



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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This document consists of **13** printed pages.

PUBLISHED**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:

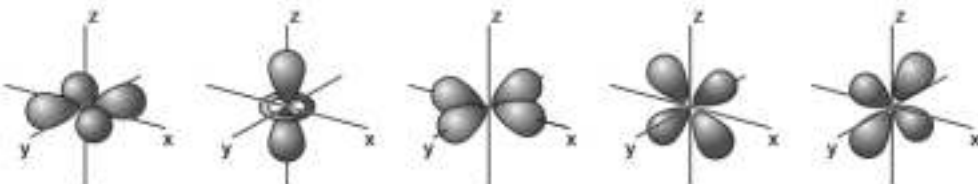
Marks awarded are based solely on the requirements as defined in the mark scheme. Marks should not be awarded with grade thresholds or grade descriptors in mind.

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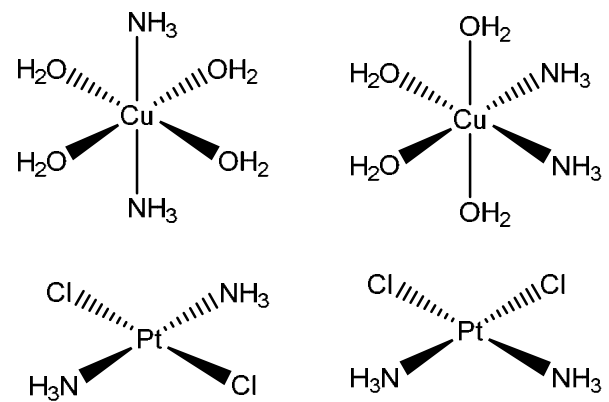
Question	Answer	Marks
1(a)(i)	$3s^2 3p^6 3d^9$ [1]	1
1(a)(ii)	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (pale) blue CuCl_4^{2-} yellow both [1]	1
1(a)(iii)	M1 energy gap / ΔE is different (for the ligands) [1] M2 different frequency / wavelength of light absorbed / transmitted / reflected [1]	2
1(b)	M1 $(\text{Cu}^+/\text{Ag}^+)$ d-shell is full / complete OR d-orbitals are full [1] M2 no electrons can be promoted [1]	2
1(c)(i)	solubility = $\sqrt{5.0 \times 10^{-13}} = 7.1 \times 10^{-7} \text{ (mol dm}^{-3}\text{)}$ [1] min 2sf	1
1(c)(ii)	M1 (in conc. NH_3) $[\text{NH}_3]$ increases and equilibrium 2 shifts to the right [1] M2 $[\text{Ag}^+]$ decreases and equilibrium 1 shifts to the right [1]	2
1(c)(iii)	$\text{AgBr} + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+ + \text{Br}^-$ [1]	1
1(c)(iv)	$K_{\text{eq}3} = K_{\text{sp}} \times K_{\text{stab}}$ [1] ALLOW $K_{\text{eq}3} = [\text{Ag}(\text{NH}_3)_2^+][\text{Br}^-]/[\text{NH}_3]^2$	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 Ag Pt 1 atm. (pressure) • • • • voltmeter / V • Ag^+ (or soluble silver salt) • H_2 (and delivery correct) + H^+ (or named strong acid) • 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

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Question	Answer	Marks
2(a)	$\text{CO}_3^{2-} \rightarrow \text{O}^{2-} + \text{CO}_2$ [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) $\text{PbCO}_3 > \text{CaCO}_3 > \text{ZnCO}_3$ (least stable) [1] ECF from atomic radii	2
2(d)	amount of $\text{CO}_2 = 125 / 24000 = 5.21 \times 10^{-3}$ mol [1] $\text{CaMg}(\text{CO}_3)_2 : \text{CO}_2$ 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 $\text{CaMg}(\text{CO}_3)_2 = 100 \times 0.480 / 0.642 = \mathbf{74.8\%}$ [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

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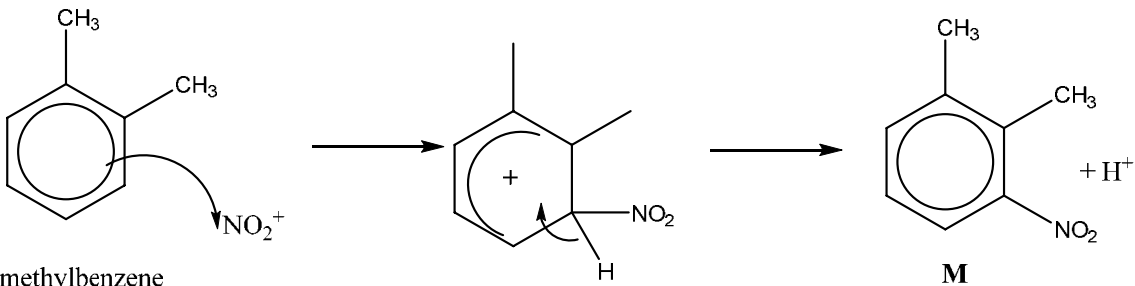
Question	Answer	Marks															
3(c)	FeO and +2 Fe ₂ O ₃ and +3 all [1] ALLOW Fe ₃ O ₄ and +3 and +2	1															
3(d)	<table><tr><th>metal ion</th><th>ligand</th><th>co-ordination number</th><th>formula of complex ion</th><th>charge of complex ion</th></tr><tr><td>Ni²⁺</td><td>CO</td><td>4</td><td>Ni(CO)₄</td><td>2+</td></tr><tr><td>Fe³⁺</td><td>CN⁻</td><td>6</td><td>Fe(CN)₆</td><td>3-</td></tr></table> mark as • ✓ • ✓ [2]	metal ion	ligand	co-ordination number	formula of complex ion	charge of complex ion	Ni ²⁺	CO	4	Ni(CO) ₄	2+	Fe ³⁺	CN ⁻	6	Fe(CN) ₆	3-	2
metal ion	ligand	co-ordination number	formula of complex ion	charge of complex ion													
Ni ²⁺	CO	4	Ni(CO) ₄	2+													
Fe ³⁺	CN ⁻	6	Fe(CN) ₆	3-													
3(e)(i)	cis-trans isomerism [1] ALLOW geometric(al)	1															
3(e)(ii)	 one correct pair [1] two correct pairs [2]	2															
3(f)(i)	$K_{\text{stab}} = \frac{[\text{Cu}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+}][\text{NH}_3]^2}$ [1] units = dm ⁶ mol ⁻² [1] ecf from M1	2															
3(f)(ii)	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]	1															

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Question	Answer	Marks
3(f)(iii)	$[\text{Cu}(\text{H}_2\text{O})_4(\text{en})]^{2+}$ and (equilibrium) constant / K_{stab} is the largest / highest [1] ALLOW $[\text{Cu}(\text{H}_2\text{O})_4(\text{en})]^{2+}$ and constant / K_{stab} of eqm 4 is greater / higher	1

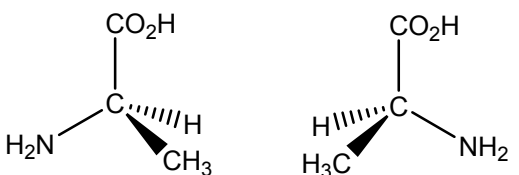
Question	Answer	Marks												
4(a)	$\text{CH}_3\text{COCH}_3 = 1$ $\text{I}_2 = 0$ $\text{H}^+ = 1$ overall order = 2 M1 3 orders [1] M2 overall order based on their M1 [1]	2												
4(b)(i)	$k = 5.40 \times 10^{-3} / (1.50 \times 10^{-2} \times 7.75 \times 10^{-1})$ $k = \mathbf{0.46(452)}$ [1] $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ [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]		decreases	no change	increases	rate constant	✓			rate of reaction	✓			1
	decreases	no change	increases											
rate constant	✓													
rate of reaction	✓													
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 $\text{rate} \propto [\text{CH}_3\text{COCH}_3]$ [1]	1												
4(e)(i)	slowest step / reaction (in the mechanism) [1]	1												
4(e)(ii)	$2\text{Ce}^{4+} + \text{Tl}^+ \rightarrow \text{Tl}^{3+} + 2\text{Ce}^{3+}$ [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><td>energy change</td><td>always positive</td><td>always negative</td><td>either negative or positive</td></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]				energy change	always positive	always negative	either negative or positive	lattice energy		✓		enthalpy of neutralisation		✓		1
energy change	always positive	always negative	either negative or positive														
lattice energy		✓															
enthalpy of neutralisation		✓															
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 $\Delta H^\circ_{\text{sol}}$ with -251 , -1284 and -2035 only and two correct signs [1] calculation of $\Delta H^\circ_{\text{sol}}$ with -251 , -1284 and -2035 only and correct signs OR calculation of $\Delta H^\circ_{\text{sol}}$ with (-251×3) , -1284 and -2035 only and two correct signs [2] $\Delta H^\circ_{\text{sol}} = (3 \times -251) + (-1284) - (-2035) = -2 \text{ (kJ mol}^{-1}\text{)}$ [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)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ [1]				1												
5(e)(ii)	$T\Delta S$ is more positive OR $-T\Delta S$ becomes more negative [1]				1												

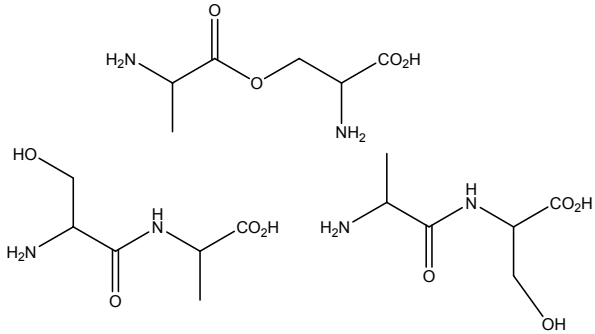
Question	Answer	Marks
6(a)	any three points from: • bond angle = 120° and shape is (hexagonal ring) planar / (trigonal) planar • carbons are sp^2 hybridised • contains <u>delocalised electrons</u> in the π bonds / system • sp^2 orbitals between C-H / C-C overlap to form σ bonds • a p orbital from each carbon atom overlap sideways with each other above and below the ring forming π bonds ALLOW labelled diagrams for bullets 1–5	3 × [1] 3
6(b)(i)	$\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{H}_2\text{O} + \text{NO}_2^+$ or $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{HSO}_4^- + \text{H}_3\text{O}^+ + \text{NO}_2^+$ [1]	1
6(b)(ii)	 1,2-dimethylbenzene first curly arrow to N of NO_2^+ [1] correct intermediate [1] 2nd curly arrow and H^+ formed / lost [1]	3
6(b)(iii)	$\text{HSO}_4^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4$ [1]	1
6(b)(iv)	$\text{Sn} + \text{conc. HCl (+ heat)}$ [1] reduction [1] IGNORE redox	2
6(c)(i)	$\text{C}_{15}\text{H}_{15}\text{NO}_2$ [1]	1
6(c)(ii)	amine and carboxylic <u>acid</u> both [1]	1

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Question	Answer	Marks
6(c)(iii)	amount of 2,3-dimethylphenylamine = $5.00 / 121 = 0.0413 \text{ mol}$ [1] amount of mefenamic acid = 0.0413 mol mass of mefenamic acid = $0.0413 \times 241 = \mathbf{9.96 / 9.95 \text{ g}}$ 3sf required [1] ECF	2
6(d)	3° carbocations are more stable than 2° 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)	$\text{H}_2\text{NCH}_2\text{CO}_2\text{H} + \text{HCl} \rightarrow \text{CH}_3\text{N}^+\text{H}_3\text{CH}_2\text{CO}_2\text{H}$ [1] $\text{H}_2\text{NCH}_2\text{CO}_2\text{H} + \text{NaOH} \rightarrow \text{H}_2\text{NCH}_2\text{CO}_2^-\text{Na}^+ + \text{H}_2\text{O}$ [1]	2
7(b)(ii)	$\text{H}_3\text{N}^+\text{CH}_2\text{CO}_2^-$ [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

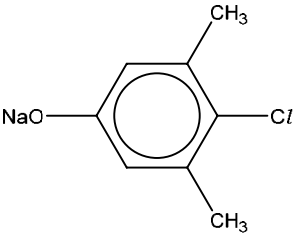
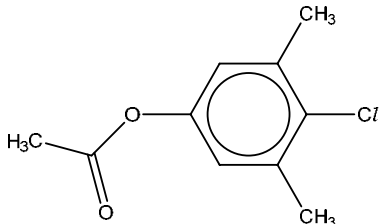
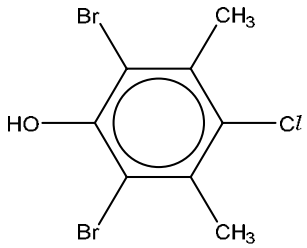
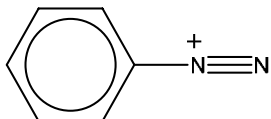
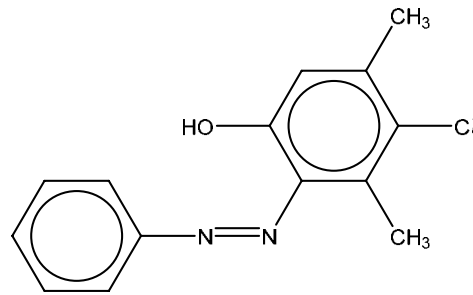
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Question	Answer	Marks
7(d)(i)	NH_3 (in ethanol) heat in a sealed tube [1] nucleophilic substitution [1]	2
7(d)(ii)	acidity of $\text{Cl}_3\text{CCO}_2\text{H} > \text{ClCH}_2\text{CO}_2\text{H} > \text{CH}_3\text{CO}_2\text{H}$ [1] any two of: Cl is electronegative / electron withdrawing group AND $\text{Cl}_3\text{CCO}_2\text{H}$ 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 $\text{CH}_3\text{CO}_2\text{H}$ OR $\text{CH}_3\text{CO}_2\text{H}$ 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

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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 ₂ O [1] ALLOW OH + D ₂ O → OD + HOD	1

Question	Answer			Marks
8(c)	reagent	organic product structure	type of reaction	6
	Na	 or ionic	redox	
	CH ₃ COCl		Condensation	
	Br ₂ (aq)		(electrophilic) substitution	
	 <i>Cl</i>		(electrophilic) substitution	
each structure [1] × 4		type of reaction • ✓ • ✓ [2]		