Cambridge Assessment International Education

Cambridge International AS & A Level

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **February/March 2023**

MARK SCHEME

Maximum Mark: 100

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.

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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.

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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.

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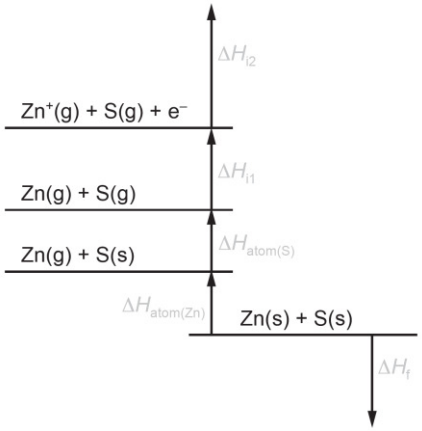
Question	Answer	Marks
1(a)(i)	[Ar] 1↓ 1↓ 1↓ 1↓ 1↓ ☐ ☐ ☐ ☐	1
1(a)(ii)	 one ● for each of the eight species (including state symbol) on the correct line **AND** one ● e^- any three [1] any six [2] all nine [3]	3
1(a)(iii)	• EA becomes **less negative/ less exothermic** (down group / S to Te) • atomic radii increases **OR** outer shell gets farther from nucleus **OR** electron added at higher energy level **OR** more shielding (of outer shells) • less **nuclear** attraction **OR** less attraction for incoming/added electron any two [1] all three [2]	2
1(a)(iv)	**M1**: O^{2-} (has same charge but) **smaller** (radius than S^{2-}) **ORA** **OR** oxygen has a **smaller ion** (than S^{2-})	1
	M2: stronger ionic bond **OR** greater attraction between Zn^{2+} and O^{2-} **ORA**	1

Question	Answer	Marks
1(b)(i)	ΔS negative **AND** more moles / molecules of **gaseous** reactants **ORA** **OR** ΔS negative **AND** moles / molecules of **gas** are reduced (in the reaction)	**1**
1(b)(ii)	ΔS = 50.8 + 197.7 – 43.7 – 5.7 = (+)**199.1** ($J\,K^{-1}\,mol^{-1}$)	**1**
1(b)(iii)	$\Delta G = \Delta H - T\Delta S$ **ALLOW** $G = \Delta H - T\Delta S$	**1**
	= +733 – (800 + 273) × 0.218 = (+)**499.086** ($kJ\,mol^{-1}$) min 3sf	**1**
1(c)(i)	$Zn(NO_3)_2 \rightarrow ZnO + 2NO_2 + ½O_2$ **OR** $2Zn(NO_3)_2 \rightarrow 2ZnO + 4NO_2 + O_2$	**1**
1(c)(ii)	**increases** (in thermal stability down the group) **AND** (cat)**ion**(ic) radius / **ion** size increases (down the group)	**1**
	less polarisation / less distortion of anion/ of nitrate ion/NO_3^- / NO_3^{2-} **OR** less weakening of N—O bond	**1**
1(c)(iii)	$Mg(NO_3)_2$ only **ALLOW** Mg^{2+} / magnesium	**1**

Question	Answer	Marks
2(a)	H_3PO_2	**1**
2(b)(i)	electrode potential E would become **more positive** / **less negative** (than $E^\ominus$)	**1**
	lower [$H_2PO_2^-$] **AND** shifts equilibrium to the right-hand side	**1**
2(b)(ii)	+1.57 – 0.74 = (+)**0.83** (V)	**1**

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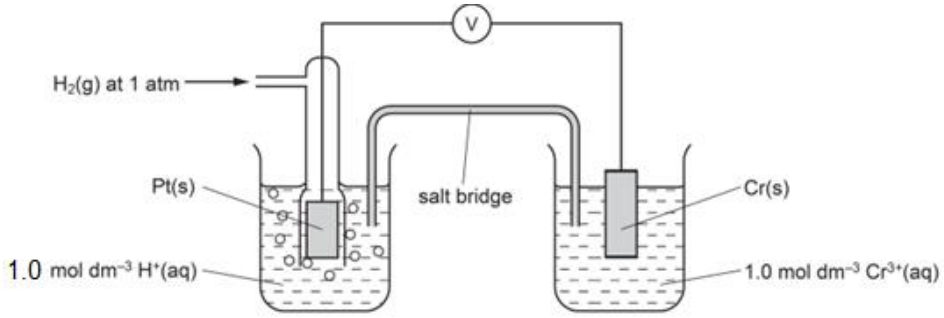
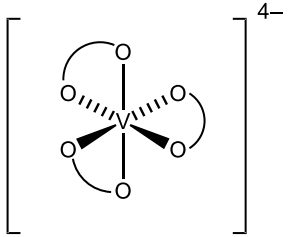
Question	Answer	Marks
2(b)(iii)	 • Pt(s) / C / graphite • Cr(s) • H^+(aq) / any strong acid • Cr^{3+}(aq) • H_2(g) • voltmeter / V • salt bridge labelled • conditions of 1 atm **AND** 1 mol dm^{-3} / 1 M / 1 mol / dm^3 • other liquid level (salt bridge) and wire to electrode any three [1] any six [2] all nine [3]	**3**
2(b)(iv)	Pt electrode positive **AND** flow of electrons anticlockwise (to the SHE)	**1**
2(b)(v)	$H_2PO_2^- + 3OH^- + Ni^{2+} \rightarrow HPO_3^{2-} + 2H_2O + Ni$	**1**
2(c)(i)	(6.4 / 24000) ÷ 60 = **4.44** × **10^{-6}** (mol dm^{-3} s^{-1}) min 2sf	**1**
2(c)(ii)	$[H_2PO_2^-]$ doubles / ×2 from experiments 1 to 2 **ORA** volume of H_2 produced doubles / ×2 (∴ first order wrt $[H_2PO_2^-]$)	**1**
	$[H_2PO_2^-]$ × 3 and $[OH^-]$ × ½ from experiments 1 to 3 **ORA** volume of H_2 produced falls to ¾ original (if first order wrt $[H_2PO_2^-]$ then must be second order wrt $[OH^-]$) **ALLOW** input data into rate equation and show *k* is the same *k* =2.8 × 10^{-6} / *k* = 6.7 × 10^{-2} (1 / 15) / *k* = 4 for all experiments [2]	**1**

Question	Answer	Marks
2(c)(iii)	$mol^{-2}\ dm^6\ s^{-1}$	**1**
2(c)(iv)	$t_{½}$ = 0.693 / 8.25 × 10^{-5} = **8400** (s) **OR** $t_{½}$ = ln2 / 8.25 × 10^{-5} = **8401.8** (s)	**1**
2(c)(v)	(k_1) **increases** (with temperature)	**1**
2(d)	• reactants **adsorb** (to surface of catalyst) • bonds (in reactant) weaken • (reaction occurs and the) **products** are desorbed **OR** reaction occurs and substances are desorbed any two [1] all three [2]	**2**

Question	Answer	Marks
3(a)	(a d-block element forms one or more) stable ions with incomplete filled d-subshell	**1**
3(b)(i)	• they behave as catalysts • they form complex ions / complexes • they form coloured compounds / salts / ions any two	**1**
3(b)(ii)	the **d** and **s** sub-shells/orbitals are close/similar in **energy**	**1**
3(c)(i)	0.02500 × 0.0300 **OR** 7.50×10^{-4} mol VO_2^+ **OR** ½(28.15 + 28.10)/1000 × 0.0400 **OR** 1.13×10^{-3} mol $C_2O_4^{2-}$	**1**
	Use of their values to show ratio of VO_2^+ : $C_2O_4^{2-}$ = **1:1.5** **ALLOW** any viable approach	**1**

Question	Answer	Marks
3(c)(ii)	 3D structure	**1**
	charge	**1**
3(d)(i)	VO_2^+ **AND** $E^\ominus$ of H_2O_2 is largest / most positive value **OR** VO_2^+ **AND** $E^\ominus$ is less positive than H_2O_2	**1**
3(d)(ii)	+5	**1**

Question	Answer	Marks
4(a)(i)	$CH_3CONH_2 + 4[H] \rightarrow CH_3CH_2NH_2 + H_2O$	**1**
4(a)(ii)	nucleophilic substitution	**1**
	(ammonia with) ethanol **AND** heat under pressure **OR** ethanol **AND** heat in a sealed tube	**1**
4(a)(iii)	$(CH_3CH_2)_2NH$ **OR** $(CH_3CH_2)_3N$	**1**

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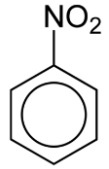
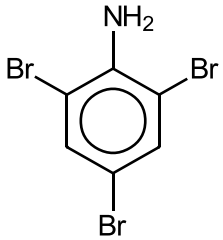
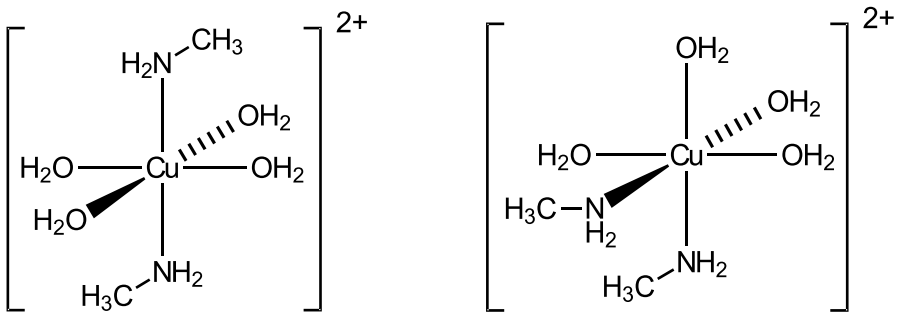
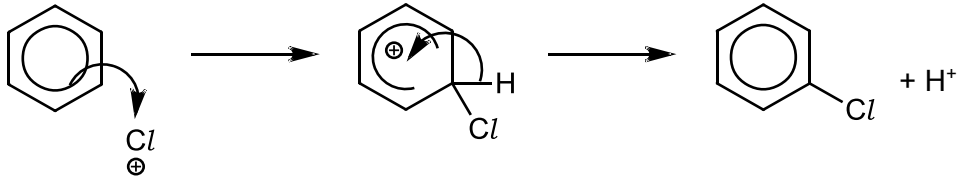
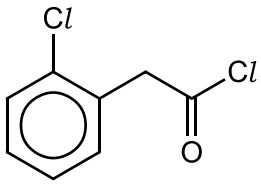
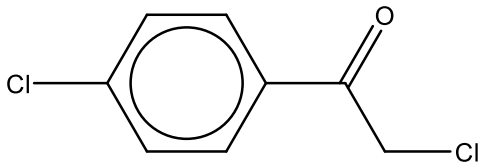
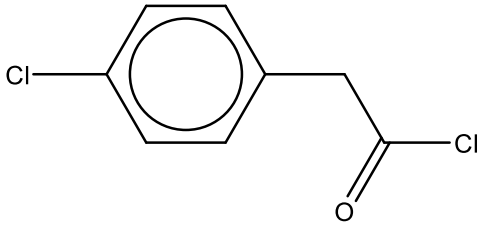
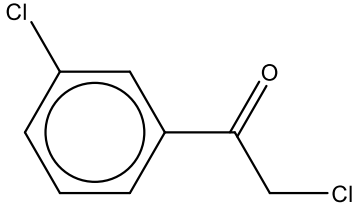
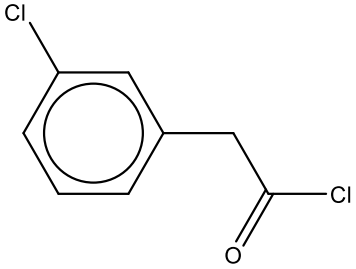
Question	Answer	Marks
4(b)	(least) phenylamine < ammonia < ethylamine (most)	**1**
	<u>explanation</u> • (order of basicity) ability of base **AND** to **accept** a **proton** **OR donate** its lone pair (to a proton) <u>phenylamine</u> • lone pair / p-orbital from N delocalised / overlaps with (π-)ring / benzene <u>ethylamine</u> • **alkyl / ethyl** group is electron donating group / +I group • increases electron density on **N** (ethylamine) **ORA** any two [1] any three [2] all four [3]	**3**
4(c)		**1**
	concentrated HNO_3 and H_2SO_4 (and 25–60 °C)	**1**
	(reduction with) Sn and concentrated HC*l* (heat)	**1**
4(d)(i)		**1**
4(d)(ii)	nitrous acid / HNO_2 **OR** $NaNO_2$ **AND** dilute HC*l*	**1**

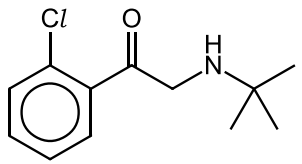
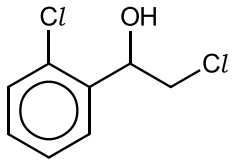
Question	Answer	Marks
4(d)(iii)	phenol	**1**
4(d)(iv)	NaOH / alkali	**1**
4(d)(v)	dyestuffs / dyes	**1**
4(e)(i)	species that uses one **lone pair** of electrons	**1**
	that **forms** a single **dative covalent** bond to a central **metal atom / ion**	**1**
4(e)(ii)		
	correct 3D cis isomer	**1**
	correct 3D trans isomer	**1**
4(e)(iii)	6	**1**
4(f)(i)	units = $mol^{-4}\,dm^{12}$	**1**
4(f)(ii)	$(K_{stab} =) \dfrac{\left[CdCl_4^{2-}\right]}{\left[Cd^{2+}\right]\left[Cl^{-}\right]^4}$	**1**
4(f)(iii)	$[CdCl_4^{2-}] = K_{stab} \times 0.043 \times 0.072^4$ **= 7.28 / 7.3 × 10^{-4}** ($mol\,dm^{-3}$) min 2sf	**1**

Question	Answer	Marks
4(f)(iv)	CH_3NH_2 (is basic so) reacts with water to produce OH^- that reacts with Cd^{2+} **OR** CH_3NH_2 acts as a base and accepts a proton from $Cd[H_2O)_6]^{2+}$ / water **OR** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightarrow [Cd(OH)_4(H_2O)_2]^{2-} + 4CH_3NH_3^+$ **OWTTE**	**1**
4(f)(v)	$Cd(OH)_4^{2-}$ = most stable (2nd box) **AND** $[Cd(H_2O)_6]^{2+}$ = least stable (first box)	**1**
	$Cd(OH)_4^{2-}$ has highest K_{stab} (and all K_{stab} values given > 1)	**1**

Question	Answer	Marks
5(a)	any **three** points from: • bond angle = 120° **AND** shape is hexagonal ring planar / trigonal planar • (carbons are) **sp^2 hybridised** • contains **delocalised electrons** in the π bonds / system • (sp^2 orbitals) **overlap end-on-end/ head-on** to form σ **bonds** • a **p orbital** (from each carbon atom) **overlaps sideways** (with each other above and below the ring) forming π **bonds**	**3**
5(b)(i)	$Cl_2 + AlCl_3 \rightarrow Cl^+ + AlCl_4^-$	**1**

Question	Answer	Marks
5(b)(ii)	 **M1** curly arrow from inside hexagon of aromatic ring to Cl^+ **CON** going to a lone pair on Cl **M2** intermediate **M3** curly arrow from C—H bond to inside the ring **AND** H^+	**3**
5(c)(i)	electrophilic substitution	**1**

Question	Answer	Marks
5(c)(ii)	 **OR** 4-substituted acyl / alkyl derivative   **ALLOW** 3-substituted acyl / alkyl derivative  	**1**

Question	Answer	Marks
5(c)(iii)	(most) acyl chloride > alkyl chloride > aryl chloride (least)	**1**
	any two from: • **acyl chlorides:** carbon (in C—C*l*) is more electron deficient **AND** it is also attached to an oxygen atom / two electronegative atoms **OR** C—C*l* bond is weakest / weakened in acyl chlorides **AND** it is also attached to an oxygen atom / two electronegative atoms • **aryl chlorides** (no hydrolysis) **C—C*l* bond** is part of delocalised system / partially double bond character so C—C*l* bond is stronger **OR** lone pair on **C*l*** delocalises with π ring so C—C*l* bond is stronger • **alkyl chlorides** carbon atom has a smaller δ+ **AND** due to the carbon being only attached to one electronegative atom **OR** C—C*l* bond strengthened **AND** by electron donating effect / positive inductive effect of alkyl / R group	**2**
5(d)	$(CH_3)_3CNH_2$ (in ethanol) [substitution] } in either order	**1**
	$LiAlH_4$ **OR** $NaBH_4$ [reduction] } in either order	**1**
	 [substitution first] **OR**  [reduction first]	**1**
5(e)(i)	**rotate** the **plane** of **polarised light** in the opposite direction **OR** stereoisomers / molecules that are **non-superimposable mirror images**	**1**
5(e)(ii)	need to separate the optical isomers to form the pure active isomer **OR** reduced / different biological activity of 'other' enantiomer **OR lower yield** of biologically active molecule / desired molecule	**1**
5(e)(iii)	chiral catalyst **OR** use of an enzyme	**1**

Question	Answer	Marks
5(f)(i)	ten / 10	**1**
5(f)(ii)	(δ = 0.9–1.7) • 9H • singlet • –C**H**$_3$ / alkane (δ = 3.2–4.0) / (δ = 2.3–3.0) • 1H • triplet • –C**H**O / alkyl next to electronegative atom **OR** Ar-CH / alkyl next to aromatic ring (δ = 6.0–9.0) • 4H • multiplet • **H**–Ar / attached to aromatic ring any three [1] any six [2] all nine [3]	**3**

Question	Answer	Marks
6(a)(i)	SiO_2 **OR** Al_2O_3 **OR** silica **OR** alumina **OWTTE**	**1**
6(a)(ii)	Cd^{2+} **AND** R_f of **M** (= 2/5) = **0.40 / same** R_f as in the Table 6.1	**1**
6(b)	metal cations are less soluble in butan-1-ol (than in water) **OR** metal cations weaker ion-dipole forces with butan-1-ol	**1**
6(c)	H_2O **AND** SCN^-	**1**
6(d)(i)	$C_8H_5O_4K$ + KOH → $C_8H_4O_4K_2$ + H_2O **OR** $C_8H_5O_4K$ + OH^- → $C_8H_4O_4K^-$ + H_2O	**1**

Question	Answer	Marks
6(d)(ii)	**M1** initially: moles of KOH = $0.150 \times 20.0 \div 1000$ $= 3.0\times10^{-3}$ **AND** moles of acid HA = $0.100 \times 50.0 \div 1000$ $= 5.0\times10^{-3}$	**1**
	M2 at equilibrium: moles of salt KA $= 3.0\times10^{-3}$ **ecf** **AND** moles of acid HA = 5.0×10^{-3} – moles of NaOH $= 2.0\times10^{-3}$ **ecf**	**1**
	M3 $K_a = 10^{-5.40} = 3.98\times10^{-6}$ $3.98\times10^{-6} = [H^+]\,[3.0\times10^{-3}] \div [2.0\times10^{-3}]$ $[H^+] = 2.65\times10^{-6}$ **ecf**	**1**
	M4 pH = $-\log(2.65\times10^{-6})$ = **5.58** / **5.6 ecf** on a calculated and identified $[H^+]$ **ALLOW** alternative approach using Henderson-Hasselbalch equation for **M3** and **M4**	**1**