** $[H^+]$	1	**ALLOW** ECF using calculated $[H^+]$ from **b(ii),** **ALLOW** 2 SF: 3.4 % up to calculator value ***Note:*** $[H^+]$ from **b(ii)** displayed *at top of answer window* ***DO NOT MARK THIS TWICE!***

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Question			Answer	Mark	Guidance
3	(c)		**ONE mark for equilibrium expression** equilibrium: $HOCH_2COOH \rightleftharpoons H^+ + HOCH_2COO^-$ ✓ --- **Four marks for action of buffer** $HOCH_2COOH$ reacts with added alkali **OR** $HOCH_2COOH + OH^- \rightarrow$ **OR** added alkali reacts with H^+ **OR** $H^+ + OH^- \rightarrow$ ✓ $\rightarrow HOCH_2COO^-$ **OR** Equilibrium $\rightarrow$ right ✓ $HOCH_2COO^-$ reacts with added acid ✓ $\rightarrow HOCH_2COOH$ **OR** Equilibrium $\rightarrow$ left ✓ --- **Two marks for preparation of buffer** Ammonia reacted with an **excess** of glycolic acid **OR** some glycolic acid remains ✓ $HOCH_2COOH + NH_3 \rightarrow HOCH_2COONH_4$ ✓	1 4 2	**ANNOTATE WITH TICKS AND CROSSES, etc** **DO NOT ALLOW** H^+, A^- and HA **ALLOW** < – > as alternative for equilibrium sign --- **ALLOW** response in terms of H^+, A^- and HA Equilibrium responses **must** refer back to a written equilibrium: **IF** more than one equilibrium shown, assume correct one **ALLOW** weak acid reacts with added alkali **DO NOT ALLOW** acid reacts with added alkali **ALLOW** conjugate base reacts with added acid **DO NOT ALLOW** salt/base reacts with added acid --- **ALLOW** as products $HOCH_2COO^-$ + NH_4^+ **ALLOW** $\rightleftharpoons$ sign instead of $\rightarrow$
	(d)		Base 1 + Acid 2 $\rightleftharpoons$ Acid 1 + Base 2 1st mark for identifying acids and bases. ✓ 2nd mark for correct pairing (ie numbers) ✓	2	**ALLOW**: Base 2 + Acid 1 $\rightleftharpoons$ Acid 2 + Base 1

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Question			Answer	Mark	Guidance
3	(e)		$2HSCH_2COO^- + R–S–S–R \longrightarrow {}^-OOCCH_2S–SCH_2COO^- + 2R–SH$ ✓ $2R–SH + H_2O_2 \longrightarrow R–S–S–R + 2H_2O$ ✓	2	**ALLOW** $(SCH_2COO^-)_2$ **ALLOW** equation with ammonium salt, ie: $2HSCH_2COONH_4$ + …… $\longrightarrow H_4NOOCCH_2S–SCH_2COONH_4$ + ……
			Total	**20**	

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Question			Answer	Mark	Guidance
4	(a)	(i)	Complete circuit with electrodes to voltmeter **AND** salt bridge between solutions ✓ Sn^{4+}/Sn^{2+} half cell with Pt electrode **AND** both solutions labelled as 1 mol dm^{-3} / 1M H^+/H_2 half cell with Pt electrode **AND** H^+ solution labelled as 1 mol dm^{-3} / 1M ✓	3	**ANNOTATE WITH TICKS AND CROSSES, etc** circuit shown **must** be complete, *ie* must be capable of working salt bridge **must** be labelled and must dip into both solutions **ALLOW** concentration label of 'equimolar' or similar wording for Sn^{4+}/Sn^{2+} half cell **ALLOW** any strong acid **IF** both half cells are correct with no concentrations, **ALLOW** 1 out of the 2 marks available for the 2 half cells **IGNORE** any stated temperature or pressure, even if wrong
		(ii)	$2Cr + 3Sn^{4+} \rightarrow 2Cr^{3+} + 3Sn^{2+}$ ✓ $Cr + 3Cu^{+} \rightarrow Cr^{3+} + 3Cu$ ✓ $Sn^{2+} + 2Cu^{+} \rightarrow Sn^{4+} + 2Cu$ ✓ Conditions not standard **OR** concentrations not 1 mol dm^{-3} ✓ High activation energy **OR** slow rate ✓	5	**ANNOTATE WITH TICKS AND CROSSES, etc** Correct species **AND** balancing needed for each mark **ALLOW** equations as shown with equilibrium sign **ALLOW multiples** but **electrons** must not be shown **IF** three equations have correct species but no balancing, **AWARD** 1 mark **ALLOW** not favoured kinetically
	(b)	(i)	$CH_3OH + 1½O_2 \rightarrow CO_2 + 2H_2O$ ✓	1	Correct species **AND** balancing needed **ALLOW** multiple, *ie* $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$ **ALLOW** CH_4O for formula of methanol
		(ii)	$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$ ✓	1	
		(iii)	less CO_2 **OR** less greenhouse gases ✓ greater efficiency ✓	2	**ALLOW** no CO_2 **OR** no greenhouse gases **ALLOW** (very) efficient **IGNORE** less pollution **OR** 'renewable fuels'
		(iv)	methanol is a **liquid** **AND** methanol is easier to store/transport ✓	1	**Both points required for mark** Response **MUST** state that methanol is a **liquid** **IGNORE** methanol has a higher boiling point Assume that '**it**' refers to methanol **IGNORE** safety issues, *eg* H_2 leakage, flammability, explosive
			Total	**13**	

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Question			Answer	Mark	Guidance
5	(a)		**A**: **forms** fewer **moles**/**molecules** of gas ✓ **B**: **forms** gas from a liquid ✓ **C**: **forms** liquid from gases ✓ **D**: **forms** more **moles**/**molecules** of gas ✓	4	**Note**: Responses must imply the key difference between the sides of the equation **IGNORE** comments about C(s)
	(b)		$\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$ $= 40 + 214 - 89 = 165$ (J K^{-1} mol^{-1}) **=** 0.165 (kJ K^{-1} mol^{-1}) ✓ At 25 ˚C, $\Delta G = +178 - 298 \times 0.165$ ✓ = (+)129 ✓ units: kJ mol^{-1} ✓ **OR** (+)129,000 ✓ units: J mol^{-1} ✓ As $\Delta G > 0$, reaction is **not** feasible **OR** as $\Delta G > 0$, $CaCO_3$ is stable ✓ --- Minimum temperature for feasibility when $0 = \Delta H - T\Delta S$ **OR** $\Delta H = T\Delta S$ **OR** $T = \frac{\Delta H}{\Delta S}$ ✓ $= \frac{178}{0.165} = 1079$ K **OR** 806 °C ✓ The units **must** be with the stated temperature	1 4 2	**ANNOTATE WITH TICKS AND CROSSES, etc** *Mark is for the working line:* $40 + 214 - 89 = 165$ **UNITS** have a separate mark **ALLOW** 129 to calculator value of 128.83 **DO NOT ALLOW** 128 (incorrect rounding) **IF** 25 ºC used rather than 298 K, credit by **ECF**, calculated ΔG = 174 to calculator value of 173.875 ***ENTROPY APPROACH***---------- **ALLOW** At 25 ˚C, $\Delta S_{total} = 0.165 - \frac{178}{298}$ ✓ = –0.432 ✓ kJ K^{-1} mol^{-1} ✓ **OR** –432 ✓ J K^{-1} mol^{-1} ✓ As $\Delta S < 0$, reaction is **not** feasible ✓ ***ENTROPY APPROACH***---------- Minimum temperature for feasibility when $0 = \Delta S_{system} + \Delta S_{surroundings}$ **OR** $\Delta S_{system} = \frac{\Delta H}{T}$ **ALLOW** 1080 K up to calculator value of 1078.787879, correctly rounded, eg 1078.79 is correct value to 6SF **DO NOT ALLOW** 1078 (incorrect rounding) **IF** 1079 K is given and additional temperature in ºC is incorrect, **IGNORE** ºC temperature (and vice versa)
			Total	**11**	

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Question			Answer	Mark	Guidance
6	(a)	(i)	(K_w =) $[H^+(aq)]$ $[OH^-(aq)]$ ✓	1	**IGNORE** state symbols **ALLOW** $[H_3O^+(aq)]$ $[OH^-(aq)]$
		(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = **2.3×10^{-10}** (mol dm^{-3}), award **2 marks** **IF** answer = **2.34×10^{-10}** (mol dm^{-3}) , award **1 mark** --- $[H^+] = 10^{-pH} = 4.27 \times 10^{-5}$ (mol dm^{-3}) ✓ $[OH^-] = \frac{1.0 \times 10^{-14}}{4.27 \times 10^{-5}}$ $= 2.34 \times 10^{-10}$ $= 2.3 \times 10^{-10}$ (mol dm^{-3}) ✓	2	**IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below **ANNOTATE WITH TICKS AND CROSSES, etc** --- **ALLOW** 4.3×10^{-5} up to calculator: $4.265795188 \times 10^{-5}$ **ALLOW** 0.0000427 Answer **MUST** be to 2 SF (in question) **ALLOW** = 2.3×10^{-x} (mol dm^{-3}) for 1 mark (must be a negative power) **ALLOW** alternative approach based on pOH: pOH = 14 – 4.27 = 9.63 ✓ (**DO NOT ALLOW** 9.6) $[OH^-] = 10^{-pOH} = 10^{-9.63} = 2.3 \times 10^{-10}$ (mol dm^{-3}) ✓
	(b)	(i)	Endothermic **because** K_w increases with temperature ✓	1	Endothermic **AND** reason required for the mark **ALLOW** Endothermic **because** increasing temperature shifts equilibrium/reaction to the right
		(ii)	K_w value from graph from 2.2 to 2.6×10^{-14} (mol^2 dm^{-6})✓ Using 2.4×10^{-14}, $[H^+] = \sqrt{2.4 \times 10^{-14}}$ **OR** 1.55×10^{-7} ✓ pH = –log (1.55×10^{-7}) = 6.81 (using $K_w = 2.4 \times 10^{-14}$) ✓	3	**ANNOTATE WITH TICKS AND CROSSES, etc** Actual $K_w = 2.38 \times 10^{-14}$ mol^2 dm^{-6} For this mark, candidate **must** use a value between 2.0 and 3.0×10^{-14} (mol^2 dm^{-6}), *ie* from the approximately correct region of the graph, **ALLOW** 6.8 up to calculator value **Note**: You will need to calculate the pH value from the candidate's estimate of K_w at 37 ºC before awarding the 3rd marking point **ONLY** award an **ECF** pH mark if candidate has generated a value of $[H^+]$ by attempting to take a square root of a value between 2.0 and 3.0×10^{-14}

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Question			Answer	Mark	Guidance
6	(b)	(iii)	(Work is) inaccurate **OR** invalid **because** K_w varies with temperature ✓	1	Response requires **reason** for inaccuracy/invalidity in terms of K_w **ALLOW** incorrect with reason **IGNORE** unreliable **ALLOW** inaccurate because wrong K_w was used For K_w varies with temperature, **ALLOW** equilibrium shifts with temperature
	(c)				**ANNOTATE WITH TICKS AND CROSSES, etc**
			Acid and alkali mixed ✓		**ALLOW** 'base' for 'alkali throughout **ALLOW** if mentioned anywhere which could be within a definition for enthalpy change of neutralisation
			Amounts of acid **AND** alkali stated ✓		Amounts could be expressed as amounts, moles, volumes **OR** concentrations
			Temperature taken at start **AND** finish ✓		**ALLOW** temperature change
			energy, $Q = mc\Delta T$ **OR** in words **AND** meaning of m, c **AND** ΔT given ✓		m = mass/volume of solution/reactants/mixture, etc (but **NOT** surroundings) c = (specific) heat capacity (of solution/water) **OR** 4.18/4.2 ΔT = temperature change
			Energy scaled up to form 1 mol of water ✓		**ALLOW** divide energy by moles
			ΔH_{neut} = –energy change ✓	6	**ALLOW** '–' sign shown in earlier part, ie $\Delta H_{neut} = -\frac{Q}{n}$ **ALLOW** a statement linking ΔH with temperature change, *ie*: **IF** temperature increases, ΔH_{neut} is **–ve** **OR IF** temperature decreases, ΔH_{neut} is +ve

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Question			Answer	Mark	Guidance
6	(d)		**Ionic radius** Potassium ion **OR** K^+ **OR** K ion is smaller **OR** K^+ has greater charge density ✓ **Lattice enthalpy** Lattice enthalpy of KF is more negative than RbF ✓ **OR** K^+ has greater attraction for F^- **Hydration enthalpy** ΔH(hydration) of K^+ is more negative than Rb^+ ✓ **OR** K^+ has greater attraction for H_2O **Enthalpy change of solution** Idea that ΔH(solution) is affected more by lattice enthalpy than by hydration enthalpy ✓	4	**ANNOTATE WITH TICKS AND CROSSES, etc** **Throughout question, ORA** in terms of Rb^+ **Throughout question, ALLOW** energy for enthalpy **DO NOT ALLOW** potassium **OR** K **OR** reference to atoms (*ie* reference to ions is required throughout a response) **ALLOW** lattice enthalpy of KF > lattice enthalpy of RbF **ALLOW** more energy needed to separate K^+ **AND** F^- **IGNORE** KF has stronger bonds **ALLOW** ΔH(hydration) of K^+ > ΔH(hydration) of Rb^+ **ALLOW** more energy needed to separate K^+ **AND** H_2O **IGNORE** K^+ has a stronger bond to H_2O **ALLOW** a correct attempt to link the contribution of lattice enthalpy and hydration enthalpy to ΔH(solution), *ie* lattice enthalpy is a more important factor than hydration enthalpy
	(e)		(During dissolving,) entropy/disorder increases **OR** disorder increases ✓ $T\Delta S > \Delta H$ **OR** $T\Delta S$ is more positive than ΔH **OR** $\Delta H - T\Delta S$ is negative ✓	2	**ALLOW** entropy change is positive **OR** ΔS is positive **OR** $T\Delta S$ is positive **ALLOW** ΔS(system) > $\Delta H/T$ **ALLOW** ΔS(system) is more positive than $\Delta H/T$ ✓ **ALLOW** ΔS(system) + ΔS(surroundings) is positive **ALLOW** Energy contribution from increase in entropy is greater than decrease in energy from enthalpy change **OR** entropy change outweighs enthalpy change **IGNORE** ΔG is negative
			Total	**20**	

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Question			Answer	Mark	Guidance
7	(a)	(i)	**amount $S_2O_3^{2-}$ used** $= 0.00100 \times \frac{24.6}{1000} = 2.46 \times 10^{-5}$ mol ✓ **amount O_2 in 25 cm^3 sample** $= \frac{2.46 \times 10^{-5}}{4} = 6.15 \times 10^{-6}$ mol ✓ **Concentration of O_2 in sample** $= 6.15 \times 10^{-6} \times \frac{1000}{25} = 2.46 \times 10^{-4}$ (mol dm^{-3}) ✓ **mass concentration of O_2 in mg dm^{-3}** $= 2.46 \times 10^{-4} \times 32$ g $= 7.872 \times 10^{-3}$ (g dm^{-3}) = 7.872 (mg dm^{-3}) ✓	4	**ANNOTATE WITH TICKS AND CROSSES, etc** **ALLOW** 0.0000246 (mol) **ECF** = $\frac{\text{answer above}}{4}$ **ALLOW** 0.00000615 g **ECF** answer above × $\frac{1000}{25}$ **ALLOW** 0.000246 g **ECF** = answer above × 32 x 1000 **ALLOW** 7.9 **OR** 7.87 **ALLOW** 2 SF up to calculator value **Must be in mg for mark** **Note:** Candidate may work out steps 3 and 4 in the opposite order, *ie* **mass of O_2 in sample** $= 6.15 \times 10^{-6} \times 32 \times 1000 = 1.968 \times 10^{-1}$ mg **mass concentration of O_2 in mg dm^{-3}** $= 1.968 \times 10^{-1} \times \frac{1000}{25} = 7.872$ (mg dm^{-3})
		(ii)	**Comment** 7.872 > 5 so fish can survive ✓	1	**ECF** If final answer > 5 fish **can** survive If final answer < 5 fish **cannot** survive
	(b)	(i)	NO ✓	1	**ALLOW** N_2H_2

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Question			Answer	Mark	Guidance
7	(b)	(ii)	$2H_2O + 2I^- + 2NO_2^- \longrightarrow 2NO + I_2 + 4OH^-$ **OR** $2H^+ + 2I^- + 2NO_2^- \longrightarrow 2NO + I_2 + 2OH^-$ **species** ✓ **balance** ✓	2	**IGNORE** state symbols **ALLOW** multiples **For species ONLY, IGNORE** any extra H_2O or e^- on either side of the equation **ALLOW** on LHS: $2HI + 2NO_2^-$ **OR** $2I^- + 2HNO_2$ **ALLOW** species and equation involving N_2H_2: $6H_2O + 8I^- + 2NO_2^- \longrightarrow N_2H_2 + 4I_2 + 10OH^-$ **OR** $6H^+ + 8I^- + 2NO_2^- \longrightarrow N_2H_2 + 4I_2 + 4OH^-$ **species** ✓ **balance** ✓
			Total	**8**	

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THIS IS A NEW SPECIFICATION

OCR
RECOGNISING ACHIEVEMENT

ADVANCED GCE
CHEMISTRY A
Equilibria, Energetics and Elements

F325

Candidates answer on the Question Paper

OCR Supplied Materials:
- *Data Sheet for Chemistry A* (inserted)

Other Materials Required:
- Scientific calculator

Thursday 17 June 2010
Afternoon

Duration: 1 hour 45 minutes

OCE/11144

Candidate Forename		Candidate Surname	

Centre Number						Candidate Number				

INSTRUCTIONS TO CANDIDATES

- Write your name clearly in capital letters, your Centre Number and Candidate Number in the boxes above.
- Use black ink. Pencil may be used for graphs and diagrams only.
- Read each question carefully and make sure that you know what you have to do before starting your answer.
- Answer **all** the questions.
- Do **not** write in the bar codes.
- Write your answer to each question in the space provided. Additional paper may be used if necessary but you must clearly show your Candidate Number, Centre Number and question number(s).

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 Lattice enthalpy can be used as a measure of ionic bond strength. Lattice enthalpies are determined indirectly using an enthalpy cycle called a Born–Haber cycle.

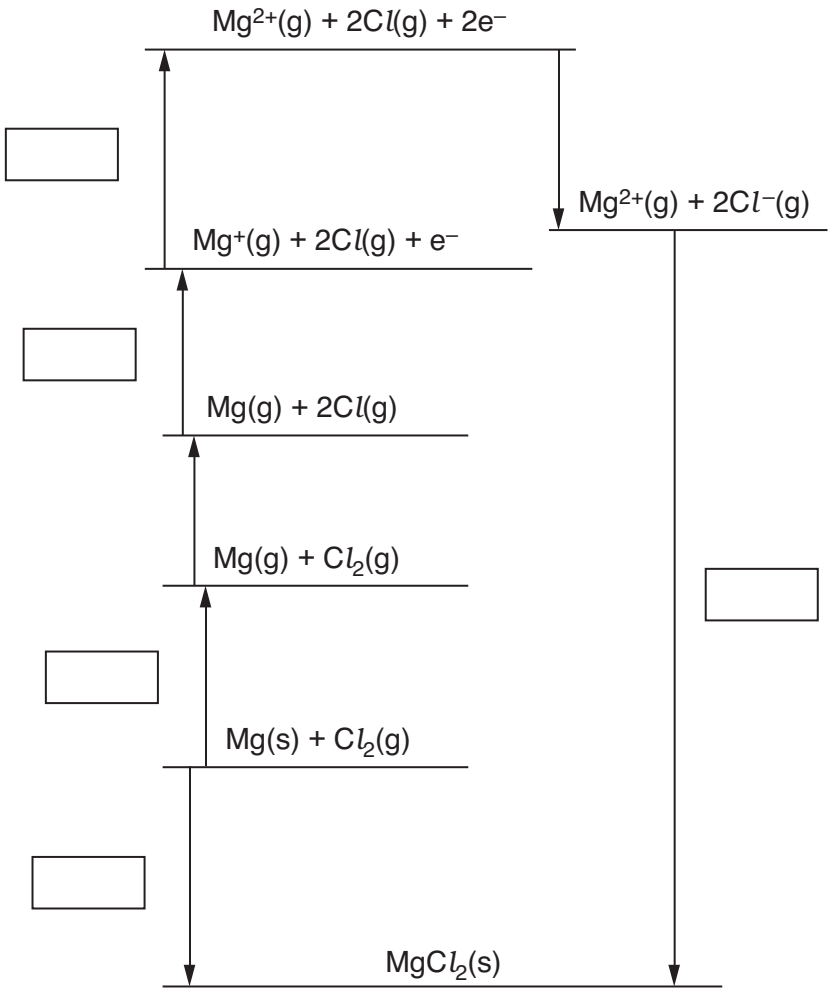
The table below shows the enthalpy changes that are needed to determine the lattice enthalpy of magnesium chloride, $MgCl_2$.

letter	enthalpy change	energy/ kJ mol^{-1}
A	1st electron affinity of chlorine	–349
B	1st ionisation energy of magnesium	+736
C	atomisation of chlorine	+150
D	formation of magnesium chloride	–642
E	atomisation of magnesium	+76
F	2nd ionisation energy of magnesium	+1450
G	lattice enthalpy of magnesium chloride	

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(a) On the cycle below, write the correct letter in each empty box.



[3]

(b) Use the Born–Haber cycle to calculate the lattice enthalpy of magnesium chloride.

answer = ... $kJ\,mol^{-1}$ **[2]**

(c) Magnesium chloride has stronger ionic bonds than sodium chloride.

Explain why.

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

[Total: 8]

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2 In the presence of acid, $H^+(aq)$, aqueous bromate(V) ions, $BrO_3^-(aq)$, react with aqueous bromide ions, $Br^-(aq)$, to produce bromine, $Br_2(aq)$.

A student carried out an investigation into the kinetics of this reaction.

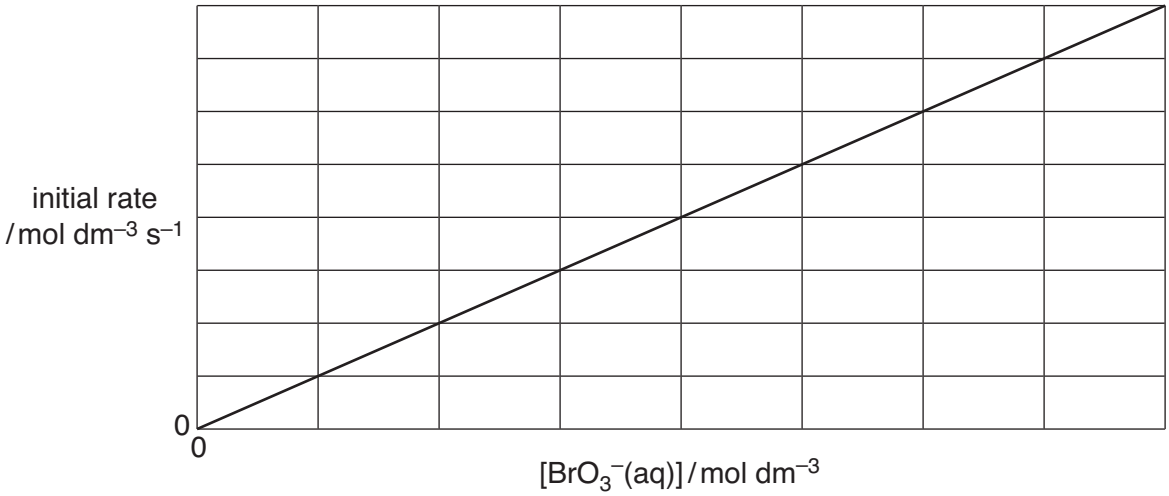
(a) Balance the ionic equation for this reaction.

$$BrO_3^- + \ldots\ldots Br^- + \ldots\ldots H^+ \longrightarrow \ldots\ldots Br_2 + \ldots\ldots H_2O$$

[1]

(b) The student investigated how different concentrations of $BrO_3^-(aq)$ affect the initial rate of the reaction.

A graph of initial rate against $[BrO_3^-(aq)]$ is shown below.



The student then investigated how different concentrations of $Br^-(aq)$ and $H^+(aq)$ affect the initial rate of the reaction.

The results are shown below.

$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
5.0×10^{-2}	1.5×10^{-1}	3.1×10^{-1}	1.19×10^{-5}
5.0×10^{-2}	3.0×10^{-1}	3.1×10^{-1}	2.38×10^{-5}
5.0×10^{-2}	1.5×10^{-1}	6.2×10^{-1}	4.76×10^{-5}

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- Using the results from the student's experiments, what conclusions can be drawn about the kinetics of this reaction? Justify your reasoning.
- Calculate the rate constant for this reaction, including the units.

In your answer you should make clear how your conclusions fit with the experimental results.

.... [9]

[Total: 10]

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3 The chemicals that we call 'acids' have been known for thousands of years. However, modern theories of acids have been developed comparatively recently. It wasn't until the early 1900s that the concept of dissociation became accepted by the scientific community and the concept of pH was introduced.

A student carried out a series of experiments with acids and alkalis.

(a) Propanoic acid, CH_3CH_2COOH, is a naturally occurring weak acid. The equation for the dissociation of propanoic acid is shown below.

$$CH_3CH_2COOH(aq) \rightleftharpoons H^+(aq) + CH_3CH_2COO^-(aq)$$

The student wanted to prove that propanoic acid is a weak acid. The student had access to a pH meter and 0.100 mol dm^{-3} propanoic acid.

- Explain how the student could prove that propanoic acid is a weak acid by taking a single pH measurement.
- Show how the student could then calculate the acid dissociation constant, K_a, for propanoic acid.

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

(b) The student measured the pH of a solution of sodium hydroxide at 25 °C.
The measured pH was 13.46.

Calculate the concentration of the aqueous sodium hydroxide.

concentration = ... mol dm^{-3} **[2]**

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(c) A student made a buffer solution by mixing an excess of propanoic acid to an aqueous solution of sodium hydroxide at 25 °C. This buffer solution contains an equilibrium system that minimises changes in pH when small amounts of acids and alkalis are added.

- Explain why a buffer solution formed when an excess of propanoic acid was mixed with aqueous sodium hydroxide.

- Explain how this buffer solution controls pH when an acid or an alkali is added.



In your answer you should explain how the equilibrium system allows the buffer solution to control the pH.

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..... **[7]**

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(d) A student added nitric acid to propanoic acid. A reaction took place to form an equilibrium mixture containing two acid–base pairs.

Complete the equilibrium below and label the two conjugate acid–base pairs.

$HNO_3 + CH_3CH_2COOH \rightleftharpoons$ ..... + ...

[2]

(e) Finally, the student reacted an aqueous solution of propanoic acid with a reactive metal and with a carbonate.

(i) Write an equation for the reaction of aqueous propanoic acid with magnesium.

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

(ii) Write an ionic equation for the reaction of aqueous propanoic acid with aqueous sodium carbonate.

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

[Total: 17]

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QUESTION 4 STARTS ON PAGE 10

PLEASE DO NOT WRITE ON THIS PAGE

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4 Electrochemical cells have been developed as a convenient and portable source of energy.

The essential components of any electrochemical cell are two redox systems, one providing electrons and the other accepting electrons. The tendency to lose or gain electrons can be quantified using values called standard electrode potentials.

Standard electrode potentials for seven redox systems are shown in **Table 4.1**.
You may need to use this information throughout this question.

Table 4.1

redox system	equation	$E^{\ominus}$/V
1	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0
2	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
3	$SO_4^{2-}(aq) + 2H^+(aq) + 2e^- \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$	+0.17
4	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.34
5	$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
6	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
7	$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54

(a) An electrochemical cell can be made based on redox systems 2 and 4.

(i) Draw a labelled diagram to show how this cell can be set up in the laboratory.

[3]

(ii) State the charge carriers that transfer current

through the wire, ...

through the solution. ..... **[1]**

(iii) Write down the overall cell reaction.

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

(iv) Write down the cell potential.

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

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(b) Select from **Table 4.1**,

(i) a species which oxidises $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$,

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

(ii) a species which reduces $Fe^{3+}(aq)$ to $Fe^{2+}(aq)$ but does **not** reduce $Ag^{+}(aq)$ to Ag(s).

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

(c) Fuel cells are a type of electrochemical cell being developed as a potential source of energy in the future.

- State **one** important difference between a fuel cell and a conventional electrochemical cell.
- Write the equation for the overall reaction that takes place in a hydrogen fuel cell.
- State **two** ways that hydrogen might be stored as a fuel for cars.
- Suggest why some people consider that the use of hydrogen as a fuel for cars consumes more energy than using fossil fuels such as petrol and diesel.

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..... **[5]**

[Total: 13]

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5 Ammonia is one of our most important chemicals, produced in enormous quantities because of its role in the production of fertilisers.

Much of this ammonia is manufactured from nitrogen and hydrogen gases using the Haber process. The equilibrium is shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

(a) (i) Write an expression for K_c for this equilibrium.

[1]

(ii) Deduce the units of K_c for this equilibrium.

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

(b) A research chemist was investigating methods to improve the synthesis of ammonia from nitrogen and hydrogen at 500 °C.

- The chemist mixed together nitrogen and hydrogen and pressurised the gases so that their total gas volume was 6.0 dm^3.
- The mixture was allowed to reach equilibrium at constant temperature and without changing the total gas volume.
- The equilibrium mixture contained 7.2 mol N_2 and 12.0 mol H_2.
- At 500 °C, the numerical value of K_c for this equilibrium is 8.00×10^{-2}.

Calculate the amount, in mol, of ammonia present in the equilibrium mixture at 500 °C.

equilibrium amount of NH_3 = ... mol **[4]**

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(c) The research chemist doubled the pressure of the equilibrium mixture whilst keeping all other conditions the same. As expected the equilibrium yield of ammonia increased.

(i) Explain in terms of le Chatelier's principle why the equilibrium yield of ammonia increased.

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

(ii) Explain in terms of K_c why the equilibrium yield of ammonia increased.

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

(d) For the industrial manufacture of ammonia, nitrogen and hydrogen gases are required in large quantities from readily available resources.

Various methods have been developed to obtain hydrogen gas for this process.

(i) Much of the hydrogen is obtained by reacting together natural gas (methane) and steam.

Construct an equation for this reaction.

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

(ii) Natural gas is a fossil fuel and the annual production of ammonia accounts for about 2% of all methane consumption. In the future, as fossil fuels become more depleted, the use of methane for ammonia production may become too expensive.

Suggest another process that might be used in the future to obtain hydrogen gas for the Haber process.

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

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(e) In the industrial production of ammonia, a temperature in the range 400–500 °C is used.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

Standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are given in the table below.

substance	$N_2(g)$	$H_2(g)$	$NH_3(g)$
S **/ J K^{-1} mol^{-1}**	191	131	192

(i) Show that the formation of ammonia from nitrogen and hydrogen gases should be feasible at room temperature (25 °C).

[6]

(ii) Explain, in terms of entropy, why this reaction is **not** feasible at very high temperatures.

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

(iii) Suggest why a temperature of 400–500 °C is used for ammonia production, despite the reaction being feasible at room temperature.

.....

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

[Total: 22]

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6 Chromium shows typical properties of a transition element. The element's name comes from the Greek word 'Chroma' meaning colour because of its many colourful compounds.

(a) Write down the electron configuration of

(i) a Cr atom, ... **[1]**

(ii) a Cr^{3+} ion. ..... **[1]**

(b) An acidified solution containing orange $Cr_2O_7^{2-}$ ions reacts with zinc in a redox reaction to form a solution containing Zn^{2+} ions and blue Cr^{2+} ions.

The unbalanced half-equations are shown below.

$$Zn \longrightarrow Zn^{2+} + e^-$$

$$Cr_2O_7^{2-} + H^+ + e^- \longrightarrow Cr^{2+} + H_2O$$

Balance these equations and construct an overall equation for this reaction.

.....

.....

.....

.....

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

(c) Aqueous solutions of Cr^{3+} ions contain ruby-coloured $[Cr(H_2O)_6]^{3+}$ complex ions. If an excess of concentrated ammonia solution is added, the solution changes to a violet colour as the hexaammine chromium(III) complex ion forms.

(i) What type of reaction has taken place?

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

(ii) Suggest an equation for this reaction.

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

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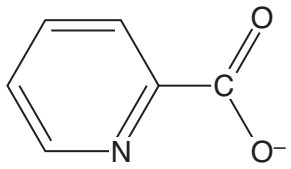
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(d) Chromium picolinate, $Cr(C_6H_4NO_2)_3$, is a bright red complex, used as a nutritional supplement to prevent or treat chromium deficiency in the human body.

In this complex,

- chromium has the +3 oxidation state,
- picolinate ions, $C_6H_4NO_2^-$, act as bidentate ligands.

The structure of the picolinate ion is shown below.



$Cr(C_6H_4NO_2)_3$ exists as a mixture of stereoisomers.

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

.....

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

(ii) How is the picolinate ion able to act as a **bidentate** ligand?

.....

.....

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

(iii) Why does $Cr(C_6H_4NO_2)_3$ exist as a mixture of stereoisomers?
Draw diagrams of the stereoisomers as part of your answer.

.....

.....

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

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(e) Compound **A** is an orange ionic compound of chromium with the percentage composition by mass N, 11.11%; H, 3.17%; Cr, 41.27%; O, 44.45%. Compound **A** does **not** have water of crystallisation.

On gentle heating, compound **A** decomposes to form three products, **B**, **C** and water.
B is a green oxide of chromium with a molar mass of 152.0 g mol^{-1}.
C is a gas. At RTP, each cubic decimetre of **C** has a mass of 1.17 g.

In the steps below, show all your working.

- Calculate the empirical formula of compound **A**.
- Deduce the ions that make up the ionic compound **A**.
- Identify substances **B** and **C**.
- Write an equation for the decomposition of compound **A** by heat.

[8]

[Total: 22]

TURN OVER FOR QUESTION 7

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7 Redox titrations using $KMnO_4$ in acidic conditions can be used to analyse reducing agents. Acidified $KMnO_4$ is a strong oxidising agent, readily removing electrons:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

A student analysed a solution of hydrogen peroxide, $H_2O_2(aq)$, using a redox titration with $KMnO_4$ under acidic conditions. Under these conditions, H_2O_2 is a reducing agent.

The overall equation for the reaction is given below.

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

(a) Deduce the simplest whole number half-equation for the oxidation of H_2O_2 under these conditions.

[2]

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(b) The student diluted 25.0 cm^3 of a solution of hydrogen peroxide with water and made the solution up to 250.0 cm^3. The student titrated 25.0 cm^3 of this solution with 0.0200 $mol\,dm^{-3}$ $KMnO_4$ under acidic conditions. The volume of $KMnO_4(aq)$ required to reach the end-point was 23.45 cm^3.

- Calculate the concentration, in $g\,dm^{-3}$, of the **undiluted** hydrogen peroxide solution.
- What volume of oxygen gas, measured at RTP, would be produced during this titration?

[6]

[Total: 8]

END OF QUESTION PAPER

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GCE

Chemistry A

Advanced GCE **F325**

Equilibria, Energetics and Elements

Mark Scheme for June 2010

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Question			Expected Answers	Marks	Additional Guidance
1	a		**F** **B** **G** **E** **D** **FIVE** correct ✓✓✓ **FOUR** correct ✓✓ **THREE** correct ✓	3	**ALLOW** **1450** **736** **G** **76** **–642**
	b		Correct calculation –642 – (+76 + (2 × 150) + 736 + 1450 + (2 × –349)) ✓ –642 – 1864 = – 2506 ✓ (kJ mol^{-1})	2	**ALLOW** for 1 mark: –2705 (2 × 150 and 2 × 349 not used for Cl) –2356 (2 × 150 not used for Cl) –2855 (2 × 349 not used for Cl) +2506 (wrong sign) **DO NOT ALLOW** any other answers
	c		Magnesium ion **OR** Mg^{2+} has greater charge (than sodium ion **OR** Na^{+}) **OR** Mg^{2+} has greater charge density ✓ Magnesium ion **OR** Mg^{2+} is smaller ✓ Mg^{2+} has a stronger attraction (than Na^{+}) to Cl^{-} ion **OR** Greater attraction between oppositely charged ions ✓	3	***ANNOTATIONS MUST BE USED*** **ALLOW** magnesium/Mg is 2+ but sodium/Na is 1+ **DO NOT ALLOW** Mg **atom** is 2+ but Na **atom** is 1+ **ALLOW** 'charge density' here **only** **ALLOW** Mg **OR** magnesium is smaller **DO NOT ALLOW** Mg^{2+} has a smaller **atomic** radius **ALLOW** anion **OR** negative ion for Cl^{-} **DO NOT ALLOW** chlorine ions **DO NOT ALLOW** Mg has greater attraction **ALLOW** 'attracts with more force' for greater attraction but **DO NOT ALLOW** 'greater force (could be repulsion) **ALLOW** reverse argument throughout in terms of Na^{+}
			Total	**8**	

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Question			Expected Answers	Marks	Additional Guidance
2	a		$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$ ✓	1	**ALLOW** multiples
	b			1	***ANNOTATIONS MUST BE USED***
			graph:		**Both** explanation and 1st order required for mark
			Straight/diagonal line through origin **OR** 0,0 **AND** 1st order with respect to BrO_3^- ✓		**DO NOT ALLOW** diagonal line **OR** straight line **OR** constant gradient on its own (no mention of origin **OR** 0,0) **ALLOW** 'As BrO_3^- doubles, rate doubles' **AND** 1st order **ALLOW** rate is proportional to concentration **AND** 1st order
			initial rates data:	4	
			When $[Br^-]$ is doubled, rate × 2 ✓ 1st order with respect to Br^- ✓		Mark order and explanation independently Mark order first, then explanation
			When $[H^+]$ × 2, rate × 4 (2^2) ✓ 2nd order with respect to H^+ ✓		
			Rate equation rate = k $[BrO_3^-]$ $[Br^-]$ $[H^+]^2$ ✓	1	**ALLOW** ECF from candidate's orders above

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Question	Expected Answers	Marks	Additional Guidance
	Calculation of rate constant (3 marks) $k = \frac{\text{rate}}{[BrO_3^-][Br^-][H^+]^2}$ **OR** $\frac{1.19 \times 10^{-5}}{(5.0 \times 10^{-2})(1.5 \times 10^{-1})(3.1 \times 10^{-1})^2}$ ✓ $= 1.7 \times 10^{-2}$ **OR** 1.65×10^{-2} ✓ $dm^9\ mol^{-3}\ s^{-1}$ ✓	3	***ANNOTATIONS MUST BE USED*** **Calculation can be from any of the experimental runs – they all give the same value of *k*** **ALLOW** $mol^{-3}\ dm^9\ s^{-1}$ **ALLOW** 1.6510579×10^{-2} and correct rounding to 1.7×10^{-2} **Correct numerical answer subsumes previous marking point** **DO NOT ALLOW** fraction: $\frac{238}{14415}$ --- **ALLOW ECF from incorrect rate equation.** Examples are given below for 1st line of initial rates data. IF other rows have been used, then calculate the rate constant from data chosen. --- **Example 1:** 1st order with respect to H^+ $rate = k[BrO_3^-][Br^-][H^+]$ $k = \frac{\text{rate}}{[BrO_3^-][Br^-][H^+]}$ **OR** $\frac{1.19 \times 10^{-5}}{(5.0 \times 10^{-2})(1.5 \times 10^{-1})(3.1 \times 10^{-1})}$ ✓ $= 5.1 \times 10^{-3}$ **OR** 5.12×10^{-3} ✓ $dm^6\ mol^{-2}\ s^{-1}$ ✓ **ALLOW** $5.11827957 \times 10^{-3}$ and correct rounding to 5.1×10^{-3} --- **Example 2:** Zero order with respect to BrO_3^- $rate = k[Br^-][H^+]^2$ $k = \frac{\text{rate}}{[Br^-][H^+]^2}$ **OR** $\frac{1.19 \times 10^{-5}}{(1.5 \times 10^{-1})(3.1 \times 10^{-1})^2}$ ✓ $= 8.3 \times 10^{-4}$ **OR** 8.26×10^{-4} ✓ $dm^6\ mol^{-2}\ s^{-1}$ ✓ **ALLOW** $8.255289629 \times 10^{-4}$ and correct rounding to 8.3×10^{-4}
	Total	**10**	

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Question			Expected Answers	Marks	Additional Guidance
3	a		measured pH > 1 **OR** $[H^+] < 0.1$ (mol dm^{-3}) ✓	4	**ALLOW** C_2H_5 throughout question **ALLOW** $[H^+] < [CH_3CH_2COOH]$ **OR** $[H^+] < [HA]$ **ALLOW** measured pH is higher than expected **ALLOW** measured pH is not as acidic as expected **ALLOW** a quoted pH value or range > 1 and < 7 **OR** between 1 and 7
			$[H^+] = 10^{-pH}$ ✓		**ALLOW** $[H^+]$ = antilog –pH **OR** $[H^+]$ = inverse log –pH
			$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$ **OR** $\frac{[H^+]^2}{[CH_3CH_2COOH]}$ ✓		**ALLOW** $\frac{[H^+][A^-]}{[HA]}$ **OR** $\frac{[H^+]^2}{[HA]}$
			Calculate K_a from $\frac{[H^+]^2}{0.100}$ ✓		**IF** K_a is **NOT** given and $K_a = \frac{[H^+]^2}{0.100}$ is shown, award mark for K_a also (i.e. $K_a = \frac{[H^+]^2}{0.100}$ is automatically awarded the last 2 marks)
	b		**Marks are for correctly calculated values.** **Working shows how values have been derived.** $[H^+] = 10^{-13.46} = 3.47 \times 10^{-14}$ (mol dm^{-3}) ✓	2	**ALLOW** $3.467368505 \times 10^{-14}$ and correct rounding to 3.5×10^{-14} **ALLOW** 0.28840315 and correct rounding to 0.29, i.e. **ALLOW** 0.288
			$[OH^-] = \frac{1.0 \times 10^{-14}}{3.47 \times 10^{-14}} = 0.29$ (mol dm^{-3}) ✓		**ALLOW** alternative approach using pOH: pOH = 14 – 13.46 = 0.54 ✓ $[OH^-] = 10^{-0.54} = 0.29$ (mol dm^{-3}) ✓ Correct answer gets **BOTH** marks

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Question	Expected Answers	Marks	Additional Guidance
c		7	***ANNOTATIONS MUST BE USED***
	Propanoic acid reacts with sodium hydroxide forming propanoate ions/sodium propanoate **OR** $CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COONa + H_2O$ ✓		**ALLOW** C_2H_5 throughout question **ALLOW** Adding NaOH forms propanoate ions/sodium propanoate (imples that the NaOH is added to the propanoic acid)
	Some propanoic acid remains **OR** propanoic acid **AND** propanoate (ions) / sodium propanoate present ✓		**ALLOW**: weak acid **AND** its conjugate base/salt present Throughout, do not penalise comments that imply that pH is constant in presence of buffer
	equilibrium: $CH_3CH_2COOH \rightleftharpoons H^+ + CH_3CH_2COO^-$ ✓		**DO NOT ALLOW** HA and A^- in this equilibrium expression For description of action of buffer below, **ALLOW** HA for CH_3CH_2COOH; **ALLOW** A^- for $CH_3CH_2COO^-$ Equilibrium responses must refer back to a written equilibrium. **IF** no equilibrium shown, use the equilibrium as written in expected answers (which is also written on page 6 of the paper)
	Added alkali CH_3CH_2COOH reacts with added alkali **OR** $CH_3CH_2COOH + OH^- \rightarrow$ **OR** added alkali reacts with H^+ **OR** $H^+ + OH^- \rightarrow$ ✓		**ALLOW** weak acid reacts with added alkali
	$\rightarrow CH_3CH_2COO^-$ **OR** Equilibrium $\rightarrow$ right ✓		
	Added acid $CH_3CH_2COO^-$ reacts with added acid **OR** $[H^+]$ increases ✓		**ALLOW** conjugate base reacts with added acid **DO NOT ALLOW** salt reacts with added acid
	$\rightarrow CH_3CH_2COOH$ **OR** Equilibrium $\rightarrow$ left ✓		
		5	

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Question			Expected Answers	Marks	Additional Guidance
	d		$HNO_3 + CH_3CH_2COOH \rightleftharpoons CH_3CH_2COOH_2^+ + NO_3^-$ ✓ acid 1 base 2 acid 2 base 1 ✓	2	State symbols **NOT** required **ALLOW** 1 **AND** 2 labels the other way around. **ALLOW** 'just acid' and 'base' labels throughout if linked by lines so that it is clear what the acid–base pairs are. **IF** proton transfer is wrong way around then **ALLOW** 2nd mark for idea of acid–base pairs, i.e. $HNO_3 + CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H_2NO_3^+$ × base 2 acid 1 base 1 acid 2 ✓
	e	i	$2CH_3CH_2COOH + Mg \rightarrow (CH_3CH_2COO)_2Mg + H_2$ ✓	1	**IGNORE** state symbols **ALLOW** ionic equation: $2H^+ + Mg \rightarrow Mg^{2+} + H_2$ **IGNORE** any random charges in formula of $(CH_3CH_2COO)_2Mg$ as long as the charges are **correct (charges are treated as working)** i.e. $(CH_3COO^-)_2Mg$ **OR** $(CH_3COO)_2^-Mg$ should **not** be penalised However, Mg^{2+} instead of Mg on the left side of equation is obviously wrong
		ii	$2H^+ + CO_3^{2-} \longrightarrow H_2O + CO_2$ **OR** $2H^+ + CO_3^{2-} \longrightarrow H_2CO_3$ **OR** $H^+ + CO_3^{2-} \longrightarrow HCO_3^-$ ✓	1	State symbols **NOT** required
			Total	**17**	

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Question			Expected Answers	Marks	Additional Guidance
4	a	i	Complete circuit (with voltmeter) and salt bridge linking two half-cells ✓ Pt electrode in solution of Fe^{2+}/Fe^{3+} ✓ Ag in solution of Ag^{+} ✓	3	**DO NOT ALLOW** 'solution of a silver halide', e.g. AgCl (as these are insoluble) but **DO ALLOW** any solution of any other silver salt (whether insoluble or not) **IF** candidate has used incorrect redox systems, then mark ECF as follows: **(i) each** incorrect system will cost the candidate **one** mark **(ii) ECF** if species have been quoted (see Additional Guidance below) **(iii) ECF** for equation **(iv) ECF** for cell potential ***YOU MAY NEED TO WORK OUT THESE ECF RESPONSES YOURSELF DEPENDING ON THE INCORRECT REDOX SYSTEMS CHOSEN***
		ii	electrons **AND** ions ✓	1	For electrons, **ALLOW** e^{-} For 'ions', **ALLOW** formula of an ion in one of the half-cells or salt bridge, e.g. Ag^{+}, Fe^{2+}, Fe^{3+} **ALLOW ECF** as in **(i)**
		iii	$Ag + Fe^{3+} \longrightarrow Ag^{+} + Fe^{2+}$ ✓	1	**ALLOW ECF** as in **(i)** **ALLOW** equilibrium sign
		iv	0.43 V ✓	1	**ALLOW ECF** as in **(i)**
	b	i	Cl_2 **OR** O_2 **AND** H^{+} ✓	1	**ALLOW** chlor**ine** **ALLOW** O_2 **AND** $4H^{+}$ **ALLOW** O_2 **AND** acid **DO NOT ALLOW** O_2 alone **DO NOT ALLOW** equation or equilibrium
		ii	I^{-} ✓	1	**ALLOW** $2I^{-}$ **OR** iod**ide** **DO NOT ALLOW** equation or equilibrium

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Question			Expected Answers	Marks	Additional Guidance
	c		A fuel cell converts energy from reaction of a fuel with oxygen into a voltage/electrical energy ✓ $2H_2 + O_2 \rightarrow 2H_2O$ ✓ Two from: • under pressure **OR** at low temperature **OR** as a liquid • adsorbed on solid • absorbed within solid ✓✓ Energy is needed to make the hydrogen **OR** energy is needed to make fuel cell ✓	5	***ANNOTATIONS MUST BE USED*** **ALLOW** combustion for reaction of fuel with oxygen/reactants **ALLOW** a fuel cell requires constant supply of fuel **OR** operates continuously as long as a fuel (and oxygen) are added **ALLOW** multiples, e.g. $H_2 + ½O_2 \rightarrow H_2O$ **IGNORE** state symbols **ALLOW** 'material' **OR** metal for solid **ALLOW** as a metal hydride
			Total	**13**	

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Question			Expected Answers	Marks	Additional Guidance
5	a	i	$(K_c =) \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$ ✓	1	Must be square brackets
		ii	$dm^6\ mol^{-2}$ ✓	1	**ALLOW** $mol^{-2}\ dm^6$ **ALLOW ECF** from incorrect K_c expression
	b		**Unless otherwise stated, marks are for correctly calculated values. Working shows how values have been derived.** $[N_2] = \frac{7.2}{6.0}$ **OR** 1.2 ($mol\ dm^{-3}$) **AND** $[H_2] = \frac{12}{6.0}$ **OR** 2.0 ($mol\ dm^{-3}$) ✓ $[NH_3] = \sqrt{(K_c \times [N_2] \times [H_2]^3)}$ **OR** $\sqrt{(8.00 \times 10^{-2} \times 1.2 \times 2.0^3)}$ ✓ = 0.876 **OR** 0.88 ($mol\ dm^{-3}$) ✓ amount NH_3 = 0.876 × 6 = 5.26 **OR** 5.3 (mol) ✓	4	***ANNOTATIONS MUST BE USED*** For **all** parts, **ALLOW** numerical answers from 2 significant figures up to the calculator value 1st mark is for realising that concentrations need to be calculated. **Correct numerical answer with no working would score all previous calculation marks** **ALLOW** calculator value: 0.876356092 down to 0.88, correctly rounded **ALLOW** calculator value down to 5.3, correctly rounded

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Question	Expected Answers	Marks	Additional Guidance
b	**EXAMPLES OF INCORRECT RESPONSES IN (b) THAT MAY BE WORTHY OF CREDIT**		---------- **ALLOW ECF from incorrect concentrations (3 marks)** For example, If concentrations **not** calculated at start, then $[NH_3] = \sqrt{(8.00 \times 10^{-2} \times 7.2 \times 12.0^3)}$ ✓ = 31.5 mol dm^{-3} ✓ Equilibrium amount of $NH_3 = 31.5 \times 6 = 189.6$ (mol) ✓ ---------- **IF** candidate has K_c expression upside down, then all **4 marks** are available in **(b)** by **ECF** Correct $[N_2]$ AND $[H_2]$ ✓ $[NH_3] = \sqrt{\frac{[N_2][H_2]^3}{K_c}} = = \sqrt{\frac{1.2 \times 2^3}{8.00 \times 10^{-2}}}$ ✓ = 11.0 mol dm^{-3} ✓ Equilibrium amount of $NH_3 = 11.0 \times 6 = 66.0$ (mol) ✓ ---------- **IF** candidate has used K_c value of 8.00×10^{-2} **AND** values for N_2 **AND** H_2 with powers wrong, mark by **ECF** from calculated as below (**3 max in (b)**) Correct $[N_2]$ AND $[H_2]$ ✓ $[NH_3]$ expression × **ECF**: Calculated $[NH_3]$ ✓ **ECF**: Equilibrium amount of NH_3 ✓

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Question			Expected Answers	Marks	Additional Guidance
	c	i	Equilibrium shifts to right **OR** Equilibrium towards ammonia ✓ Right hand side has fewer number of (gaseous) moles ✓	2	**ALLOW** 'moves right' **OR** 'goes right' **OR** 'favours right' **OR** 'goes forwards' **ALLOW** 'ammonia side' has fewer moles **ALLOW** 'there are more (gaseous) moles on left'
		ii	K_c does not change ✓ Increased pressure increases concentration terms on bottom of K_c expression more than the top **OR** system is now no longer in equilibrium ✓ top of K_c expression increases and bottom decreases until K_c is reached ✓	3	***ANNOTATIONS MUST BE USED*** Any response in terms of K_c changing scores **ZERO** for Part **(ii)** **ALLOW** K_c is temperature dependent only **OR** K_c does not change with pressure **ALLOW** $\frac{[NH_3]^2}{[N_2]\ [H_2]^3}$ no longer equal to K_c
	d	i	$CH_4 + H_2O \longrightarrow 3H_2 + CO$ ✓	1	State symbols **NOT** required **ALLOW**: $CH_4 + H_2O \longrightarrow CH_3OH + H_2$ $CH_4 + 2H_2O \longrightarrow 4H_2 + CO_2$ $CH_4 + H_2O \longrightarrow 2H_2 + HCHO$ $CH_4 + 2H_2O \longrightarrow 3H_2 + HCOOH$
		ii	Electrolysis of water **OR** $H_2O \longrightarrow H_2 + ½O_2$ ✓	1	**ALLOW** electrolysis of brine **DO NOT ALLOW** reforming **DO NOT ALLOW** cracking **DO NOT ALLOW** reaction of metal with acid

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Question			Expected Answers	Marks	Additional Guidance
	e	i	**Unless otherwise stated, marks are for correctly calculated values.** **Working shows how values have been derived.** $\Delta S = \Sigma S$(products) – ΣS(reactants) / = (2 × 192) – (191 + 3 × 131) ✓ = –200 (J K^{-1} mol^{-1}) **OR** –0.200 (kJ K^{-1} mol^{-1}) ✓ Use of 298 K (could be within ΔG expression below) ✓ $\Delta G = \Delta H - T\Delta S$ **OR** ΔG = –92 – (298 × –0.200) **OR** ΔG = –92000 – (298 × –200) ✓ = –32.4 kJ mol^{-1} **OR** –32400 J mol^{-1} ✓ **(Units must be shown)** For feasibility, $\Delta G < 0$ **OR** ΔG is negative ✓	5 1	***ANNOTATIONS MUST BE USED*** See **Appendix 1** for extra guidance for marking **5e(i)** and **5e(ii)** **NO UNITS** required at this stage **IGNORE** units **ALLOW** –32.4 kJ **OR** –32400 J **(Units must be shown)** Award all 5 marks **above** for correct answer with no working **IF** 25 ºC has been used instead of 298 K, correctly calculated ΔG values are = –87 kJ mol^{-1} **OR** –87000 J mol^{-1} **4 marks** are still available up to this point and maximum possible from **(e)(i)** is 5 marks
		ii	As the temperature increases, $T\Delta S$ becomes more negative **OR** $T\Delta S$ becomes more negative than ΔH **OR** $T\Delta S$ becomes more significant ✓ Eventually $\Delta H - T\Delta S$ becomes positive ✓	2	**ALLOW** $T\Delta S > \Delta H$ (i.e. assume no sign at this stage) **ALLOW** 'entropy term' as alternative for $T\Delta S$ **ALLOW –** $T\Delta S$ becomes more positive **ALLOW –** $T\Delta S$ decreases **ALLOW** ΔG becomes positive **OR** $\Delta G > 0$

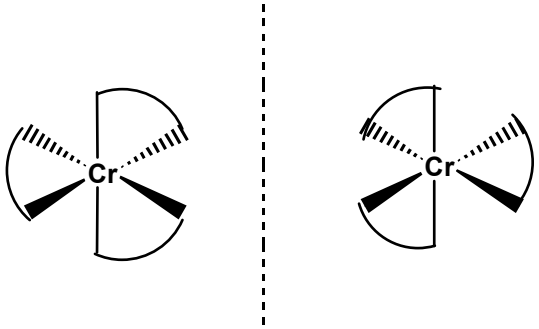
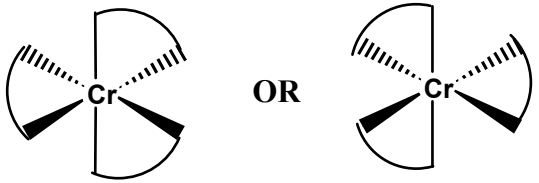
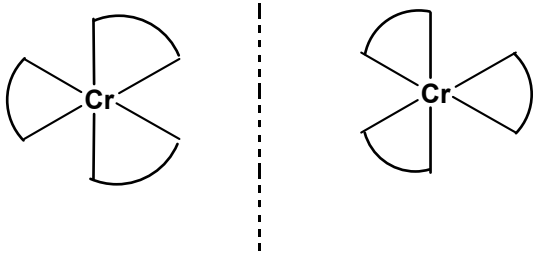
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Question			Expected Answers	Marks	Additional Guidance
		iii	Activation energy is too high **OR** reaction too slow ✓	1	**ALLOW** increases the rate **OR** more molecules exceed activation energy **OR** more successful collisions **ALLOW** rate constant increases **IGNORE** comments on yield
			Total	**22**	

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Question			Expected Answers	Marks	Additional Guidance
6	a	i	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ ✓	1	**ALLOW** $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ (i.e. 4s before 3d) **ALLOW** $[Ar]4s^1 3d^5$ **OR** $[Ar]3d^5 4s^1$
		ii	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ ✓	1	**ALLOW** $[Ar]3d^3$ **ALLOW** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^0$ **OR** $[Ar]3d^3 4s^0$
	b		$Zn \longrightarrow Zn^{2+} + 2e^-$ ✓ $Cr_2O_7^{2-} + 14H^+ + 8e^- \longrightarrow 2Cr^{3+} + 7H_2O$ ✓ $4Zn + Cr_2O_7^{2-} + 14H^+ \longrightarrow 4Zn^{2+} + 2Cr^{3+} + 7H_2O$ ✓	3	**ALLOW** multiples **WATCH** for balancing of the equations printed on paper **IF** printed equations and answer lines have different balancing numbers **OR** electrons, **IGNORE** numbers on printed equations (i.e. treat these as working) and mark responses on answer lines **only** **NO ECF** for overall equation i.e. the expected answer is the **ONLY** acceptable answer
	c	i	Ligand substitution ✓	1	**ALLOW** ligand exchange
		ii	$[Cr(H_2O)_6]^{3+} + 6NH_3 \longrightarrow [Cr(NH_3)_6]^{3+} + 6H_2O$ ✓ ✓	2	1 mark is awarded for each side of equation **ALLOW** equilibrium sign **ALLOW** 1 mark for 2+ shown instead of 3+ on both sides of equation **ALLOW** 1 mark for substitution of 4 NH_3: $[Cr(H_2O)_6]^{3+} + 4NH_3 \longrightarrow [Cr(NH_3)_4(H_2O)_2]^{3+} + 4H_2O$
	d	i	Donates an electron pair to a metal ion **OR** forms a coordinate bond to a metal ion ✓	1	**ALLOW** donates an electron pair to a metal **ALLOW** dative (covalent) bond for coordinate bond
		ii	Donates **two** electron pairs **OR** forms **two** coordinate bonds ✓ Lone pairs on two O atoms ✓	2	First mark is for the idea of two coordinate bonds **ALLOW** lone pair on O and N **DO NOT ALLOW** lone pairs on COO^- (could involve C) Second mark is for the atoms that donate the electron pairs Look for the atoms with lone pairs also on response to **(d)(iii)** and credit here if not described in **(d)(ii)**

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Question	Expected Answers	Marks	Additional Guidance
iii	Forms two optical isomers **OR** two enantiomers **OR** two non-superimposable mirror images ✓  ✓✓ For each structure	3	**IGNORE** any charges shown **ALLOW** any attempt to show bidentate ligand. Bottom line is the diagram on the left. 1 mark for 3D diagram with ligands attached for ONE stereoisomer. Must contain 2 out wedges, 2 in wedges and 2 lines in plane of paper:  2nd mark for reflected diagram of SECOND stereoisomer. The diagram below would score the 2nd mark but not the first 

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Question	Expected Answers	Marks	Additional Guidance
e		8	***ANNOTATIONS MUST BE USED***
	N : H : Cr : O 11.1/14 : 3.17/1 : 41.27/52 : 44.45/16 **OR** 0.793 : 3.17 : 0.794 : 2.78 ✓		
	A: $N_2H_8Cr_2O_7$ ✓		**ALLOW A**: $(NH_4)_2Cr_2O_7$
	Ions: NH_4^+ ✓ $Cr_2O_7^{2-}$ ✓		**IF** candidate has obtained NH_4CrO_4 for A, **ALLOW** NH_4^+ **DO NOT ALLOW** CrO_4^-
	B: Cr_2O_3 ✓		
	Correctly calculates molar mass of **C** = 1.17 × 24.0 = 28.08 (g mol^{-1}) ✓		**ALLOW**: (relative) molecular mass **ALLOW**: 28 **ALLOW**: '**C** is 28'
	C: N_2 ✓		
	Equation: $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4H_2O + N_2$ ✓		**ALLOW** $N_2H_8Cr_2O_7$ in equation.
	Total	**22**	

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Question			Expected Answers	Marks	Additional Guidance
7	a	i	$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ ✓✓	2	All other multiples score 1 mark e.g. ½ $H_2O_2 \longrightarrow$ ½ $O_2 + H^+ + e^-$ $5H_2O_2 \longrightarrow 5O_2 + 10H^+ + 10e^-$
	b		**Marks are for correctly calculated values.** **Working shows how values have been derived.**		***ANNOTATIONS MUST BE USED***
			$n(KMnO_4) = \frac{0.0200 \times 23.45}{1000} = 4.69 \times 10^{-4}$ (mol) ✓		**DO NOT ALLOW** 4.7×10^{-4}
			$n(H_2O_2) = 5/2 \times 4.69 \times 10^{-4} = 1.1725 \times 10^{-3}$ (mol) ✓		**ALLOW** 1.173 x 10^{-3} OR 1.17 x 10^{-3} (i.e. 3 significant figures upwards) **ALLOW** by **ECF**: 5/2 × ans above
			$n(H_2O_2)$ in 250 cm^3 solution $= 10 \times 1.1725 \times 10^{-3} = 1.1725 \times 10^{-2}$ (mol) ✓		**ALLOW** by **ECF** 10 × ans above **ALLOW** concentration H_2O_2 = 0.0469 mol dm^{-3}
			concentration in g dm^{-3} of original H_2O_2 $= 40 \times 1.1725 \times 10^{-2} \times 34 = 15.9$ (g dm^{-3}) ✓	4	**ALLOW** by **ECF** 40 × $n(H_2O_2)$ × 34 **ALLOW** 0.0469 x 10 x 34 = 15.9 g dm^{-3} ✓ **ALLOW** two significant figures, 16 (g dm^{-3}) up to calculator value of 15.946 g dm^{-3}
			$n(O_2) = 5/2 \times 4.69 \times 10^{-4} = 1.1725 \times 10^{-3}$ (mol) ✓		**ALLOW** 0.028 dm^3 **OR** 0.02814 dm^3 **ALLOW** 28 cm^3 **OR** 28.14 cm^3 Value **AND** units required **DO NOT ALLOW** 0.03 dm^3
			volume $O_2 = 24.0 \times 1.1725 \times 10^{-3} = 0.0281$ dm^3 ✓	2	**ALLOW** by **ECF**: 24.0 × calculated moles of O_2 (2 significant figures up to calculator value)
			Total	**8**	

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Appendix 1

Extra guidance for marking atypical responses to **5e(i)** and **5e(ii)**

Question			Expected Answer	Mark	Additional Guidance
5	e	i	**TOTAL ENTROPY APPROACH:** **ALL MARKS AVAILABLE** **Unless otherwise stated, marks are for correctly calculated values.** **Working shows how values have been derived.**		***ANNOTATIONS MUST BE USED***
			$\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$ / $= (2 \times 192) - (191 + 3 \times 131)$ ✓ $= -200$ (J K^{-1} mol^{-1}) **OR** -0.200 (kJ K^{-1} mol^{-1}) ✓		**NO UNITS** required at this stage **IGNORE** units
			Use of 298 K (could be within expression below) ✓		
			$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ $\Delta S_{surroundings} = -\frac{\Delta H}{T}$ **OR** $\Delta S_{total} = \Delta S_{system} - \frac{\Delta H}{T}$ **OR** $\Delta S_{total} = -0.200 - \frac{-92}{298}$ **OR** $\Delta S_{total} = -200 - \frac{-92000}{298}$ ✓ $=$ 0.109 kJ (K^{-1} mol^{-1}) **OR** 109 J (K^{-1} mol^{-1}) ✓	5	**ALLOW** 0.109 kJ **OR** 109 J **IF** 25ºC has been used instead of 298 K, correctly calculated ΔS_{total} values are = 3.48 kJ K^{-1} mol^{-1} **OR** 3,480 J K^{-1} mol^{-1}
			Feasible when $\Delta S_{total} > 0$ ✓	1	

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Question			Expected Answer	Mark	Additional Guidance
5	e	i	**MAX/MIN TEMPERATURE APPROACH:** **5 MARKS MAX AVAILABLE** **Unless otherwise stated, marks are for correctly calculated values.** **Working shows how values have been derived.**		***ANNOTATIONS MUST BE USED*** **This candidate has not answered the question but many marks are still available.**
			$\Delta S = \Sigma S$(products) – ΣS(reactants) / = (2 × 192) – (191 + 3 × 131) ✓ = –200 (J K^{-1} mol^{-1}) **OR** –0.200 (kJ K^{-1} mol^{-1}) ✓		**NO UNITS** required at this stage **IGNORE** units
			Use of 298 K (could be within ΔG expression below) ✓		
			$\Delta G = \Delta H - T\Delta S$ **OR** When $\Delta G = 0$, $0 = \Delta H - T\Delta S$; **OR** $T = \frac{\Delta H}{\Delta S} = \frac{-92}{-0.200}$ **OR** $T = \frac{\Delta H}{\Delta S} = \frac{-92000}{-200}$ ✓ = 460 K ✓ = 187 ºC (use of 298) ✓		
			The condition $\Delta G = 0$ because temperature at which $\Delta G = 0$ is the maximum temperature for feasibility **AND** justification for the being the maximum ✓		By this approach, the calculated temperature is the switchover between feasibility and non-feasibility but it cannot be assumed that this is the maximum temperature

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Question			Expected Answer	Mark	Additional Guidance
5	e	ii	As the temperature increases, $\Delta H/T$ becomes **less** negative **OR** $\Delta H/T$ becomes **more** negative than ΔS(system) **OR** $\Delta H/T$ becomes **less** significant **OR** ΔS(surroundings) becomes **less** significant **OR** ΔS(system) > $\Delta H/T$ **OR** ΔS(system) > ΔS(surroundings) ✓ Eventually ΔS(total) becomes **negative** ✓	2	**ALLOW** $\Delta H/T > \Delta S_{system}$ (i.e. assume no sign at this stage) **ALLOW –**$\Delta H/T$ becomes more positive **ALLOW –**$\Delta H/T$ increases

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