

Example Candidate Responses

Cambridge
International
AS & A Level

Cambridge International AS & A Level Chemistry

9701

Paper 4 – A Level Structured Questions

In order to help us develop the highest quality Curriculum Support resources, we are undertaking a continuous programme of review; not only to measure the success of our resources but also to highlight areas for improvement and to identify new development needs.

We invite you to complete our survey by visiting the website below. Your comments on the quality and relevance of Cambridge Curriculum Support resources are very important to us.

<https://www.surveymonkey.co.uk/r/GL6ZNJB>

Do you want to become a Cambridge consultant and help us develop support materials?

Please follow the link below to register your interest.

<http://www.cie.org.uk/cambridge-for/teachers/teacherconsultants/>

Cambridge International Examinations retains the copyright on all its publications. Registered Centres are permitted to copy material from this booklet for their own internal use. However, we cannot give permission to Centres to photocopy any material that is acknowledged to a third party even for internal use within a Centre.

Contents

Contents	3
Introduction	4
Assessment at a glance	6
Paper 4 – A Level Structured Questions	7
Question 1	7
Question 2	13
Question 3	21
Question 4	27
Question 5	33
Question 6	41
Question 7	49
Question 8	57
Question 9	66
Question 10	72

Introduction

The main aim of this booklet is to exemplify standards for those teaching Cambridge International AS and A Level Chemistry (9701), and to show how different levels of candidates' performance (high, middle and low) relate to the subject's curriculum and assessment objectives.

In this booklet candidate responses have been chosen to exemplify a range of answers. Each response is accompanied by a brief commentary explaining the strengths and weaknesses of the answers.

For each question, each response is annotated with a clear explanation of where and why marks were awarded or omitted. This, in turn, is followed by examiner comments on how the answer could have been improved. In this way it is possible for you to understand what candidates have done to gain their marks and what they will have to do to improve their answers. At the end there is a list of common mistakes candidates made in their answers for each question.

This document provides illustrative examples of candidate work. These help teachers to assess the standard required to achieve marks, beyond the guidance of the mark scheme. Some question types where the answer is clear from the mark scheme, such as short answers and multiple choice, have therefore been omitted.

The questions, mark schemes and pre-release material used here are available to download as a zip file from Teacher Support as the Example Candidate Responses Files. These files are:

Question Paper 22, June 2016	
Question paper	9701_s16_qp_22.pdf
Mark scheme	9701_s16_ms_22.pdf
Question Paper 33, June 2016	
Question paper	9701_s16_qp_33.pdf
Mark scheme	9701_s16_ms_33.pdf
Question Paper 42, June 2016	
Question paper	9701_s16_qp_42.pdf
Mark scheme	9701_s16_ms_42.pdf
Question Paper 52, June 2016	
Question paper	9701_s16_qp_52.pdf
Mark scheme	9701_s16_ms_52.pdf

Past papers, Examiner Reports and other teacher support materials are available on Teacher Support at <https://teachers.cie.org.uk>

How to use this booklet

Example candidate response – high	Examiner comments
<p>3 Acidified potassium dichromate(VI) can oxidise ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$. The relevant half-equations are shown.</p> $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ $\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \times 3$ $3\text{H}_2\text{C}_2\text{O}_4 \rightarrow 6\text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ <p>(a) State the overall equation for the reaction between acidified dichromate(VI) ions and ethanedioic acid.</p> $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 3\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{CO}_2 + 6\text{H}^+ \quad [2]$ <p>...ted ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, was reacted with potassium dichromate(VI). ...e(VI) solution was required for complete oxidation ...omate(VI) ions used to react with the sample of amount = 6.4×10^{-4} mol [1]</p>	<p>1 This equation contains all the correct species from the half-equations given so one mark has been awarded. The</p> <p>Examiner comments are alongside the answers, linked to specific part of the answer. These explain where and why marks were awarded. This helps you to interpret the standard of Cambridge exams and helps your learners to refine their exam technique.</p>

Answers by real candidates in exam conditions. These show you the types of answers for each level. Discuss and analyse the answers with your learners in the classroom to improve their skills.

How the candidate could have improved their answer

In (a) the candidate needed to remember that the key loss in one half-equation must balance the electron gain.

In (b)(iii) the candidate used the correct method but the number of significant figures in the answer must correspond to the data provided.

This explains how the candidate could have improved their answer and helps you to interpret the standard of Cambridge exams and helps your learners to refine exam technique.

Common mistakes candidates made in this question

(a) The skills needed to combine two half-equations and balance them are often tricky for many candidates. Good candidates often got them out, while weaker candidates failed to recognise the

(b) The first two parts of the calculation were generally correct but the M_r calculation depended on the previous answer to

This lists the common mistakes candidates made in answering each question. This will help your learners to avoid these mistakes at the exam and give them the best chance of achieving a high mark.

Assessment at a glance

Candidates for Advanced Subsidiary (AS) certification take Papers 1, 2 and 3 (either Advanced Practical Skills 1 or Advanced Practical Skills 2) in a single examination series.

Candidates who, having received AS certification, wish to continue their studies to the full Advanced Level qualification may carry their AS marks forward and take Papers 4 and 5 in the examination series in which they require certification.

Candidates taking the full Advanced Level qualification at the end of the course take all five papers in a single examination series.

Candidates may only enter for the papers in the combinations indicated above.

Candidates may not enter for single papers either on the first occasion or for resit purposes.

All components are externally assessed.

Component	Weighting	
	AS Level	A Level
Paper 1 Multiple Choice 1 hour This paper consists of 40 multiple choice questions, 30 of the direct choice type and 10 of the multiple completion type, all with four options. All questions will be based on the AS Level syllabus content. Candidates will answer all questions. Candidates will answer on an answer sheet. [40 marks]	31%	15.5%
Paper 2 AS Level Structured Questions 1 hour 15 minutes This paper consists of a variable number of questions of variable mark value. All questions will be based on the AS Level syllabus content. Candidates will answer all questions. Candidates will answer on the question paper. [60 marks]	46%	23%
Paper 3 Advanced Practical Skills 2 hours This paper requires candidates to carry out practical work in timed conditions. Candidates will be expected to collect, record and analyse data so that they can answer questions related to the activity. The paper will consist of two or three experiments drawn from different areas of chemistry. Candidates will answer all questions. Candidates will answer on the question paper. [40 marks]	23%	11.5%
Paper 4 A Level Structured Questions 2 hours This paper consists of a variable number of free response style questions of variable mark value. All questions will be based on the A Level syllabus but may require knowledge of material first encountered in the AS Level syllabus. Candidates will answer all questions. Candidates will answer on the question paper. [100 marks]	–	38.5%
Paper 5 Planning, Analysis and Evaluation 1 hour 15 minutes This paper consists of a variable number of questions of variable mark value based on the practical skills of planning, analysis and evaluation. The context of the questions may be outside the syllabus content, but candidates will be assessed on their practical skills of planning, analysis and evaluation rather than their knowledge of theory. Candidates will answer all questions. Candidates will answer on the question paper. [30 marks]	–	11.5%

Teachers are reminded that the latest syllabus is available on our public website at www.cie.org.uk and Teacher Support at <https://teachers.cie.org.uk>

Paper 4 – A Level Structured Questions

Question 1

Example candidate response – high	Examiner comments
<p>1 (a) Magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, is very soluble in water. When a hot saturated solution of magnesium nitrate is cooled, crystals of the hydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, are formed. In the crystals, six water molecules bond to each Mg^{2+} ion, and some of these water molecules are also bonded to the nitrate ions.</p> <p>(i) Suggest the type of bonding that occurs between</p> <p>H_2O and Mg^{2+}, <u>covalent bond</u> 1</p> <p>H_2O and NO_3^- <u>ionic bond</u> [2]</p> <p>(ii) Describe the arrangement of the water molecules around the Mg^{2+} ion. 2</p> <p>..... <u>The arrangement arrangement is such that the shape is octahedral.</u> [1]</p> <p>(iii) Describe in detail what you would observe when crystals of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are heated in a boiling tube, gently at first and then more strongly. Write equations for any reactions that occur.</p> <p>..... <u>Initially, water water vapour is produced.</u></p> <p>..... <u>$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$</u></p> <p>..... <u>After more stronger heating, brown fumes are produced (NO_2) and a white solid is left. (MgO).</u> 3</p> <p>..... <u>$\text{Mg}(\text{NO}_3)_2 \rightarrow \text{MgO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$</u></p> <p>..... [4]</p> <p>(iv) Calculate the percentage <u>loss</u> in mass when $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is heated strongly to constant mass.</p> <p>Molar mass of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = 24.3 + 2[14 + 3(16)] + 6[2 + 16]$</p> <p>..... <u>$= 256.3$</u></p> <p>Molar mass of $\text{MgO} = 24.3 + 16 = 40.3$</p> <p>..... <u>$\therefore$ Percentage loss $= \frac{256.3 - 40.3}{256.3} \times 100\%$</u> 4</p> <p>..... <u>$= 84.3\%$</u></p> <p>percentage loss = <u>84.3</u> % [2]</p>	<p>1 The first answer is correct, but the second is incorrect. Hydrogen bond or ion-dipole forces are required.</p> <p>Mark for (a) (i) = 1/2</p> <p>2 The correct answer is given.</p> <p>Mark for (a) (ii) = 1/1</p> <p>3 The candidate gives two correct balanced equations and three viable observations for four marks. The two other allowed observations are: on gentle heating the solid turns to liquid; on strong heating a gas is formed that relights a glowing splint.</p> <p>Mark for (a) (iii) = 4/4</p> <p>4 A clear, well presented calculation. Full working shown.</p> <p>Mark for (a) (iv) = 2/2</p>

Example candidate response – high, continued	Examiner comments
<p>(b) Explain why the Group 2 nitrates become more stable to heat down the group.</p> <p>Going down the group, size of cation increases. 5</p> <p>Polarizing power of cation decreases down Group 2.</p> <p>Bonding between nitrate ion and Group 2 cation becomes more ionic and so thermal stability increases.</p> <p>[2]</p>	<p>5 The candidate answers correctly for the first mark in the mark scheme. They do not earn the second mark, as the polarising power of the cation is not linked to the relative distortion of the electron cloud of the anion.</p>
<p>(c) Magnesium nitrate and silver nitrate, AgNO_3, decompose on heating to produce the same gases. Silver nitrate also produces silver metal during decomposition.</p> <p>Write an equation for the decomposition of AgNO_3.</p> <p>$\text{AgNO}_3 \rightarrow \text{Ag} + \text{NO}_2 + \frac{1}{2}\text{O}_2$ 6</p> <p>[1]</p> <p>[Total: 12]</p>	<p>Mark for (b) = 1/2</p> <p>6 The correct equation is given. Multiplies are allowed.</p>
	<p>Mark for (c) = 1/1</p> <p>Total marks awarded = 10 out of 12</p>

How the candidate could have improved their answer

(a) (i) The candidate should have given the type of bonding between H_2O and NO_3^- as hydrogen bonding or ion-dipole forces.

(a) (iii) The candidate was awarded full marks here, although they omitted two other viable observations: (on gentle heating) the solid turns to liquid and (on strong heating) a gas is formed that relights a glowing splint.

(b) The candidate was not awarded the second mark here. This could have been earned by stating that there is less distortion (less polarisation) of the anion by the cation down the group.

Mark awarded = (a) (i) 1/2, (ii) 1/1, (iii) 4/4, (iv) 2/2

Mark awarded = (b) 1/2

Mark awarded = (c) 1/1

Total marks awarded = 10 out of 12

Example candidate response – middle	Examiner comments
<p>1 (a) Magnesium nitrate, $Mg(NO_3)_2$, is very soluble in water. When a hot saturated solution of magnesium nitrate is cooled, crystals of the hydrate, $Mg(NO_3)_2 \cdot 6H_2O$, are formed. In the crystals, six water molecules bond to each Mg^{2+} ion, and some of these water molecules are also bonded to the nitrate ions.</p> <p>(i) Suggest the type of bonding that occurs between. 1</p> <p>H_2O and Mg^{2+}, ionic bonding Co-ordinate bonding H_2O and NO_3^-, Covalent bonding [2]</p> <p>(ii) Describe the arrangement of the water molecules around the Mg^{2+} ion. 2</p> <p>..... Hexagonal [1]</p> <p>(iii) Describe in detail what you would observe when crystals of $Mg(NO_3)_2 \cdot 6H_2O$ are heated in a boiling tube, gently at first and then more strongly. Write equations for any reactions that occur. 3</p> <p>At first, when $Mg(NO_3)_2 \cdot 6H_2O$ are heated, steam would be seen on the inside of the boiling tube as the crystals are dehydrated. 3</p> <p>$Mg(NO_3)_2 \cdot 6H_2O \rightleftharpoons Mg(NO_3)_2 + 6H_2O(g)$</p> <p>when heated strongly, a brown gas is seen on the inside of the tube and being emitted, this is the Nitrogen gas which has a strong smell. $Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \frac{1}{2} O_2$</p> <p>$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$ [4]</p> <p>(iv) Calculate the percentage loss in mass when $Mg(NO_3)_2 \cdot 6H_2O$ is heated strongly to constant mass. 4</p> <p>$A = \frac{m}{m-m}$</p> <p>$m = 108 \text{ g of } H_2O$ $(NO_3)_2 = 124 \text{ g}$ $Mg = 24 \text{ g}$ <u>256.</u></p> <p>$\begin{array}{r} 256 \\ - 108 \\ \hline 148 \\ - 92 \\ \hline 56 \\ \hline 40 \end{array}$</p> <p>$\begin{array}{r} 256 \\ - 40 \\ \hline 216 \rightarrow \text{lost} \end{array}$</p> <p>$\therefore \frac{216}{256} \times 100 = \frac{89.875}{5} = 84\%$</p> <p>percentage loss = 84.875 % [2]</p>	<p>1 The first answer is correct, but the second is incorrect. Hydrogen bond or ion-dipole forces are required.</p> <p>Mark for (a) (i) = 1/2</p> <p>2 'Hexagonal' is not sufficient here: 'octahedral' is required.</p> <p>Mark for (a) (ii) = 0/1</p> <p>3 Two correct balanced equations are shown for the dehydration and subsequent decomposition of magnesium nitrate. Only two viable observations are given (steam and brown gas). Examiners ignored the comment about 'nitrogen gas' as the identities of the product are marked in the equations.</p> <p>Mark for (a) (iii) = 3/4</p> <p>4 Two marks awarded. Examiners credited 84.325 shown in the working and ignored the rounding to two significant figures. Candidates should give their answers to three significant figures unless instructed otherwise.</p> <p>Mark for (a) (iv) = 2/2</p>

Example candidate response – middle, continued	Examiner comments
<p>(b) Explain why the Group 2 nitrates become <u>more</u> stable to heat <u>down</u> the group.</p> <p><i>As the lattice energy increases down the group, Group 2 nitrates become more stable to heat and don't decompose easily.</i> 5</p> <p>.....</p> <p>.....</p> <p>..... [2]</p>	<p>5 There is no comment about the increasing cation size or that the anion becomes less polarised down the group.</p> <p>Mark for (b) = 0/2</p>
<p>(c) Magnesium nitrate and silver nitrate, AgNO₃, decompose on heating to produce the same gases. Silver nitrate also produces silver metal during decomposition.</p> <p>Write an equation for the decomposition of AgNO₃.</p> <p><i>2 AgNO₃ $\xrightarrow{\Delta}$ 2 Ag + 2 NO₂ + O₂</i> 6</p> <p>..... [1]</p> <p>[Total: 12]</p>	<p>6 A correct balanced equation. Examiners ignored the use of the reversible sign in the equation.</p> <p>Mark for (c) = 1/1</p> <p>Total marks awarded = 7 out of 12</p>

How the candidate could have improved their answer

(a) (i) The candidate should have given the type of bonding between H₂O and NO₃⁻ as hydrogen bonding or ion-dipole forces.

(a) (ii) 'Octahedral' was the only valid answer here.

(a) (iii) The candidate could have made more viable observations here: (on gentle heating) the solid turns to liquid, a white solid is formed, and (on strong heating) a gas is formed that relights a glowing splint.

(b) The candidate needed to relate the increase in thermal stability of the Group II nitrates to the increasing cation size and the anion becoming less polarised down the group.

Mark awarded = (a) (i) 1/2, (ii) 0/1, (iii) 3/4, (iv) 2/2

Mark awarded = (b) 0/2

Mark awarded = (c) 1/1

Total marks awarded = 7 out of 12

Example candidate response – low	Examiner comments
<p>1 (a) Magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, is very soluble in water. When a hot saturated solution of magnesium nitrate is cooled, crystals of the hydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, are formed. In the crystals, six water molecules bond to each Mg^{2+} ion, and some of these water molecules are also bonded to the nitrate ions.</p> <p>(i) Suggest the type of bonding that occurs between H_2O and Mg^{2+}, <u>dative set covalent bond</u> 1 H_2O and NO_3^- <u>hydrogen bond</u> [2]</p> <p>(ii) Describe the arrangement of the water molecules around the Mg^{2+} ion. <u>In octahedral shape.</u> 2 [1]</p> <p>(iii) Describe in detail what you would observe when crystals of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are heated in a boiling tube, gently at first and then more strongly. Write equations for any reactions that occur. <u>When $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is heated, at first the water will evaporate leaving $\text{Mg}(\text{NO}_3)_2$ in crystals form. Heating strongly will give a colour that at the end the H_2O is evaporated.</u> 3 <u>$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$.</u> [4]</p> <p>(iv) Calculate the percentage loss in mass when $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is heated strongly to constant mass. <u>$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{NO}_3^- + 6\text{H}_2\text{O}$</u> 4</p>	<p>1 Both answers are correct. 'Ion-dipole forces' would be a valid alternative to both of these answers. Mark for (a) (i) = 2/2</p> <p>2 Correct answer given. Mark for (a) (ii) = 1/1</p> <p>3 One correct equation for the dehydration of the salt, but both equations are required for the mark. Only one viable observation ('water will evaporate') is given. The candidate does not describe the decomposition of $\text{Mg}(\text{NO}_3)_2$. Mark for (a) (iii) = 1/4</p> <p>4 The calculation has not been attempted. The correct answer, 84.3%, without working, would have been awarded full marks. Mark for (a) (iv) = 0/2</p>
<p>(b) Explain why the Group 2 nitrates become more stable to heat down the group. <u>As we go down the group the ionic size increase as the valence shell increases so there is less attraction. As a result polarisation decreases as lattice energy and hydration energy decrease.</u> 5 [2]</p> <p>(c) Magnesium nitrate and silver nitrate, AgNO_3, decompose on heating to produce the same gases. Silver nitrate also produces silver metal during decomposition. Write an equation for the decomposition of AgNO_3. <u>$\text{AgNO}_3 \rightarrow \text{Ag} + \text{NO}_2$</u> 6 [1]</p> <p>[Total: 12]</p>	<p>5 A mark is awarded for the ionic size increasing going down the group. The second mark is not awarded, as there is no mention of less distortion (less polarisation) of the anion by the cation down the group. Mark for (b) = 1/2</p> <p>6 The candidate does not identify the gases produced, oxygen and nitrogen dioxide, from the nitrate ion. Mark for (c) = 0/1</p> <p>Total marks awarded = 5 out of 12</p>

How the candidate could have improved their answer

(a) (iii) The candidate should have given the equation for the decomposition of $\text{Mg}(\text{NO}_3)_2$, which results in $\text{MgO} + 2\text{NO}_2 + \frac{1}{2} \text{O}_2$. More viable observations should have been included: a brown gas is seen and a white solid remains at the end of the experiment.

(a) (iv) The candidate needed to recall that MgO is produced during the decomposition of $\text{Mg}(\text{NO}_3)_2$ in (a) (iii) and use this information in their calculation, showing clear working, to give 84.3%.

(b) The second mark could have been gained if the candidate had stated that there is less distortion (less polarisation) of the anion by the cation down the group.

(c) A balanced equation for the decomposition of copper(II) nitrate should have been given.

Mark awarded = **(a) (i) 2/2, (ii) 1/1, (iii) 1/4, (iv) 0/2**

Mark awarded = **(b) 1/2**

Mark awarded = **(c) 0/1**

Total marks awarded = 5 out of 12

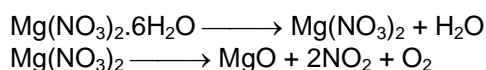
Common mistakes candidates made in this question

(a) (i) Common errors for H_2O and Mg^{2+} were covalent and ionic. More candidates were awarded the mark for the second part of the question (hydrogen bonding) than the first.

(a) (ii) Many candidates just wrote 'hexagonal'.

(a) (iii) Many candidates omitted viable observations in the decomposition and dehydration of magnesium nitrate.

There were a number of unbalanced equations. For example, equations where the water was omitted or not balanced:



Some candidates thought the decomposition product was $\text{Mg}(\text{OH})_2$.

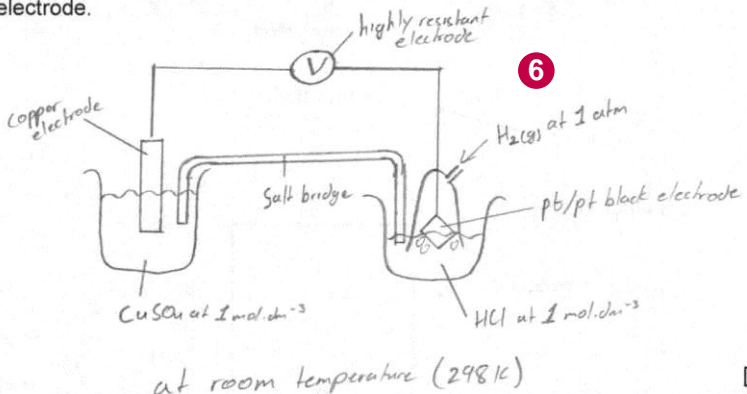
(a) (iv) Common errors were 15.7% (% of mass remaining), 42.1% (thought that the final solid was $\text{Mg}(\text{NO}_3)_2$), and 72.8 (M_r of 148.3 for $\text{Mg}(\text{NO}_3)_2$ used instead of 256.3).

(b) Some candidates answered in terms of atomic, rather than cationic, size and did not clearly specify that the anion was undergoing polarisation.

(c) Some candidates did not read the question carefully and gave Ag_2O as the product.

Question 2

Example candidate response – high	Examiner comments															
<p>2 Ethanoic acid is a weak acid.</p> <p>(a) Explain what is meant by the term <i>weak acid</i>.</p> <p><i>Is an acid that does not dissociate completely in a solution.</i> 1</p> <p>..... [1]</p> <p>(b) The pK_a values of four acids are listed below.</p> <table border="1" data-bbox="418 600 804 779"> <thead> <tr> <th>acid</th> <th>structural formula</th> <th>pK_a</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>CH_3CO_2H</td> <td>4.8</td> </tr> <tr> <td>2</td> <td>$CH_3CH_2CO_2H$</td> <td>4.9</td> </tr> <tr> <td>3</td> <td>$CH_3CHClCO_2H$</td> <td>2.8</td> </tr> <tr> <td>4</td> <td>$CH_2ClCH_2CO_2H$</td> <td>4.0</td> </tr> </tbody> </table> <p>(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a.</p> <p><i>$pK_a = -\log_{10}(K_a)$.</i> 2</p> <p>..... [1]</p> <p>(ii) With reference to acidity, explain the difference in pK_a values between</p> <ul style="list-style-type: none"> acid 1 and acid 2, 3 <i>acid 2 is less acidic than acid 1 because of its more powerful inductive effect. Therefore its K_a is lower and its pK_a is greater.</i> acid 2 and acid 3, 4 <i>acid 2 is less acidic than acid 3 because the chlorine atom is electron withdrawing and weakens the O-H bond increasing K_a and decreasing pK_a.</i> acid 3 and acid 4, 5 <i>acid 3 is more acidic than acid 4, because the chlorine atom is closer to the carboxylic acid group and therefore has higher K_a and lower pK_a.</i> <p>..... [3]</p>	acid	structural formula	pK_a	1	CH_3CO_2H	4.8	2	$CH_3CH_2CO_2H$	4.9	3	$CH_3CHClCO_2H$	2.8	4	$CH_2ClCH_2CO_2H$	4.0	<p>1 The correct definition is given.</p> <p>Mark for (a) = 1/1</p> <p>2 The correct relationship is shown. Candidates do not need to indicate that the logarithm is base 10 so $pK_a = -\log K_a$ would be credited.</p> <p>Mark for (b) (i) = 1/1</p> <p>3 The correct trend in acidity is given without an explanation. Candidates were expected to state that acid 2 is less acidic due to the presence of a larger electron-donating (alkyl/R) group.</p> <p>4 An excellent answer. Candidates did not need to mention that the presence of the Cl electron-withdrawing weakens the O–H bond.</p> <p>5 The correct answer is given. The candidate could have extended their answer to state this weakens the O–H bond making it easier for the acid to dissociate.</p> <p>Mark for (b) (ii) = 2/3</p>
acid	structural formula	pK_a														
1	CH_3CO_2H	4.8														
2	$CH_3CH_2CO_2H$	4.9														
3	$CH_3CHClCO_2H$	2.8														
4	$CH_2ClCH_2CO_2H$	4.0														

Example candidate response – high, continued	Examiner comments
<p>(c) (i) Draw a fully labelled diagram of the equipment needed to measure the voltage of an electrochemical cell consisting of the standard hydrogen electrode and the standard Cu/Cu²⁺ electrode.</p>  <p>(ii) For the cell drawn in (i), calculate the E_{cell}° and state which electrode is positive.</p> $\text{Cu}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Cu} \quad E^{\circ} = +0.34 \text{ V}$ $\text{H}_2 \rightleftharpoons 2\text{H}^{+} + 2\text{e}^{-} \quad E = 0.00 \text{ V}$ <p>$E_{\text{cell}}^{\circ} = \dots + 0.34 \dots$ identity of the positive electrode \dots Copper electrode \dots [1]</p>	<p>6 Full marks for a correct, fully labelled diagram. Examiners ignored the label 'highly resistant electrode' and credited 'V' for voltmeter and salt bridge for the first mark. Cu²⁺(aq) was accepted as an alternative for CuSO₄ for the second mark. Likewise, H⁺(aq) for HCl for the third mark. Pt alone + 1 atm is acceptable for the fourth mark.</p> <p>Mark for (c) (i) = 4/4</p> <p>7 A correct answer.</p> <p>Mark for (c) (ii) = 1/1</p>
<p>(d) A monobasic acid, D, has $K_{\text{a}} = 1.23 \times 10^{-5} \text{ mol dm}^{-3}$.</p> <p>(i) Calculate the pH of a 0.100 mol dm⁻³ solution of D.</p> $K_{\text{a}} = \frac{[\text{H}^{+}]^2}{[\text{D}]}, \quad [\text{H}^{+}] = \sqrt{[\text{D}] \times K_{\text{a}}}$ $= \sqrt{(0.1)(1.23 \times 10^{-5})}$ $= 1.11 \times 10^{-3}$ $\text{pH} = -\log_{10}([\text{H}^{+}])$ $= -\log_{10}(1.11 \times 10^{-3})$ $= 2.95$ <p>pH = $\dots 2.95 \dots$ [2]</p> <p>(ii) An electrochemical cell similar to the one you have drawn in (c)(i) was set up using a 0.100 mol dm⁻³ solution of D in the hydrogen electrode instead of the standard solution.</p> <p>Use the data and the Nernst equation, $E = E^{\circ} + 0.059 \log [\text{H}^{+}(\text{aq})]$, to calculate the new E_{cell} in this experiment.</p> $E_{\text{cell}} = E_{\text{reduced}}^{\circ} - E_{\text{oxidised}}^{\circ}$ $E_{\text{cell}} = 0.34 - (0 + 0.059 \log(1.11 \times 10^{-3}))$ $= 0.34 - (-0.17) = 0.51 \text{ V}$ <p>$E_{\text{cell}} = \dots 0.51 \dots \text{ V}$ [2]</p> <p>[Total: 14]</p>	<p>8 Clear working with the correct answer given. A minimum of two significant figures is required here.</p> <p>Mark for (d) (i) = 2/2</p> <p>9 The candidate uses the Nernst equation correctly to give the correct answer. Clear working given.</p> <p>Mark for (d) (ii) = 2/2</p>
<p>[Total: 14]</p>	<p>Total marks awarded = 13 out of 14</p>

How the candidate could have improved their answer

(b) (ii) The candidate should have stated that acid 2 is less acidic due to the presence of a larger electron-donating (alkyl/R) group. This answer could have been extended to mention that this will strengthen the O–H bond in acid 2. This means the O–H bond in acid 2 is more difficult to dissociate.

In the comparison between acid 3 and acid 4, the candidate could have extended their answer and stated that this weakens the O–H bond in acid 3 making it easier for the acid to dissociate.

Mark awarded = **(a) 1/1**

Mark awarded = **(b) (i) 1/1, (ii) 2/3**

Mark awarded = **(c) (i) 4/4, (ii) 1/1**

Mark awarded = **(d) (i) 2/2, (ii) 2/2**

Total marks awarded = 13 out of 14

Example candidate response – middle

Examiner comments

2 Ethanoic acid is a weak acid.

(a) Explain what is meant by the term *weak acid*:

Acid which dissociates partially in a solution to form a low concentration of H^+ ion. 1 [1]

1 A correct definition.

Mark for (a) = 1/1

(b) The pK_a values of four acids are listed below.

acid	structural formula	pK_a
1	CH_3CO_2H	4.8
2	$CH_3CH_2CO_2H$	4.9
→ 3	$CH_3CHClCO_2H$	2.8
4	$CH_2ClCH_2CO_2H$	4.0

← more acidic

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a .

$pK_a = -\lg(K_a)$. $-\log_{10} K_a$. 2 [1]

2 A correct answer.

Mark for (b) (i) = 1/1

(ii) With reference to acidity, explain the difference in pK_a values between

- acid 1 and acid 2,

3 Ethyl groups of acid 2 is more electron releasing than methyl group of acid 1. Bonding between $CH_3CH_2CO_2^-$ and H^+ is stronger and so, acid 2 dissociates less extensively than acid 1.

- acid 2 and acid 3,

4 Acid 3 has an electronegative atom chlorine which is electron withdrawing, stabilizing the anion of acid 3. Acid 3 ionizes more extensively than acid 2.

- acid 3 and acid 4.

5 The position of chlorine atom in acid 3 is at carbon atom adjacent to CO_2^- group while for acid 4, the chlorine atom is further from CO_2^- group. Anion of acid 3 is more stable than that of acid 4. [3]

3 A correct answer.

Examiners allowed 'dissociates less extensively' for 'less acidic'.

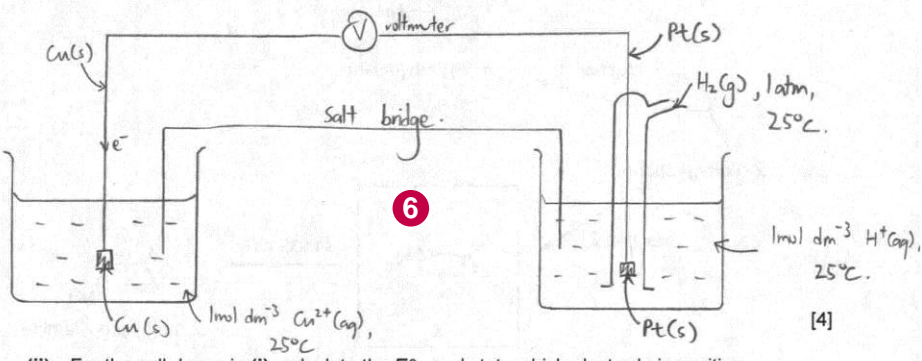
4 A correct answer.

Examiners allowed 'ionises more extensively' for 'more acidic'.

5 The candidate does

not link the relative acidity of the acids to their correct reasoning for why acid 3 is more acidic than acid 4. Examiners ruled that 'the anion is more stable' was not sufficient for 'more acidic' here.

Mark for (b) (ii) = 2/3

Example candidate response – middle, continued	Examiner comments
<p>(c) (i) Draw a fully labelled diagram of the equipment needed to measure the voltage of an electrochemical cell consisting of the standard hydrogen electrode and the standard Cu/Cu²⁺ electrode.</p>  <p>(ii) For the cell drawn in (i), calculate the E_{cell}° and state which electrode is positive.</p> <p style="text-align: center;">7</p> <p>$E_{\text{cell}}^{\circ} = \dots\dots\dots + 0.34 \text{ V} \dots\dots\dots$ identity of the positive electrode $\dots\dots\dots$ Platinum (hydrogen electrode) $\dots\dots\dots$ [1]</p> <p>(d) A monobasic acid, D, has $K_a = 1.23 \times 10^{-5} \text{ mol dm}^{-3}$.</p> <p>(i) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of D.</p> $[\text{H}^+] = \sqrt{(0.1)(1.23 \times 10^{-5})} = 1.109 \times 10^{-3} \text{ mol dm}^{-3}$ $\therefore \text{pH} = -\lg(1.109 \times 10^{-3}) = 2.96$ <p style="text-align: right;">pH = $\dots\dots\dots 2.96 \dots\dots\dots$ [2]</p> <p>(ii) An electrochemical cell similar to the one you have drawn in (c)(i) was set up using a $0.100 \text{ mol dm}^{-3}$ solution of D in the hydrogen electrode instead of the standard solution.</p> <p>Use the data and the Nernst equation, $E = E^{\circ} + 0.059 \log[\text{H}^+(\text{aq})]$, to calculate the new E_{cell} in this experiment.</p> $E = 0.34 + 0.059 \lg(1.109 \times 10^{-3})$ $= 0.166 \text{ V}$ <p style="text-align: right;">$E_{\text{cell}} = \dots\dots\dots 0.166 \dots\dots\dots \text{ V}$ [2]</p> <p style="text-align: right;">[Total: 14]</p>	<p>6 An excellent clear, labelled diagram. For marking points two and three, Cu²⁺(aq) is an alternative to CuSO₄ and H⁺ to HCl(aq) here.</p> <p>Mark for (c) (i) = 4/4</p> <p>7 The correct value for the cell potential, but the identity of the positive electrode should be copper.</p> <p>Mark for (c) (ii) = 0/1</p> <p>8 Clear working shown and the correct answer is given.</p> <p>Mark for (d) = 2/2</p> <p>9 One mark awarded. There is a sign error in the calculation. It should be: $E_{\text{cell}} = E_{\text{red}} - E_{\text{oxid}}$ $E_{\text{cell}} = 0.34 - (-0.17) = +0.51 \text{ V}.$</p> <p>Mark for (d) (ii) = 1/2</p> <p>Total marks awarded = 11 out of 14</p>

How the candidate could have improved their answer

(b) (ii) This candidate should have stated that acid 3 is more acidic than acid 4 (the consequence of Cl atom being closer to the -CO₂H group in acid 3).

(c) (ii) The copper electrode is positive here.

(d) (ii) The correct answer is +0.51 V. This is calculated as shown:

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{oxid}}$$

$$E_{\text{cell}} = E_{\text{red}} - 0.059 \log_{10}(1.11 \times 10^{-3})$$

$$E_{\text{cell}} = 0.34 - (-0.17) = +0.51 \text{ V}$$

Mark awarded = (a) 1/1

Mark awarded = (b) (i) 1/1, (ii) 2/3

Mark awarded = (c) (i) 4/4, (ii) 0/1

Mark awarded = (d) (i) 2/2, (ii) 1/2

Total marks awarded = 11 out of 14

Example candidate response – low

Examiner comments

2 Ethanoic acid is a weak acid.

(a) Explain what is meant by the term weak acid.

~~Weak acid produces the products less H⁺ ions~~ **1**
 Weak acid dissociates to produce ~~less~~ H⁺ ions and doesn't ionise completely. [1]

(b) The pK_a values of four acids are listed below.

acid	structural formula	pK _a
1	CH ₃ CO ₂ H	4.8
2	CH ₃ CH ₂ CO ₂ H	4.9
3	CH ₃ CHClCO ₂ H	2.8
4	CH ₂ ClCH ₂ CO ₂ H	4.0

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

$pK_a = -\log_{10} K_a$ **2** [1]

(ii) With reference to acidity, explain the difference in pK_a values between

- acid 1 and acid 2,

Acid 2 is a ^{slightly} weak acid compared to acid 1

as the Acid's 2 pKa value is higher than that of Acid 1
 as ethyl group is electron withdrawing group

- acid 2 and acid 3,

3 higher the pKa value, lesser the acidity. Therefore, Acid 3 is a stronger acid than Acid 2 due to the ethyl group present in Acid 2 and Cl in Acid 3 which is electron donating group -

- acid 3 and acid 4.

Acid 3 is ~~the~~ acidic than Acid 4 as ethene is present in & Acid 3. [3]

1 A correct definition.

Mark for (a) = 1/1

2 The correct answer.

Mark for (b) (i) = 1/1

3 The candidate is awarded credit for the correct trend in acidity for the three bullet points, but has given incorrect reasoning. Acid 1 is more acidic than acid 2 due to the smaller electron donating alkyl group. Acid 3 is more acidic than acid 2 due to the presence of the electron-withdrawing Cl group. Acid 3 is more acidic than acid 4 since the Cl group is closer to the CO₂H group.

Mark for (b) (ii) = 1/3

Example candidate response – low, continued	Examiner comments
<p>(c) (i) Draw a fully labelled diagram of the equipment needed to measure the voltage of an electrochemical cell consisting of the standard hydrogen electrode and the standard Cu/Cu²⁺ electrode.</p> <p style="text-align: right;">[4]</p>	<p>4 Two marks are awarded for marking points three and four. The presence of the 'cell' in the circuit is a contradiction so negates the first marking point. For the second marking point, the solution in the copper half-cell should have been identified as Cu²⁺ or CuSO₄.</p> <p>Mark for (c) (i) = 2/4</p>
<p>(ii) For the cell drawn in (i), calculate the E_{cell}^o and state which electrode is positive.</p> <p>E_{cell}^o = 0.34 + 0.34 identity of the positive electrode <u>copper</u> [1]</p>	<p>5 The correct answer is given.</p> <p>Mark for (c) (ii) = 1/1</p>
<p>(d) A monobasic acid, D, has K_a = 1.23 × 10⁻⁵ mol dm⁻³.</p> <p>(i) Calculate the pH of a 0.100 mol dm⁻³ solution of D.</p> <p><i>Handwritten work:</i> $K_a = 1.23 \times 10^{-5}$ $pK_a = -\log_{10} 1.23 \times 10^{-5} = -8.99 \times 10^{-7}$ $pH = pK_a + \log_{10} \left[\frac{\text{salt}}{\text{acid}} \right]$ $pH = -\log_{10} [H^+]$ $pH = \dots \dots \dots$ [2]</p> <p>(ii) An electrochemical cell similar to the one you have drawn in (c)(i) was set up using a 0.100 mol dm⁻³ solution of D in the hydrogen electrode instead of the standard solution.</p> <p>Use the data and the Nernst equation, $E = E^o + 0.059 \log [H^+(aq)]$, to calculate the new E_{cell} in this experiment.</p>	<p>6 An incorrect answer. D is a weak acid (very small K_a) so the pH is calculated as shown in the mark scheme. The correct answer, pH = 2.96, should be given to a minimum of two significant figures.</p> <p>Mark for (d) = 0/2</p>
<p><i>Handwritten work:</i> $E = 0.34 + 0.059 \log \sqrt{0.100}$ $= 0.3105$ E_{cell} = <u>0.3105</u> V [2]</p> <p style="text-align: right;">[Total: 14]</p>	<p>7 An incorrect answer. The candidate should have used 1.11×10^{-3} for the [H⁺] and the Nernst equation is not used correctly. The correct answer is +0.51 V.</p> <p>Mark for (a) (i) = 0/2</p> <p>Total marks awarded = 6 out of 14</p>

How the candidate could have improved their answer

(b) (ii) The candidate should have explained the difference in acidity as shown:

Acid 1 is more acidic than acid 2 due to the smaller electron donating alkyl group.

Acid 3 is more acidic than acid 2 due to the presence of the electron-withdrawing Cl group.

Acid 3 is more acidic than acid 4 since the Cl group is closer to the CO₂H group.

(c) (i) The candidate should have had no cell present in their circuit and the solution in the copper half-cell should have been identified as Cu²⁺ or CuSO₄.

(d) (i) The correct answer is 2.96. This is calculated as shown:

$$[\text{H}^+] = \sqrt{K_a \cdot c} = \sqrt{(1.23 \times 10^{-5} \times 0.1)} = 1.11 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = 2.96$$

(d) (ii) The candidate should have used 1.11×10^{-3} for the [H⁺] and the Nernst equation is not used correctly. The correct answer is +0.51 V. This is calculated as shown:

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{oxid}}$$

$$E_{\text{cell}} = E_{\text{red}} - 0.059 \log_{10}(1.11 \times 10^{-3})$$

$$E_{\text{cell}} = 0.34 - (-0.17) = +0.51 \text{ V}$$

Mark awarded = **(a) 1/1**

Mark awarded = **(b) (i) 1/1, (ii) 1/3**

Mark awarded = **(c) (i) 2/4, (ii) 1/1**

Mark awarded = **(d) (i) 0/2, (ii) 0/2**

Total marks awarded = 6 out of 14

Common mistakes candidates made in this question

(a) A few candidates incorrectly described a weak acid in terms of dissolving, that it is a substance that was partially dissolved.

(b) (i) A common error was stating that $\text{p}K_a$ had an inverse proportional to K_a .

(b) (ii) A number of candidates did not comment on the acidity of the two acids. For marking point one, many candidates did not compare the relative electron-donating ability of alkyl groups. For marking points two and three, some candidates said the Cl group acted as an electron-donating group. Many candidates' explanations lacked clarity.

(c) (i) Some common errors were:

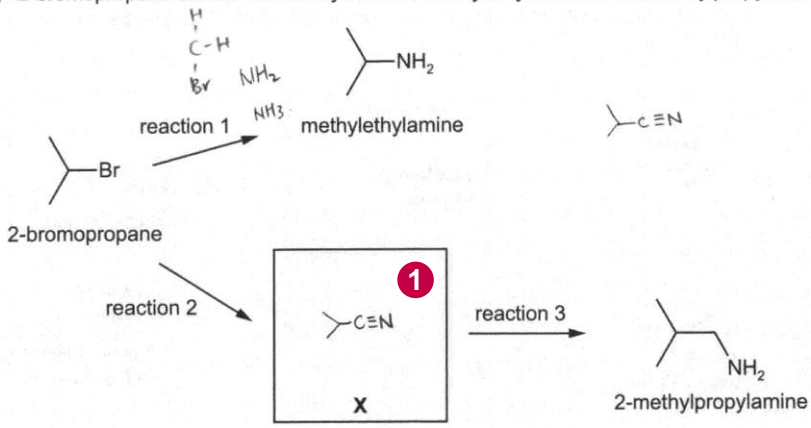
- the inclusion of a battery in the external circuit
- omitting the salt bridge from their diagram
- labelling the solutions as Cu²⁺/Cu or H₂/H⁺ instead of Cu²⁺ and H⁺
- omitting a standard condition, 1 atm or 1 mol dm⁻³.

(c) (ii) Some candidates identified the hydrogen half-cell as the positive electrode.

(d) (i) A common error was 5.91 (no square root taken).

(d) (ii) The electrode potential and the cell potential were confused. Common errors seen were 0.40, 0.17 and -0.17 (worth 1 mark) and 0.28 (no marks).

Question 3

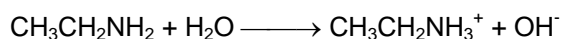
Example candidate response – high	Examiner comments
<p>3 (a) 2-bromopropane can be used to synthesise methylethylamine and 2-methylpropylamine.</p>  <p>(i) Draw the structure of the intermediate X in the box above. $\begin{array}{c} \\ -\text{C}-\text{NH}_2 \\ \\ \text{NH} \end{array}$ [1]</p> <p>(ii) Suggest reagents and conditions for</p> <ul style="list-style-type: none"> • reaction 1, <u>alcoholic NH_3</u>. 2 • reaction 2, <u>alcoholic KCN, reflux</u> • reaction 3, <u>LiAlH_4</u> [3] <p>(b) (i) Write an equation showing why aqueous solutions of ethylamine are alkaline. <u>$\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{NH}_3^+$</u> 3 [1]</p> <p>(ii) Compare the basicities of ethylamine and ammonia. Explain your answer. <u>Ethylamine is more basic than ammonia. Ethylamine contains ethyl group, which is an electron donating group. Lone pair on N is more readily available to H^+ ion compared to ammonia.</u> 4 [2]</p>	<p>1 A correct answer. Mark for (a) (i) = 1/1</p> <p>2 Two marks for reactions 2 and 3. The candidate omits the need to heat in a sealed tube for reaction 1. Mark for (a) (ii) = 2/3</p> <p>3 An incorrect answer. This shows ethylamine acting as a base, rather than why aqueous ethylamine solutions are alkaline (an equation releasing hydroxide ions). Mark for (b) (i) = 0/1</p> <p>4 A correct answer. Mark for (b) (ii) = 2/2</p>

Example candidate response – high, continued	Examiner comments
<p>(c) Solutions containing mixtures of amines and their salts are buffer solutions.</p> <p>(i) Explain what is meant by the term <i>buffer solution</i>. 5</p> <p>A solution consists of positive and negatively charged ions which are readily to take up & H⁺ ions and OH⁻ ions to resist small change in pH when a small amount of H⁺ ions and OH⁻ ions are added to the solution. [1]</p> <p>(ii) Write two equations to show how a solution containing a mixture of CH₃NH₂ and CH₃NH₃⁺Cl⁻ acts as a buffer. 6</p> <p>$\text{CH}_3\text{NH}_3^+ + \text{OH}^- \rightarrow \text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$</p> <p>$\text{CH}_3\text{NH}_2 + \text{H}^+ \rightarrow \text{CH}_3\text{NH}_3^+$</p> <p style="text-align: right;">[2]</p> <p style="text-align: right;">[Total: 10]</p>	<p>5 A correct answer.</p> <p>Mark for (c) (i) = 1/1</p> <p>6 A correct answer. The equations can be ionic or not ionic.</p> <p>Mark for (c) (ii) = 2/2</p> <p>Total marks awarded = 8 out of 10</p>

How the candidate could have improved their answer

(a) (ii) The conditions for reaction 1 should be 'alcoholic NH₃ heated in a sealed tube'.

(b) (i) The candidate should have included an equation showing how aqueous ethylamine solutions are alkaline (an equation releasing hydroxide ions):

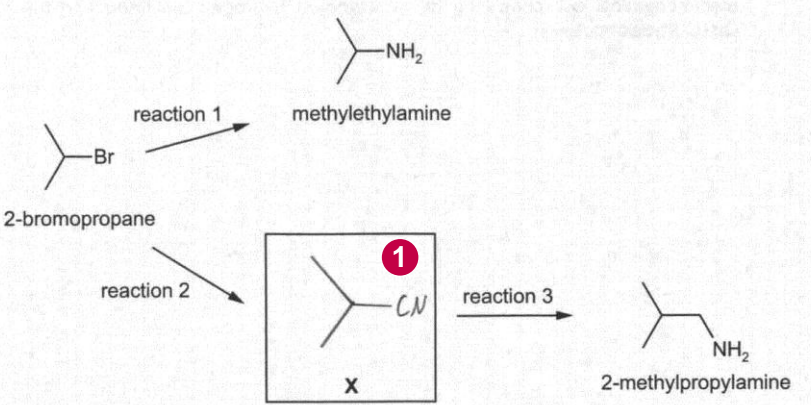


Mark awarded = (a) (i) 1/1, (ii) 2/3

Mark awarded = (b) (i) 0/1, (ii) 2/2

Mark awarded = (c) (i) 1/1, (ii) 2/2

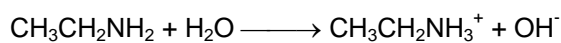
Total marks awarded = 8 out of 10

Example candidate response – middle	Examiner comments
<p>3 (a) 2-bromopropane can be used to synthesise methylethylamine and 2-methylpropylamine.</p>  <p>(i) Draw the structure of the intermediate X in the box above. [1]</p> <p>(ii) Suggest reagents and conditions for</p> <ul style="list-style-type: none"> reaction 1, <i>heat with ethanolic ammonia (NH₃(ethanol))</i>..... [1] reaction 2, <i>heat with ethanolic KCN</i>..... 2 reaction 3, <i>pass over nickel catalyst with hydrogen gas.</i>..... [3] <p>(b) (i) Write an equation showing why aqueous solutions of ethylamine are alkaline. $C_2H_5NH_2(aq) + H^+(aq) \rightleftharpoons C_2H_5NH_3^+(aq)$..... 3 [1]</p> <p>(ii) Compare the basicities of ethylamine and ammonia. Explain your answer. <i>ethylamine is more basic than ammonia, because ethyl is an electron donating group and increases the ability of nitrogen to form dative bond with proton, while hydrogen is not as strong of an electron donating group as ethyl</i>..... 4 [2]</p> <p>(c) Solutions containing mixtures of amines and their salts are buffer solutions.</p> <p>(i) Explain what is meant by the term <i>buffer solution</i>. <i>A solution that keeps pH constant when small amounts of alkalis and or acid are added.</i>..... 5 [1]</p> <p>(ii) Write two equations to show how a solution containing a mixture of CH₃NH₂ and CH₃NH₃Cl acts as a buffer. $CH_3NH_2(aq) + HCl(aq) \rightleftharpoons CH_3NH_3Cl(aq)$..... 6 $CH_3NH_3Cl(aq) + NaOH(aq) \rightleftharpoons CH_3NH_2(aq) + NaCl(aq) + H_2O(l)$..... [2]</p> <p>[Total: 10]</p>	<p>1 A correct answer. Mark for (a) (i) = 1/1</p> <p>2 Two marks for reactions 2 and 3. The candidate omits the need to heat in a sealed tube for reaction 1. Mark for (a) (ii) = 2/3</p> <p>3 Incorrect answer. This shows ethylamine acting as a base, rather than why aqueous ethylamine solutions are alkaline (an equation releasing hydroxide ions). Mark for (b) (i) = 0/1</p> <p>4 One mark is awarded for 'ethylamine being more basic due to the presence of the electron-donating ethyl group'. The candidate should also have stated that this makes the lone pair on the N more available to accept a proton. Mark for (b) (ii) = 1/2</p> <p>5 No mark, as the candidate states that a buffer solution 'keeps the pH constant'. A buffer solution minimises changes in pH when small amounts of acid and alkali are added to it. Mark for (c) (i) = 0/1</p> <p>6 Both equations are correct. Mark for (c) (ii) = 2/2</p> <p>Total marks awarded = 6 out of 10</p>

How the candidate could have improved their answer

(a) (ii) The conditions for reaction 1 should be alcoholic NH_3 heated in a sealed tube.

(b) (i) The candidate should have included an equation showing how aqueous ethylamine solutions are alkaline (an equation releasing hydroxide ions):



(b) (ii) The second mark would have been awarded if the candidate had stated that this makes the lone pair on the N (in ethylamine) more available to accept a proton.

(c) (i) A buffer solution should be described as a solution that minimises changes in pH when small amounts of acid and alkali are added to it.

Mark awarded = **(a) (i) 1/1, (ii) 2/3**

Mark awarded = **(b) (i) 0/1, (ii) 1/2**

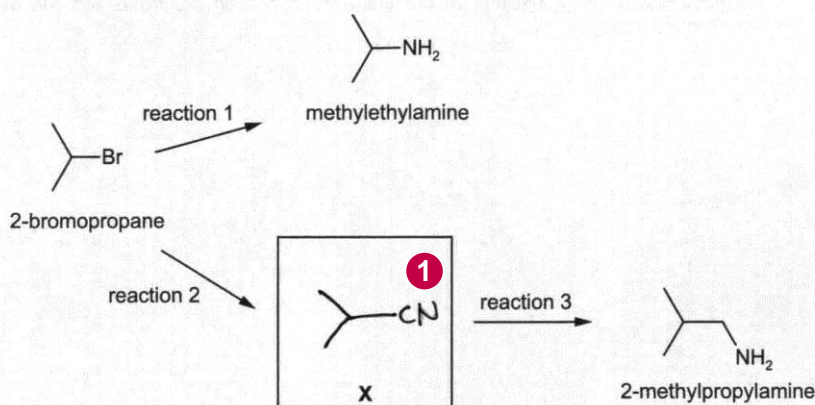
Mark awarded = **(c) (i) 0/1, (ii) 2/2**

Total marks awarded = 6 out of 10

Example candidate response – low

Examiner comments

- 3 (a) 2-bromopropane can be used to synthesise methylethylamine and 2-methylpropylamine.



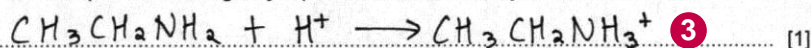
- (i) Draw the structure of the intermediate X in the box above. [1]

- (ii) Suggest reagents and conditions for

- reaction 1, Ammonia gas excess, sealed tube 2
- reaction 2, aqueous NaCN with a trace of alcohol.
- reaction 3, Sn + HCl

[3]

- (b) (i) Write an equation showing why aqueous solutions of ethylamine are alkaline.



- (ii) Compare the basicities of ethylamine and ammonia. Explain your answer.

Ethylamine is more basic as compared to ammonia because the alkyl group is electron releasing which facilitates the removal of a lone pair of electrons.

4

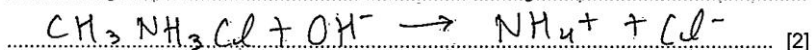
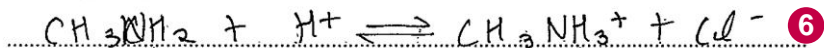
[2]

- (c) Solutions containing mixtures of amines and their salts are buffer solutions.

- (i) Explain what is meant by the term *buffer solution*. 5

A solution which resists changes in pH when small quantities of acid or alkali are added to it. [1]

- (ii) Write two equations to show how a solution containing a mixture of CH_3NH_2 and $\text{CH}_3\text{NH}_3\text{Cl}$ acts as a buffer.



[Total: 10]

- 1 Correct structure identified.

Mark for (a) (i) = 1/1

- 2 Credit is awarded for identifying the main reagent in reactions 1 and 2. The candidate omits the need to heat reactions 1 and 2. The reagents Sn/HCl were not accepted for reaction 3. LiAlH_4 or H_2/Ni catalyst was required.

Mark for (a) (ii) = 1/3

- 3 An incorrect answer. This shows ethylamine acting as a base rather than why aqueous ethylamine solutions are alkaline (an equation releasing hydroxide ions).

Mark for (b) (i) = 0/1

- 4 One mark is awarded for 'ethylamine being more basic due to the presence of the electron-releasing alkyl group'. The candidate should have stated that this makes the lone pair on the N more available to accept a proton.

Mark for (b) (ii) = 1/2

- 5 A correct answer.

Mark for (c) (i) = 1/1

- 6 Both equations are incorrect. The first equation has an extra Cl^- ion on the right. The second equation has incorrect products.

Mark for (c) (ii) = 0/2

Total marks awarded = 4 out of 10

How the candidate could have improved their answer

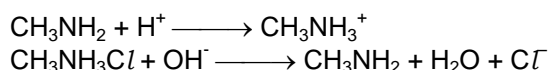
(a) (ii) The candidate omitted the need to heat for reactions 1 and 2. LiAlH_4 or H_2/Ni catalyst was required for reaction 3.

(b) (i) The candidate should have included an equation showing how aqueous ethylamine solutions are alkaline (an equation releasing hydroxide ions):



(b) (ii) The second mark could have been awarded for stating that this would make the lone pair on the N (in ethylamine) more available to accept a proton.

(c) (ii) The correct equations are shown:



Mark awarded = **(a) (i) 1/1, (ii) 1/3**

Mark awarded = **(b) (i) 0/1, (ii) 1/2**

Mark awarded = **(c) (i) 1/1, (ii) 0/2**

Total marks awarded = 4 out of 10

Common mistakes candidates made in this question

(a) (i) A few candidates included an additional CH_2 group or NO_2 group instead of CN group.

(a) (ii) Some common errors by candidates were:

- using $\text{NH}_3(\text{aq})$ instead of $\text{NH}_3(\text{alcoholic})$ in reaction 1
- omitting the need for high pressure as a condition in reaction 1
- the use of heat in reactions 1 and 2
- using HCN in reaction 2.

(b) (i) A common error was the equation $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{NH}_3^+$.

(b) (ii) Many candidates omitted sufficient detail about the lone pair on the nitrogen being more available to protonation or donation.

(c) (i) A common error was stating that a buffer solution maintains constant pH.

(c) (ii) Some candidates gave equations for CH_3NH_2 and $\text{CH}_3\text{NH}_2\text{Cl}$ ionising in water, and the formation of $\text{CH}_3\text{NH}_2\text{Cl}$ as a product in the second equation, $\text{CH}_3\text{NH}_3\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{NH}_2\text{Cl} + \text{H}_2\text{O}$.

Question 4

Example candidate response – high/middle 1	Examiner comments
<p>4 (a) There are two isomeric complexes with the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, one of which is an anti-cancer drug.</p>	
<p>(i) Draw diagrams to show the three-dimensional structures of the two isomers.</p>	
	<p>1 The correct structures of the cis- and trans-isomers are given.</p>
<p>[2]</p>	<p>Mark for (a) (i) = 2/2</p>
<p>(ii) Comment on the polarity of the two isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. Explain your answer.</p>	<p>2 An incorrect answer. Only the dipoles on the trans isomer cancel. The cis isomer is polar.</p>
<p><i>Isomers are polar. The structure is square planar. The net dipoles on both isomers cancel out. They are both non-polar.</i></p>	<p>Mark for (a) (ii) = 0/1</p>
<p>Oxaloplatin is another successful anti-cancer drug in which the stereochemistry around the platinum atom is the same as that in $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.</p>	<p>3 This answer is not sufficient for the mark. The candidate should have stated that the mirror image of this isomer is superimposable/ the same.</p>
	<p>Mark for (a) (iii) = 0/1</p>
<p>(iii) Explain why there are no isomers of oxaloplatin.</p>	<p>4 A correct answer.</p>
<p><i>No cis trans isomers can exist because the rings prevent the angles between the two ends of the rings changing. The need for e.g. cannot be across each other.</i></p>	<p>Mark for (b) (i) = 1/1</p>
<p>(b) Only one structure of the complex $[\text{Ni}(\text{R}_3\text{P})_2\text{Cl}_2]$ is known. ($\text{R} = \text{CH}_3$, R_3P is a monodentate ligand)</p>	<p>5 A correct three-dimensional tetrahedral diagram.</p>
<p>(i) What does this indicate about the stereochemistry around the nickel atom?</p>	<p>Mark for (b) (ii) = 1/1</p>
<p><i>It is tetrahedral (if square planar there could be isomers).</i></p>	<p>Total marks awarded = 4 out of 6</p>
<p>(ii) Draw a three-dimensional diagram showing the structure of this complex.</p>	<p>[Total: 6]</p>
	<p>[1]</p>

How the candidate could have improved their answer

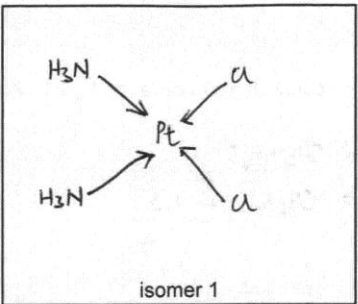
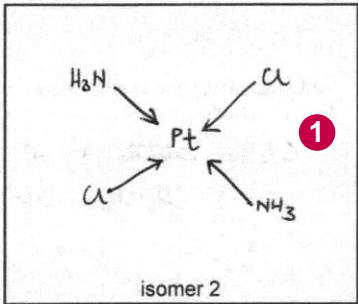
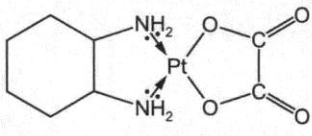
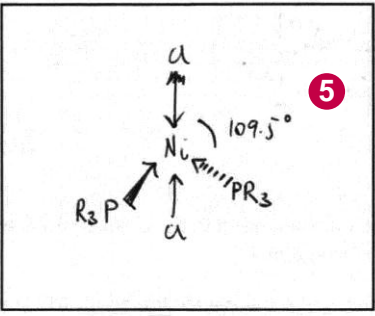
(a) (ii) The candidate should have stated that the **cis** is (more) **polar** due to both $C\delta^-$ on the same side or the **cis** is (more) **polar** as the dipoles do not cancel.

(a) (iii) The candidate should have stated that the mirror image of this isomer is the superimposable.

Mark awarded = **(a) (i) 2/2, (ii) 0/1, (iii) 0/1**

Mark awarded = **(b) (i) 1/1, (ii) 1/1**

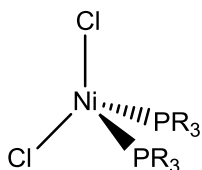
Total marks awarded = 4 out of 6

Example candidate response – high/middle 2	Examiner comments
<p>4 (a) There are two isomeric complexes with the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, one of which is an anti-cancer drug.</p> <p>(i) Draw diagrams to show the three-dimensional structures of the two isomers.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>isomer 1</p> </div> <div style="text-align: center;">  <p>isomer 2</p> </div> </div> <p style="text-align: right;">[2]</p> <p>(ii) Comment on the polarity of the two isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. Explain your answer. 2</p> <p>Isomer 1 is more polar than isomer 2 since in both of the electronegative chlorine atoms are at the same side of complex. [1]</p> <p>Oxaloplatin is another successful anti-cancer drug in which the stereochemistry around the platinum atom is the same as that in $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.</p> <div style="text-align: center;">  <p>oxaloplatin</p> </div> <p>(iii) Explain why there are no isomers of oxaloplatin. 3</p> <p>The orientation position of bonds around platinum are fixed and cannot be changed. [1]</p>	<p>1 A correct answer. Mark for (a) (i) = 2/2</p> <p>2 A correct answer. Mark for (a) (ii) = 1/1</p> <p>3 This answer is not sufficient. The required answer is that its mirror image is the same or superimposable. Mark for (a) (iii) = 0/1</p>
<p>(b) Only one structure of the complex $[\text{Ni}(\text{R}_3\text{P})_2\text{Cl}_2]$ is known. ($\text{R} = \text{CH}_3$, R_3P is a monodentate ligand)</p> <p>(i) What does this indicate about the stereochemistry around the nickel atom? 4</p> <p>It shows a tetrahedral shape and has no isomers. [1]</p> <p>(ii) Draw a three-dimensional diagram showing the structure of this complex.</p> <div style="text-align: center;">  <p>5</p> </div> <p style="text-align: right;">[1] [Total: 6]</p>	<p>4 A correct answer. Mark for (b) (i) = 1/1</p> <p>5 An incorrect 3D structure, as the two bonds outside the plane should be adjacent to one another. Mark for (b) (ii) = 0/1</p> <p>Total marks awarded = 4 out of 6</p>

How the candidate could have improved their answer

(a) (iii) The candidate should have stated that the mirror image of this isomer is the superimposable.

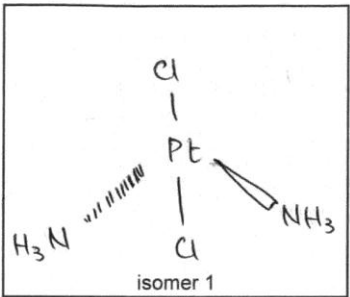
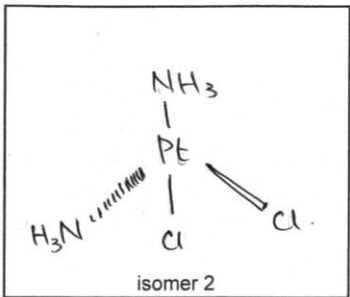
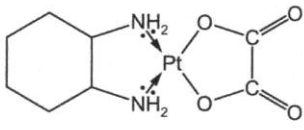
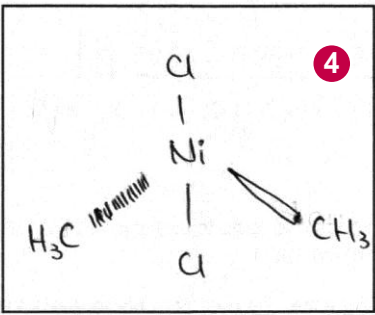
(b) (ii) A three-dimensional tetrahedral structure was required here. The two bonds outside the plane should be adjacent to one another, as shown.



Mark awarded = **(a) (i) 2/2, (ii) 1/1, (iii) 0/1**

Mark awarded = **(b) (i) 1/1, (ii) 0/1**

Total marks awarded = 4 out of 6

Example candidate response – low	Examiner comments
<p>4 (a) There are two isomeric complexes with the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, one of which is an anti-cancer drug.</p> <p>(i) Draw diagrams to show the three-dimensional structures of the two isomers.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>isomer 1</p> </div> <div style="text-align: center;">  <p>isomer 2</p> </div> </div> <p>[2]</p> <p>(ii) Comment on the polarity of the two isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. Explain your answer.</p> <p style="text-align: center;">Both have same polarity</p> <p>..... [1]</p> <p>Oxaloplatin is another successful anti-cancer drug in which the stereochemistry around the platinum atom is the same as that in $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.</p> <div style="text-align: center;">  <p>oxaloplatin</p> </div> <p>(iii) Explain why there are no isomers of oxaloplatin.</p> <p style="text-align: center;">Because there is no possibility to switch the atoms</p> <p>..... [1]</p> <p>(b) Only one structure of the complex $[\text{Ni}(\text{R}_3\text{P})_2\text{Cl}_2]$ is known. ($\text{R} = \text{CH}_3$, R_3P is a monodentate ligand)</p> <p>(i) What does this indicate about the stereochemistry around the nickel atom?</p> <p style="text-align: center;">It will either have a trigonal a a planar shape.</p> <p>..... [1]</p> <p>(ii) Draw a three-dimensional diagram showing the structure of this complex.</p> <div style="text-align: center;">  <p>4</p> </div> <p>[1]</p> <p>[Total: 6]</p>	<p>1 The diagrams in (i) are incorrect and in (ii) the candidate gives an incorrect answer. The candidate could have received an error carried forward mark from (a) (i) if they had added 'as the dipoles do not cancel'.</p> <p>Mark for (a) (i) = 0/2</p> <p>Mark for (a) (ii) = 0/1</p> <p>2 This answer is not sufficient for the mark. The required answer is that its mirror image is the same or superimposable.</p> <p>Mark for (a) (iii) = 0/1</p> <p>3 'Tetrahedral' is the answer required.</p> <p>Mark for (b) (i) = 0/1</p> <p>4 An incorrect 3D structure, as the two bonds outside the plane should be adjacent to one another.</p> <p>Mark for (b) (ii) = 0/1</p> <p>Total marks awarded = 0 out of 6</p>

How the candidate could have improved their answer

(a) (i) The candidate should have drawn the two different square planar isomers here. Examiners wanted candidates to label the isomers as *cis* and *trans*.

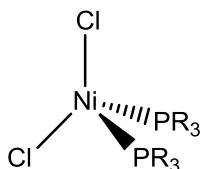


(a) (ii) The candidate should have stated that the *cis* is (more) polar due to both $\text{Cl}^{\delta-}$ on the same side or the *cis* is (more) polar as the dipoles do not cancel. The candidate could have received an error carried forward mark from two tetrahedral structures in (a) (i) if they had stated that 'both isomers have the same/similar polarity as their dipoles do not cancel'.

(a) (iii) The candidate should have stated that the mirror image of this isomer is the same or superimposable.

(b) (i) Tetrahedral is the only correct answer here.

(b) (ii) A three-dimensional tetrahedral structure was required. The two bonds outside the plane should be adjacent to one another as shown.



Mark awarded = **(a) (i) 0/2, (ii) 0/1, (iii) 0/1**

Mark awarded = **(b) (i) 0/1, (ii) 0/1**

Total marks awarded = 0 out of 6

Common mistakes candidates made in this question

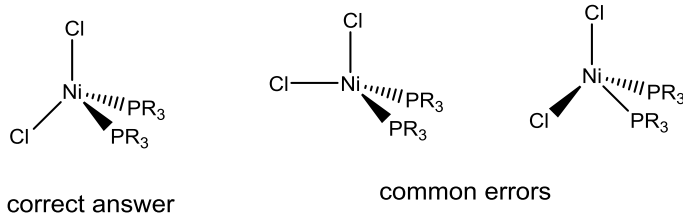
(a) (i) Some candidates identified the structure as tetrahedral.

(a) (ii) Some candidates did not comment about dipoles. Some stated that the Pt^{2+} and 2Cl^- charges cancel so no overall charge or polarity.

(a) (iii) Many candidates gave answers which were vague and not related to the structure of the complex.

(b) (i) Many candidates did not refer to any stereochemistry. A common error was 'cis-trans' or 'optical isomerism'.

(b) (ii) Many candidates gave a square planar structure. Some common errors with a tetrahedral structure are shown here:



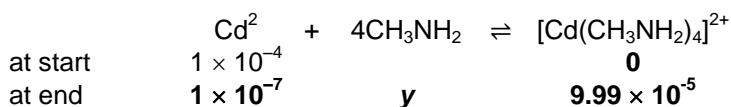
Question 5

Example candidate response – high	Examiner comments
<p>5 Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.</p> $\text{Cd}^{2+}(\text{aq}) + 4\text{CH}_3\text{NH}_2(\text{aq}) \rightleftharpoons [\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}(\text{aq}) \quad K_{\text{stab}} = 3.6 \times 10^6 \quad \text{equilibrium I}$ $\text{Cd}^{2+}(\text{aq}) + 2\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq}) \rightleftharpoons [\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}(\text{aq}) \quad K_{\text{stab}} = 4.2 \times 10^{10} \quad \text{equilibrium II}$ <p>(a) (i) Write an expression for the stability constant, K_{stab}, for equilibrium I, and state its units.</p> $K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}(\text{aq})}{[\text{CH}_3\text{NH}_2(\text{aq})]^4 [\text{Cd}^{2+}(\text{aq})]}$ <p style="text-align: right;">mol⁻⁴ dm¹² 1 units [2]</p> <p>Cadmium ions are poisonous and need to be removed from some water supplies. This is often done by adding a complexing agent.</p> <p>(ii) In a sample of ground water the concentration of $\text{Cd}^{2+}(\text{aq})$ is $1.00 \times 10^{-4} \text{ mol dm}^{-3}$.</p> <p>Calculate the concentration of $\text{CH}_3\text{NH}_2(\text{aq})$ needed to reduce the concentration of $\text{Cd}^{2+}(\text{aq})$ in this dilute solution by a factor of one thousand. $\times 1000 \rightarrow 1 \times 10^{-7}$</p> $\begin{array}{ccccccc} \text{Cd}^{2+} & + & 4\text{CH}_3\text{NH}_2 & \rightleftharpoons & [\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+} & & \\ 1 & : & 4 & & & & \\ 1.00 \times 10^{-4} & & & & & & \end{array}$ <p style="text-align: right;">2</p> $(1 \times 10^{-4}) - 4x = (1 \times 10^{-7}) =$ $4x = 9.99 \times 10^{-5}$ $x = 2.4975 \times 10^{-5}$ $= 2.50 \times 10^{-5} \text{ mol dm}^{-3} \quad \text{concentration of } \text{CH}_3\text{NH}_2(\text{aq}) = \dots\dots\dots \text{ mol dm}^{-3} \quad [2]$	<p>1 A correct answer. Mark for (a) (i) = 2/2</p> <p>2 An incorrect answer. The candidate does not calculate the new concentration of $[\text{Cd}^{2+}]$ and $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}]$ and substitute into their expression in (a) (i). The correct answer is 0.129. Mark for (a) (ii) = 0/2</p>

Example candidate response – high, continued				Examiner comments												
<p>(b): Values for ΔH° and ΔG° for equilibria I and II, and the value of ΔS° for equilibrium I, are given in the table below. All values are at a temperature of 298 K.</p> <table border="1"> <thead> <tr> <th>equilibrium</th> <th>$\Delta H^\circ / \text{kJ mol}^{-1}$</th> <th>$\Delta G^\circ / \text{kJ mol}^{-1}$</th> <th>$\Delta S^\circ / \text{JK}^{-1} \text{mol}^{-1}$</th> </tr> </thead> <tbody> <tr> <td>I</td> <td>-57.3</td> <td>-37.4</td> <td>-66.8</td> </tr> <tr> <td>II</td> <td>-56.5</td> <td>-60.7</td> <td>to be calculated</td> </tr> </tbody> </table>				equilibrium	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{JK}^{-1} \text{mol}^{-1}$	I	-57.3	-37.4	-66.8	II	-56.5	-60.7	to be calculated	
equilibrium	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{JK}^{-1} \text{mol}^{-1}$													
I	-57.3	-37.4	-66.8													
II	-56.5	-60.7	to be calculated													
<p>(i) Suggest a reason why the ΔH° values for the two equilibria are very similar.</p> <p>3 In both complexes, 4 nitrogen atoms donate four lone pairs to make dative bonds with cadmium. So the energy released is very similar. [1]</p>				<p>3 A correct reference to bond breaking or bond forming is credited here.</p> <p>Mark for (b) (i) = 1/1</p>												
<p>(ii) Calculate ΔS° for equilibrium II.</p> <p>$\Delta G = \Delta H - T\Delta S$</p> <p>$(-60.7 \times 1000) = (-56.5 \times 1000) - (298)(\Delta S)$</p> <p>$\Delta S = 14.09395$ 4 $\Delta S^\circ = +14.1 \text{ JK}^{-1} \text{mol}^{-1}$ [1]</p> <p>$= 14.1 \text{ JK}^{-1} \text{mol}^{-1}$</p>				<p>4 A correct answer.</p> <p>Mark for (b) (ii) = 1/1</p>												
<p>(iii) Suggest a reason for the difference between the ΔS° you have calculated for equilibrium II and that for equilibrium I given in the table.</p> <p>5 Increase in entropy for equilibrium 2 because fewer moles of reactant (2) converting to product (1). In equilibrium 1, a decrease in entropy because more moles of reactant (5) converting to product (1). [1]</p>				<p>5 A correct answer. The examiners credited the answer of 'fewer moles of reactant were converted to the complex in equilibrium II'. They ignored the slight slip ('2') here.</p> <p>Mark for (b) (iii) = 1/1</p>												
<p>(iv) Which of the two complexes is the more stable? Give a reason for your answer.</p> <p>The complex from equilibrium 2 because its formation is favored energetically (ΔG is much more negative so reaction is more spontaneous in forward direction) and also because its K_{stab} value is higher. [Total: 8]</p> <p>6 [1]</p>				<p>6 An excellent answer.</p> <p>Mark for (b) (iv) = 1/1</p> <p>Total marks awarded = 6 out of 8</p>												

How the candidate could have improved their answer

(a) (ii) The candidate did not calculate the new concentrations of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]$ and $[\text{Cd}^{2+}]$. These values should have been substituted into their expression in (a) (i). The correct answer is 0.129 as shown.



$$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$$

$$9.99 \times 10^{-5} / (y^4 \times 1 \times 10^{-7}) = 3.6 \times 10^6$$

$$\text{and } y = \sqrt[4]{(9.99 \times 10^{-5}) / (1 \times 10^{-7} \times 3.6 \times 10^6)} = \mathbf{0.129}$$

Mark awarded = (a) (i) 2/2, (ii) 0/2

Mark awarded = (b) (i) 1/1, (ii) 1/1, (iii) 1/1, (iv) 1/1

Total marks awarded = 6 out of 8

Example candidate response – middle	Examiner comments
<p>5 Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.</p> $\text{Cd}^{2+}(\text{aq}) + 4\text{CH}_3\text{NH}_2(\text{aq}) \rightleftharpoons [\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}(\text{aq}) \quad K_{\text{stab}} = 3.6 \times 10^6 \quad \text{equilibrium I}$ $\text{Cd}^{2+}(\text{aq}) + 2\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq}) \rightleftharpoons [\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}(\text{aq}) \quad K_{\text{stab}} = 4.2 \times 10^{10} \quad \text{equilibrium II}$ <p>(a) (i) Write an expression for the stability constant, K_{stab}, for equilibrium I, and state its units.</p> $K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$ <p style="text-align: right;"> $\frac{(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^4} \Rightarrow \text{mol}^{-4} \text{dm}^{12}$ units $\text{mol}^{-4} \text{dm}^{12}$ [2] </p> <p>Cadmium ions are poisonous and need to be removed from some water supplies. This is often done by adding a complexing agent.</p> <p>(ii) In a sample of ground water the concentration of $\text{Cd}^{2+}(\text{aq})$ is $1.00 \times 10^{-4} \text{ mol dm}^{-3}$.</p> <p>Calculate the concentration of $\text{CH}_3\text{NH}_2(\text{aq})$ needed to reduce the concentration of $\text{Cd}^{2+}(\text{aq})$ in this dilute solution by a factor of one thousand.</p> $\frac{1.00 \times 10^{-4} \times 4}{1000} \Rightarrow 4 \times 10^{-7} \quad \text{2}$ <p style="text-align: right;">concentration of $\text{CH}_3\text{NH}_2(\text{aq}) = 4 \times 10^{-7} \text{ mol dm}^{-3}$ [2]</p>	<p>1 A correct answer. Mark for (a) (i) = 2/2</p> <p>2 An incorrect answer. The candidate does not calculate the new concentration of $[\text{Cd}^{2+}]$ and $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ and substitute into their expression in (a) (i). The correct answer is 0.129. Mark for (a) (ii) = 0/2</p>

Example candidate response – middle, continued

- (b) Values for ΔH° and ΔG° for equilibria I and II, and the value of ΔS° for equilibrium I, are given in the table below. All values are at a temperature of 298 K.

equilibrium	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{JK}^{-1} \text{mol}^{-1}$
I	-57.3	-37.4	-66.8
II	-56.5	-60.7	to be calculated

- (i) Suggest a reason why the ΔH° values for the two equilibria are very similar.

The values are very similar because the energy required by reactant to form a product for both equilibrium [1] is nearly same.

- (ii) Calculate ΔS° for equilibrium II.

$$\Delta G = -T\Delta S$$

$$\frac{-60.7 \times 1000}{-298} = \Delta S$$

$$\Delta G = \Delta H_{\text{reaction}} - T\Delta S$$

$$\frac{(-60.7 \times 1000) + (56.5 \times 1000)}{-298} = \Delta S$$

$$\Delta S^\circ = 14.1 \text{ JK}^{-1} \text{mol}^{-1} [1]$$

- (iii) Suggest a reason for the difference between the ΔS° you have calculated for equilibrium II and that for equilibrium I given in the table.

=> The difference in equilibrium of II and equilibrium I is because equilibrium II is more random and spontaneous than that of equilibrium I. [1]

- (iv) Which of the two complexes is the more stable? Give a reason for your answer.

=> Equilibrium II is more stable (1,2-diaminoethane) as K_{stab} is more and Gibbs energy also shows more energy or work is to be done in experiment II. [1]

[Total: 8]

Examiner comments

- 3 This answer is not sufficient. The candidate needed to reference bond breaking or making in their answer. For example, the same number of bonds are forming and breaking.

Mark for (b) (i) = 0/1

- 4 A correct answer.

Mark for (b) (ii) = 1/1

- 5 No marks. The candidate needed to answer in terms of the number of moles of reactants or quoting the molar ratio of reactants in equilibria I and II.

Mark for (b) (iii) = 0/1

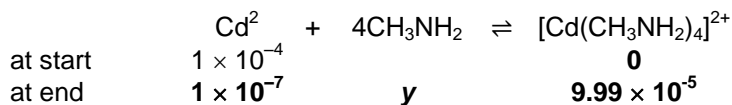
- 6 A correct answer.

Mark for (b) (iv) = 1/1

Total marks awarded = 4 out of 8

How the candidate could have improved their answer

(a) (ii) The candidate did not calculate the new concentrations of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]$ and $[\text{Cd}^{2+}]$. These values should have been substituted into their expression in (a) (i). The correct answer is 0.129 as shown.



$$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$$

$$9.99 \times 10^{-5} / (y^4 \times 1 \times 10^{-7}) = 3.6 \times 10^6$$

$$\text{and } y = \sqrt[4]{(9.99 \times 10^{-5}) / (1 \times 10^{-7} \times 3.6 \times 10^6)} = \mathbf{0.129}$$

(b) (i) The candidate should have referenced bond breaking and forming in their answer. For example, the same types of or similar bonds forming/breaking or the same number of bonds forming/breaking.

(b) (iii) The candidate needed to answer in terms of the number of moles of reactants. For example, fewer moles of reactants are forming the complex in equilibrium II than in equilibrium I.

Mark awarded = **(a) (i) 2/2, (ii) 0/2**

Mark awarded = **(b) (i) 0/1, (ii) 1/1, (iii) 0/1, (iv) 1/1**

Total marks awarded = 4 out of 8

Example candidate response – low	Examiner comments
<p>5 Cadmium ions form complexes with primary amines and with 1,2-diaminoethane:</p> $\text{Cd}^{2+}(\text{aq}) + 4\text{CH}_3\text{NH}_2(\text{aq}) \rightleftharpoons [\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}(\text{aq}) \quad K_{\text{stab}} = 3.6 \times 10^6 \quad \text{equilibrium I}$ $\text{Cd}^{2+}(\text{aq}) + 2\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq}) \rightleftharpoons [\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}(\text{aq}) \quad K_{\text{stab}} = 4.2 \times 10^{10} \quad \text{equilibrium II}$ <p>(a) (i) Write an expression for the stability constant, K_{stab}, for equilibrium I, and state its units.</p> $K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4]}{[\text{Cd}][\text{CH}_3\text{NH}_2]^4}$ <p style="text-align: right;">units $\text{mol}^{-4} \text{dm}^{12}$ [2]</p> <p>Cadmium ions are poisonous and need to be removed from some water supplies. This is often done by adding a complexing agent.</p> <p>(ii) In a sample of ground water the concentration of $\text{Cd}^{2+}(\text{aq})$ is $1.00 \times 10^{-4} \text{mol dm}^{-3}$.</p> <p>Calculate the concentration of $\text{CH}_3\text{NH}_2(\text{aq})$ needed to reduce the concentration of $\text{Cd}^{2+}(\text{aq})$ in this dilute solution by a factor of one thousand.</p> $\frac{(4.2 \times 10^{10})}{1000} = \frac{1}{(1 \times 10^{-4})^2} x$ $\frac{(3.6 \times 10^6)}{1000} = \frac{1}{(1 \times 10^{-4})^2} x$ <p style="text-align: right;">concentration of $\text{CH}_3\text{NH}_2(\text{aq}) = 0.36 \text{mol dm}^{-3}$ [2]</p>	<p>1 One mark is awarded for giving the correct units. The mark for the stability constant expression has not been awarded as the charges have been omitted on the two ions.</p> <p>Mark for (a) (i) = 1/2</p> <p>2 An incorrect answer. The candidate does not calculate a new concentration of $[\text{Cd}^{2+}]$ and $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}]$ and substitute into their expression in (a) (i). The correct answer is 0.129.</p> <p>Mark for (a) (ii) = 0/2</p>

Example candidate response – low, continued

Examiner comments

(b) Values for ΔH° and ΔG° for equilibria I and II, and the value of ΔS° for equilibrium I, are given in the table below. All values are at a temperature of 298 K.

equilibrium	$\Delta H^\circ / \text{kJ mol}^{-1}$	$\Delta G^\circ / \text{kJ mol}^{-1}$	$\Delta S^\circ / \text{JK}^{-1} \text{mol}^{-1}$
I	-57.3	-37.4	-66.8
II	-56.5	-60.7	to be calculated

(i) Suggest a reason why the ΔH° values for the two equilibria are very similar.

Because it has the same transition metal involved. [1]

(ii) Calculate ΔS° for equilibrium II.

$$\begin{aligned}
 &= -60.7 - (-56.5) - (298 \times x) \\
 -60.700 &= -56.500 - (298x) \\
 -4200 &= -298x \\
 \Delta S^\circ &= 14.1 \text{ JK}^{-1} \text{mol}^{-1} \quad [1]
 \end{aligned}$$

(iii) Suggest a reason for the difference between the ΔS° you have calculated for equilibrium II and that for equilibrium I given in the table.

More Equilibrium I has more disorder ~~and~~ arrangement on its reactant side while II has more disorder on its product side. [1]

(iv) Which of the two complexes is the more stable? Give a reason for your answer.

Equilibrium I $[\text{Cd}(\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ because of its higher K_{stab} . [1]

[Total: 8]

3 An incorrect answer. The candidate needed to reference bond breaking or making. For example, the same number of bonds are forming and breaking.

Mark for (b) (i) = 0/1

4 A correct answer.

Mark for (b) (ii) = 1/1

5 This answer is not sufficient for the mark. The candidate needed to answer in terms of the number of moles of reactants or quoting the molar ratio of reactants in equilibria I and II.

Mark for (b) (iii) = 0/1

6 A correct answer.

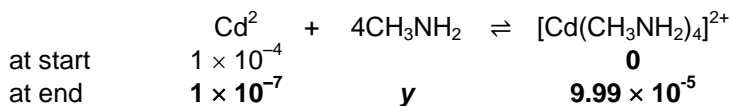
Mark for (b) (iv) = 1/1

Total marks awarded = 3 out of 8

How the candidate could have improved their answer

(a) (i) The candidate should have included the charges for both ions in the stability constant, K_{stab} , expression.

(a) (ii) The candidate did not calculate the new concentrations of $[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]$ and $[\text{Cd}^{2+}]$. These values should have been substituted into their expression in (a) (i). The correct answer is 0.129 as shown.



$$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$$

$$9.99 \times 10^{-5} / (y^4 \times 1 \times 10^{-7}) = 3.6 \times 10^6$$

$$\text{and } y = \sqrt[4]{(9.99 \times 10^{-5}) / (1 \times 10^{-7} \times 3.6 \times 10^6)} = \mathbf{0.129}$$

(b) (i) The candidate should have referenced bond breaking and forming in their answer. For example, the same types of or similar bonds forming/breaking or the same number of bonds forming/breaking.

(b) (iii) The candidate needed to answer in terms of the number of moles of reactants. For example, fewer moles of reactants are forming the complex in equilibrium II than in equilibrium I.

Mark awarded = **(a) (i) 1/2, (ii) 0/2**

Mark awarded = **(b) (i) 0/1, (ii) 1/1, (iii) 0/1, (iv) 1/1**

Total marks awarded = 3 out of 8

Common mistakes candidates made in this question

(a) (i) A common error was putting charges outside the square brackets in the expression.

(a) (ii) Many candidates did not calculate the new $[\text{Cd}^{2+}]$ correctly and used 1×10^{-4} instead 1×10^{-7} in their expression.

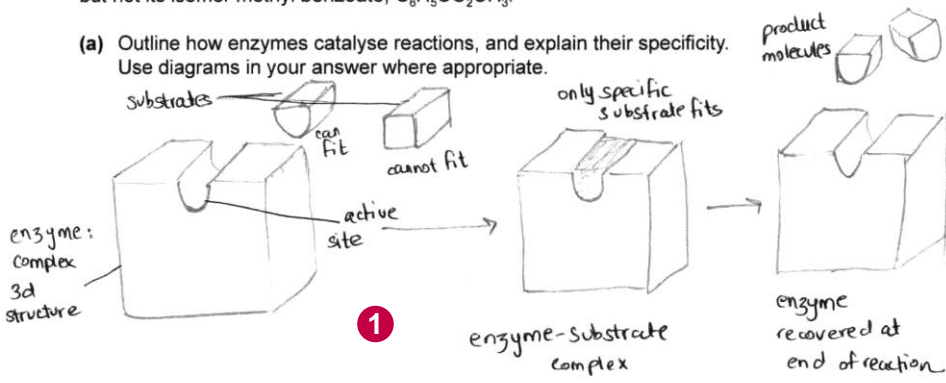
(b) (i) Many candidates omitted any reference to bond making/breaking.

(b) (ii) A common error was -14.1 .

(b) (iii) Some candidates answered in terms of increased disorder of the product or increased entropy, rather than comparing the number of gaseous moles of the reactants.

(b) (iv) Many candidates gave a reason based on increased ΔS rather than larger K_{stab} or more negative ΔG .

Question 6

Example candidate response – high	Examiner comments
<p>6 Esterases are enzymes that hydrolyse esters.</p> $\text{R}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{O}-\text{R}' \end{array} + \text{H}_2\text{O} \longrightarrow \text{R}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{O}-\text{H} \end{array} + \text{HO}-\text{R}$ <p>Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould <i>Aspergillus niger</i> will hydrolyse phenyl ethanoate, $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5$, but not its isomer methyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3$.</p> <p>(a) Outline how enzymes catalyse reactions, and explain their specificity. Use diagrams in your answer where appropriate.</p>  <p>Enzymes are biological catalysts. They reduce the activation energy for a reaction by providing an alternative pathway for reaction. Now more many more substrate molecules have the E_a required and reaction rate increases. Enzymes are highly specific, with an active site only certain substrates can fit into. An enzyme-substrate complex is formed, the product is made and enzyme is recovered unchanged.</p> <p>[3]</p>	<p>1 An excellent answer. The clear, labelled diagrams and the text obtain the essential marking point and all four of the other points on the mark scheme.</p> <p>Mark for (a) = 3/3</p>

Example candidate response – high, continued

Examiner comments

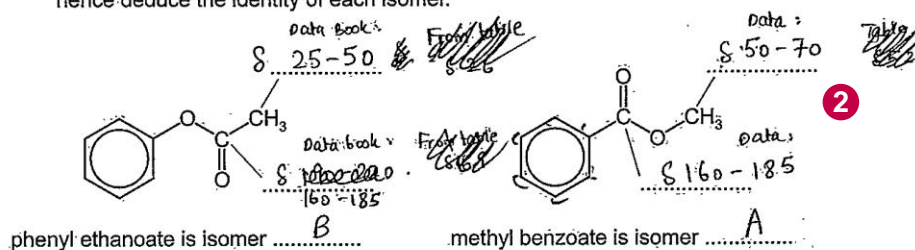
(b) Sample bottles of each of the isomers phenyl ethanoate and methyl benzoate have lost their labels and so have been named isomer A and isomer B.

(i) The carbon-13 NMR spectra of isomers A and B contain the following peaks.

isomer A	isomer B
δ 52	δ 26
δ 128	δ 122
δ 129	δ 126
δ 130	δ 129
δ 133	δ 151
δ 167	δ 169

The identity of the compound responsible for each spectrum can be deduced by studying the chemical shifts (δ) of the peaks in the spectra.

Use the *Data Booklet* to assign the correct peaks to the labelled carbon atoms in the structures of the isomers below. Write each value next to the relevant carbon atom and hence deduce the identity of each isomer.



[2]

(ii) These two isomers are difficult to distinguish chemically.

Describe a method of converting them to suitable products in step 1 which can then be tested in step 2.

You should state the reagents and conditions for each step, and any observations you would make.

step 1 hydrolyse with dil. HCl and heat A phenol and a benzoic acid will result **3**

step 2 React with Br₂ (aq) The phenol will form a white ppt precipitate of tribromophenol and lactone. The benzoic acid will not. So phenyl ethanoate will be the white ppt compound parent. [3]

[Total: 8]

2 A correct answer. Examiners allowed the use of the *Data Booklet* range as an alternative to quoting the correct value from the table.

Mark for (b) (i) = 2/2

3 Three marks awarded. Dil HCl is equivalent to HCl(aq) for the first marking point.

Mark for (b) (ii) = 3/3

Total marks awarded = 8 out of 8

How the candidate could have improved their answer

(a) The candidate could have stated in words that 'enzymes are specific because the substrate has a complementary shape to the active site of the enzyme'.

Mark awarded = (a) 3/3

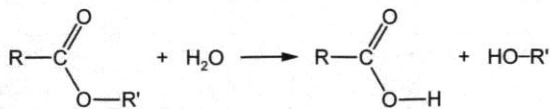
Mark awarded = (b) (i) 2/2, (ii) 3/3

Total marks awarded = 8 out of 8

Example candidate response – middle

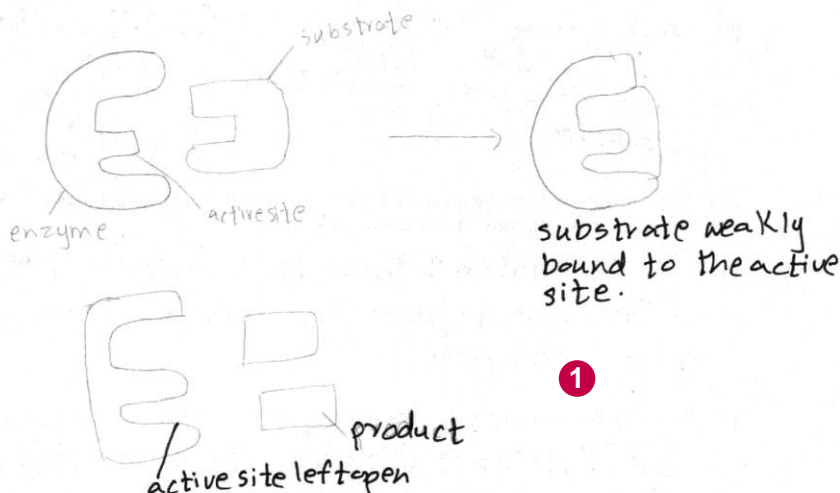
Examiner comments

6 Esterases are enzymes that hydrolyse esters.



Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould *Aspergillus niger* will hydrolyse phenyl ethanoate, $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5$, but not its isomer methyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3$.

(a) Outline how enzymes catalyse reactions, and explain their specificity. Use diagrams in your answer where appropriate.



The enzymes have an active site with a specific three-dimensional shape which is complementary to the substrate. The substrate weakly binds to it and is converted to product after which the active site is left open for another substrate molecule. [3]

1 The clear, labelled diagrams along with the text obtain the essential marking point and three of the four other points on the mark scheme. The candidate could have stated that the interaction of the substrate with the active site causes a specific bond to be weakened or lowers the activation energy.

Mark for (a) = 3/3

Example candidate response – middle, continued

Examiner comments

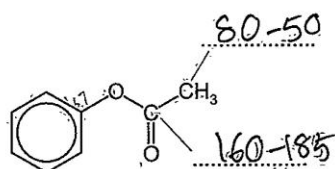
(b) Sample bottles of each of the isomers phenyl ethanoate and methyl benzoate have lost their labels and so have been named isomer A and isomer B.

(i) The carbon-13 NMR spectra of isomers A and B contain the following peaks.

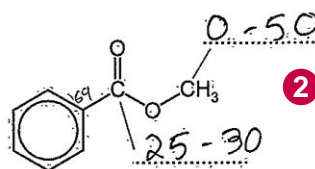
isomer A	isomer B
δ 52	δ 26
δ 128	δ 122
δ 129	δ 126
δ 130	δ 129
δ 133	δ 151
δ 167	δ 169

The identity of the compound responsible for each spectrum can be deduced by studying the chemical shifts (δ) of the peaks in the spectra.

Use the *Data Booklet* to assign the correct peaks to the labelled carbon atoms in the structures of the isomers below. Write each value next to the relevant carbon atom and hence deduce the identity of each isomer.



phenyl ethanoate is isomerA.....



methyl benzoate is isomerB.....

[2]

(ii) These two isomers are difficult to distinguish chemically.

Describe a method of converting them to suitable products in step 1 which can then be tested in step 2.

You should state the reagents and conditions for each step, and any observations you would make.

step 1 NaOH (aq)
Add a carboxylic acid to it. It will lead to the formation of phenol

step 2 Phenol can be tested with aq. Bromine it will form a white ppt.

[3]

[Total: 8]

Examiner comments

2 Three incorrect data range values are quoted here. Phenyl ethanoate is B with values 26 and 169. Methyl benzoate is A with values 52 and 167.

Mark for (b) (i) = 0/2

3 One mark is awarded for identifying that a white precipitate will be given (the third marking point). For the first marking point, the condition of heat has been omitted. If alkaline hydrolysis is used, candidates need to acidify before reacting with $\text{Br}_2(\text{aq})$ because NaOH would react with $\text{Br}_2(\text{aq})$.

Mark for (b) (ii) = 1/3

Total marks awarded = 4 out of 8

How the candidate could have improved their answer

(a) The candidate could have stated that the interaction of the substrate with the active site causes a specific bond to be weakened or lowers the activation energy for this process.

(b) (i) The candidate should have used the Data Booklet to identify the values for these peaks. Phenyl ethanoate is B with values of δ 26 for $\text{CH}_3\text{-CO}$ and δ 169 for CH_3CO . Methyl benzoate is A with values of δ 52 for $\text{CH}_3\text{-O}$ and δ 167 for phenyl-CO.

(b) (ii) The candidate should have included 'heat' and 'followed by acidification' in the alkaline hydrolysis step.

Mark awarded = **(a) 3/3**

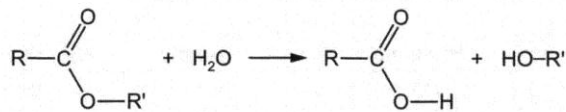
Mark awarded = **(b) (i) 0/2, (ii) 1/3**

Total marks awarded = 4 out of 8

Example candidate response – low

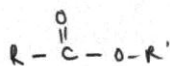
Examiner comments

6 Esterases are enzymes that hydrolyse esters.



Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould *Aspergillus niger* will hydrolyse phenyl ethanoate, $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5$, but not its isomer methyl benzoate, $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3$.

(a) Outline how enzymes catalyse reactions, and explain their specificity. Use diagrams in your answer where appropriate.



1

Enzymes have a specific site called active site, which provides adsorption for specific reactant only. They act as a catalyst and speed up the esterification. [3]

1 No marks awarded, The candidate needed to include labelled diagrams illustrating the lock-and-key mechanism. They should also have stated that the enzymes are specific because the substrate has a complementary shape to the active site of the enzyme.

Mark for (a) = 0/3

Example candidate response – low, continued

Examiner comments

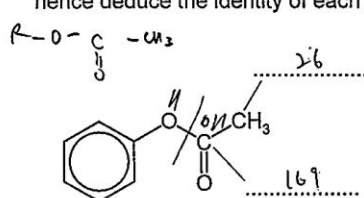
(b) Sample bottles of each of the isomers phenyl ethanoate and methyl benzoate have lost their labels and so have been named isomer A and isomer B.

(i) The carbon-13 NMR spectra of isomers A and B contain the following peaks.

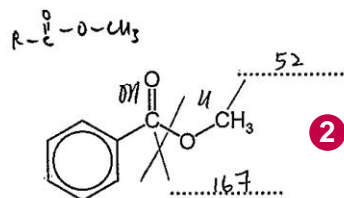
isomer A	isomer B
δ 52	δ 26
δ 128	δ 122
δ 129	δ 126
δ 130	δ 129
δ 133	δ 151
δ 167	δ 169

The identity of the compound responsible for each spectrum can be deduced by studying the chemical shifts (δ) of the peaks in the spectra.

Use the *Data Booklet* to assign the correct peaks to the labelled carbon atoms in the structures of the isomers below. Write each value next to the relevant carbon atom and hence deduce the identity of each isomer.



phenyl ethanoate is isomerB.....



methyl benzoate is isomerA.....

[2]

(ii) These two isomers are difficult to distinguish chemically.

Describe a method of converting them to suitable products in step 1 which can then be tested in step 2.

You should state the reagents and conditions for each step, and any observations you would make.

step 1 ~~Use concentrated hydrochloric acid~~ Hydrolysis is used to produce 2 different products for each compound. 3
Dilute $H^+(aq)$ and heat under reflux.

step 2 Use $I_2(aq) + NaOH(aq)$. The products of isomer B from step 1 will give yellow precipitate as positive result.

[3]

[Total: 8]

2 A correct answer.

Mark for (b) (i) = 2/2

3 One mark is awarded for step one, the first marking point in the mark scheme. The iodoform reaction would not give a yellow precipitate with any of the hydrolysis products. Candidates should have used aqueous bromine, which would give a white precipitate with hydrolysis product, phenol, from phenyl ethanoate.

Mark for (b) (ii) = 1/3

Total marks awarded = 3 out of 8

How the candidate could have improved their answer

(a) The candidate should have included labelled diagrams illustrating the lock-and-key mechanism as shown below.



They should also have stated that the enzymes are specific because the substrate has a complementary shape to the active site of the enzyme.

(b) (ii) The candidate should have used aqueous bromine, which would give a white precipitate with hydrolysis product, phenol, from phenyl ethanoate. The hydrolysis products from methyl benzoate would show no change.

Mark awarded = **(a) 0/3**

Mark awarded = **(b) (i) 2/2, (ii) 1/3**

Total marks awarded = 3 out of 8

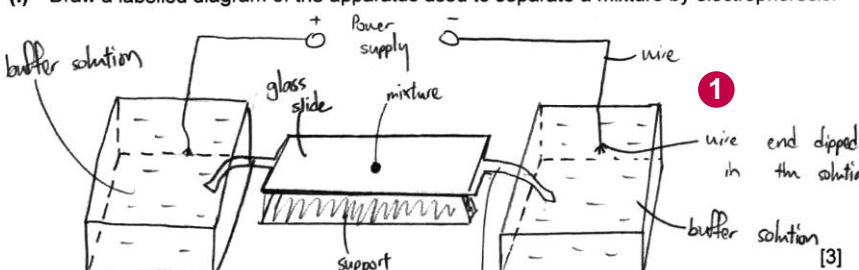
Common mistakes candidates made in this question

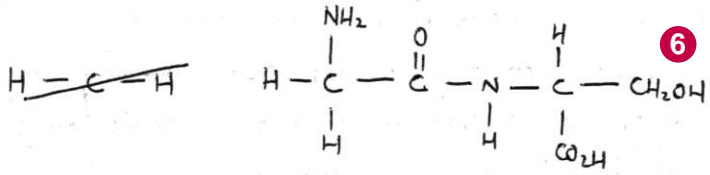
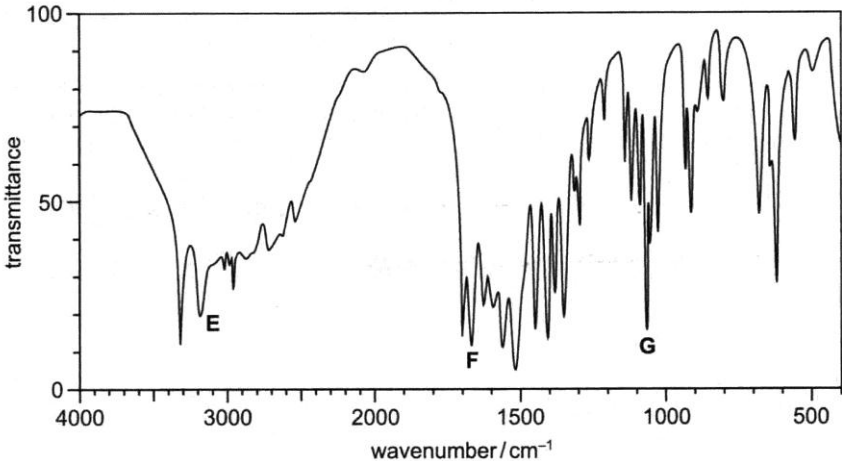
(a) Common errors were omitting any reference to 'active site' or 'enzyme specificity' in their explanation and drawing unlabelled diagrams with little explanation.

(b) (i) Some candidates identified the isomers but incorrectly assigned their δ values.

(b) (ii) Some candidates omitted dilute/aq with the acid and heat in step 1. Common errors in step 2 were use of the iodoform reaction or aqueous sodium carbonate.

Question 7

Example candidate response – high	Examiner comments
<p>7 (a) Amino acids can be separated by electrophoresis.</p> <p>(i) Draw a labelled diagram of the apparatus used to separate a mixture by electrophoresis.</p>  <p>(ii) Explain the principles of the separation of amino acids by electrophoresis.</p> <p>It is based on acid-base reaction. [1]</p> <p>Amino acid will move to either end depending on its isoelectric point and charges on amino acid. [2]</p> <p>(b) Electrophoresis is usually carried out in a buffer solution.</p> <p style="text-align: center;">H^+ OH^-</p> <p>Given three buffers, with pH values of 2.0, 7.0 and 12.0, suggest, with a reason, which buffer would be the most suitable for the separation of the following amino acid mixtures. Your reasons should refer to the structure of each molecule. (The structures of these amino acids are given in the Data Booklet.)</p> <p>(i) Asp and Val</p> <p style="text-align: center;">(-) neutral</p> <p>buffer pH 7.0 [3]</p> <p>reason Since valine is zwitterion, it will not move. For aspartic acid, it carries a negatively charged and will move to positive pole. due to its $-COO^-$ group.</p> <p>(ii) Lys and Ser</p> <p style="text-align: center;">+</p> <p>buffer pH 7.0 [4]</p> <p>reason Serine is a zwitter ion and will not move in a neutral solution. Lysine carries a positive charge due to NH_3^+ and will move to the negative pole.</p> <p>(iii) Tyr and Phe</p> <p>buffer pH 7.0 [5]</p> <p>reason Phenylalanine will gain a negative charge ($-COO^- + OH^-$). Phenylalanine is a zwitterion and will not move. Tyrosine is slightly acidic due to the phenolic group, hence there is a negative charge (O^-) and it will move to positive pole. [3]</p>	<p>1 A clear, correctly labelled diagram which earns all the marking points from the mark scheme.</p> <p>Mark for (a) (i) = 3/3</p> <p>2 One mark is awarded for the direction of movement related to the charge on the amino acid. The candidate has omitted the effect of size/Mr on the distance travelled.</p> <p>Mark for (a) (ii) = 1/2</p> <p>3 A correct answer.</p> <p>Mark for (b) (i) = 1/1</p> <p>4 A correct answer.</p> <p>Mark for (b) (ii) = 1/1</p> <p>5 An incorrect answer. The candidate should have chosen pH 12. Tyr would move further (towards the positive electrode) than Phe (as Tyr has a charge of 2- and Phe a charge of 1-).</p> <p>Mark for (b) (iii) = 0/1</p>

Example candidate response – high, continued	Examiner comments
<p>(c) (i) Draw the structure of the dipeptide Gly-Ser, showing the peptide bond in full.</p> <p style="text-align: center;">  </p> <p style="text-align: right;">[2]</p> <p>The infra-red spectrum of Gly-Ser is shown below.</p> <p style="text-align: center;">  </p> <p>(ii) Use the <i>Data Booklet</i> to identify the bond in the molecule of Gly-Ser that is responsible for each of the peaks indicated on the above infra-red spectrum.</p> <p>E N-H O-H 7</p> <p>F C=O</p> <p>G C-O</p> <p style="text-align: right;">[2]</p> <p style="text-align: right;">[Total: 12]</p>	<p>6 A correct answer. Only the peptide bond needed to be shown as a displayed formula.</p> <p>Mark for (c) (i) = 2/2</p> <p>7 A correct answer. An alternative answer for E is N-H.</p> <p>Mark for (c) (ii) = 2/2</p> <p style="text-align: right;">Total marks awarded = 10 out of 12</p>

How the candidate could have improved their answer

(a) (i) The candidate should have labelled their power supply as 'DC power supply'. Examiners accepted 'power supply' with '+' and '-' charges.

(a) (ii) The candidate should have stated the effect of size/ M_r of the amino acid on the distance travelled.

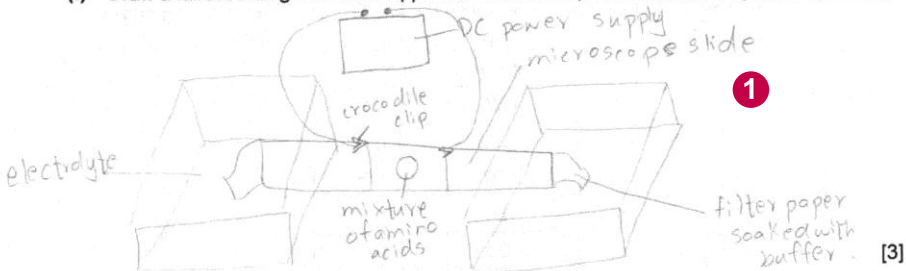
(b) (iii) A pH 12 should have been chosen here. Tyr would move further (towards the positive electrode) than Phe (as Tyr has a charge of 2- and Phe a charge of 1-).

Mark awarded = (a) (i) 3/3, (ii) 1/2

Mark awarded = (b) 2/3

Mark awarded = (c) (i) 2/2, (ii) 2/2

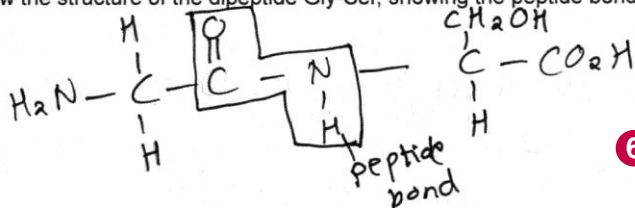
Total marks awarded = 10 out of 12

Example candidate response – middle	Examiner comments
<p>7 (a) Amino acids can be separated by electrophoresis.</p> <p>(i) Draw a labelled diagram of the apparatus used to separate a mixture by electrophoresis.</p>  <p>(ii) Explain the principles of the separation of amino acids by electrophoresis.</p> <p>A DC can voltage is provided which causes the amino acids to move according to their charge that is +ve towards cathode, -ve towards anode. The bigger the molecule slower it will move, less distance covered. [2]</p> <p>(b) Electrophoresis is usually carried out in a buffer solution.</p> <p>Given three buffers, with pH values of 2.0, 7.0 and 12.0, suggest, with a reason, which buffer would be the most suitable for the separation of the following amino acid mixtures. Your reasons should refer to the structure of each molecule. (The structures of these amino acids are given in the <i>Data Booklet</i>.)</p> <p>(i) Asp and Val buffer pH 12.0 [3] reason They both are acidic in nature and will therefore move better in alkaline conditions.</p> <p>(ii) Lys and Ser [4] buffer pH reason</p> <p>(iii) Tyr and Phe buffer pH 7.0 [5] reason The difference in negativity is so great that the mixture will be separated. [3]</p>	<p>1 Two marks awarded for marking points two and three. The candidate should have connected the DC power supply to the ends of the slide or in electrolyte tanks.</p> <p>Mark for (a) (i) = 2/3</p> <p>2 A correct answer.</p> <p>Mark for (a) (ii) = 2/2</p> <p>3 The correct pH is given here but the reasoning is incorrect. At pH 12 Asp is more negative so moves further (towards the positive electrode).</p> <p>Mark for (b) (i) = 0/1</p> <p>4 No response. The candidate could have chosen pH 2 where Lys is more positive so moves further (towards the negative electrode).</p> <p>Mark for (b) (ii) = 0/1</p> <p>5 The pH given is incorrect. The candidate should have chosen pH 12 where Tyr is more negative so moves further (towards the positive electrode).</p> <p>Mark for (b) (iii) = 0/1</p>

Example candidate response – middle, continued

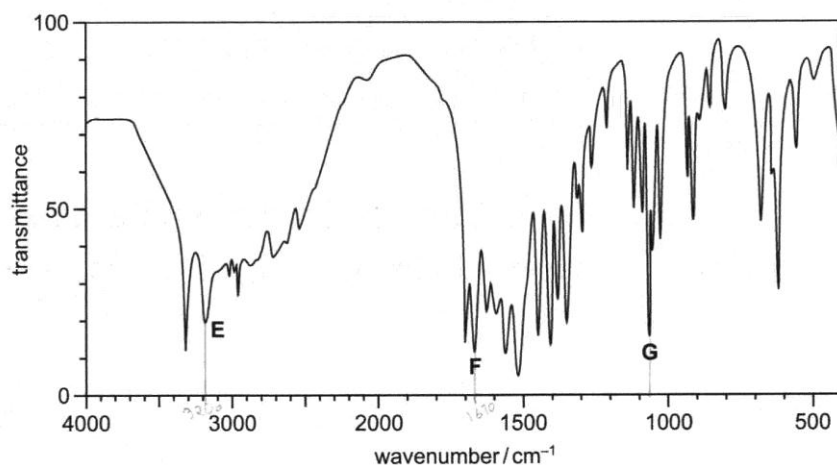
Examiner comments

(c) (i) Draw the structure of the dipeptide Gly-Ser, showing the peptide bond in full.



[2]

The infra-red spectrum of Gly-Ser is shown below.



(ii) Use the *Data Booklet* to identify the bond in the molecule of Gly-Ser that is responsible for each of the peaks indicated on the above infra-red spectrum.

E R-OH
 F C=O
 G C-O

7

[2]

[Total: 12]

6 A correct answer.

Mark for (c) (i) = 2/2

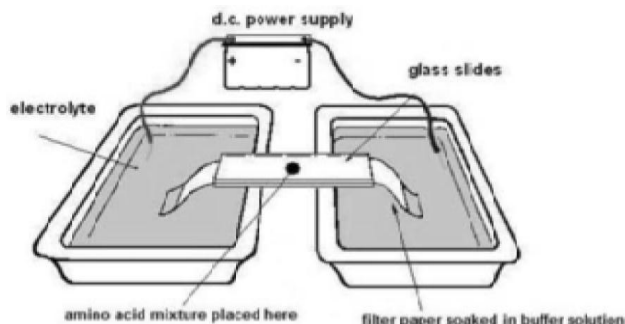
7 One mark is awarded for F and G. The answer for E is incorrect. Candidates should have chosen either the O-H bond or the N-H bond for E.

Mark for (c) (ii) = 1/2

Total marks awarded = 7 out of 12

How the candidate could have improved their answer

(a) (i) The candidate should have connected the DC power supply to the ends of the slide or in electrolyte tanks as shown.



(b) The candidate could have chosen:

- for Asp and Val a pH 12 where Asp is more negative (as a 2⁻ charge) so moves further (towards the positive electrode),
- for Lys and Ser, a pH 2 where Lys is more positive (as a 2⁺ charge) so moves further (towards the negative electrode),
- Tyr and Phe, a pH 12 where Tyr is more negative (as a 2⁻ charge) so moves further (towards the positive electrode).

(c) (ii) The candidate should have chosen either the O–H bond or the N–H bond for **E**.

Mark awarded = **(a) (i) 2/3, (ii) 2/2**

Mark awarded = **(b) 0/3**

Mark awarded = **(c) (i) 2/2, (ii) 1/2**

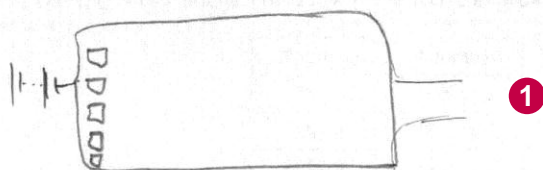
Total marks awarded = 7 out of 12

Example candidate response – low

Examiner comments

7 (a) Amino acids can be separated by electrophoresis.

(i) Draw a labelled diagram of the apparatus used to separate a mixture by electrophoresis.



[3]

(ii) Explain the principles of the separation of amino acids by electrophoresis.

1. By the principles of separation of amino acids by electrophoresis amino acid separates by forming ions. First COOH separates followed by NH₂ [2]

(b) Electrophoresis is usually carried out in a buffer solution.

Given three buffers, with pH values of 2.0, 7.0 and 12.0, suggest, with a reason, which buffer would be the most suitable for the separation of the following amino acid mixtures.

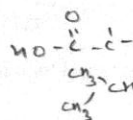
Your reasons should refer to the structure of each molecule.

(The structures of these amino acids are given in the *Data Booklet*.)

(i) Asp and Val

buffer pH ~~7.0~~ 12.0 [3]

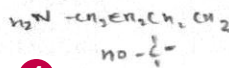
reason pH value 2.0 as ~~the~~ the structure of carboxylic group and alkane group ~~of~~ which becomes acidic can be separated by ~~acidic~~ basic buffer.



(ii) Lys and Ser

buffer pH ~~12.0~~ 12.0 [4]

reason Presence of amine makes the solution basic and basic and acidic buffer would release the base due to common ion effect.



(iii) Tyr and Phe

buffer pH ~~12.0~~ 7.0 [5]

reason The appear to be neutral which can ~~be~~ help to ~~bring~~ bring about a charge in both the compounds. [3]

1 No marks awarded. The candidate should have drawn a clear, labelled diagram of the electrophoresis apparatus.

Mark for (a) (i) = 0/3

2 No marks awarded. The candidate needed to relate the direction of movement to the charge on the amino acid, and the distance travelled to the Mr of the amino acid.

Mark for (a) (ii) = 0/2

3 The correct pH is given, but with incorrect reasoning. At pH 12, Asp is more negative so moves further (towards the positive electrode).

Mark for (b) (i) = 0/1

4 The correct pH is given, but with incorrect reasoning. At pH 2, Lys is more positive so moves further (towards the negative electrode).

Mark for (b) (ii) = 0/1

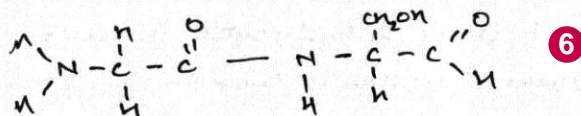
5 An incorrect answer. The candidate should have chosen pH 12 where Tyr is more negative so moves further (towards the positive electrode).

Mark for (b) (iii) = 0/1

Example candidate response – low, continued

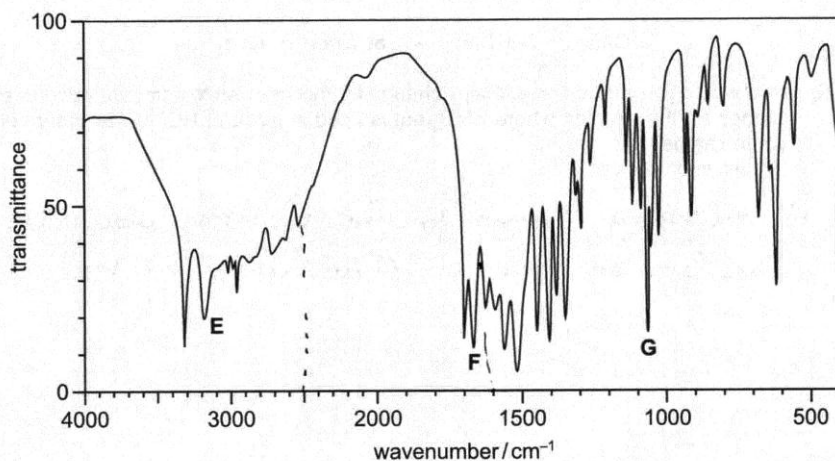
Examiner comments

(c) (i) Draw the structure of the dipeptide Gly-Ser, showing the peptide bond in full.



[2]

The infra-red spectrum of Gly-Ser is shown below.



(ii) Use the *Data Booklet* to identify the bond in the molecule of Gly-Ser that is responsible for each of the peaks indicated on the above infra-red spectrum.

E O-H carboxylic
 F C=O amides
 G C-O carbonyl

7

[2]

[Total: 12]

6 One mark is awarded for the peptide bond. The candidate has drawn an aldehyde functional group instead of a carboxylic acid in the Ser unit of the dipeptide.

Mark for (c) (i) = 1/2

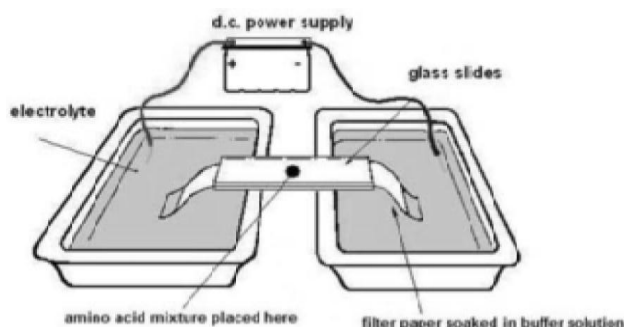
7 A correct answer.

Mark for (c) (ii) = 2/2

Total marks awarded = 3 out of 12

How the candidate could have improved their answer

(a) (i) The candidate should have drawn a clear labelled diagram as shown below.



(a) (ii) The candidate should have related the direction of movement to the charge on the amino acid, and the distance travelled to the M_r of the amino acid.

(b) The candidate could have chosen:

- for Asp and Val a pH 12 where Asp is more negative (as a 2⁻ charge) so moves further (towards the positive electrode),
- for Lys and Ser, a pH 2 where Lys is more positive (as a 2⁺ charge) so moves further (towards the negative electrode),
- Tyr and Phe, a pH 12 where Tyr is more negative (as a 2⁻ charge) so moves further (towards the positive electrode).

(c) (i) The candidate should have drawn a carboxylic acid group instead of an aldehyde group in the Ser unit of the dipeptide.

Mark awarded = (a) (i) 0/3, (ii) 0/2

Mark awarded = (b) 0/3

Mark awarded = (c) (i) 1/2, (ii) 2/2

Total marks awarded = 3 out of 12

Common mistakes candidates made in this question

(a) (i) Common errors included an incomplete circuit and omitting the filter paper or gel.

(a) (ii) Some candidates did not relate the size/ M_r /magnitude of the charge to the speed of movement/distance travelled. Mass was often stated instead of M_r , which was not sufficient.

(b) Many candidates had difficulty identifying the charge on the amino acid at a particular pH and chose an incorrect pH. Some candidates referred only to the R group in their explanation and omitted the effect of pH on the COOH and NH₂ groups. For example, for Asp and Val at pH 12 Val does not move as it has no charge and Asp has a negative charge and moves towards the positive electrode.

(c) (i) Common errors were connectivity errors linked to the CH₂OH and COOH groups and drawing a polymer unit with continuation bonds.

(c) (ii) Common errors included giving the structure or naming the functional group without highlighting the specific bond responsible for the peak.

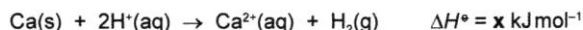
Question 8

Example candidate response – high	Examiner comments
<p>8 (a) Describe and explain the trend in the solubility of the hydroxides down Group 2.</p> <p>So going down group Group 2, both lattice energy and hydration energy decreases. Lattice energy decreases more significantly than hydration energy. Et Enthalpy of solution becomes more exothermic and so, solubility of Group 2 hydroxide increases. 1 [3]</p> <p>(b) Calcium reacts vigorously with HCl(aq) producing H₂(g).</p> $\text{Ca(s)} + 2\text{HCl(aq)} \rightarrow \text{CaCl}_2\text{(aq)} + \text{H}_2\text{(g)}$ <p>(i) How would you expect the enthalpy change for this reaction to compare with the enthalpy change for the reaction where HNO₃(aq) is used in place of HCl but all other conditions are the same? Explain your answer.</p> <p>It will be about the same since both HCl and HNO₃ are strong acid and ionizes monoprotic acid. 2 [1]</p>	<p>1 A correct answer. Mark for (a) = 3/3</p> <p>2 A correct answer. Mark for (b) (i) = 1/1</p>

Example candidate response – high, continued

Examiner comments

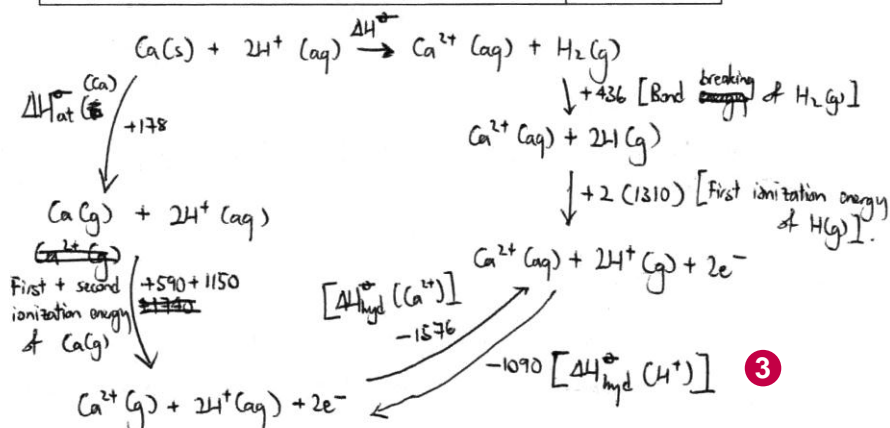
(ii) The ionic equation for this reaction is shown.



Construct a **fully labelled** Hess' Law cycle to connect each side of this equation to the relevant gas phase ions.

Use your cycle, the following data, and data from the *Data Booklet*, to calculate a value for **x**.

standard enthalpy of atomisation of Ca(s), $\Delta H_{\text{at}}^\ominus(\text{Ca})$	+178 kJ mol ⁻¹
standard enthalpy of hydration of Ca ²⁺ (g), $\Delta H_{\text{hyd}}^\ominus(\text{Ca}^{2+})$	-1576 kJ mol ⁻¹
standard enthalpy of hydration of H ⁺ (g), $\Delta H_{\text{hyd}}^\ominus(\text{H}^+)$	-1090 kJ mol ⁻¹



$$\Delta H^\ominus + 436 + 2(1310) = 178 + 1740 - 1576 + 1090$$

$$\therefore \Delta H^\ominus = -1624 \text{ kJ mol}^{-1}$$

$$x = -1624 \text{ kJ mol}^{-1} \text{ [4]}$$

(c) The standard enthalpy change for the reaction between Ca(s) and CH₃CO₂H(aq) is **less negative** than **x** by 2 kJ mol⁻¹.

Suggest an explanation for this.

CH₃CO₂H is a ~~tot~~ weak acid and produces lower concentrations of H⁺ ion. Hence, reaction is less exothermic since less energy is released. [2]

[Total: 10]

3 One mark for a clear, correct Hess cycle diagram. Two marks for -1624. The candidate only uses 1 × -1090 in the calculation instead of 2 × -1090.

Mark for (b) (ii) = 3/4

4 This earns the first marking point. For the other mark, the candidate should have linked the less negative enthalpy change to the energy needed to dissociate the weak acid.

Mark for (c) = 1/2

Total marks awarded = 8 out of 10

How the candidate could have improved their answer

(b) (ii) The candidate should have used 2×-1090 in the calculation of x as shown.

$$x = \Delta H_{\text{at}}(\text{Ca}) + \text{IE}(1) + \text{IE}(2) - 2\Delta H_{\text{hyd}}(\text{H}^+) + \Delta H_{\text{hyd}}(\text{Ca}^{2+}) - 2\text{IE}(\text{H}) - E(\text{H-H})$$

$$x = 178 + 590 + 1150 + 2(1090) - 1576 - 2(1310) - 436$$

$$x = -534 \text{ kJ mol}^{-1}$$

(c) The candidate should have linked the less negative enthalpy change to the energy needed to dissociate $\text{CH}_3\text{CO}_2\text{H}$.

Mark awarded = **(a) 3/3**

Mark awarded = **(b) (i) 1/1, (ii) 3/4**

Mark awarded = **(c) 1/2**

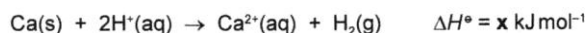
Total marks awarded = 8 out of 10

Example candidate response – middle/low	Examiner comments
<p>8 (a) Describe and explain the trend in the solubility of the hydroxides down Group 2.</p> <p>1 They get more soluble going down the group. As ΔH_{hyd} and $\Delta H_{\text{L.E}}$ both decrease but $\Delta H_{\text{L.E}}$ decreases at faster rate hence ΔH_{sol} gets more exothermic. [3]</p> <p>(b) Calcium reacts vigorously with $\text{HCl}(\text{aq})$ producing $\text{H}_2(\text{g})$.</p> $\text{Ca}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2(\text{g})$ <p>(i) How would you expect the enthalpy change for this reaction to compare with the enthalpy change for the reaction where $\text{HNO}_3(\text{aq})$ is used in place of HCl but all other conditions are the same? Explain your answer.</p> <p>2 The enthalpy would be higher as it requires more energy for HNO_3 [1]</p>	<p>1 A correct answer. Mark for (a) = 3/3</p> <p>2 An incorrect answer. HNO_3 or HCl are both strong acids so the enthalpy change should be similar. The ionic equation for the reaction of Ca with HNO_3 or HCl is the same. Mark for (b) (i) = 0/1</p>

Example candidate response – middle/low, continued

Examiner comments

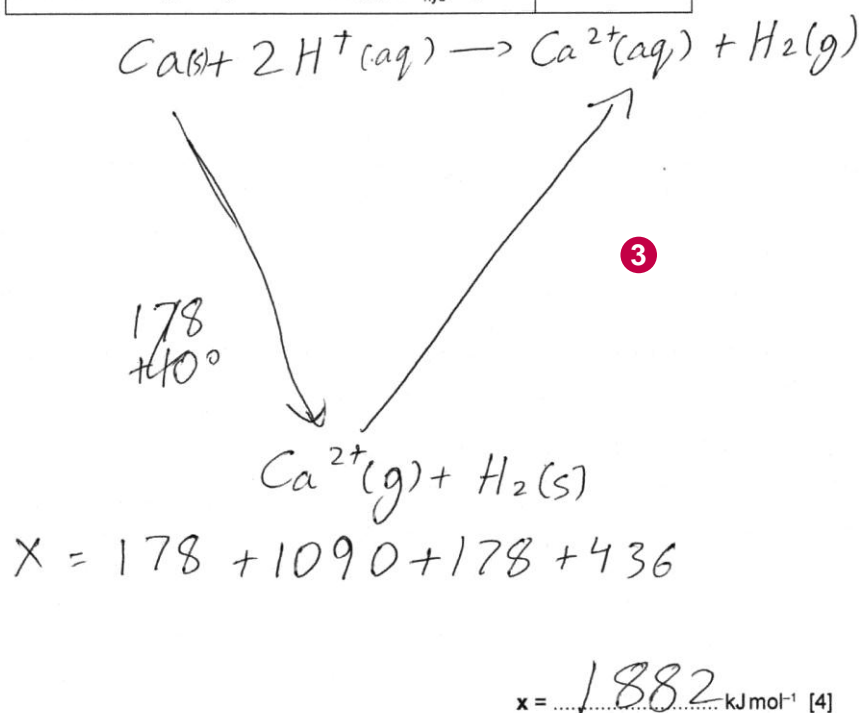
(ii) The ionic equation for this reaction is shown.



Construct a **fully labelled** Hess' Law cycle to connect each side of this equation to the relevant gas phase ions.

Use your cycle, the following data, **and** data from the *Data Booklet*, to calculate a value for **x**.

standard enthalpy of atomisation of Ca(s), $\Delta H_{\text{at}}^\circ(\text{Ca})$	+178 kJ mol ⁻¹
standard enthalpy of hydration of Ca ²⁺ (g), $\Delta H_{\text{hyd}}^\circ(\text{Ca}^{2+})$	-1576 kJ mol ⁻¹
standard enthalpy of hydration of H ⁺ (g), $\Delta H_{\text{hyd}}^\circ(\text{H}^+)$	-1090 kJ mol ⁻¹



(c) The standard enthalpy change for the reaction between Ca(s) and CH₃CO₂H(aq) is **less negative** than **x** by 2 kJ mol⁻¹.

Suggest an explanation for this.

Because of its bigger ionic radi.

[Total: 10]

3 No marks. The Hess cycle should have '2H⁺(g)' instead of 'H₂(s)'. The answer for **x** is -534. The candidate makes at least three errors in their calculation.

Mark for (b) (ii) = 0/4

4 No marks. CH₃CO₂H is a weak acid so some energy is needed to dissociate the acid.

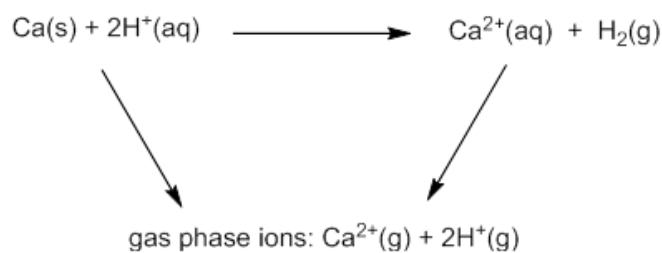
Mark for (c) = 0/2

Total marks awarded = 3 out of 10

How the candidate could have improved their answer

(b) (i) The candidate should have suggested that the enthalpy change would be similar since they are both strong acids.

(b) (ii) The Hess cycle should have had '2H⁺(g)' instead of 'H₂(s)':



The answer to **x** is -534 and can be calculated as shown:

$$x = \Delta H_{\text{at}}(\text{Ca}) + \text{IE}(1) + \text{IE}(2) - 2\Delta H_{\text{hyd}}(\text{H}^+) + \Delta H_{\text{hyd}}(\text{Ca}^{2+}) - 2\text{IE}(\text{H}) - E(\text{H}-\text{H})$$

$$x = 178 + 590 + 1150 + 2(1090) - 1576 - 2(1310) - 436$$

$$x = -534 \text{ kJ mol}^{-1}$$

(c) The candidate should have stated that CH₃CO₂H is a weak acid so some energy is needed to dissociate the acid.

Mark awarded = **(a) 3/3**

Mark awarded = **(b) (i) 0/1, (ii) 0/4**

Mark awarded = **(c) 0/2**

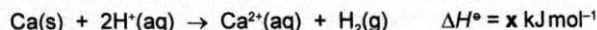
Total marks awarded = 3 out of 10

Example candidate response – low	Examiner comments
<p>8 (a) Describe and explain the trend in the solubility of the hydroxides down Group 2.</p> <p>Their solubility is decreases as we go down the group because ΔH of hydration decreases down the group due to greater ionic radius and ΔH of hydration becomes more positive down the group so ΔH of solution decreases. [3]</p> <p>(b) Calcium reacts vigorously with $\text{HCl}(\text{aq})$ producing $\text{H}_2(\text{g})$.</p> $\text{Ca}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2(\text{g})$ <p>(i) How would you expect the enthalpy change for this reaction to compare with the enthalpy change for the reaction where $\text{HNO}_3(\text{aq})$ is used in place of HCl but all other conditions are the same? Explain your answer. [1]</p> <p>Enthalpy change would increase because HNO_3 acid is a strong acid and reacts vigorously.</p>	<p>1 Credit is earned for the enthalpy of solution becoming less negative linked to the solubility decreasing. The solubility of the hydroxides increases down Group 2 as lattice energy decreases faster than enthalpy of hydration. So enthalpy of solution becomes more negative.</p> <p>Mark for (a) = 1/3</p> <p>2 An incorrect answer. As HNO_3 or HCl are both strong acids the enthalpy change should be similar.</p> <p>Mark for (b) (i) = 0/1</p>

Example candidate response – low, continued

Examiner comments

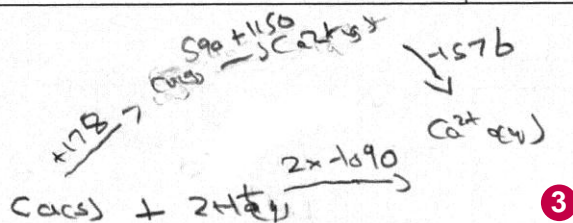
(ii) The ionic equation for this reaction is shown.



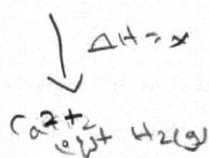
Construct a **fully labelled** Hess' Law cycle to connect each side of this equation to the relevant gas phase ions.

Use your cycle, the following data, and data from the *Data Booklet*, to calculate a value for **x**.

standard enthalpy of atomisation of Ca(s), $\Delta H_{\text{at}}^\circ(\text{Ca})$	+178 kJ mol ⁻¹
standard enthalpy of hydration of Ca ²⁺ (g), $\Delta H_{\text{hyd}}^\circ(\text{Ca}^{2+})$	-1576 kJ mol ⁻¹
standard enthalpy of hydration of H ⁺ (g), $\Delta H_{\text{hyd}}^\circ(\text{H}^+)$	-1090 kJ mol ⁻¹



3



$$x = 178 + 1150 + (-1576) + (2 \times -1090)$$

$$x = 1918 - 3756$$

$$x = -1838$$

$$x = -1838 \text{ kJ mol}^{-1} \text{ [4]}$$

(c) The standard enthalpy change for the reaction between Ca(s) and CH₃CO₂H(aq) is **less negative** than **x** by 2 kJ mol⁻¹.

Suggest an explanation for this.

4

CH₃CO₂H does not fully decompose into H⁺ ions
 as CH₃CO₂⁻ + H⁺ The number of CH₃CO₂⁻ ions is less.
 so less water occur

[Total: 10]

3 No marks. The Hess cycle is incorrect and it is not a cycle. The answer for x is -534. The candidate makes three errors in their calculation.

Mark for (b) (ii) = 0/4

4 Examiners allowed marking point one for 'CH₃CO₂H does not fully decompose into H⁺ and CH₃CO₂⁻' as alternative wording for 'is incompletely ionised'. For the second mark, the candidate needed to state that this dissociation requires energy.

Mark for (c) = 1/2

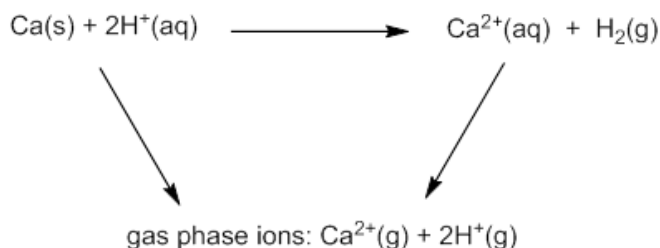
Total marks awarded = 2 out of 10

How the candidate could have improved their answer

(a) The candidate should have stated that solubility increases (down the group) because lattice energy decreases faster than ΔH_{hyd} . This results in the enthalpy of solution becoming more exothermic.

(b) (i) The candidate should have stated that HNO_3 and HCl are both strong acids so the enthalpy change would be similar.

(b) (ii) The Hess cycle should have been drawn as follows:



The answer to **x** is -534 and can be calculated as shown:

$$\begin{aligned}
 x &= \Delta H_{\text{at}}(\text{Ca}) + \text{IE}(1) + \text{IE}(2) - 2\Delta H_{\text{hyd}}(\text{H}^+) + \Delta H_{\text{hyd}}(\text{Ca}^{2+}) - 2\text{IE}(\text{H}) - E(\text{H}-\text{H}) \\
 x &= 178 + 590 + 1150 + 2(1090) - 1576 - 2(1310) - 436 \\
 x &= \mathbf{-534 \text{ kJ mol}^{-1}}
 \end{aligned}$$

(c) The candidate should have described the breakdown of $\text{CH}_3\text{CO}_2\text{H}$ into H^+ ions and CH_3CO_2^- ions as a dissociation. For full marks, examiners required candidates to suggest that this would require some energy.

Mark awarded = **(a) 1/3**

Mark awarded = **(b) (i) 0/1, (ii) 0/4**

Mark awarded = **(c) 1/2**

Total marks awarded = 2 out of 10

Common mistakes candidates made in this question

(a) A common error was omitting any reference to the enthalpy of solution, ΔH_{sol} . Some candidates stated the solubility decreased down the group.

(b) (i) Many candidates did not appreciate that both acids would be fully ionised.

(b) (ii) Many candidates did not draw a complete Hess cycle. A wide range of answers was seen for the calculation. Common errors included missing out necessary values, multiples and using incorrect signs.

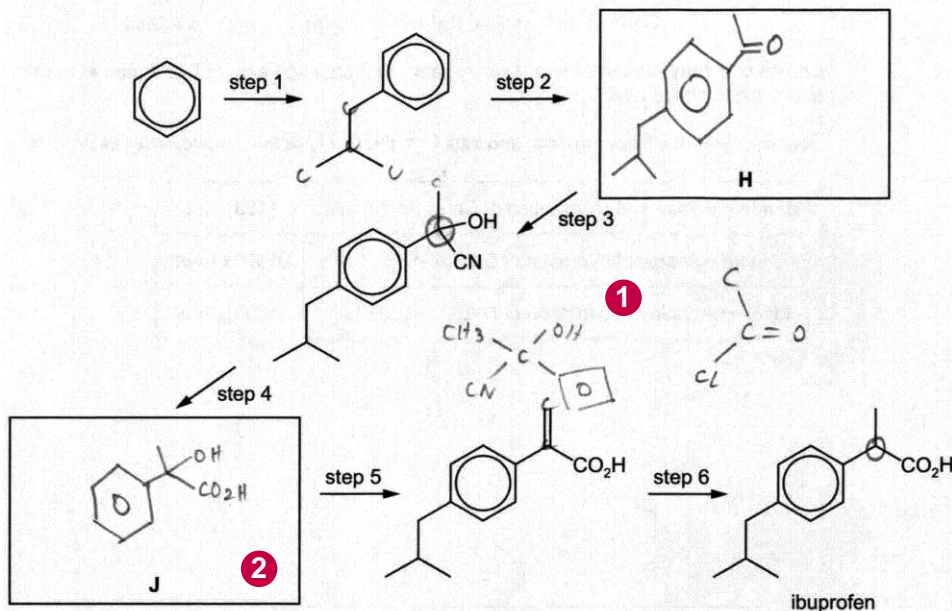
(c) Many candidates did not explain the difference in standard enthalpy change between the two acids.

Question 9

Example candidate response – high

Examiner comments

9 The anti-inflammatory drug ibuprofen can be synthesised from benzene via the following six steps.



(a) Draw circles around any chiral carbon atoms in the above five formulae. [1]

(b) Suggest the structures of compounds H and J and draw them in the boxes above. [2]

(c) Suggest reagents and conditions for steps 1-6.

step 1 ... $(\text{CH}_3)_2\text{CHCH}_2\text{Cl} + \text{AlCl}_3$.

step 2 ... $\text{CH}_3\text{COCl} + \text{AlCl}_3$.

step 3 ... HCN in NaCN + heat under reflux. **3**

step 4 ... dil HCl + heat under reflux,

step 5 ... Al_2O_3 conc HCl + heat to 300°C . dehydrate

step 6 ... Ni + $\text{H}_2(\text{g})$ at 100°C . hydrogenate [6]

(d) Name the mechanism of step 1 and state the type of reaction for step 6.

step 1 ... Electrophilic substitution

step 6 ... Reduction **4**

[2]

[Total: 11]

1 One mark for identifying both chiral centres.

Mark for (a) = 1/1

2 One mark for the correct structure of compound H. The alkyl group has been omitted from compound J.

Mark for (b) = 1/2

3 Correct reagents and conditions are given for all six steps.

Mark for (c) = 6/6

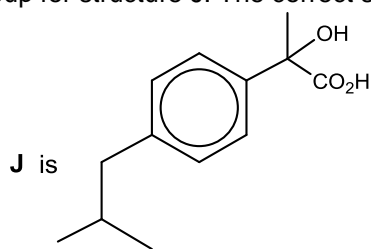
4 Two marks for identifying the correct name of the mechanism and type of reaction here.

Mark for (d) = 2/2

Total marks awarded = 10 out of 11

How the candidate could have improved their answer

(b) The candidate omitted the alkyl group for structure J. The correct structure of J is as shown:



Mark awarded = (a) 1/1

Mark awarded = (b) 1/2

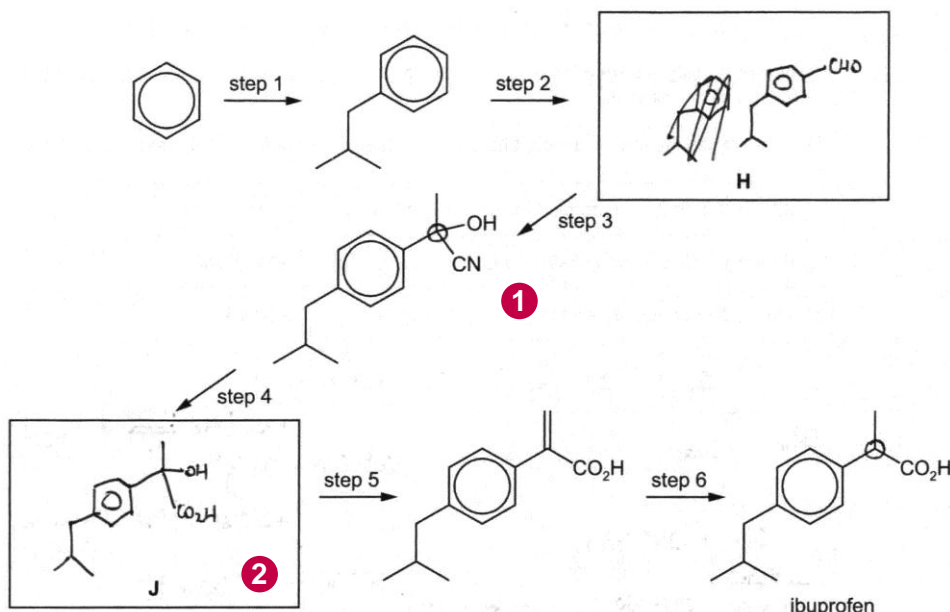
Mark awarded = (c) 6/6

Mark awarded = (d) 2/2

Total marks awarded = 10 out of 11

Example candidate response – middle

9 The anti-inflammatory drug ibuprofen can be synthesised from benzene via the following six steps.



(a) Draw circles around any chiral carbon atoms in the above five formulae. [1]

(b) Suggest the structures of compounds H and J and draw them in the boxes above. [2]

(c) Suggest reagents and conditions for steps 1-6.

step 1 $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Cl}$ in AlCl_3 heat under reflux

step 2 $\text{Cl}-\text{CHO}$ with AlCl_3 heat under reflux

step 3 HCN with a little NaCN heat under reflux. 3

step 4 HCl (aq) heat under reflux.

step 5 concentrated H_2SO_4 heat ~~to~~ heat at 180°C .

step 6 H_2 (g) + Pt (s) [6]

(d) Name the mechanism of step 1 and state the type of reaction for step 6.

step 1 Electrophilic substitution 4

step 6 Electrophilic addition. [2]

[Total: 11]

Examiner comments

1 Both chiral centres are correctly identified.

Mark for (a) = 1/1

2 Structure J is correct. Structure H is incorrect; it should be the methylketone substituted product, $-\text{COCH}_3$ instead of $-\text{CHO}$.

Mark for (b) = 1/2

3 The reagents and conditions are correct for steps 3, 4 and 5. In step 1 the chloroalkane should be $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$. In step 2 the reagent should be CH_3COCl . In step 6 a nickel catalyst should be used (H_2/Pt would also cause the hydrogenation of the benzene ring).

Mark for (c) = 3/6

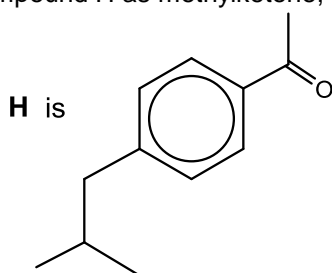
4 Two marks awarded. Examiners ignored the term 'electrophilic' for step 6; 'addition' only is required here.

Mark for (d) = 2/2

Total marks awarded = 7 out of 11

How the candidate could have improved their answer

(b) The candidate needed to identify compound H as methylketone, as shown below:



(c) The candidate should have suggested the reagents and conditions for steps 1, 2 and 6 as shown below:

- step 1 the chloroalkane should be $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$ with AlCl_3
- step 2 the reagent should be CH_3COCl with AlCl_3
- step 6 a nickel catalyst should be used with H_2 to avoid hydrogenation of the benzene ring.

(d) The type of reaction for step 6 should be 'addition' or 'reduction'.

Mark awarded = (a) 1/1

Mark awarded = (b) 1/2

Mark awarded = (c) 3/6

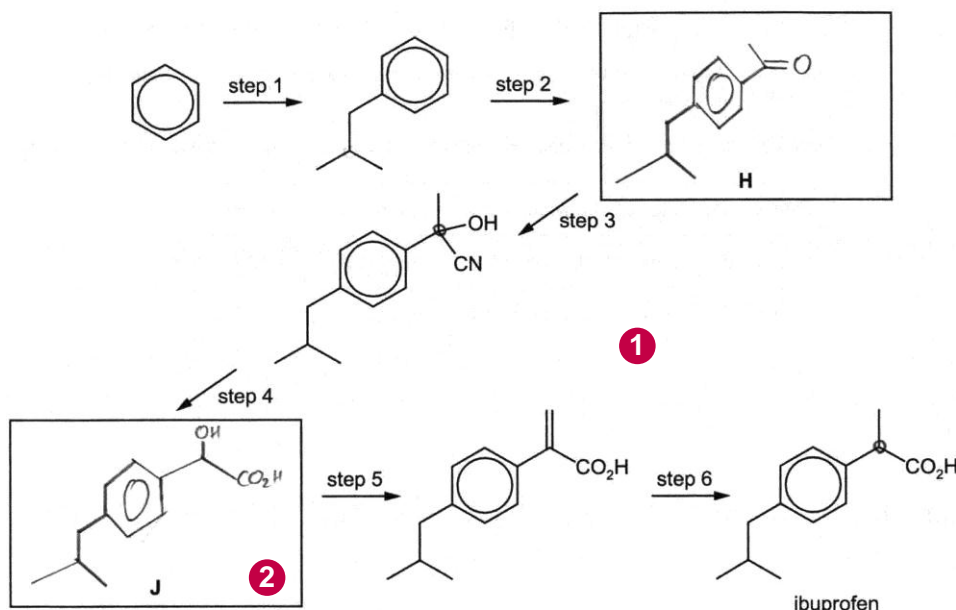
Mark awarded = (d) 2/2

Total marks awarded = 7 out of 11

Example candidate response – low

Examiner comments

9 The anti-inflammatory drug ibuprofen can be synthesised from benzene via the following six steps.



(a) Draw circles around any chiral carbon atoms in the above five formulae. [1]

(b) Suggest the structures of compounds H and J and draw them in the boxes above. [2]

(c) Suggest reagents and conditions for steps 1-6.

step 1 3-methyl (CH₃)₂CHCH₂Cl + AlCl₃ + heat

step 2 CH₃COCl + AlCl₃ + heat

step 3 HCN in sulphuric acid

step 4 KMnO₄ + heat

step 5 LiAlH₄ in dry ether

step 6 CH₃CHO + LiAlH₄ in dry ether

[6]

(d) Name the mechanism of step 1 and state the type of reaction for step 6.

step 1 electrophilic substitution

step 6 nucleophilic substitution

[2]

[Total: 11]

1 Both chiral centres are identified.

Mark for (a) = 1/1

2 One mark for the correct structure of compound H. Structure J is incorrect as a methyl group has been omitted.

Mark for (b) = 1/2

3 Two marks are awarded for steps 1 and 2. The reagents and conditions for the other steps should be: step 3 HCN + NaCN, step 4 aqueous HCl + heat, step 5 conc. H₂SO₄ + heat and step 6 H₂ + Ni catalyst (+ heat).

Mark for (c) = 2/6

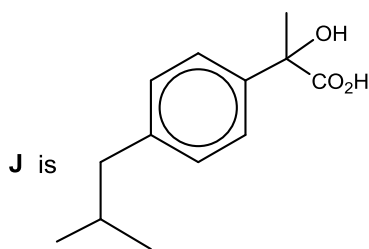
4 One mark for the correct mechanism. The type of reaction for step 6 is reduction.

Mark for (d) = 1/2

Total marks awarded = 5 out of 11

How the candidate could have improved their answer

(b) Structure J should have been identified as shown below:



(c) The candidate should have suggested the reagents and conditions for steps 3–6 as shown below:

- step 3 HCN + NaCN
- step 4 aqueous HCl + heat
- step 5 conc. H₂SO₄ + heat
- step 6 H₂ + Ni catalyst (+ heat).

(d) The candidate should have identified the type of reaction for step 6 as 'reduction'.

Mark awarded = (a) 1/1

Mark awarded = (b) 1/2

Mark awarded = (c) 2/6

Mark awarded = (d) 1/2

Total marks awarded = 5 out of 11

Common mistakes candidates made in this question

(a) A number of candidates gave no response for this question. Some candidates failed to identify the chiral centre in ibuprofen.

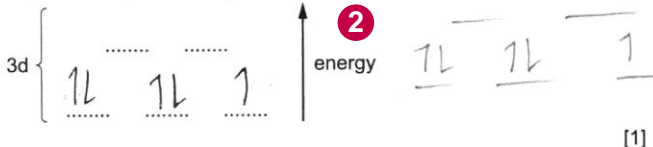
(b) A common error was identifying compound H as an alcohol.

(c) Common errors were:

- incorrect structures for the halogenoalkane and acyl chlorides
- omitting AlCl₃ in steps 1 and 2
- omitting 'concentrated' with H₂SO₄/H₃PO₄
- the use of LiAlH₄ in step 6.

(d) Some candidates identified the mechanism as electrophilic addition and the type of reaction as an elimination or substitution reaction.

Question 10

Example candidate response – high	Examiner comments
<p>10 (a) (i) Complete the electronic configuration of the iron atom.</p> <p>Fe $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ 1 [1]</p> <p>(ii) In some of its complexes, the Fe^{3+} ion has only one unpaired electron in its d orbitals.</p> <p>Using the symbols \uparrow and \downarrow to represent electrons of opposite spins, complete the following diagram to show the d orbital electronic configuration of this Fe^{3+} ion.</p>  <p>2 [1]</p> <p>(b) A solution containing a mixture of $Sn^{2+}(aq)$ and $Sn^{4+}(aq)$ is added to a solution containing a mixture of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$.</p> <p>Use E° data from the <i>Data Booklet</i> to predict the reaction that might take place when the two solutions are mixed, and write an equation for the reaction.</p> <p>$Fe^{3+} + e^- \rightarrow Fe^{2+} + 0.77$</p> <p>$Sn^{4+} + 2e^- \rightarrow Sn^{2+} + 0.15$ 3</p> <p>[2]</p> <p>$Sn^{2+} + 2Fe^{3+} \rightarrow 2Fe^{2+} + Sn^{4+}$ $E^\circ_{cell} = +0.62V$</p> <p>(c) Hexaquairon(III) ions are pale violet. They form a colourless complex with fluoride ions, F^-, equilibrium 1, and a deep-red complex with thiocyanate ions, SCN^-, equilibrium 2.</p> <p>$[Fe(H_2O)_6]^{3+} + F^- \rightleftharpoons [Fe(H_2O)_5F]^{2+} + H_2O$ equilibrium 1 $K_{stab} = 2.0 \times 10^9 \text{ mol}^{-1} \text{ dm}^3$ violet colourless</p> <p>$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(H_2O)_5SCN]^{2+} + H_2O$ equilibrium 2 $K_{stab} = 1.0 \times 10^9 \text{ mol}^{-1} \text{ dm}^3$ violet deep-red</p> <p>(i) Predict and explain the sequence of colour changes you would observe in each of the following experiments.</p> <ul style="list-style-type: none"> A few drops of $KSCN(aq)$ are added to 5 cm^3 of $Fe^{3+}(aq)$, followed by a few drops of $KF(aq)$. <p>violet color to deep red purple to pale purple.</p> <p>A few drops of $KSCN$ forms a deep red complex but color mixing makes it purple. Adding KF forms a colorless complex through substitution but color mixing makes it paler. Higher K_{stab} from KF has a greater effect. <ul style="list-style-type: none"> A few drops of $KF(aq)$ are added to 5 cm^3 of $Fe^{3+}(aq)$, followed by a few drops of $KSCN(aq)$. <p>Violet to pale violet to pale purple. 4</p> <p>The adding of KF makes a colorless complex that makes the color paler. Adding a few drops of $KSCN$ makes a deep red complex which makes the color a pale purple due to color mixing. [4]</p> <p>(ii) What type of reaction is occurring during the experiments in (i)?</p> <p>Ligand substitution reaction 5 [1]</p> <p>[Total: 9]</p> </p>	<p>1 The correct electronic configuration of Fe.</p> <p>Mark for (a) (i) = 1/1</p> <p>2 A correct answer.</p> <p>Mark for (a) (ii) = 1/1</p> <p>3 Correct use of the data and a balanced equation given.</p> <p>Mark for (b) = 2/2</p> <p>4 Three correct colour changes identified but not explained. The examiner expected candidates to give the reasons for these colour changes. For example, the stability of the complex ion of $[Fe(H_2O)_5F]^{2+}$ is greater than $[Fe(H_2O)_5SCN]^{2+}$.</p> <p>Mark for (c) (i) = 2/4</p> <p>5 A correct type of reaction identified.</p> <p>Mark for (c) (ii) = 1/1</p> <p>Total marks awarded = 7 out of 9</p>

How the candidate could have improved their answer

(c) (i) The candidate needed to say that when a few drops of KSCN(aq) are added to the colourless solution of $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$, there is no change and the solution stays colourless. This is because the stability constant for $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$ is greater than $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^+$.

Mark awarded = **(a) (i) 1/1, (ii) 1/1**

Mark awarded = **(b) 2/2**

Mark awarded = **(c) (i) 2/4, (ii) 1/1**

Total marks awarded = 7 out of 9

Example candidate response – middle

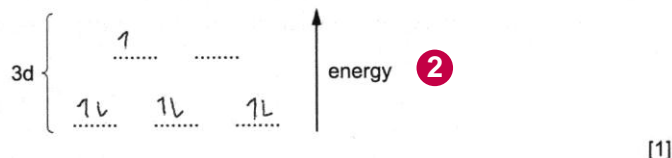
Examiner comments

10 (a) (i) Complete the electronic configuration of the iron atom.



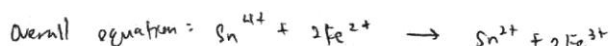
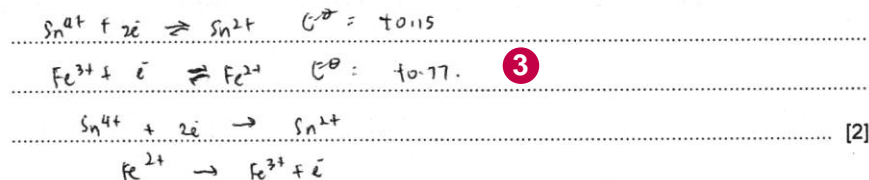
(ii) In some of its complexes, the Fe^{3+} ion has **only one** unpaired electron in its d orbitals.

Using the symbols \uparrow and \downarrow to represent electrons of opposite spins, complete the following diagram to show the d orbital electronic configuration of **this** Fe^{3+} ion.

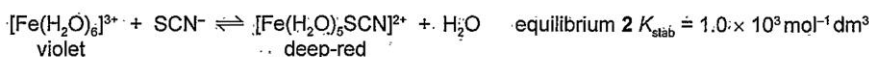


(b) A solution containing a mixture of $Sn^{2+}(aq)$ and $Sn^{4+}(aq)$ is added to a solution containing a mixture of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$.

Use E^\ominus data from the *Data Booklet* to predict the reaction that might take place when the two solutions are mixed, and write an equation for the reaction.



(c) Hexaquairon(III) ions are pale violet. They form a colourless complex with fluoride ions, F^- , equilibrium 1, and a deep-red complex with thiocyanate ions, SCN^- , equilibrium 2.



(i) Predict and explain the **sequence** of colour changes you would observe in each of the following experiments.

- A few drops of $KSCN(aq)$ are added to 5 cm^3 of $Fe^{3+}(aq)$, followed by a few drops of $KF(aq)$.

From violet to deep red to colourless. [4]

SCN^- ligand is exchanged with H_2O . Then F^- is exchanged with SCN^- .

- A few drops of $KF(aq)$ are added to 5 cm^3 of $Fe^{3+}(aq)$, followed by a few drops of $KSCN(aq)$.

From violet to colourless to deep red.

F^- ligand is exchanged with H_2O then SCN^- is exchanged with F^- .

[4]

(ii) What *type* of reaction is occurring during the experiments in (i)?

Ligand exchange. [5] [1]

1 An incorrect answer. It should be $3d^6$.

Mark for (a) (i) = 0/1

2 One mark is awarded for an error carried forward here. This diagram has only one unpaired electron and shows the loss of three electrons (two from the 4s and one from the 3d subshells).

Mark for (a) (ii) = 1/1

3 One mark for extracting relevant E^\ominus data from the *Data Booklet*. The candidate gives the equation for the reverse (non-spontaneous) reaction.

Mark for (b) = 1/2

4 Three correct colour changes identified, but not explained. The examiner expected candidates to give the reasons for these colour changes. For example, the stability constant for equilibrium 1 is greater than equilibrium 2.

Mark for (c) (i) = 2/4

5 A correct answer.

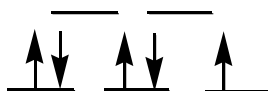
Mark for (c) (ii) = 1/1

Total marks awarded = 5 out of 9

How the candidate could have improved their answer

(a) (i) The electronic configuration of an iron atom should have been completed by $3s^23p^63d^64s^2$.

(a) (ii) The candidate was awarded this mark for the error carried forward from their incorrect answer to (a)(i). The correct answer is as shown:



(b) The correct equation is: $\text{Sn}^{2+} + 2\text{Fe}^{3+} \longrightarrow \text{Sn}^{4+} + 2\text{Fe}^{2+}$

(c) (i) When a few drops of $\text{KSCN}(\text{aq})$ are added to the colourless solution of $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$, there is no change and the solution stays colourless. This is because the stability of the complex ion $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$ is greater than $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^+$.

Mark awarded = **(a) (i) 0/1, (ii) 1/1**

Mark awarded = **(b) 1/2**

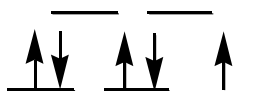
Mark awarded = **(c) (i) 2/4, (ii) 1/1**

Total marks awarded = 5 out of 9

Example candidate response – low	Examiner comments
<p>10 (a) (i) Complete the electronic configuration of the iron atom.</p> <p>Fe $1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^2 3d^6$ ① [1]</p> <p>(ii) In some of its complexes, the Fe^{3+} ion has only one unpaired electron in its d orbitals.</p> <p>Using the symbols \uparrow and \downarrow to represent electrons of opposite spins, complete the following diagram to show the d orbital electronic configuration of this Fe^{3+} ion.</p> <div style="text-align: center;"> <p style="text-align: right;">② [1]</p> </div> <p>(b) A solution containing a mixture of $Sn^{2+}(aq)$ and $Sn^{4+}(aq)$ is added to a solution containing a mixture of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$.</p> <p>Use E^\ominus data from the <i>Data Booklet</i> to predict the reaction that might take place when the two solutions are mixed, and write an equation for the reaction.</p> <p>$E^\ominus = 0.77 - 0.15 = +0.62V$, the reaction is feasible. Sn^{2+} ③ [2]</p> <p>$2Fe^{3+} + Sn^{2+} \rightarrow Sn^{4+} + 2Fe^{2+}$</p> <p style="text-align: right;">$Sn = +0.15$ $+0.77$</p> <p style="text-align: center;">$0.77 - 0.15$</p> <p>$(Fe^{3+} + e^- \rightarrow Fe^{2+}) \times 2$</p> <p>$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$</p>	<p>① A correct answer.</p> <p>Mark for (a) (i) = 1/1</p> <p>② An incorrect answer. The candidate should have a $3d^5$ configuration in the lower three d orbitals.</p> <p>Mark for (a) (ii) = 0/1</p> <p>③ Two marks awarded for a correct answer.</p> <p>Mark for (b) = 2/2</p>

How the candidate could have improved their answer

(a) (ii) The candidate should have drawn a $3d^5$ configuration in the lower three d orbitals as shown:



(c) (i) The candidate should have given the following colour changes:

- KSCN added to Fe^{3+} followed by KF: (violet) \longrightarrow deep-red \longrightarrow colourless
- KF added to Fe^{3+} followed by KSCN: (violet) \longrightarrow colourless \longrightarrow stays colourless

This is due to the fact that the stability constant for $[Fe(H_2O)_5F]^{2+}$ is greater than $[Fe(H_2O)_5SCN]^+$.

Mark awarded = **(a) (i) 1/1, (ii) 0/1**

Mark awarded = **(b) 2/2**

Mark awarded = **(c) (i) 0/4, (ii) 1/1**

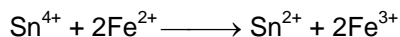
Total marks awarded = 4 out of 9

Common mistakes candidates made in this question

(a) (i) Occasionally $3s^23p^63d^8$ was seen.

(a) (ii) Many candidates completed the diagram with more than one unpaired electron or electrons not in their lowest energy state.

(b) Common errors included an unbalanced equation, and writing the equation for the reverse reaction as shown:



(c) (i) Many candidates found it difficult to apply the information in the question and gave a wide range of different colour changes in their answers. Most candidates omitted any explanation for their colour changes.

(c) (ii) The most common error was 'displacement' on its own without 'ligand'.

Cambridge International Examinations
1 Hills Road, Cambridge, CB1 2EU, United Kingdom
t: +44 1223 553554 f: +44 1223 553558
e: info@cie.org.uk www.cie.org.uk

© Cambridge International Examinations 2017
Version 3.0

