

#### CHEMISTRY

9701/42 March 2019

Paper 4 A Level Structured Questions 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)	natural: lightning, bacterial decomposition, volcanic emissions man-made: exhaust fumes, power stations, jet / car/ vehicle engines	1
1(b)(i)	$4NO \longrightarrow N_2O + N_2O_3$	1
1(b)(ii)	+2 to +1 <b>AND</b> +2 to +3	1
1(b)(iii)	$\Delta S = (\Delta H - \Delta G) / T$ = (-195.2+102.8) / 298 = -0.310 kJ mol <sup>-1</sup> K <sup>-1</sup>	2
	M1 numerical answer M2 units	
1(b)(iv)	yes as there is a decrease in no. of moles of gas OR yes as moles of (gaseous) reactants is greater than moles of (gaseous) products	1
1(c)(i)	$K_p = p(NO)p(NO_2) / p(N_2O_3)$ AND units: atm OR Pa	1
1(c)(ii)	M1 $p(NO) = p(NO_2) = 0.48 \text{ atm}$ $p(N_2O_3)_{eqm} = p(N_2O_3)_o - 0.48 = 0.12 \text{ atm}$	2
	<b>M2</b> $K_p = 0.48^2 / 0.12 = 1.92 \text{ (atm)}$	
1(d)(i)	<b>M1</b> from 3rd and 1st rows as [NO] $\times$ 2, rate increases $\times$ 4, so order = 2	2
	<b>M2</b> from 3rd and 2nd rows as $[O_2] \times 2$ , rate also $\times 2$ , so order = 1	
1(d)(ii)	rate = $k[NO]^2[O_2]$	3
	<i>k</i> = rate / ([NO] <sup>2</sup> [O <sub>2</sub> ]) = 3.5 / (0.01 × 0.05) = 7000	
	units: mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup>	

Question	Answer	Marks
1(e)(i)	the number of dative bonds formed with / by the central metal atom / ion OR number of bonds between the ligands and the central metal atom / ion	1
1(e)(ii)	from 5 to 4	1
1(e)(iii)	tetrahedral	1
1(f)(i)	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2
1(f)(ii)	geometric(al) OR cis-trans	1

Question	Answer	Marks
2(a)(i)	<b>M1</b> $\Delta H_{\text{latt}}$ and $\Delta H_{\text{hyd}}$ both decrease OR $\Delta H_{\text{latt}}$ and $\Delta H_{\text{hyd}}$ both become less exothermic / more endothermic	3
	<b>M2</b> $\Delta H_{\text{latt}}$ decreases more than $\Delta H_{\text{hyd}}$ (as OH <sup>-</sup> being smaller than M <sup>2+</sup> )	
	<b>M3</b> $\Delta H_{sol}$ becomes more exothermic / more negative	
2(a)(ii)	(for MCO <sub>3</sub> ) change / decrease in $\Delta H_{hyd}$ is larger than decrease in $\Delta H_{latt}$	1
2(a)(iii)	M1 Sr and Ba could be used AND Mg could not be used	2
	<b>M2</b> solubility of MgCO <sub>3</sub> is more than Mg(OH) <sub>2</sub> OR SrCO <sub>3</sub> / BaCO <sub>3</sub> is less than Sr(OH) <sub>2</sub> / Ba(OH) <sub>2</sub>	

Question	Answer	Marks
2(b)(i)	$K_{\rm sp} = [Mg^{2+}(aq)][OH^{-}(aq)]^2  OR  K_{\rm sp} = (2.0 \times 10^{-4})(4.0 \times 10^{-4})^2$	2
	$= 3.2 \times 10^{-11}$	
2(b)(ii)	M1 (white) ppt. / solid (of BaCO <sub>3</sub> ) will appear	2
	<b>M2</b> due to the common ion effect OR the BaCO <sub>3</sub> (s) $\Rightarrow$ Ba <sup>2+</sup> (aq) + CO <sub>3</sub> <sup>2–</sup> (aq) equilibrium shifts to the left	
2(c)	elements $AH_f$ $Mg^{2+}(g) + 2OH(g)$ $LE$ $\Delta H_f$ $Mg(OH)_2(s)$	3
	$\begin{array}{l} -2993 + 148 + 736 + 1450 + 2 \Delta H_{\rm f}(\rm OH^-(g)) = -925 \\ 2 \Delta H_{\rm f}(\rm OH^-(g)) = -266 \\ \Delta H_{\rm f}(\rm OH^-(g)) = -133 \ (kJ \ mol^{-1}) \end{array}$	

Question	Answer	Marks
3(a)(i)	<b>M1</b> pH = -log[H <sup>+</sup> ]	2
	<b>M2</b> <i>K</i> <sub>a</sub> = [H <sup>+</sup> ][A <sup>-</sup> ]/[HA]	
3(a)(ii)	<b>M1</b> $A^-$ + $H^+ \rightarrow HA$ <b>OR</b> NaA + $H^+ \rightarrow HA$ + Na <sup>+</sup>	2
	$\mathbf{M2} \text{ HA} + \text{OH}^{-} \rightarrow \text{H}_2\text{O} + \text{A}^{-}$	
3(b)	remaining $n(HClO) = 0.17 - 0.03 = 0.14 \text{ mol} (dm^{-3})$	3
	$[H^+]$ = 1.35 × 10 <sup>-7</sup> mol dm <sup>-3</sup> OR calculate pK <sub>a</sub> (7.54) from K <sub>a</sub>	
	pH = -log(1.35 × 10 <sup>-7</sup> ) = 6.87/ 6.9 OR pH = 7.54 + log(0.03/0.14) = 6.87	

Question	Answer	Marks
4(a)(i)	(1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> )3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>1</sup>	1
4(a)(ii)	M1 d orbitals / sub-shell split into two levels by repulsion of approaching ligands	4
	M2 light absorbed and complementary colour observed	
	M3 (d) electron(s) promoted / excited OR (d) electron(s) moves to higher (d) orbital	
	<b>M4</b> (in Cu(I) complexes) all the orbitals in Cu are full OR Cu(I) is $d^{10}$	
4(b)	$n(S_2O_3^{2-}) = 28.35 \times 0.5 / 1000 = 0.0142 (0.014175)$	3
	this also equals $n(Cu^{2+})$ mass of Cu = 0.014175 × 63.5 = 0.90 g	
	% of Cu = $100 \times 0.90 / 1.5 = 60\%$	
4(c)(i)	$E_{\text{cell}}^{\Theta} = 0.15 - 0.54 = -0.39 \text{ (V)}$	1
4(c)(ii)	since $E_{cell}^{e}$ is negative (reaction is not likely to occur) OR since $E_{cell}^{e} < 0$ (reaction is not feasible / not spontaneous)	1
4(c)(iii)	$E = E^{\circ} + (0.059 / 1) \log(1.0 / 1.3 \times 10^{-6})$ = +0.15 + 0.059 × 5.89 = +0.50/0.497 V	2
4(c)(iv)	$E_{\text{cell}}^{\text{e}}$ is very negative OR calculation ( $E_{\text{cell}}^{\text{e}} = 0.15 - 1.36 = ) - 1.21 \text{ V}$	1
4(d)(i)	Cu <sup>2+</sup> (aq) is (light) blue AND [CuC4] <sup>2–</sup> (aq) is yellow	1
4(d)(ii)	ligand displacement / replacement / substitution / exchange	1
4(d)(iii)	$K_{\text{stab}} = [CuC4]^{2-} / ([Cu^{2+}][Ct^{-}]^4)$ units: mol <sup>-4</sup> dm <sup>12</sup>	2

Question	Answer	Marks
5(a)(i)	$\begin{pmatrix} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	2
	M1 correct C–C backbone (with correct side groups) M2 continuation bonds and two repeat units	
5(a)(ii)	addition	1
5(a)(iii)	<i>Any two of:</i> permanent dipole (attraction): C, N, O, OR CO, CN, CO <sub>2</sub> CH <sub>3</sub> , OCH <sub>3</sub>	2
	H-bonding: N, O OR CO, CN	
	London/van der Waals: N, C, H, O OR CH <sub>3</sub> , CN, CO <sub>2</sub> CH <sub>3</sub> , C–C chains	
5(b)(i)	Y CH <sub>3</sub> COCO <sub>2</sub> CH <sub>3</sub>	2
	Z CH <sub>3</sub> C(OH)(CN)CO <sub>2</sub> CH <sub>3</sub>	
5(b)(ii)	M1/M2 step 1: CH <sub>3</sub> OH and (conc) H <sub>2</sub> SO <sub>4</sub> + heat	4
	M3 step 2: HCN + NaCN catalyst	
	<b>M4</b> step 3: T > 100°C / heat with $Al_2O_3$ (or heat with c. $H_2SO_4$ )	

Question	Answer	Marks
6(a)	Any two of: chloro amine / amino alcohol / hydroxyl / phenol benzene / phenyl ring / aryl / arene	1
6(b)(i)	ketamine is acting as a base	1
6(b)(ii)	carbonyl group	1
6(b)(iii)	n = (100 / 1.1) x (14.3 / 100) = 13.0  OR  n = (14.3 / 1.1) = 13.0	1
6(b)(iv)	the ratio of the (M:M+2) peaks is 3:1 <b>AND</b> halogen is chlorine / Cl	1
6(b)(v)	relative abundance = 14.3 / 3 = 4.77 (4.8) OR RA = 14.3 × 33.3 / 100 = 4.76 (4.8)	1
6(b)(vi)	C <sub>13</sub> H <sub>16</sub> NOC <i>l</i>	1
6(c)(i)	six	1
6(c)(ii)	M1 peak at $\delta$ 0.9 is due to 12 H M2 peak at 2.2 is due to 2 H M3/M4 peaks at 1.2, 1.4 and 1.7 are all singlets	4
6(c)(iii)	$\begin{array}{c} CH_3 \\ H_2C \\ H_3C \\ H_3C \\ H_3C \\ H_3C \\ \hline CH_2 \\ \hline CH_3 \\$	2

Question	Answer	Marks
6(c)(iv)	$NH/NH_2$ protons <b>AND</b> exchange with $D_2O/D$	1
	$OR - NH_2 + D_2O \rightarrow -ND_2 + H_2O$	

Question	Answer	Marks
7(a)(i)	HO <sub>2</sub> C-CO <sub>2</sub> H OR HO <sub>2</sub> C-COC <i>l</i>	1
7(a)(ii)	SOC12 OR PC15	1
7(b)(i)	$B \xrightarrow{CI} CI \xrightarrow{O \xrightarrow{H}} CI$	4
7(b)(ii)	<b>M1</b> step 1: $Cl_2 + AlCl_3$	5
	<b>M2</b> step 3: conc. $HNO_3 + H_2SO_4$	
	M3 step 4: Sn + conc. HCl	
	<b>M4</b> step 6: LiA <i>t</i> H <sub>4</sub>	
	<b>M5</b> any two of: heat / T $\ge$ 60 °C / reflux for step 1 T $\le$ 60 °C / warm for step 3 heat / T $\ge$ 60 °C / reflux for step 4	

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