

Cambridge International AS & A Level

CHEMISTRY

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

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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.

Cambridge International is publishing the mark schemes for the May/June 2022 series for most Cambridge IGCSE, Cambridge International A and AS Level and Cambridge Pre-U components, and some Cambridge O Level components.

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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.

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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)	M1 ΔH_{latt} and ΔH_{hyd} both become less exothermic / less negative	3
	M2 ΔH_{hyd} changes less / becomes less exothermic by a smaller extent OR ΔH_{latt} changes more / dominant factor / changes faster	
	M3 ΔH_{sol} becomes more exothermic / more negative OR ΔH_{sol} becomes less endothermic / less positive	
1(b)(i)	M1 $K_{sp} = [Be^{2+}][OH^{-}]^2$ M2 mol ³ dm ⁻⁹ ecf	2
1(b)(ii)	M1 solubility of Be(OH) ₂ = $2.40 \times 10^{-6} / 43 = 5.58 \times 10^{-8}$ (mol dm ⁻³) ecf (b)(i) M2 $K_{sp} = 4 \times (5.58 \times 10^{-8})^3 = 6.95 \times 10^{-22}$ ecf min 2sf	2
1(c)(i)	as a molecule or ion formed by a central metal atom / metal ion dative bonded to / surrounded by one or more ligands	1
1(c)(ii)	HO OH HO OH OH tetrahedral and correct 3D structure	1
1(d)(i)	d orbitals that are energetically accessible OR empty / vacant d orbitals AND form dative bonds / accept a lone pair from a ligand	1

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Question	Answer					
1(d)(ii)	complex ion	shape	coordination number	polarity		2
	cis-[Pt(en)Cl ₂]	square planar	4	polar		
	[Ag(NH ₃) ₂] ⁺	linear	2	non-polar		
	[Fe(C ₂ O ₄) ₃] ³⁻	octahedral	6	non-polar		
	three for one mark	, six for two marks		·		
1(e)(i)	the equilibrium constant for the formation of the complex ion in a solvent (from its constituent ions or molecules)				1	
1(e)(ii)	M1 $K_{\text{stab}} = [\text{Ni}(\text{en})_3^{2+}] / [\text{Ni}(\text{H}_2\text{O})_6^{2+}][\text{en}]^3$ M1 units = mol ⁻³ dm ⁹ ecf			2		
1(e)(iii)	the equilibria lie to the right / product side OR equilibrium 1 lies more to the right AND <i>en</i> complex is more stable / [Ni(en) ₃] ²⁺ is more stable				1	

Question	Answer	Marks
2(a)	the d and s sub-shells / orbitals are close / similar in energy	1
2(b)	The star	1

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Question	Answer	Marks		
2(c)	M1 (in a complex / in the presence of ligands) the d-orbitals are split into two sets of orbitals	3		
	M2 as an electron is excited / promoted			
	M3 visible light is absorbed AND colour seen is complementary			
2(d)(i)) Cu(OH) ₂ : (pale / light) blue [Cu(H ₂ O) ₂ (NH ₃) ₄] ²⁺ : dark / deep blue			
2(d)(ii)	(addition of OH ⁻) increases [OH ⁻] AND shifts equilibrium to the right	1		
2(e)	$H_{2}O_{III_{III_{III_{III_{III_{III_{III_{I$	2		

Question	Answer	
3(a)(i)	 enthalpy change / energy change one mole of electrons (gained by) one mole of gaseous atoms two for one mark, three for two marks 	2
3(a)(ii)	(energy required to overcome) the repulsion between the electron and anion / negative ion	

Question	Answer	Marks
3(a)(iii)	 less negative / less exothermic down the group greater the distance between the nucleus and (the shells of the) electrons OR atomic radii increases OR more shielding by inner shells the less attraction between nucleus and incoming electron (and the less energy released) two for one mark, three for two marks 	2
3(b)	M1 use of correct seven numbers only in calculation / energy cycle M2 only 2 × used correctly M3 correct signs and evaluation ecf -208 = 131 + 906 + 1733 + 62 + 151 + 2x - 2605 2x = -586 $x = -293 \text{ kJ mol}^{-1}$	3
3(c)	first box ticked AND Cd ²⁺ larger / Cd ²⁺ lower charge density AND less attraction between the ions / weaker ionic bonds	1

Question	Answer	
4(a)(i)	M1 all five points plotted correctly M2 best-fit straight line (ruler) with negative gradient drawn	
4(a)(ii)	a)(ii) M1 gradient correctly calculated OR gradient working seen	
	M2 gradient = $-\Delta S^{\circ}$ ΔS° evaluated correctly ecf ΔS° = (+)160 ± 10 (J K ⁻¹ mol ⁻¹)	
4(b)(i)	$2\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O}$	1

Question	Answer	Marks
4(b)(ii)	M1 ionic radius of M ⁺ / cationic radius increases OR charge density of ion / M ⁺ decreases down Group 1	2
	M2 less distortion / polarisation of the anion / HCO ₃ ⁻ OR CO bond / C-O / C=O less weakened	
4(c)(i)	M1 solution which resists changes in pH when opposes / resists change in pH	2
	M2 when small amount of acid / H ⁺ or alkali / base / OH ⁻ is added	
4(c)(ii)	M1 (with acid) $HCO_3^- + H^+ \rightarrow H_2CO_3$ OR $HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O$	2
	M2 (with alkali) $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$	
4(c)(iii)	M1 $K_{\rm a} = 10^{-6.35} = 4.47 \times 10^{-7}$	3
	M2 [H ⁺] = $4.47 \times 10^{-7} / 14.1 = 3.17 \times 10^{-8}$ ecf	
	M3 pH = $-\log [H^+] = 7.5$ ecf from a calculated [H ⁺] min 2sf	

Question		Answer			
5(a)	electrolyte	substance liberated at the anode	substance liberated at the cathode		
	PbBr ₂ (I)	Br ₂ /bromine	Pb/lead		
	concentrated NaCl(aq)	Cl ₂ / chlorine	H ₂ / hydrogen		
	Cu(NO ₃) ₂ (aq)	O ₂ / oxygen (+ H ₂ O)	Cu/copper		
	two for one mark, four for	two marks, six for three	e marks		

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Question	Answer			
5(b)(i)	$F = Le \ \mathbf{OR} \ \mathbf{F}$ is directly proportional to L	1		
5(b)(ii)	number of Cu ²⁺ formed = $0.35 / 63.5 = 5.51 \times 10^{-3}$	4		
	$Q = I \times t = 0.60 \times 30 \times 60 = 1080 \text{ C}$			
	number of electrons = $1080 / 1.6 \times 10^{-19} = 6.75 \times 10^{21} \text{ ecf}$			
	number of Cu ²⁺ ions = $6.75 \times 10^{21}/2 = 3.375 \times 10^{21}$ ecf			
	number of Cu ²⁺ ions per mole (L) = $3.375 \times 10^{21} / 5.51 \times 10^{-3} = 6.12 \times 10^{23}$ ecf min 2sf			
	all five points for four marks ALLOW valid alternate calculations of <i>L</i>			

Question	Answer	
6(a)(i)	$M_{NO_{2}^{+}} \longrightarrow (++)^{NO_{2}^{+}} \longrightarrow (++)^{N$	3
6(a)(ii)	$HSO_4^- + H^+ \rightarrow H_2SO_4$	1

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Question	Answer	Marks
6(b)	M1 benzoic acid M2 phenol $\downarrow \bigcirc \bigcirc$	2
	OR	
6(c)	 M1 phenol > benzene > benzoic acid M2 / M3 <u>phenol:</u> lone pair / p-orbital on oxygen delocalises into the ring / overlaps with π-delocalised ring accepts / attracts / polarises NO₂* / electrophiles better benzoic acid: COOH / C=O is an electron-withdrawing / positive inductive effect two for one mark, three for two marks M4 (phenol-oxygen) increases electron density in the ring (as compared to benzene as a result of the OH group) OR (benzoic acid–COOH) decreases electron density in the ring (as compared to benzene as a result of the COOH group) 	4

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Question	Answer	Marks
6(d)(i)		3
	$z N \equiv N + N + N = N$	
	\mathbf{Y} \mathbf{V}	
6(d)(ii)	step 1 M1 Sn and hydrochloric acid / HC <i>1</i> M2 concentrated (HC <i>1</i>) + heat / reflux (followed by NaOH)	3
	step 2 M3 HNO ₂ and (HC <i>l</i>) $\leq 10^{\circ}$ C OR NaNO ₂ , HC <i>l</i> and $\leq 10^{\circ}$ C	

Question	Answer	Marks
7(a)	TMSreference OR standard OR to define $d = 0$ D ₂ Osolvent OR identification of O-H/N-H protons/group	

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Question			Answer	Marks
7(b)(i)	ketone	number of peaks observed in proton NMR spectrum	number of peaks observed in carbon-13 NMR spectrum	2
	pentan-2-one	4	5	
	pentan-3-one	2	3	
	3-methylbutanone	3	4	
	three for one mark, s	six for two marks		
7(b)(ii)	M1 3-methylbutanon M2 3-methylbutanon	ne Ne AND pentan-2-one		2
7(c)(i)	six/6			1
7(c)(ii)	C ₂₁ H ₃₄ O ₅			1
7(c)(iii)	a substance that is a	able to <u>rotate</u> the plane of pola	rised light in opposite directions	1

Question	Answer	Marks
8(a)	M1 chloroethanoic acid > ethanoic acid > phenol > ethanol	4
	M2 correct link of acidity once can be implied from M1 weakens O—H / carboxylate anion stabilised	
	 M3 / M4 explanation linked to structure (ClCH₂CO₂H > ethanoic acid) due to electronegative / electron withdrawing / negative inductive effect of Cl (ethanoic acid > phenol) due to electronegative / electron withdrawing / negative inductive effect of COOH / C=O (phenol > ethanol) due to lone pair of oxygen overlapping / delocalised into the ring (ethanol weakest) alkyl group is electron donating / positive inductive effect 	

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Question	Answer	Marks
8(b)	oxidation	2
	 (solution) decolourises OR purple → colourless / pale pink OR bubbles 	
	• HOOCCOOH + [O] \rightarrow 2CO ₂ + H ₂ O OR 5HOOCCOOH + 2MnO ₄ ⁻ + 6H ⁺ \rightarrow 10CO ₂ + 8H ₂ O + 2Mn ²⁺	
	two for one mark, three for two marks	
8(c)		2
	HO HO OH OR HO CI	
8(d)	$\begin{array}{c c} & OH \\ H_2C \\ \hline \\ \\ H_2C \\ \hline \\ \\ H_2C \\ \hline \\ \\ \\ H_2C \\ \hline \\ \\ \\ \\ H_2C \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	2
	M1 peptide linkage shown displayed with saturated C each side	
	M2 rest of structure correct AND continuation bonds	

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Question	Answer	Marks
8(e)	addition polymers do not hydrolyse OR condensation polymers can hydrolyse	1
9(a)	 cyclohexylamine > ammonia > phenylamine (order of basicity) linked to ability of N to accept a proton / donate its lone pair (to a proton) alkyl / cyclo / hexyl group is electron donating group / positive inductive group (and increases electron density on N) lone pair / p-orbital from N in phenylamine delocalised / overlaps with ring (and decreases electron density on N) two for one mark, three for two marks 	3
9(b)(i)	(nucleophilic) addition-elimination	1
9(b)(ii)	$H_{3C} \xrightarrow{\delta^{-}}_{C_{1}} \xrightarrow{C_{1}}_{R_{1}} \xrightarrow{H_{1}}_{R_{2}} \xrightarrow{C_{1}}_{R_{1}} \xrightarrow{H_{1}}_{R_{2}} \xrightarrow{H_{1}}_{R_{2}} \xrightarrow{H_{1}}_{R_{1}} \xrightarrow{H_{2}}_{R_{2}} \xrightarrow{H_{1}}_{R_{1}} \xrightarrow{H_{2}}_{R_{2}} \xrightarrow{H_{1}}_{R_{2}} \xrightarrow{H_{1}}_{R_{2$	4
	 M1 / M2 lone pair on N correct arrow from (lone pair) N to C (of C=O) dipole on C=O correct arrow on C=O two for one mark, four for two marks M3 correct intermediate 	
	M4 arrow from lone pair on O ⁻ to C-O bond AND arrow from C-C <i>l</i> to C <i>l</i>	

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Question	Answer	Marks
9(b)(iii)	H_3C C CH_3	1