Cambridge International AS & A Level

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CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2019**

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.

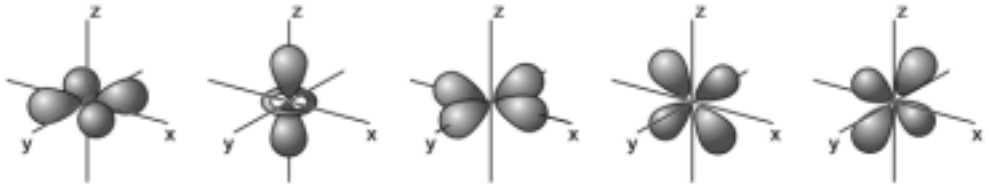
GENERIC MARKING PRINCIPLE 4:

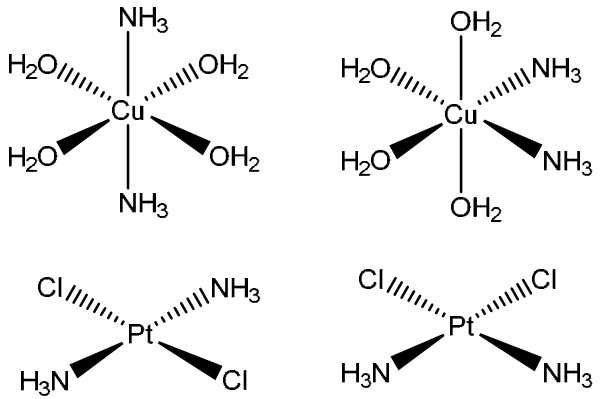
Rules must be applied consistently e.g. in situations where candidates have not followed instructions or in the application of generic level descriptors.

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.

Question	Answer	Marks
1(a)(i)	$3s^2 3p^6 3d^9$ [1]	**1**
1(a)(ii)	$[Cu(H_2O)_6]^{2+}$ (pale) blue $CuCl_4^{2-}$ yellow **both** [1]	**1**
1(a)(iii)	M1 energy gap / ΔE is **different** (for the ligands) [1] M2 different frequency / wavelength of light **absorbed / transmitted / reflected** [1]	**2**
1(b)	M1 (Cu^+/Ag^+) d-shell is full / complete **OR** d-orbital**s** are full [1] M2 no electrons can be promoted [1]	**2**
1(c)(i)	solubility = $\sqrt{5.0 \times 10^{-13}}$ = **7.1×10^{-7}** ($mol\ dm^{-3}$) [1] min 2sf	**1**
1(c)(ii)	M1 (in conc. NH_3) [NH_3] increases **and** equilibrium 2 shifts to the right [1] M2 [Ag^+] decreases **and** equilibrium **1** shifts to the right [1]	**2**
1(c)(iii)	$AgBr + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Br^-$ [1]	**1**
1(c)(iv)	$K_{eq3} = K_{sp} \times K_{stab}$ [1] **ALLOW** $K_{eq3} = [Ag(NH_3)_2^+][Br^-]/[NH_3]^2$	**1**
1(d)	The potential difference when a half-cell is connected to a (standard) hydrogen electrode under standard conditions [1] **OR** the potential difference / voltage / EMF between a hydrogen electrode and another half-cell under standard conditions [1]	**1**
1(e)(i)	salt bridge • voltmeter / V • Ag • Ag^+ (or soluble silver salt) • Pt • H_2 (and delivery correct) + H^+ (or named strong acid) • 1 atm. (pressure) • 1 $mol\ dm^{-3}$ (and 298 K) • mark as • ✓ • ✓ • ✓ • ✓ [4]	**4**
1(e)(ii)	Ag electrode labelled **and** arrow (in the external circuit moving towards this electrode) [1]	**1**

Question	Answer	Marks
2(a)	$CO_3^{2-} \rightarrow O^{2-} + CO_2$ [1]	**1**
2(b)	Increases (with increasing atomic number / implied) [1] cationic radius / ion size **increases** (down the group) [1] less polarisation / distortion of anion/CO_3^{2-} [1]	**3**
2(c)	(Pb^{2+}) 0.120 nm; (Ca^{2+}) 0.099 nm; (Zn^{2+}) 0.075 nm [1] (most stable) $PbCO_3$ > $CaCO_3$ > $ZnCO_3$ (least stable) [1] **ECF** from atomic radii	**2**
2(d)	amount of CO_2 = 125 / 24000 = 5.21×10^{-3} mol [1] $CaMg(CO_3)_2$:CO_2 1:2 amount of carbonate = $2.60(4) \times 10^{-3}$ mol [1] ECF mass of carbonate = $184(.4) \times 2.60(4) \times 10^{-3}$ = 0.480 g % of $CaMg(CO_3)_2$ = $100 \times 0.480 / 0.642$ = **74.8** % [1] ECF	**3**

Question	Answer	Marks
3(a)	 any diagram [1]	**1**
3(b)(i)	(elements) forming one or more (stable) **ions** with incomplete / partially filled **d** orbital(s) / sub-shell [1]	**1**
3(b)(ii)	dative covalent / coordinate [1]	**1**

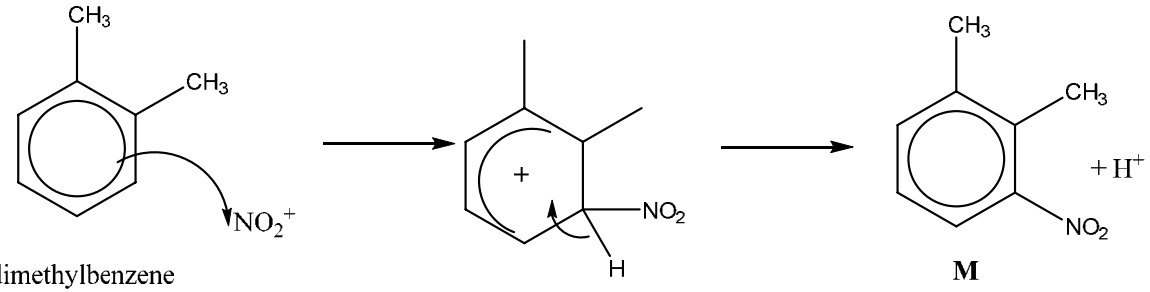
<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>3(c)</td><td>FeO and +2
Fe_2O_3 and +3 all [1] ALLOW Fe_3O_4 and +3 and +2</td><td>1</td></tr>
<tr><td>3(d)</td><td>
<table>
<tr><th>metal ion</th><th>ligand</th><th>co-ordination number</th><th>formula of complex ion</th><th>charge of complex ion</th></tr>
<tr><td>Ni^{2+}</td><td>CO</td><td>4</td><td>$Ni(CO)_4$</td><td>2+</td></tr>
<tr><td>Fe^{3+}</td><td>CN^-</td><td>6</td><td>$Fe(CN)_6$</td><td>3-</td></tr>
</table>
mark as • ✓ • ✓ [2]</td><td>2</td></tr>
<tr><td>3(e)(i)</td><td>cis-trans isomerism [1] ALLOW geometric(al)</td><td>1</td></tr>
<tr><td>3(e)(ii)</td><td> 

one correct pair [1] two correct pairs [2]</td><td>2</td></tr>
<tr><td>3(f)(i)</td><td>$K_{stab} = \frac{[Cu(H_2O)_4(NH_3)_2^{2+}]}{[Cu(H_2O)_6^{2+}][NH_3]^2}$ [1] units = $dm^6\ mol^{-2}$ [1] ecf from M1</td><td>2</td></tr>
<tr><td>3(f)(ii)</td><td>equilibrium 4 has a (net) increase in moles of product / 2 moles goes to 3 moles whereas equilibrium 5 has same number of moles of reactants and products / 3 moles vs 3 moles [1]</td><td>1</td></tr>
</table>

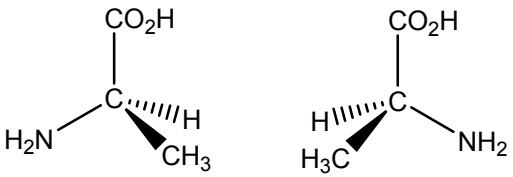
Question	Answer	Marks
3(f)(iii)	$[Cu(H_2O)_4(en)]^{2+}$ **and** (equilibrium) constant / K_{stab} is the larg**est** / high**est** [1] **ALLOW** $[Cu(H_2O)_4(en)]^{2+}$ **and** constant / K_{stab} of eqm 4 is greate**r** / high**er**	**1**

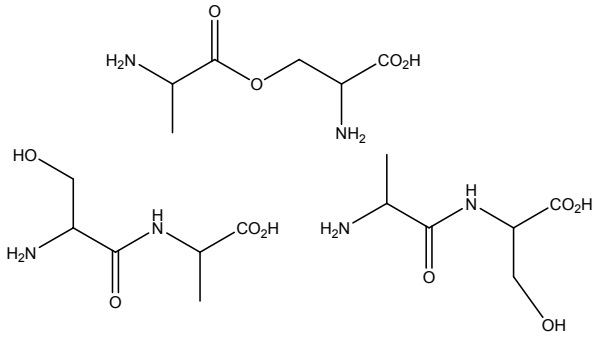
Question	Answer	Marks
4(a)	CH_3COCH_3 = 1 I_2 = 0 H^+ = 1 overall order = 2 M1 3 orders [1] M2 overall order based on their M1 [1]	**2**
4(b)(i)	$k = 5.40 \times 10^{-3} / (1.50 \times 10^{-2} \times 7.75 \times 10^{-1})$ k = **0.46(452)** [1] $dm^3\ mol^{-1}\ s^{-1}$ [1] 2sf min	**2**
4(b)(ii)	<table><tr><td></td><td>decreases</td><td>no change</td><td>increases</td></tr><tr><td>rate constant</td><td>✓</td><td></td><td></td></tr><tr><td>rate of reaction</td><td>✓</td><td></td><td></td></tr></table> **both** [1]	**1**
4(c)	draw **a tangent** at **time, t=0** [1] measure the **gradient / slope** of the tangent [1]	**2**
4(d)	straight line graph **starting at 0,0** and showing rate α $[CH_3COCH_3]$ [1]	**1**
4(e)(i)	slowest step / reaction (in the mechanism) [1]	**1**
4(e)(ii)	$2Ce^{4+} + Tl^{+} \rightarrow Tl^{3+} + 2Ce^{3+}$ [1] catalyst **and** (used in step 1 and) regenerated / reformed in **step 3 / end of the reaction** [1]	**2**

Question	Answer	Marks
5(a)	<table><tr><th>energy change</th><th>always positive</th><th>always negative</th><th>either negative or positive</th></tr><tr><td>lattice energy</td><td></td><td>✓</td><td></td></tr><tr><td>enthalpy of neutralisation</td><td></td><td>✓</td><td></td></tr></table> **both** [1]	**1**
5(b)	(energy change) when **1 mole** of solute is dissolved in an infinite amount of **water** to form a dilute solution	**1**
5(c)	calculation of $\Delta H^{\ominus}_{sol}$ with –251, –1284 and –2035 only and two correct signs [1] calculation of $\Delta H^{\ominus}_{sol}$ with –251, –1284 and –2035 only and correct signs **OR** calculation of $\Delta H^{\ominus}_{sol}$ with (–251 × 3), –1284 and –2035 only and two correct signs [2] $\Delta H^{\ominus}_{sol}$ = (3 × –251) + (–1284) – (–2035) = **–2** (kJ mol^{-1}) [3]	**3**
5(d)	Ca^{2+} have a higher charge / greater charge density [1] **ora** **stronger** electrostatic forces between Br^- and Ca^{2+} [1]	**2**
5(e)(i)	$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ [1]	**1**
5(e)(ii)	$T\Delta S$ is more positive **OR** $-T\Delta S$ becomes more negative [1]	**1**

Question	Answer	Marks
6(a)	any **three** points from: 3 × [1] • bond angle = 120° **and** shape is (hexagonal ring) planar / (trigonal) planar • carbons are sp^2 hybridised • contains <u>delocalised electrons</u> in the π bonds / system • sp^2 orbitals between C-H / C-C overlap to form **σ bonds** • a **p orbital** from each carbon atom overlap sideways with each other above and below the ring forming **π bonds** **ALLOW** labelled diagrams for bullets 1–5	**3**
6(b)(i)	$HNO_3 + H_2SO_4 \rightarrow HSO_4^- + H_2O + NO_2^+$ ***or*** $HNO_3 + 2H_2SO_4 \rightarrow 2HSO_4^- + H_3O^+ + NO_2^+$ [1]	**1**
6(b)(ii)	 1,2-dimethylbenzene **M** first curly arrow to N of NO_2^+ [1] correct intermediate [1] 2nd curly arrow **and** H^+ formed / lost [1]	**3**
6(b)(iii)	$HSO_4^- + H^+ \rightarrow H_2SO_4$ [1]	**1**
6(b)(iv)	Sn + conc. HC*l* (+ heat) [1] reduction [1] **IGNORE** redox	**2**
6(c)(i)	$C_{15}H_{15}NO_2$ [1]	**1**
6(c)(ii)	amine **and** carboxylic <u>acid</u> **both** [1]	**1**

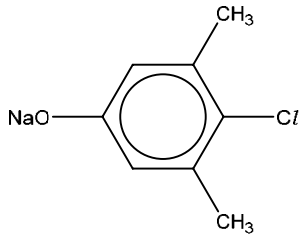
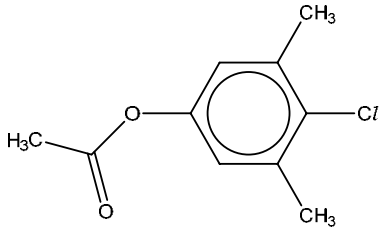
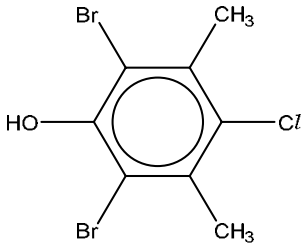
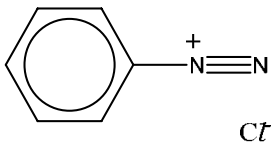
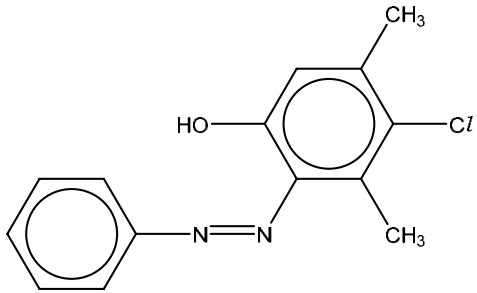
Question	Answer	Marks
6(c)(iii)	amount of 2,3-dimethylphenylamine = 5.00 / 121 = 0.0413 mol [1] amount of mefenamic acid = 0.0413 mol mass of mefenamic acid = 0.0413 × 241 = **9.96 / 9.95** g 3sf required [1] ECF	**2**
6(d)	**3º** carbocations are more stable than **2º** carbocations [1] due to the methyl group acting as an electron donating group (leading to an increase in electron density on the cation stabilising it) [1]	**2**

Question	Answer	Marks
7(a)(i)	A= leucine B= glutamic acid **both** [1]	**1**
7(a)(ii)	greater **and** more soluble in the solvent / mobile phase **OR** greater **and** form more H-bonds with the solvent [1]	**1**
7(b)(i)	$H_2NCH_2CO_2H + HCl \rightarrow Cl^-H_3N^+CH_2CO_2H$ [1] $H_2NCH_2CO_2H + NaOH \rightarrow H_2NCH_2CO_2^-Na^+ + H_2O$ [1]	**2**
7(b)(ii)	$H_3N^+CH_2CO_2^-$ [1] Proton is transferred from the CO_2H group to the NH_2 group [1]	**2**
7(c)	 two non-superimposable mirror images for alanine drawn [1]	**1**

Question	Answer	Marks
7(d)(i)	NH_3 (in ethanol) heat in a sealed tube [1] nucleophilic substitution [1]	**2**
7(d)(ii)	acidity of Cl_3CCO_2H > $ClCH_2CO_2H$ > CH_3CO_2H [1] **any two of:** Cl is electronegative / electron withdrawing group **AND** Cl_3CCO_2H has more / 3 Cl groups [1] weakens O-H bond **so** more likely to ionise / dissociate **OR negative** charge on anion is more stabilised **OR** charge / electron density on COO^- decreases so anion is (more) stabilised [1] CH_3 is electron donating **so** O-H bond is stronger so less likely to ionise in CH_3CO_2H **OR** CH_3CO_2H has no -I group **so** O-H bond is stronger and less likely to ionise [1]	**3**
7(e)	 One mark for each structure. [1] [1] [1]	**3**

Question	Answer	Marks
8(a)	4-chloro-3,5-dimethylphenol **OR** 3,5-dimethyl-4-chlorophenol [1] **ALLOW** 2,6-dimethyl-4-hydroxychlorobenzene and 2-chloro-5-hydroxy-1,3-dimethylbenzene	**1**
8(b)(i)	carbon-13 NMR = 5 peaks [1] proton NMR = 3 peaks [1]	**2**
8(b)(ii)	**OH** proton had disappeared due to proton exchange with D / D_2O [1] **ALLOW** $OH + D_2O \rightarrow OD + HOD$	**1**

Question	Answer	Marks
8(c)		**6**

reagent	organic product structure	type of reaction
Na	 or ionic	redox
CH_3COCl		Condensation
$Br_2(aq)$		(electrophilic) substitution
		(electrophilic) substitution

each structure [1] × 4 type of reaction • ✓ • ✓ [2]