Cambridge International AS & A Level

CHEMISTRY 9701/42
Paper 4 A Level Structured Questions May/June 2021

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.
- 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.

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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) | [1s ²] 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ³ | | | | 1 |
| 1(a)(ii) | (a molecule or ion form | med by a central) metal atom/ion surrounded | by / bonded to one or more | ligands | 1 |
| 1(b) | [Cr(H ₂ O) ₆] ³⁺ (aq) | formula of chromium species formed | type of reaction | | 5 |
| | + NaOH(aq) | Cr(OH) ₃ or Cr(OH) ₃ (H ₂ O) ₃ | precipitation | | |
| | + H ₂ O ₂ (aq) | Cr ₂ O ₇ ²⁻ /CrO ₄ ²⁻ | redox / oxidation | | |
| | + excess NH ₃ (aq) | Cr(NH ₃) ₆ ³⁺ | ligand substitution | | |
| | • | ne mark for each correct species correct for one mark and three correct for two | marks | | |
| 1(c) | M1: ΔE is different OR | R energy gap between d-orbitals is different | | | 2 |
| | | cy / wavelength is absorbed ight in visible region is absorbed | | | |
| 1(d)(i) | OR ethanoate ions for | dentate whereas as H ₂ O are monodentate rm two dative bonds whereas H ₂ O forms one mate two lone pairs whereas H ₂ O donates on | ` | | 1 |
| 1(d)(ii) | (coordination number) | six AND (geometry around Cr) octahedral | | | 1 |
| 1(d)(iii) | coordinate / (dative) co | ovalent | | | 1 |
| 1(e)(i) | $4Cr^{2+} + O_2 + 4H^+ \rightarrow 40$ | $Cr^{3+} + 2H_2O$ OR $2Cr^{2+} + O_2 + 2H^+ \rightarrow 2Cr^{3+} +$ | H ₂ O ₂ | | 2 |
| | M1: correct species M2: balancing | | | | |
| 1(e)(ii) | $E_{\text{cell}}^{\text{e}} = 1.23 - (-0.41)$ value linked to (e)(i) | = (+)1.64 V OR E_{cell}^{θ} = 0.68 - (-0.41) = (+)1 | .09 V | | 1 |

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| Question | Answer | Marks |
|----------|---|-------|
| 2(a) | M1: increases down the group | 3 |
| | M2: radius / size of cation / M ²⁺ increases OR charge density of cation / M ²⁺ decreases | |
| | M3: less polarisation / less distortion of anion / NO ₃ ⁻ ion OR less weakening of NO bond | |
| 2(b)(i) | $Pb(NO_3)_2 \rightarrow PbO + 2NO_2 + \frac{1}{2}O_2$ | 1 |
| 2(b)(ii) | lead nitrate / Pb(NO ₃) ₂ would decompose more / easier AND as Pb ²⁺ is smaller / Pb ²⁺ has larger charge density (so more polarising) | 1 |
| 2(c)(i) | $BaC_2O_4 \rightarrow BaO + CO_2 + CO$ OR $BaC_2O_4 \rightarrow BaO + 2CO + \frac{1}{2}O_2$ | 1 |
| 2(c)(ii) | M1: [a] initial moles $MnO_4^- = 0.0200 \times 0.050 = 1.00 \times 10^{-3}$ [b] moles $Fe^{2+} = 0.050 \times 0.0304 = 1.52 \times 10^{-3}$ | 4 |
| | M2: [a] moles MnO ₄ ⁻ unreacted = $1.52 \times 10^{-3} / 5 = 3.04 \times 10^{-4}$ [b] moles MnO ₄ ⁻ reacted = $1.00 \times 10^{-3} - 3.04 \times 10^{-4} = 6.96 \times 10^{-4}$ | |
| | M3: moles $C_2O_4^{2-}$ reacted = $6.96 \times 10^{-4} \times 5/2 = 1.74 \times 10^{-3}$ | |
| | M4: mass of BaC ₂ O ₄ = $225.3 \times 1.74 \times 10^{-3} = 0.392$ g % Purity of BaC ₂ O ₄ = $100 \times 0.392/0.50 = 78.4$ | |
| 2(d) | M1: $[OH^-] = 2 \times 0.12 = 0.24 \text{ (mol dm}^{-3})$ $[H^+] = 1 \times 10^{-14}/0.24 = 4.17 \times 10^{-14} \text{/ pOH} = -log(0.24)$ OR 0.62 | 2 |
| | M2: pH = $-\log[H^+]$ = 13.4 OR pH = 14 - 0.6 = 13.4 | |

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| Question | | Answer | Marks |
|-----------|--|---|-------|
| 3(a)(i) | • | mol / dm ³ AND (pressure of) 1 atm / 101 kPa (or in Pa) AND 298 K / 25°C | 2 |
| 3(a)(ii) | E → redox system | | 1 |
| | Most B negative | | |
| | ↑ C | | |
| | Least A negative | | |
| 3(a)(iii) | M1 / M2: two 3D isomers o | | 3 |
| 3(b)(i) | $E^{\Theta}_{cell} = 1.07 - 0.80 = (+)0.2$ AND direction of electron fl | 7 V | 1 |
| 3(b)(ii) | M1: E ^e cell 3rd box ticked | | 2 |
| | OR | Ag ⁺ /Ag) equilibrium shifts to the left (Ag ⁺ /Ag) becomes less positive/more negative | |

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| Question | Answer | Marks |
|-----------|---|-------|
| 3(c)(i) | (a species) that uses / shares a lone pair of electrons to form a coordinate bond to a metal atom / ion | 1 |
| 3(c)(ii) | $K_c = [Ag(S_2O_3)_2^{3-}][Br^-]/[S_2O_3^{2-}]^2$ | 1 |
| 3(c)(iii) | M1: $K_c = K_{stab} \times K_{sp} = 15.7$ M2: 1 OR none / no units | 2 |
| 3(d) | M1 : highest [Ag(CN) ₂] ⁻ [Ag(S ₂ O ₃) ₂] ³⁻ [Ag(NH ₃) ₂] ⁺ lowest | 2 |
| | M2: K_{stab} [Ag(CN) ₂] ⁻ is highest / [Ag(CN) ₂] ⁻ is the most stable OR higher K_{stab} forms the more stable complex | |

| Question | Answer | Marks |
|-----------|--|-------|
| 4(a)(i) | M1: energy change when 1 mole of a ionic compound is formed M2: from its gaseous ions under standard conditions | 2 |
| 4(a)(ii) | $\Delta H_{\text{sol}} = (-2099) + (2 \times -378) - (-2824)$ $\Delta H_{\text{sol}} = -31 \text{ kJ mol}^{-1}$ | 2 |
| | M1: use of ×2 as only multiplier M2: correct signs and evaluation | |
| 4(a)(iii) | M1: Cu ²⁺ is smaller OR Cu ²⁺ has a higher charge density | 2 |
| | M2: Cu ²⁺ attracts water molecules more / stronger OR (Cu ²⁺) forms stronger ion-dipole forces to water molecules | |
| 4(b)(i) | anode: chlorine / Cl_2 cathode: hydrogen / H_2 | 1 |
| 4(b)(ii) | M1 : Q = 0.75 × 60 × 60 = 2700 C AND 96 500 or 193 000 used | 2 |
| | M2: [a] moles of Ca = 2700 / 193 000 = 0.0140 [b] mass = 0.0140 × 40.1 = 0.56 g | |

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| Question | | | A | nswer | | Marks |
|-----------|---|--|-------------------------|------------------------|---------|-------|
| 4(c)(i) | measure / degree of (dis)order / randomness (of a system) OR the number of possible arrangements of the particles and their energy (in a given system) | | 1 | | | |
| 4(c)(ii) | | ΔS is negative | ΔS is zero | ΔS is positive | | 1 |
| | solid dissolving in water | | | ✓ | | |
| | water solidifying to ice | ✓ | | | | |
| 4(c)(iii) | negative two correct for 1 mark, three starting at +8.6 kJ/in po line passes through x-ax negative gradient straight | ositive region clos xis around 100°C | se to the <i>y</i> -axi | | exions) | 2 |
| 4(d) | M1: ΔH negative $/-$, ΔS neg M2: as temperature increase OR at low(er) T, (ΔH more now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high(er) T, (ΔH less now OR at high (ΔH le | e, ΔG becomes (egative than T ΔS | S) so ΔG is ne | gative | | 2 |

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| Question | Answer | Marks |
|----------|--|-------|
| 5(a) | M1: ethylamine phenylamine 4-nitrophenylamine most basic least basic | 4 |
| | M2 / 3 / 4: explanation two correct for one mark, three correct for two marks, four correct for three marks • (basicity linked to) lone pair / p orbital on N AND being able accept / donate to / coordinate to a proton / H+ | |
| | ethyl / alkyl group is electron donating / has a positive inductive effect (so lone pair on N is more able to accept a proton) | |
| | (phenylamines are less basic than ethylamine as) p orbital / lone pair on N is delocalised (into the ring so less able to accept a proton) | |
| | • (4-nitrophenylamine is less basic than phenylamine as) nitro / NO ₂ group is electron withdrawing (so lone pair on N is less able to accept a proton) | |
| 5(b)(i) | O_2N \longrightarrow N | 1 |
| 5(b)(ii) | M1: step 1: HNO_2 , \leq 10°C OR $NaNO_2$, $HCl(aq)$, \leq 10°C | 2 |
| | M2: step 2: NaOH / alkaline AND 1-naphthol / α-naphthol / structure below | |
| 5(c)(i) | 4-bromo-2-nitrobenzoic acid OR 4-bromo-2-nitro(-1-)benzenecarboxylic acid | 1 |

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| Question | Answer | Marks |
|-----------|---|-------|
| 5(c)(ii) | $\mathbf{E} = \begin{array}{c} CH_3 \\ NO_2 \\ R \end{array}$ $\mathbf{F} = \begin{array}{c} CH_3 \\ NO_2 \\ R \end{array}$ | 2 |
| 5(c)(iii) | M1: step 1 conc. H ₂ SO ₄ and conc. HNO ₃ | 3 |
| | M2: step 2 Br ₂ and A <i>l</i> Br ₃ | |
| | M3: step 3 hot (alkaline / acidified) MnO ₄ ⁻ / KMnO ₄ | |

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| Question | Answer | Marks |
|----------|---|-------|
| 6(a) | three peaks four peaks | 4 |
| | | |
| | five peaks six peaks | |
| | | |
| | correct isomers and correct assignment to peaks: mark as • ✓ • ✓ • ✓ | |
| 6(b)(i) | $RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$ | 1 |
| | OR $Cl(CH_2)_3COOH + AlCl_3 \rightarrow {}^+(CH_2)_3COOH + AlCl_4^-$ | |
| 6(b)(ii) | X C ₁₀ H ₁₀ O | 2 |
| | OR OR | |

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| Question | Answer | Marks |
|-----------|--|-------|
| 6(b)(iii) | SOC l ₂ OR PC l ₅ ALLOW PC l ₃ AND heat | 1 |
| 6(b)(iv) | intermediate H R H R H H H H H M1: arrow to R+ OR arrow to positive carbon of +(CH ₂) ₃ COOH M2: correct structure of intermediate M3: arrow from C-H bond into the ring AND H+ | 3 |

| Question | Answer | |
|-----------|--|---|
| 7(a)(i) | the power to which a concentration of a reactant is raised in the rate equation / law | 1 |
| 7(a)(ii) | M1 : (using expt 1 and 3) as $[ClO_2] \times 2.5$ rate $\times 6.25$ so 2nd order | 2 |
| | M2: (using expt 1 and 2) as $[OH^-] \times 4$ rate $\times 4$ so 1st order | |
| 7(a)(iii) | $rate = k[ClO_2]^2[OH^-]$ | 1 |
| 7(a)(iv) | M1: $k = \text{rate} / [ClO_2]^2[OH^-]$ $k = 7.20 \times 10^{-4} / (0.02)^2(0.03)$ k = 60 | 2 |
| | M2: mol ⁻² dm ⁶ min ⁻¹ | |

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| Question | Answer | Marks |
|----------|---|-------|
| 7(b)(i) | structure of phenol: C ₆ H ₅ OH OR | 1 |
| 7(b)(ii) | tangent drawn correctly AND rate = $0.015/260 = 5.8 \times 10^{-5}$ ALLOW values consistent with tangent drawn at 100 sec | 1 |
| 7(c) | AND half-life decreases (1st box) | 1 |

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| Question | Answer | | |
|----------|---|---|--|
| 8(a) | M1: acyl chlorides > alkyl chlorides > aryl chlorides fastest slowest | 3 | |
| | M2 / 3: Any two from: acyl chlorides carbon in C-Cl bond is more electron deficient since it is also attached to an oxygen atom OR C-Cl bond is weakest / weakened in acyl chlorides since it is also attached to an oxygen atom / two electronegative atoms aryl chlorides (no hydrolysis) C-Cl bond is part of delocalised system / partially double bond character (so C-Cl bond is | | |
| | stronger) OR lone pair / p-orbital on Cl delocalises with π ring (so C-Cl bond is stronger) alkyl chlorides C-Cl bond strengthened by electron donating effect / positive inductive effect of alkyl / R group (as compared to acyl chlorides) OR carbon atom has a smaller δ+ and the C-Cl bond is stronger (than the C-Cl bond in COCl) due to (the carbon) being only attached to one electronegative atom | | |
| 8(b) | ОН H ₃ C—ОН НО Н | 3 | |
| | ALLOW amine salt for the third structure – mono or di ion | | |
| 8(c)(i) | ОН | 1 | |

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| Answer | | | | | Marks |
|--------------------|--|---|---|--|--|
| chemical shift (δ) | environment of proton | splitting pattern (words required) | number of ¹ H atoms responsible for the peak | | 3 |
| 0.95 | alkane / CH ₃ | doublet | 6 | | |
| 1.90 | alkane / CH ALLOW alkyne | multiplet | 1 | | |
| 2.20 | R / alkyl / CH ₂ next to C=O / COOH | doublet | 2 | | |
| | shift (δ) 0.95 1.90 | shift (δ) 0.95 alkane / CH ₃ 1.90 alkane / CH ALLOW alkyne 2.20 R / alkyl / CH ₂ next to | | | chemical shift (δ) environment of proton splitting pattern (words required) number of ¹H atoms responsible for the peak 0.95 alkane / CH ₃ doublet 6 1.90 alkane / CH ALLOW alkyne multiplet 1 2.20 R / alkyl / CH ₂ next to doublet 2 |

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