

# **Cambridge International AS & A Level**

#### CHEMISTRY

Paper 4 A Level Structured Questions MARK SCHEME Maximum Mark: 100 9701/42 February/March 2022

Published

This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began, which would have considered the acceptability of alternative answers.

Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

Cambridge International will not enter into discussions about these mark schemes.

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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 descriptors 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 <u>'List rule' guidance</u>

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 <u>Calculation specific guidance</u>

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 <u>Guidance for chemical equations</u>

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.

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Question	Answer	Marks
1(a)(i)	oxidising agent [1] H <sub>2</sub> O <sub>2</sub> + $2H^+$ + 2I <sup>-</sup> $\rightarrow$ 2H <sub>2</sub> O + I <sub>2</sub> [1]	2
1(a)(ii)	M1: $K_{pc}$ (93.8) = [I <sub>2</sub> (cyclohexane)] ÷ [I <sub>2</sub> (aq)] 93.8 = (0.390 / 15) ÷ (x / 20)	2
1(a)(iii)	<ul> <li>M2: mass of I<sub>2</sub>(aq), x = 5.54 × 10<sup>-3</sup>(g) ecf</li> <li><i>K</i><sub>pc</sub> would be lower</li> <li>hexan-2-one is more polar (than cyclohexane) OR hexan-2-one is polar AND cyclohexane is non-polar</li> <li>I<sub>2</sub> is (therefore) less soluble in hexan-2-one <i>All three correct for two marks</i></li> </ul>	2
1(b)(i)	enthalpy change when one mole of a solute AND dissolves in water to form a solution of infinite dilution	1
1(b)(ii)	$-(-629) + (-322) + (-293) = (+)14 (kJ mol^{-1})$	1
1(b)(iii)	(cationic) charge density decreases Li⁺ to K⁺ [1] so lattice energies become less negative / less exothermic <b>AND</b> because less <b>attraction</b> between ions [1]	2
1(c)(i)	M1: moles of thiosulfate = $0.02230 \times 0.150 = 3.345 \times 10^{-3}$ M2: $[Cu^{2+}] = 2 \times \frac{1}{2} \times 3.345 \times 10^{-3} \div 0.0250 = 0.134 \text{ (mol dm}^{-3}\text{) ecf}$	2
1(c)(ii)	starch	1
1(c)(iii)	3d <sub>xy</sub>	1
1(d)	$\begin{array}{ll} \textit{Reduction of Fe}^{3+}: & 2\text{Fe}^{3+} + 2\text{I}^{-} \rightarrow 2\text{Fe}^{2+} + \text{I}_2 \ [1] \\ \textit{Regeneration of Fe}^{3+}: 2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-} \ [1] \end{array}$	2

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Question		Answer	Marks
1(e)	M1: ([Hg <sup>2+</sup> ]) = 1.00 × 10 <sup>-7</sup> ÷ 454.4	= $2.20 \times 10^{-10}$ (mol dm <sup>-3</sup> )	3
	M2: $K_{sp} = [Hg^{2+}][I^{-}]^2 = 4[Hg^{2+}]^3$	= <b>4.26</b> × <b>10</b> <sup>-29</sup> ecf	
	M3: units = mol <sup>3</sup> dm <sup>-9</sup> ecf		

Question	Answer	Marks
2(a)(i)	1 mol liquid and 2 mol gas formed from 3 mol solid <b>OR</b> two solid compounds converted to a liquid and a gas	1
2(a)(ii)	M1: (as T increases) $T\Delta S$ becomes greater (than $\Delta H$ ) <b>OR</b> (as T increases) $T\Delta S$ becomes more positive	2
	M2: (as T increases) feasibility will increase as $\Delta G$ becomes more negative	
2(b)(i)	M1: = $314 + 131 - (19 + 3 \times 187)$ use of values and correct stoichiometry	2
	M2: <b>= –135</b> (J K <sup>-1</sup> mol <sup>-1</sup> )	
2(b)(ii)	M1: $\Delta G = 0 \therefore T = \Delta H / \Delta S = +219.3 \times 10^3 \div -(b)(i)$	2
	M2: = <b>1624</b> (.4) (K)	
2(c)	M1: 1.00 g Si is 1/28.1 = 0.0356 mol ∴ moles of e⁻ needed = 4 × mol Si = 0.142 faraday (3 sf)	2
	M2: $Q = It$ $\therefore t = M1 \times 96500 \div 6 = 2289$ (s) ecf	

Question	Answer	Marks
3(a)(i)	(d-block) element that forms one or more stable ions with incomplete d subshell / incomplete d orbitals	1

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Question	Answer	Marks
3(a)(ii)	<ul> <li>variable oxidation states</li> <li>behave as catalysts</li> <li>form complex ions / complexes</li> <li>form coloured compounds / ions</li> <li><i>Any two for one mark</i></li> </ul>	1
3(b)(i)	Ti is in +4 oxidation state so no d electrons / d <sup>0</sup> <b>OR</b> Ti in TiO <sup>2+</sup> has no d electrons / d <sup>0</sup> [1] cannot absorb photons / light in visible spectrum <b>OR</b> no wavelength / frequency absorbed in visible spectrum [1]	2
3(b)(ii)	(1s <sup>2</sup> ) 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>1</sup> (4s <sup>0</sup> )	1
3(b)(iii)	$2\text{TiO}^{2+} + 4\textbf{H}^{+} + \text{Zn} \rightarrow 2\text{Ti}^{3+} + 2\text{H}_2\text{O} + \text{Zn}^{2+}$	1
3(c)(i)	M1: $\Delta G = - nE \ominus_{cell} F$ AND n = 4 M2: $\therefore E \ominus_{cell} = -436100 / -4(96500) = 1.13 \vee ecf$ M3: $E \ominus_{cell} = E \ominus (O_2, 4H^+ H_2O) - E \ominus (TiO^{2+} Ti^{3+}) = 1.23 - E \ominus (TiO^{2+} Ti^{3+})$	3
	$\therefore E^{\ominus}(TiO^{2+} Ti^{3+}) = (+)0.1 (V) ecf$	
3(c)(ii)	Ti <sup>3+</sup> empty / vacant d orbitals can form dative bonds / accept a lone pair from a ligand <b>OR</b> Ti <sup>3+</sup> has vacant d-orbitals which are energetically accessible	1
3(c)(iii)	the $E^{\ominus}$ of the half-cell must be <b>greater</b> than +1.23 V / $E^{\ominus}$ of the O <sub>2</sub>  H <sup>+</sup> half-cell as $E^{\ominus}_{cell} < 0$ and the reaction does not occur	1
3(d)(i)	the number of co-ordinate bonds being formed by the metal <b>atom/ion</b>	1
3(d)(ii)	$\begin{array}{l} \text{TiO}_2 + 6\text{HF} \rightarrow \text{TiF}_6{}^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ \\ \textbf{OR} \ \text{TiO}_2 + 6\text{HF} \rightarrow \text{TiF}_6{}^{2-} + 2\text{H}_3\text{O}^+ \end{array}$	1
3(d)(iii)	species with <b>two lone pairs</b> (of electrons) [1] that form <b>dative covalent / co-ordinate bonds</b> to a central <b>metal atom/ion</b> [1]	2

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Question	Answer		Marks
3(d)(iv)	mirror image of isomer I	trans isomer	2
3(d)(v)	isomer <b>I AND</b> cis isomer drawn by candi dipoles do not cancel / <b>partial</b> charges d		2

Question	Answer	Marks
4(a)(i)	In F: (phenyl)amine AND carboxylic acid In J: phenol AND ester <i>Any two for one mark</i> <i>All four for two marks</i>	2
4(a)(ii)	0 (zero) in <b>F AND</b> 2 (two) in <b>J</b>	1

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Question	Answer	Marks
4(b)(i)	step 1 $CH_3Cl \text{ AND } AlCl_3$ [1] step 2 $\mathbf{D} = {}^{O_2N}$ [1] step 4 (hot) Sn <b>AND</b> concentrated <b>AND</b> HCl [1]	3
4(b)(ii)	$ \begin{array}{c}     \hline                                $	2
4(c)(i)	C <sub>9</sub> H <sub>18</sub> O	1
4(c)(ii)	hydrolysis [1] acid–base / neutralisation [1]	2
4(d)(i)	$C_6H_5OH + Na \rightarrow C_6H_5O^{(-)}Na^{(+)} + \frac{1}{2}H_2$	1
4(d)(ii)	Br OH Br Br	1
4(d)(iii)	<ul> <li>(CO)O—H bond weaker / more easy to donate H<sup>+</sup> in K</li> <li>owing to negative inductive / electron withdrawing effect of C=O / COOH group</li> <li>carboxylate anion stabilised / phenoxide anion is less stabilised</li> <li>All three for two marks</li> </ul>	2

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Question	Answer	Marks
4(e)	p-orbital on oxygen overlaps with ring / π system <b>OR</b> lone pair of e⁻ on oxygen is delocalised into the ring [1] electron density in <b>ring</b> increases [1] attracts/polarises electrophile better [1]	3

Question	Answer	Marks
5(a)(i)	$CH_{3}CHClCOOH + H_{2}O \rightleftharpoons CH_{3}CHClCOO^{-} + H_{3}O^{+}$ $OR CH_{3}CHClCOOH \rightleftharpoons CH_{3}CHClCOO^{-} + H^{+}$	
5(a)(ii)	M1: $[H^+] = 10^{-1.51} = 0.0309 \text{ (mol dm}^{-3}\text{)}$ M2: $K_a = 0.0309^2/0.60 = 1.592 \times 10^{-3} \text{ ecf}$ $pK_a = -\log 1.592 \times 10^{-3} = 2.80 \text{ ecf}$	2
5(a)(iii)	CH₃CHC <i>l</i> COOH is a stronger acid (than propanoic acid, owing to higher [H⁺] [1] because electron-withdrawing effect of C <i>l</i> (substituent) <b>AND</b> weakens O—H / carboxylate anion stabilised [1]	2
5(b)(i)	<b>pH</b> at which a molecule has no overall charge / is neutral <b>OR pH</b> at which it exists as a zwitterion / dipolar ion	1
5(b)(ii)	CH₃CH(N⁺H₃)COOH	1
5(b)(iii)	H IIII C NH <sub>2</sub> HOOC	1
5(b)(iv)	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2

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Question	Answer	Marks
5(b)(v)	condensation	1
5(b)(vi)	<b>C</b> is biodegradable / easily hydrolysed	1
5(c)(i)	pair I = $CH_3CHClCOOH$ (acid) and $CH_3CHClCOO^-$ (c.base) pair II = $NH_3$ (base) and $NH_4^+$ (c.acid)	1
5(c)(ii)	evidence on graph / paper of one half-life (use of data) / $t_{1/2}$ = 500 s [1] <b>constant half-life</b> (= first order) [1]	2
5(c)(iii)	so that [NH <sub>3</sub> ] is (effectively) constant <b>AND</b> doesn't affect the rate / zero order	1
5(c)(iv)	M1: when $[NH_3]$ increases ×1.5, rate increase ×1.5 <b>AND</b> first order (w.r.t. $[NH_3]$ ) / rate is proportional to $[NH_3]$	2
	M2: $S_N 2$ <b>DEP on M1</b> (because rate is first order w.r.t. to [2-chloropropanoate] and [NH <sub>3</sub> ])	
5(c)(v)	greater proportion of <b>particles</b> have $E \ge E_A$ [1] frequency of (effective) collisions increases <b>AND</b> rate increases <b>OR</b> rate of collisions increases <b>AND</b> rate increases [1]	2
5(c)(vi)		1

Question	Answer	Marks
6(a)	$HOCH_2COOH + 2SOCl_2 \rightarrow ClCH_2COCl + 2SO_2 + 2HCl$	1
6(b)	to remove / neutralise excess H <sup>+</sup> / acid produced OR to react with any acidic by-products / HCl/ SO <sub>2</sub> OR to react with any unreacted W	1

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Question	Answer	Marks
6(c)	$ \begin{array}{c} \overbrace{l} \overbrace{l} \overbrace{l} \overbrace{l} \overbrace{l} \overbrace{l} \overbrace{l} l$	4
6(d)	N / nitrogen can donate its lone pair / LP / pair of electrons	1
6(e)(i)	mobile = ethyl ethanoate stationary = $SiO_2$ / silica or $Al_2O_3$ / alumina	1
6(e)(ii)	<i>R</i> <sub>f</sub> = distance travelled by solute / substance / compound / component ÷ distance travelled by solvent (front)	1
6(e)(iii)	X is more attracted / more affinity / adsorbed more to the <b>stationary phase</b> OR lidocaine dissolves better in the solvent ORA	1
6(f)(i)	quartet AND triplet	1
6(f)(ii)	<ul> <li>δ 7.1 = attached to aromatic ring / H—Ar</li> <li>δ 3.0 = alkyl next to C=O / —CH<sub>(2)</sub>—C=O</li> <li>δ 2.3 = alkyl next to aromatic ring / H<sub>(3)</sub>C–Ar</li> <li>All three correct for two marks</li> </ul>	2
6(f)(iii)	9 (nine)	1