CAMBRIDGE
International Education

Cambridge International AS & A Level

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 2024**

MARK SCHEME

Maximum Mark: 100

Published

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Generic Marking Principles

These general marking principles must be applied by all examiners when marking candidate answers. They should be applied alongside the specific content of the mark scheme or generic level descriptions for a question. Each question paper and mark scheme will also comply with these marking principles.

GENERIC MARKING PRINCIPLE 1:

Marks must be awarded in line with:

- the specific content of the mark scheme or the generic level descriptors for the question
- the specific skills defined in the mark scheme or in the generic level descriptors for the question
- the standard of response required by a candidate as exemplified by the standardisation scripts.

GENERIC MARKING PRINCIPLE 2:

Marks awarded are always **whole marks** (not half marks, or other fractions).

GENERIC MARKING PRINCIPLE 3:

Marks must be awarded **positively**:

- marks are awarded for correct/valid answers, as defined in the mark scheme. However, credit is given for valid answers which go beyond the scope of the syllabus and mark scheme, referring to your Team Leader as appropriate
- marks are awarded when candidates clearly demonstrate what they know and can do
- marks are not deducted for errors
- marks are not deducted for omissions
- answers should only be judged on the quality of spelling, punctuation and grammar when these features are specifically assessed by the question as indicated by the mark scheme. The meaning, however, should be unambiguous.

GENERIC MARKING PRINCIPLE 4:

Rules must be applied consistently, e.g. in situations where candidates have not followed instructions or in the application of generic level descriptors.

GENERIC MARKING PRINCIPLE 5:

Marks should be awarded using the full range of marks defined in the mark scheme for the question (however; the use of the full mark range may be limited according to the quality of the candidate responses seen).

GENERIC MARKING PRINCIPLE 6:

Marks awarded are based solely on the requirements as defined in the mark scheme. Marks should not be awarded with grade thresholds or grade descriptors in mind.

Science-Specific Marking Principles

1 Examiners should consider the context and scientific use of any keywords when awarding marks. Although keywords may be present, marks should not be awarded if the keywords are used incorrectly.

2 The examiner should not choose between contradictory statements given in the same question part, and credit should not be awarded for any correct statement that is contradicted within the same question part. Wrong science that is irrelevant to the question should be ignored.

3 Although spellings do not have to be correct, spellings of syllabus terms must allow for clear and unambiguous separation from other syllabus terms with which they may be confused (e.g. ethane / ethene, glucagon / glycogen, refraction / reflection).

4 The error carried forward (ecf) principle should be applied, where appropriate. If an incorrect answer is subsequently used in a scientifically correct way, the candidate should be awarded these subsequent marking points. Further guidance will be included in the mark scheme where necessary and any exceptions to this general principle will be noted.

5 ‘List rule’ guidance

For questions that require ***n*** responses (e.g. State **two** reasons …):

- The response should be read as continuous prose, even when numbered answer spaces are provided.
- Any response marked *ignore* in the mark scheme should not count towards ***n***.
- Incorrect responses should not be awarded credit but will still count towards ***n***.
- Read the entire response to check for any responses that contradict those that would otherwise be credited. Credit should **not** be awarded for any responses that are contradicted within the rest of the response. Where two responses contradict one another, this should be treated as a single incorrect response.
- Non-contradictory responses after the first ***n*** responses may be ignored even if they include incorrect science.

6 Calculation specific guidance

Correct answers to calculations should be given full credit even if there is no working or incorrect working, **unless** the question states ‘show your working’.

For questions in which the number of significant figures required is not stated, credit should be awarded for correct answers when rounded by the examiner to the number of significant figures given in the mark scheme. This may not apply to measured values.

For answers given in standard form (e.g. $a \times 10^n$) in which the convention of restricting the value of the coefficient (a) to a value between 1 and 10 is not followed, credit may still be awarded if the answer can be converted to the answer given in the mark scheme.

Unless a separate mark is given for a unit, a missing or incorrect unit will normally mean that the final calculation mark is not awarded. Exceptions to this general principle will be noted in the mark scheme.

7 Guidance for chemical equations

Multiples / fractions of coefficients used in chemical equations are acceptable unless stated otherwise in the mark scheme.

State symbols given in an equation should be ignored unless asked for in the question or stated otherwise in the mark scheme.

Question	Answer	Marks
1(a)(i)	(enthalpy change when) one mole of a substance / solute **AND** dissolves in water / turns into an aqueous solution (to form a solution of infinite dilution)	**1**
1(a)(ii)	there is a (large) increase in entropy **OR** ΔS is positive **OR** $T\Delta S$ is positive	**1**
	so ΔG is negative / $T\Delta S$ outweighs ΔH	**1**
1(b)(i)	anionic charge density decreases (down the group / Cl^- to I^-)	**1**
	(so hydration enthalpies become less negative / less exothermic because) **less attraction** of **ion to water** / the **dipole–ion force weakens**	**1**
1(b)(ii)	the difference between ΔH_{latt} and ΔH_{hyd} remains roughly constant **OR** ΔH_{latt} and ΔH_{hyd} become less exothermic by a similar amount	**1**
1(b)(iii)	$\Delta H_{hyd}(K^+(g))$ = –629 + 21.0 –(–293) = **–315** kJ mol^{-1}	**1**
1(b)(iv)	solubility of PbI_2 = $7.1 \times 10^{-9} = x\cdot(2x)^2$ $\therefore x = \sqrt[3]{(\frac{1}{4} \times 7.1 \times 10^{-9})}$	**1**
	solubility of PbI_2 = **1.21×10^{-3}** mol dm^{-3} min 2sf	**1**
1(b)(v)	• Pb^{2+} has a greater charge • Pb^{2+} is smaller (than K^+) **OR** (Pb^{2+}) smaller ionic radius • greater attraction between Pb^{2+} and I^- **OR** ionic bond between Pb^{2+} and I^- is stronger **OR** lattice energy is more exothermic / more negative mark as • ✓ ✓	**2**
1(c)(i)	ΔS = 2(155.5) + 2(116.1) – 4(106.3) – 2(213.6) – 205.2	**1**
	ΔS = –514.4 (J K^{-1} mol^{-1}) min 3sf **ECF**	**1**

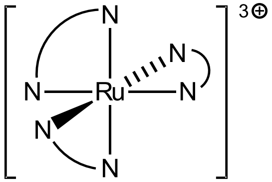
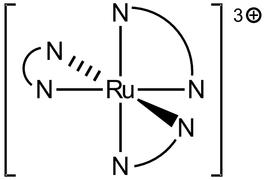
Question	Answer	Marks
1(c)(ii)	$\Delta G = \Delta H - T\Delta S$ **AND** use of 298 K for T **OR** clear working to represent this	**1**
	$\Delta G = -203.4 - 298(-514.4 / 1000)$ ΔG = **–50.1 OR –50.2** (kJ mol^{-1}) **OR** ΔG = **–50 108.8 J** min 3sf **ECF from (c)(i)** (negative so spontaneous)	**1**
1(c)(iii)	increases (in thermal stability down the group) **AND** (cat)ionic radius / ion size increases (down the group)	**1**
	less polarisation of anion / C—O bond / distortion of carbonate ion / CO_3^{2-} **OR** C–O is less weakened / stronger (down the group)	**1**
1(d)(i)	$2H^+(aq) + 2e^- \rightarrow H_2(g)$ **state symbols required**	**1**
1(d)(ii)	M1 moles of $S_2O_3^{2-} = \frac{21.35}{1000} \times 0.100 = 2.135 \times 10^{-3}$	**1**
	M2 calc of Q $= 2.135 \times 10^{-3} \times 0.5 \times 2 \times 96500 = 206.02 / 205.68$ **ECF**	**1**
	M3 = answer $I = 206 / (8 \times 60) = 0.428$ **OR** 0.429 A min 2sf **ECF**	**1**
1(e)(i)	reaction 1 concentrated HNO_3 **AND** concentrated H_2SO_4 (concentrated seen once)	**1**
	reaction 2 Sn **AND** (concentrated) HCl	**1**
1(e)(ii)	step 1 $NaNO_2 + HCl \rightarrow HNO_2 + NaCl$	**1**
	step 2 $C_6H_5NH_2 + HNO_2 + H^+ \rightarrow C_6H_5N_2^+ + 2H_2O$	**1**
1(e)(iii)	nucleophilic (aromatic) substitution	**1**

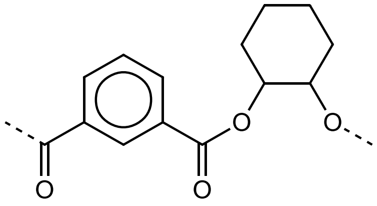
Question	Answer	Marks
2(a)(i)	● conjugate base of acid I = OH^- ● acid II = HNO_2 ● conjugate base of acid II = NO_2^-	**1**
2(a)(ii)	lone pair on the **N** can be donated to a proton /H^+ **OR** lone pair on the **N** can accept / gain a proton /H^+ **OR** lone pair on the **N** can form a dative bond to a proton/H^+	**1**
2(a)(iii)	$H_2O + CH_3COOH \rightarrow H_3O^+ + CH_3COO^-$	**1**
2(b)(i)	(K_w) = $[H^+][OH^-]$ **ALLOW** (K_w) = $K_a \times K_b$	**1**
2(b)(ii)	endothermic **AND** equilibrium position moves right **OR** as water dissociates more **OR** K_w increases with temperature	**1**
2(b)(iii)	M1 (K_w increases with temperature so) pH of neutral solution decreases **OR** (from graph) $K_w = 1.50 \times 10^{-14} = [H^+]^2$ ∴ neutral pH = $-\frac{1}{2}\log(1.50 \times 10^{-14}) = 6.91$ **OR** $[H^+] = 10^{-7.00}$ ∴ $[OH^-] = 1.50 \times 10^{-14} / 10^{-7.00} = 1.50 \times 10^{-7}$	**1**
	M2 pH 7 is therefore above neutral pH / is alkaline **OR** $[OH^-] > [H^+]$ (so alkaline)	**1**
2(c)(i)	$H_2O(l)$ **particles / molecules** has **more** randomness / disorder **OR** $H_2O(l)$ has more ways to arrange **particles** / **energy** (than in solid)	**1**
2(c)(ii)	$H_2O(g)$ **particles / molecules** has **much more** randomness / disorder **OR** $H_2O(g)$ has **many** more ways to arrange **particles** / **energy** (than in liquid)	**1**
2(c)(iii)	+6030 / (70.1 – 48.0) = 272.85 / 272.9 / 273 K (which is 0 °C)	**1**
2(d)(i)	(+)1.62 V	**1**

Question	Answer	Marks
2(d)(ii)	$[OH^-] = 10^{-14}/10^{-11} = 1 \times 10^{-3}$	**1**
	$E = +0.40 - ½ \times 0.059 \times \log (10^{-3})^2 = +0.40 - 0.059(-3) =$ **+0.577 (V)** min 2sf	**1**

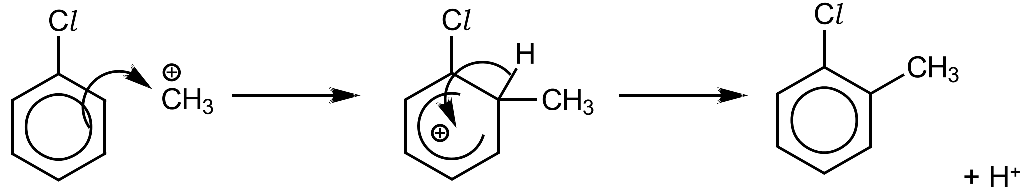
Question	Answer	Marks
3(a)(i)	energies / energy levels of the 3d and the 4s (sub-shells / orbitals) are similar **OR** the difference between the 3d and the 4s is small	**1**
3(a)(ii)	Fe = [Ar] $3d^6$ $4s^2$ **AND** Fe^{3+} = [Ar] $3d^5$	**1**
3(b)(i)	(a molecule or ion formed by a central) metal atom / ion surrounded / bonded by one or more ligands	**1**
3(b)(ii)	6 / six	**1**
3(b)(iii)	bond angle 106–108° **AND** lone pair from O is donated (in a bond) **OR** one more of O's electron pairs is now a bond/bonding pair (so repels less)	**1**
3(b)(iv)	M1 (degenerate) **d** orbitals split (into two energy levels) **OR** (degenerate) **d** orbitals become non-degenerate	**1**
	M2 as an electron moves up / to a higher energy level	**1**
	M3 absorption of light energy / energy in the visible region **AND** colour seen is complementary (to colour absorbed)	**1**
3(b)(v)	(d–d) energy gap / ΔE / Δ_{oct} is different	**1**
	different frequency / wavelength (of light) absorbed / transmitted / reflected	**1**
3(c)(i)	$[Fe(H_2O)_6]^{3+}$ + $\mathbf{H_3PO_4}$ $\rightarrow$ $[Fe(H_2O)_5(H_2PO_4)]^{2+}$ + H_3O^+	**1**

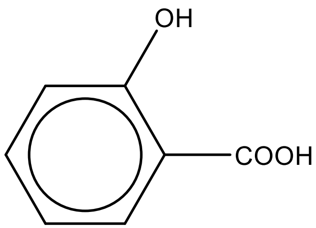
Question	Answer	Marks
3(c)(ii)	$K_{\text{stab}} = \dfrac{[[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}]}{[[\text{Fe}(\text{H}_2\text{O})_6]^{3+}]\,[\text{SCN}^-]}$	1
	$\text{mol}^{-1}\ \text{dm}^3$ u/c	1
3(c)(iii)	$1.30 \times 10^2 / 59.0$ = **2.2**(03) min 2sf	1

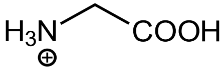
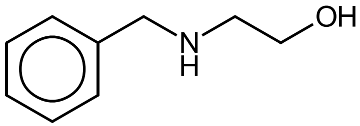
Question	Answer	Marks
4(a)(i)	**X** $[\text{Ru}(\text{H}_2\text{O})_5\text{C}l]^{2+}$	1
	Y $[\text{Ru}(\text{H}_2\text{O})_4\text{C}l_2]^+$ **ECF** [1] if reversed	1
4(a)(ii)	 	2
4(b)(i)	(pyrazine has) a **lone** pair on each N (atoms) / **two lone** pairs (on the N's) **AND** which can be donated / form a coordinate / dative bond (with Ru)	1
4(b)(ii)	• shape is (hexagonal ring) planar / (trigonal) planar / 120° • carbons and nitrogens are sp^2 hybridised • a **p orbital (**from each atom) **overlaps** sideways/laterally (with each other above and below the ring forming π bonds) mark as • ✓ ✓	2

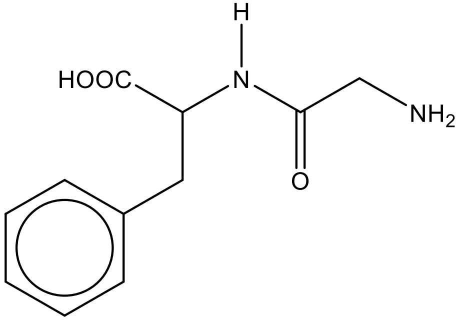
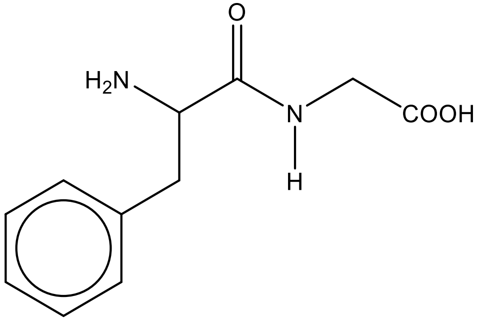
Question	Answer	Marks
4(b)(iii)	1/one	**1**
	all the carbon atoms are equivalent / in same environment **OR** pyrazine is a symmetrical molecule u/c	**1**
4(b)(iv)	+2 / 2+ **AND** +3 / 3+ **OR** +4 / 4+ **AND** +1 / 1+	**1**
4(c)(i)	$SOCl_2$ **OR** PCl_3 **OR** PCl_5	**1**
4(c)(ii)		
	M1 correct ester linkage in the middle of the polymer (displayed C=O bond attached to benzene ring)	**1**
	M2 rest of structure	**1**

Question	Answer	Marks
5(a)(i)	$AlCl_3 + CH_3Cl \rightarrow AlCl_4^- + CH_3^+$	**1**

Question	Answer	Marks
5(a)(ii)	 curly arrow from inside hexagon to electrophile (CH_3^+)	1
	intermediate	1
	curly arrow from C—H bond into the hexagon **AND** H^+ formed	1
5(a)(iii)	$C_6H_4(Cl)CH_3$ + **2**[O] → $C_6H_4(Cl)CHO$ + H_2O	1
5(a)(iv)	step 3 HCN **AND** KCN (cat) **OR** KCN **AND** H_2SO_4/HC*l*	1
	step 4 H_2SO_4(aq) **OR** HC*l* (aq)	1
5(a)(v)	addition–elimination / condensation	1
5(a)(vi)	(a strong base) it would hydrolyse the **ester**	1
5(a)(vii)	(a substance able to) **rotate** the **plane** of plane-**polarised light**	1
5(a)(viii)	any two of: • reduced / different biological activity of 'other' enantiomer **ORA** • avoids need to separate the optical isomers to form the pure active isomer • lower dosage required **OR** (drug is) more potent • higher yield (of biologically-active molecule) • *no / less* (harmful) side effects **OR** *other isomer* can have side effects	2
5(b)(i)	**M1** [HA] = $(75 \times 10^{-3} / 180) \div 0.100 = 4.17 \times 10^{-3}$ **OR** 1 / 240 ($mol\,dm^{-3}$)	1
	M2 $[H^+] = (K_a \times [HA])^{½} = (10^{-3.49} \times 4.17 \times 10^{-3})^{½} = 1.16 \times 10^{-3}$ ($mol\,dm^{-3}$)	1
	M3 pH = –log $[H^+]$ = 2.93 to 2.94 min 2sf	1

Question	Answer	Marks
5(b)(ii)	 CH_3COOH	1 1

Question	Answer	Marks
6(a)(i)	**pH** at which a molecule has no overall charge / is neutral/ is a Zwitterion / charges cancel out	1
6(a)(ii)		1
6(b)(i)	ethanol **AND** heat in a sealed tube **OR** ethanol **AND** high pressure	1
6(b)(ii)	C_6H_5COCl / benzoyl chloride / benzoyl anhydride	1
6(b)(iii)	 • carboxylic acid to primary alcohol COOH to CH_2OH • amide to amine CONH to CH_2NH • rest of the molecule is correct (carbons and benzene ring) mark as • ✓ ✓	2

<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>6(b)(iv)</td><td> </td><td>2</td></tr>
<tr><td rowspan="2">6(c)(i)</td><td>M1 nitrogen lone pair in amides is delocalised with C=O</td><td>1</td></tr>
<tr><td>M2 lone pair less available for donation / to accept H^+
OR less electron density on N / NH_2 so less able to accept H^+</td><td>1</td></tr>
<tr><td rowspan="2">6(c)(ii)</td><td>chloroethanoic acid is a stronger acid (than ethanoic acid)</td><td>1</td></tr>
<tr><td>because electron-withdrawing (–I / inductive) effect of C<i>l</i> substituent
AND weakens O—H / carboxylate anion stabilised</td><td>1</td></tr>
<tr><td>6(d)(i)</td><td>
<table>
<tr><td>proton</td><td>a</td><td>b</td><td>c</td><td>d</td><td>e</td></tr>
<tr><td>δ</td><td>9.0–13.0</td><td>6.0–9.0</td><td>2.3–3.0</td><td>3.2–4.0</td><td>1.0–5.0</td></tr>
<tr><td>splitting</td><td>singlet</td><td>multiplet</td><td>triplet</td><td>triplet</td><td>singlet</td></tr>
<tr><td colspan="6">any three [1] any five [2] any seven [3] all nine [4]</td></tr>
</table>
</td><td>4</td></tr>
<tr><td>6(d)(ii)</td><td>
<table>
<tr><td>proton</td><td>a</td><td>b</td><td>c</td><td>d</td><td>e</td></tr>
<tr><td>present in D_2O</td><td></td><td>✓</td><td>✓</td><td>✓</td><td></td></tr>
</table>
</td><td>1</td></tr>
</table>