Cambridge Assessment International Education
Cambridge International Advanced Subsidiary and Advanced Level

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CHEMISTRY **9701/41**

Paper 4 A Level Structured Questions **October/November 2017**

MARK SCHEME

Maximum Mark: 100

Published

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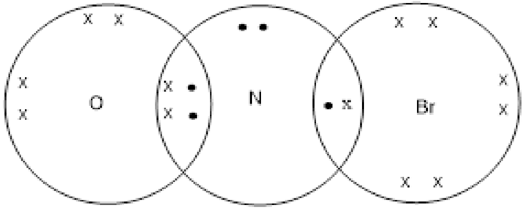
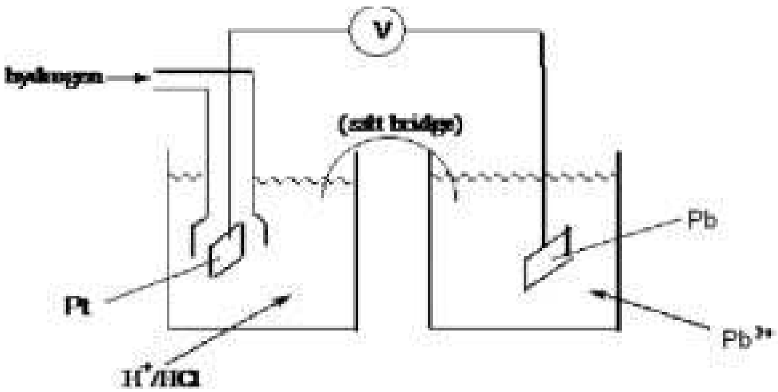
This document consists of **13** printed pages.

Question	Answer	Marks
1(a)	N +2 to +3 (and oxidised)	**1**
	Br_2 / Br 0 to –1 (and reduced)	**1**
1(b)		
	3 bonding pairs around N (in a structure involving NOBr)	**1**
	rest of molecule correct	**1**
1(c)(i)	the **power** to which a concentration of a reactant is raised in the **rate equation**	**1**
1(c)(ii)	using expt. 2 and 3 a = 2 **or** [NO] 2nd order **and** conc × 3 rate × 9 **or** $6.1 \times 10^{-2} / 6.8 \times 10^{-3} = (0.09 / 0.03)^a$	**1**
	using expt. 1 and 2 b = 1 **or** $[Br_2]$ 1st order **and** conc × 2 rate × 2 **or** $6.8 \times 10^{-3} / 3.4 \times 10^{-3} = (0.04 / 0.02)^b$	**1**
(c)(iii)	initial rate = 0.16(32)	**1**
1(c)(iv)	$(0.0034 = k(0.03)^2(0.02))$ k = **188.9**	**1**
	$mol^{-2}\,dm^6\,s^{-1}$	**1**
1(c)(v)	*k* decreases (as rate decreases)	**1**

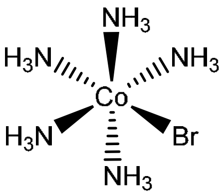
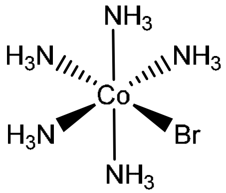
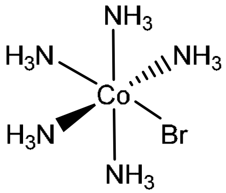
Question	Answer	Marks
1(d)	m = 2 **and** n = 0	**1**

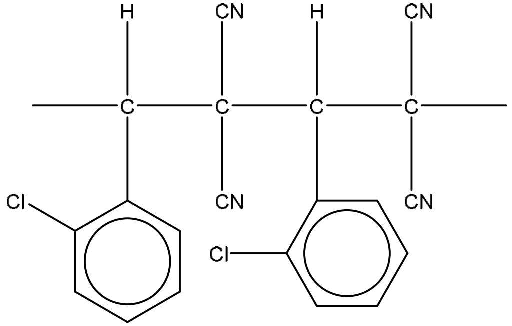
Question	Answer	Marks
2(a)	it / solubility **decreases** down the group **and** K_{sp} decreases	**1**
2(b)(i)	$MgCO_3$**(s)** ⇌ Mg^{2+}**(aq)** + CO_3^{2-}**(aq)**	**1**
2(b)(ii)	(white) solid appears / precipitation (of $MgCO_3$)	**1**
	as $[CO_3^{2-}]$ increases shifting equilibrium to the LHS (precipitating out $MgCO_3$)	**1**
2(c)	solubility = $\sqrt{1.0 \times 10^{-5}} = 3.16 \times 10^{-3}$ mol dm^{-3}	**1**
	solubility= $3.2 \times 10^{-3} \times 84.3 =$ **0.27** g dm^{-3}	**1**
2(d)(i)	Mg^{2+} ion is smaller than Ba^{2+} ion **or** ionic radii increase down group ora	**1**
	(Mg^{2+}) distorts / polarises / the anion / nitrate group / nitrate **ion** / $NO_3^{(1)-}$ / NO_3 ion more easily (than Ba^{2+}) ora	**1**
2(d)(ii)	$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + ½O_2$	**1**
2(d)(iii)	$BaO + H_2O \rightarrow Ba(OH)_2$	**1**
	$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$	**1**

Question	Answer	Marks
3(a)	the potential **difference** between two half-cells / two electrodes (in a cell)	1
	under standard conditions of 1 atm., 298 K, (all) solutions being 1 mol dm^{-3}	1
3(b)(i)	 8 marking points, any 2 points for each mark H_2 / hydrogen correct delivery system for H_2 Pb^{2+} (aq) Pb electrode Pt electrode H^+(aq) solution salt bridge voltmeter / V labelled	4
3(b)(ii)	more negative	1
	shifts Pb^{2+} (+ $2e^-$) $\leftrightharpoons$ Pb equilibrium / reaction to the left	1

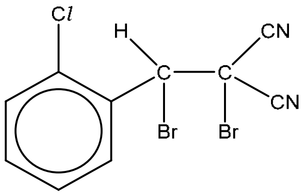
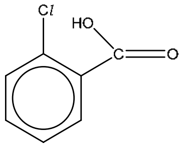
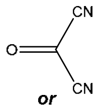
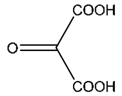
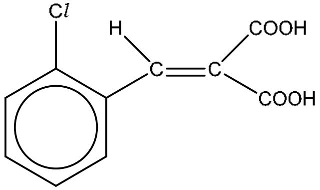
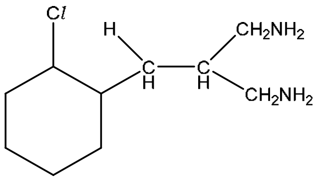
Question	Answer	Marks
3(c)(i)	Q = 0.4 × 80 × 60 = **1920** C **and** use of 96500 / 193000 Moles of Pb = 1920 / 193000 = 9.95×10^{-3} Mass of Pb = 207.2 × 9.95×10^{-3} = **2.1 g** **OR** Q = 0.4 × 80 × 60 = **1920** C **and** use of 1.6×10^{-19} / 1.2×10^{22} atoms Pb = 6×10^{21}; moles of Pb = $6 \times 10^{21} / 6 \times 10^{23}$ = 0.01 Mass of Pb = 207.2 × 0.01 = **2.1 g**	2
3(c)(ii)	$PbO_2(s) + SO_4^{2-}(aq) + \mathbf{4H^+} + \mathbf{2e^-} \rightarrow PbSO_4(s) + \mathbf{2H_2O}$	1
3(d)	reagents / PbO_2 / H_2SO_4 **and** used up / concentration decreases	1
	as fuel / hydrogen is being continuously supplied / fuel has not run out	1

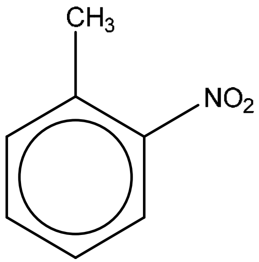
Question	Answer	Marks
4(a)	density is higher **and** melting point is higher	1
	(density) due to A_r being larger **and** smaller atomic radii **or** (Co) **atoms / ions** heavier **and** smaller	1
	(melting point) due to stronger attraction to cations as more delocalised electrons	1
4(b)	(a molecule or ion) formed by a **central** metal **atom / ion** surrounded by (one or more) **ligands**	1
4(c)(i)	same number and type of <u>atoms</u> **and** different structural formula	1

<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>4(c)(ii)</td><td>octahedral AND 3D structure of $[Co(NH_3)_5Br]^{2+}$
e.g.


</td><td>1</td></tr>
<tr><td>4(c)(iii)</td><td>co-ordinate / dative covalent</td><td>1</td></tr>
<tr><td>4(c)(iv)</td><td>+3 for both</td><td>1</td></tr>
<tr><td>4(d)</td><td>(HNO_3) Ag^+ / $AgNO_3$ cream(–yellow) ppt. (of AgBr) and no reaction / white ppt. for other isomer</td><td>1</td></tr>
<tr><td></td><td>$Ba(OH)_2$ / Ba^{2+}(aq) / $BaCl_2$ / $Ba(NO_3)_2$ white ppt. (of $BaSO_4$) and no reaction for other isomer</td><td>1</td></tr>
<tr><td>4(e)</td><td>(d-d) energy gap / ΔE is different</td><td>1</td></tr>
<tr><td></td><td><u>absorb</u> different wavelength / frequency (of light)</td><td>1</td></tr>
<tr><td>4(f)</td><td><table>
<tr><th></th><th>heterogeneous</th><th>homogeneous</th></tr>
<tr><td>Fe in the Haber process</td><td>✓</td><td></td></tr>
<tr><td>Fe^{2+} in the I^- / $S_2O_8^{2-}$ reaction</td><td></td><td>✓</td></tr>
<tr><td>NO_2 in the oxidation of SO_2</td><td></td><td>✓</td></tr>
<tr><td>V_2O_5 in the Contact process</td><td>✓</td><td></td></tr>
</table></td><td>2</td></tr>
</table>

Question	Answer	Marks
5(a)	nitrile; alkene; chloro; benzene / arene	2
5(b)		1
	addition (polymerisation)	1

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

reagent	structure of product	type of organic reaction
excess Br_2(aq)	 [1]	(electrophilic) addition
excess hot, conc. MnO_4^-(aq)	  *or*  [1] + [1]	oxidation
excess hot, aqueous HCl	 [1]	hydrolysis
excess H_2 / Pt catalyst	 both CH_2NH_2 formed [1] both arene and alkene reduced [1]	reduction / hydrogenation
	structures [6]	2 correct for 1 mark total [2]

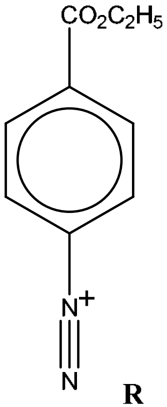
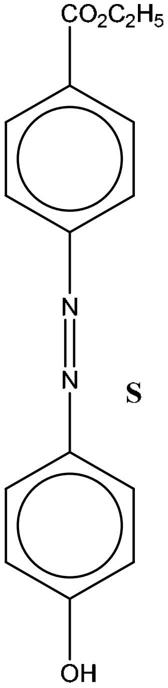
Question	Answer	Marks
6(a)(i)		**1**
6(a)(ii)	$HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$	**1**
6(a)(iii)	**any three** from: Point 1: bonds / electrons are **partially** delocalised in **T** **or** delocalised / π system / π bonding extends over only five carbons Point 2: four π-electrons in the (delocalised system of **T**) **or** methylbenzene has (two) more π-electrons / (two) more delocalised electrons Point 3: contains a carbon that is sp^3 hybridised in **T** ***or*** (all the) carbons are sp^2 hybridised in methylbenzene Point 4**:** one carbon has a bond angle of 109.5° / tetrahedral (in **T)** ***or*** (C-C) bond strengths / lengths are not all the same **or** not all the bond angles are 120° (in **T**)	**3**
6(b)(i)	4-aminobenzoic acid	**1**
6(b)(ii)	step 1 Sn + HC*l* [1] concentrated / reflux / heat [1] step 2 CH_3COCl [1] step 3 $KMnO_4$ / manganate(VII) / MnO_4^- (acidified / alkaline) **and** heat [1] step 4 aqueous HC*l* **and** heat [1] step 5 ethanol, H_2SO_4, concentrated / reflux / heat [1]	**6**

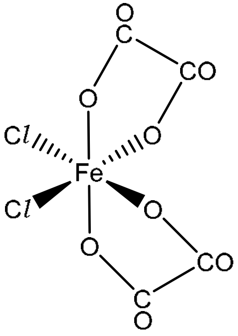
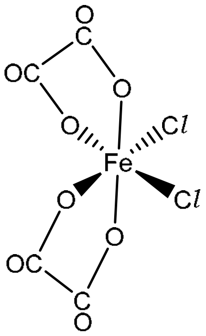
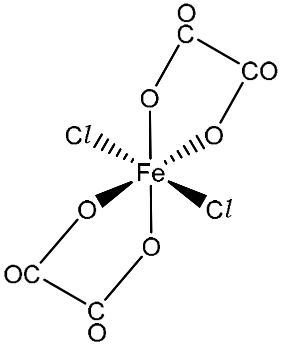
<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>6(c)</td><td>(benzocaine) is less (basic than ethylamine) **AND**
lone pair (on N) is less available to **accept** a proton / H^+

since (lone pair on N) is delocalised over the ring
or phenyl ring is electron withdrawing group

OR
ethylamine is more basic (than benzocaine) **AND**
lone pair (on N) is more available to **accept** a proton / H^+

since ethyl / alkyl group is electron-donating group</td><td>**2**</td></tr>
<tr><td>6(d)(i)</td><td>7 peaks</td><td>**1**</td></tr>
<tr><td>6(d)(ii)</td><td>$CDCl_3$ will produce no signal in the spectrum
or $CHCl_3$ would produce a signal / would be detected</td><td>**1**</td></tr>
<tr><td>6(d)(iii)</td><td>
<table>
<tr><th>δ/ppm</th><th>group responsible for the peak</th><th>number of H atoms responsible for the peak</th><th>splitting pattern</th></tr>
<tr><td>*1.2*</td><td>$CH_{(3)}$</td><td>3</td><td>triplet</td></tr>
<tr><td>*3.5*</td><td>$CH_{(2)}O$</td><td>2</td><td>quartet</td></tr>
<tr><td>*5.5*</td><td>NH_2</td><td>2</td><td>singlet (broad)</td></tr>
<tr><td>*7.1–7.4*</td><td>H attached to aromatic / benzene ring</td><td>4</td><td>*multiplet*</td></tr>
</table>
</td><td>**4**</td></tr>
<tr><td>6(d)(iv)</td><td>neighbouring / adjacent carbon **atom** has two protons / H (attached to it)
or there is an adjacent $CH_2(O)$ group</td><td>**1**</td></tr>
<tr><td>6(d)(v)</td><td>peak at 5.5 / NH_2 peak will disappear
and
NH_2 / protons exchange / swap with deuterium</td><td>**1**</td></tr>
</table>

Question	Answer	Marks
6(e)(i)	$NaNO_2 + HCl$ ***or*** HNO_2	1
6(e)(ii)	 **R**  **S**	
	structure of diazonium salt **R**	1
	structure of azo dye **S**	1

Question	Answer	Marks
7(a)	Fe atom= $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^6 4s^2$ Fe^{3+} ion= $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^5$	**1**
7(b)	$([H^+]^2 = 8.9 \times 10^{-4} \times 0.25$ ***or*** $2.225 \times 10^{-4})$ $[H^+] = 0.0149$	**1**
	pH = –log(0.0149) = **1.83**	**1**
7(c)(i)	(K_{stab} is) the **equilibrium constant** for the formation of a complex (ion) (in a solvent from its constituent ions / molecules)	**1**
7(c)(ii)	$[Fe(H_2O)_5F]^{2+}$ **and** $[Hg(H_2O)_5Cl]^+$	**1**
7(d)	$K_{stab} = \dfrac{[Fe(ed)_2Cl_2^{\ 3-}]}{[Fe(H_2O)_4Cl_2^{\ +}][ed]^2}$	**1**
	$mol^{-2}\,dm^6$	**1**
7(e)(i)	 cis  cis  trans	**3**

Question	Answer	Marks
7(e)(ii)	any cis isomer **and** the trans isomer identified	**1**
7(e)(iii)	**both** correct cis isomers identified	**1**
7(e)(iv)	trans isomer identified	**1**