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**CHEMISTRY**

**9791/03**

Paper 3 Part B Written

**May/June 2018**

MARK SCHEME

Maximum Mark: 100

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**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.

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This document consists of **10** 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:**

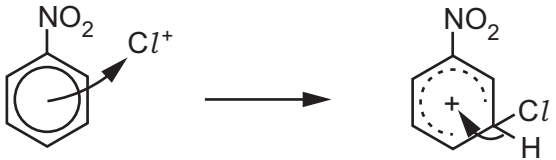
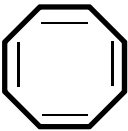
Rules must be applied consistently e.g. in situations where candidates have not followed instructions or in the application of generic level descriptors.

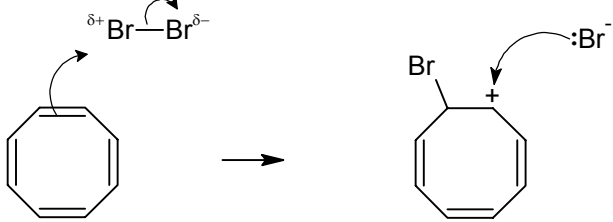
**GENERIC MARKING PRINCIPLE 5:**

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.

Question	Answer	Marks
1(a)	<p>p orbitals (one each carbon) overlap above and below the ring (1)  Less electron density cf. alkene or reverse argument (1)  Electrons are <u>delocalised</u> (1)  Less susceptible to attack by electrophiles or reverse argument (1)</p>	4
1(b)	<p><math>AlCl_3 + Cl_2 \rightarrow Cl^+ + AlCl_4^-</math> (1)  Arrow from double bond or conjugated ring of benzene to <math>Cl^+</math> (1)  Intermediate cation (with nitro group) (1)  Arrow from C-H bond to reform delocalised ring (1)</p> 	4
1(c)(i)	<u>Conc</u> $H_2SO_4$ and <u>conc</u> $HNO_3$ (1)	1
1(c)(ii)	<u>Cl</u> group is 2,4 – directing (1)	1
1(c)(iii)	Steric congestion disfavors 2 substitution (1)	1
1(d)(i)	 (1)	1
1(d)(ii)	<p>In COT (C=C) &lt; (C–C) (1)  Benzene (all C–C are the same and) are between values for COT (1)</p>	2

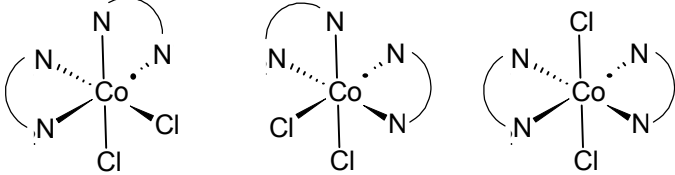
Question	Answer	Marks
1(d)(iii)	<p>Induced dipole shown <math>\text{Br}^{\delta+} - \text{Br}^{\delta-}</math> (1)            Arrow from <math>\text{C} = \text{C}</math> to <math>\text{Br}^{\delta+}</math> and from bond to <math>\text{Br}^{\delta-}</math> (1)            Correct carbocation shown (1)            Arrow from lone pair of <math>\text{Br}^-</math> to <math>\text{C}^+</math> of carbocation (1)</p>  <p>The diagram illustrates the mechanism of electrophilic aromatic substitution. On the left, a benzene ring is shown with a curved arrow pointing from a double bond to the <math>\delta^+</math> bromine atom of a <math>\text{Br}-\text{Br}</math> molecule. Another curved arrow points from the <math>\text{Br}-\text{Br}</math> bond to the <math>\delta^-</math> bromine atom. An arrow points to the right, where a carbocation intermediate is shown: a benzene ring with a positive charge on one carbon and a bromine atom attached to the adjacent carbon. A curved arrow points from a lone pair on a bromide ion (<math>:\text{Br}^-</math>) to the positively charged carbon of the carbocation.</p>	4
1(e)	<p>Correct unambiguous structure for <math>\text{C}_6\text{H}_5\text{CHCH}_2</math> (1)            Correct unambiguous structure for <math>\text{CH}_2\text{CHCN}</math> (1)</p>	2

Question	Answer	Marks
2(a)	$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \quad (1)$	1
2(b)	Ester (1)	1
2(c)	Catalyst (1)	1
2(d)(i)	Mass of $\text{CH}_3\text{COOC}_2\text{H}_5 = 20 \times 0.902 = 18.04 \text{ g} \quad (1)$ Initial moles of $\text{CH}_3\text{COOC}_2\text{H}_5 = 20 \times \frac{(0.902)}{88} = 0.205 \quad (1)$	2
2(d)(ii)	Moles of $\text{HCl} = \left(\frac{1}{1000}\right) \times 15.0 = 0.0150 \quad (1)$	1
2(d)(iii)	Reaction is slow <b>OR</b> to allow (time needed) to reach equilibrium (1)	1
2(d)(iv)	Moles of $\text{NaOH} = \left(\frac{0.25}{1000}\right) \times 11.30 \times 95 = 0.268 \quad (1)$	1
2(d)(v)	Moles of $\text{CH}_3\text{COOH}$ at $\text{eq}^m = [\text{ans(iv)}] - [\text{ans(ii)}] = 0.253 \quad (1)$	1
2(d)(vi)	$\Delta(\text{initial moles of } \text{CH}_3\text{COOH} - \text{eq}^m \text{ moles}) = 0.438 - 0.253 = 0.185 \quad (1)$ Moles of $\text{C}_2\text{H}_5\text{OH} = 0.601 - 0.185 = 0.416 \quad (1)$ Moles of $\text{CH}_3\text{COOC}_2\text{H}_5 = 0.205 + 0.185 = 0.390 \quad (1)$ (Moles of $\text{H}_2\text{O} = 0.833 + 0.185 = 1.018$ ) $K_c = \frac{(1.018 \times 0.390)}{(0.416 \times 0.253)} = 3.77 \quad (1)$	4
2(d)(vii)	$\Delta H$ is exothermic AND $\text{eq}^m$ moves to LHS / $K_c$ decreases / to make more acid (1)  (More acid means) greater titre of $\text{NaOH} \quad (1)$	2

Question	Answer	Marks
3(a)(i)	Slowest step of a reaction (1)	1
3(a)(ii)	First step identified and linked to rate equation (1)	1
3(b)(i)	Minimum / least energy required for reaction (1)	1
3(b)(ii)	Use of $k = A \exp(-E_a / RT)$ (1) $-\ln(0.0421) - \ln(5.52 \times 10^5)] \times 8.31 \times 298$ (1) $= 40.59 \text{ (kJ mol}^{-1}\text{)}$ (1)	3
3(b)(iii)	$k = (5.52 \times 10^5) \exp\left(\frac{-40.59 \times 10^3}{8.31 \times 315}\right)$ (1) $k = 0.102$ (1) Rate = $0.102 (0.500)^2 = 0.0255$ (1) mol dm <sup>-3</sup> s <sup>-1</sup> (1)	4
3(b)(iv)	$A$ is independent of $T$ (1) $E_a$ is independent of $T$ (1)	2

Question	Answer	Marks
4(a)	$K_a = \frac{[\text{H}^+][(\text{CH}_3)_2\text{AsO}_2^-]}{[(\text{CH}_3)_2\text{AsO}_2\text{H}]} (1)$	1
4(b)	Buffer resists change / minimises change / small change in pH when small amounts of acid or alkali are added (1)  $\text{HA} = \text{H}^+ + \text{A}^- (1)$ Add $\text{H}^+$ : $\text{A}^-$ reacts with $\text{H}^+$ (1) equilibrium moves to LHS (1)  Add $\text{OH}^-$ : $\text{OH}^-$ reacts with $\text{H}^+$ (1) equilibrium moves to RHS (1)	6
4(c)(i)	$\text{Na}(\text{CH}_3)_2\text{AsO}_2 + \text{HCl} \rightarrow (\text{CH}_3)_2\text{AsO}_2\text{H} + \text{NaCl}$ correct product as $(\text{CH}_3)_2\text{AsO}_2\text{H} (1)$ Correct equation (1)	2
4(c)(ii)	$M_r$ of $\text{Na}(\text{CH}_3)_2\text{AsO}_2 \cdot 3\text{H}_2\text{O} = 213.9 (1)$ $\frac{4.87}{213.9} (= 0.0228)$ moles of salt (1) $\frac{75}{1000} \times 0.2 (= 0.0150)$ moles of $\text{HCl} =$ moles of $(\text{CH}_3)_2\text{AsO}_2\text{H} (1)$ $0.0228 - 0.0150 (= 0.0078)$ moles of $(\text{CH}_3)_2\text{AsO}_2^- (1)$ $K_a = 10^{-6.27} = 5.37 \times 10^{-7} (1)$ $[\text{H}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]} (1)$  $[\text{H}^+] = (5.37 \times 10^{-7}) \times \frac{(0.0150)}{(0.0078)} (= 1.03 \times 10^{-6}) (1)$ pH = 5.98 or 5.99 (1) 2 dp	8



Question	Answer	Marks
5(a)(i)	Donates a pair of electrons / forms dative bond / coordinate bond to a metal atom / ion (1)	1
5(a)(ii)	Lone pair on N (1) Each N can form a dative covalent bond / each N can donate pair of electrons (1)	2
5(b)(i)	Correct representation of an octahedron once (1) Each isomer shown correctly (3) 	4
5(b)(ii)	Correctly identifies BOTH pairs of geometric isomers (1) (States Cl groups) cis / trans or 90° / 180° or opposite and adjacent (1)	2
5(b)(iii)	Correctly identifies pair of optical isomers (1) Optical isomers are non-superimposable on their mirror image (1)	2
5(c)(i)	$4\text{Co}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightarrow 4\text{Co}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ Correct reactant and product species (only) (1) All correct with state symbols and balancing (1)	2
5(c)(ii)	$E = 1.23 - 1.82 = -0.59$ (1) $n = 4$ (1) $\Delta G = -(4)(-0.59)(96500) = +228$ (1) $\text{kJ mol}^{-1}$ sign (1)	4
5(c)(iii)	$\Delta G$ is positive (so reaction is not feasible) (1)	1
5(c)(iv)	$4\text{Co}^{2+}(\text{aq}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \rightleftharpoons 4\text{Co}^{3+}(\text{aq}) + 2\text{H}_2\text{O}$ moves to LHS as $[\text{H}^+]$ is reduced (1)  So reaction less feasible / even less feasible <b>AND</b> $\Delta G$ becomes more positive (1)	2

Question	Answer	Marks
6(a)	Minus charge on NH <sub>2</sub> (1) Two bonding pairs (to 2 H atoms) and two lone pairs on N (1) Triangle symbol as one of the N electrons AND rest correct (1)	3
6(b)(i)	Related by gain / loss of H <sup>+</sup> (1)	1
6(b)(ii)	NH <sub>2</sub> <sup>-</sup> + H <sub>2</sub> O → OH <sup>-</sup> + NH <sub>3</sub> (1) base 2 acid 1 base 1 acid 2 (1)	2
6(c)	Na + NH <sub>3</sub> → NaNH <sub>2</sub> + ½H <sub>2</sub> (1) Na is oxidised from 0 to +1 (1) H is reduced from +1 to 0 (1)	3
6(d)(i)	π-bond / overlap of p-orbital AND above and below prevents rotation (can be on diagram) (so molecule forced to be planar) (1)	1
6(d)(ii)	Correct 3d shape drawn (1) 2 p orbitals on central carbon involved in π bond must be orthogonal (1)	2
6(e)(i)	Correct structures of benzoyl chloride AND benzamide (1) Arrow from lone pair of N of NH <sub>2</sub> <sup>-</sup> to C of CO (1) Arrow from C-Cl bond to Cl (1) 	3
6(e)(ii)	Ammonia (1)	1