Cambridge International AS & A Level

Cambridge Assessment International Education
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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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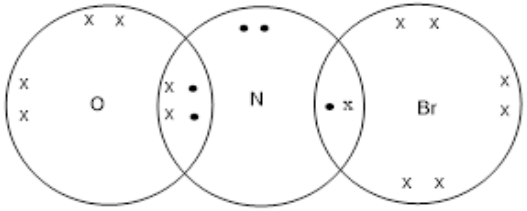
Question	Answer	Marks
1(a)	N +2 to +3 (and oxidised)	**1**
	Br_2 / Br 0 to –1 (and reduced)	**1**
1(b)		
	3 bonding pairs around N (in a structure involving NOBr)	**1**
	rest of molecule correct	**1**
1(c)(i)	the **power** to which a concentration of a reactant is raised in the **rate equation**	**1**
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**

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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**

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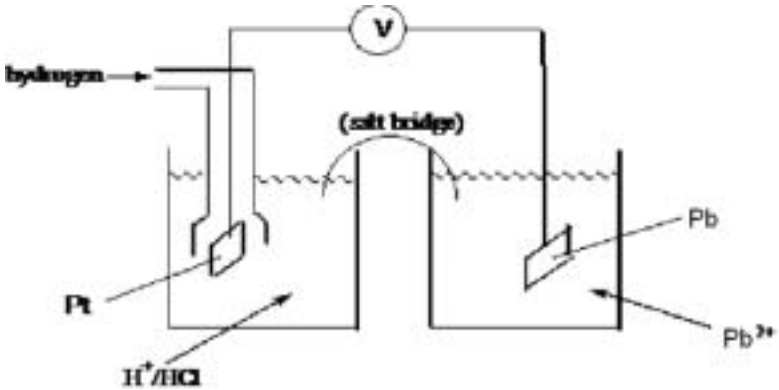
Question	Answer	Marks
3(a)	the potential **difference** between two half-cells / two electrodes (in a cell)	**1**
	under standard conditions of 1 atm., 298 K, (all) solutions being 1 mol dm^{-3}	**1**
3(b)(i)	 8 marking points, any 2 points for each mark H_2 / hydrogen correct delivery system for H_2 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+} (+ $2e^-$) ⇋ Pb equilibrium / reaction to the left	**1**

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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 = $207.2 \times 9.95 \times 10^{-3}$ = **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**

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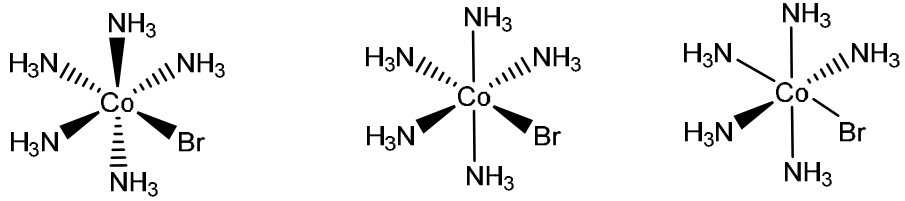
<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>4(c)(ii)</td><td>octahedral AND 3D structure of $[Co(NH_3)_5Br]^{2+}$
e.g.
</td><td>1</td></tr>
<tr><td>4(c)(iii)</td><td>co-ordinate / dative covalent</td><td>1</td></tr>
<tr><td>4(c)(iv)</td><td>+3 for both</td><td>1</td></tr>
<tr><td rowspan="2">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>$Ba(OH)_2$ / $Ba^{2+}(aq)$ / $BaCl_2$ / $Ba(NO_3)_2$ white ppt. (of $BaSO_4$) and no reaction for other isomer</td><td>1</td></tr>
<tr><td rowspan="2">4(e)</td><td>(d-d) energy gap / ΔE is different</td><td>1</td></tr>
<tr><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>

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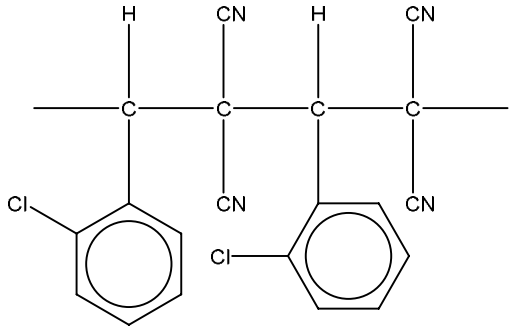
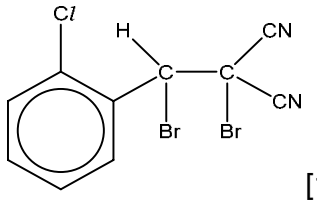
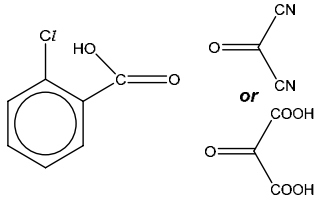
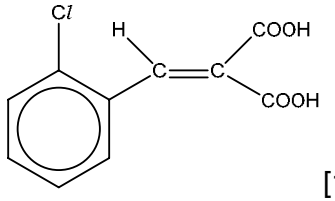
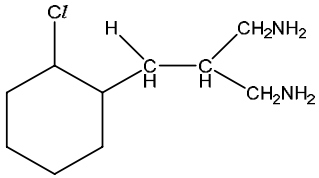
Question	Answer	Marks
5(a)	nitrile; alkene; chloro; benzene / arene	**2**
5(b)		**1**
	addition (polymerisation)	**1**

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

reagent	structure of product	type of organic reaction
excess $Br_2(aq)$	 [1]	(electrophilic) addition
excess hot, conc. $MnO_4^-(aq)$	 [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]

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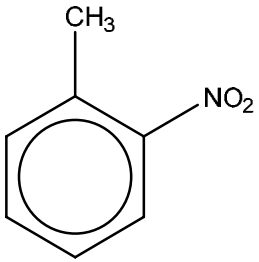
Question	Answer	Marks
6(a)(i)		**1**
6(a)(ii)	$HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$	**1**
6(a)(iii)	**any three** from: Point 1: bonds / electrons are **partially** delocalised in **T** **or** delocalised / π system / π bonding extends over only five carbons Point 2: four π-electrons 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**

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<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>

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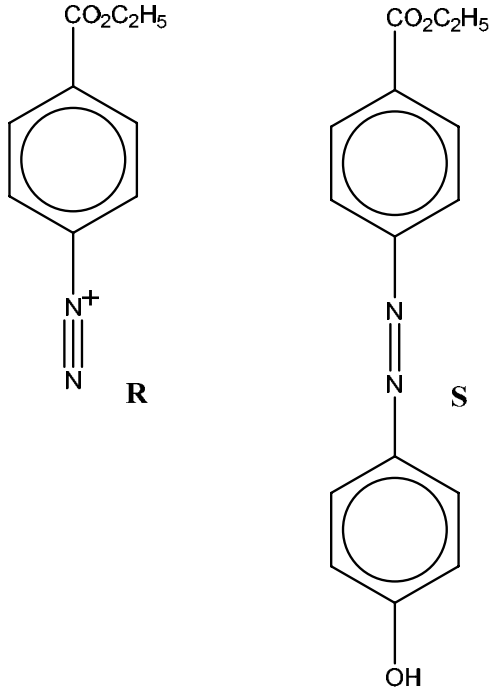
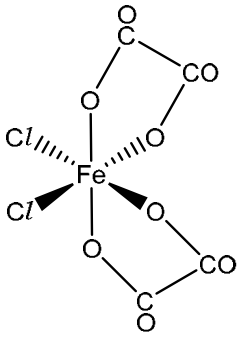
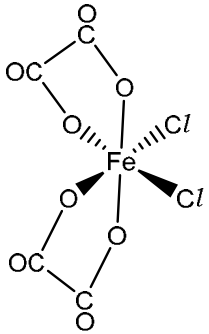
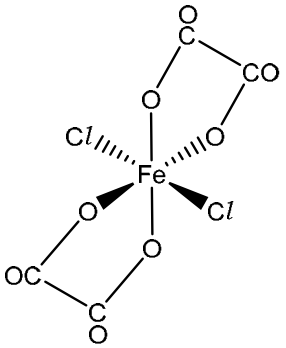
Question	Answer	Marks
6(e)(i)	$NaNO_2 + HCl$ ***or*** HNO_2	**1**
6(e)(ii)		
	structure of diazonium salt **R**	**1**
	structure of azo dye **S**	**1**

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**

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