CHEMISTRY **9701/41**

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

MARK SCHEME

Maximum Mark: 100

Published

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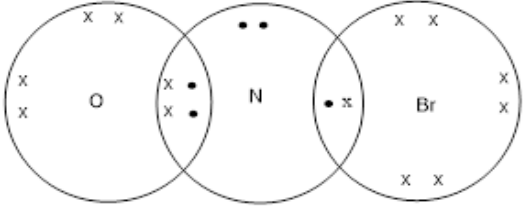
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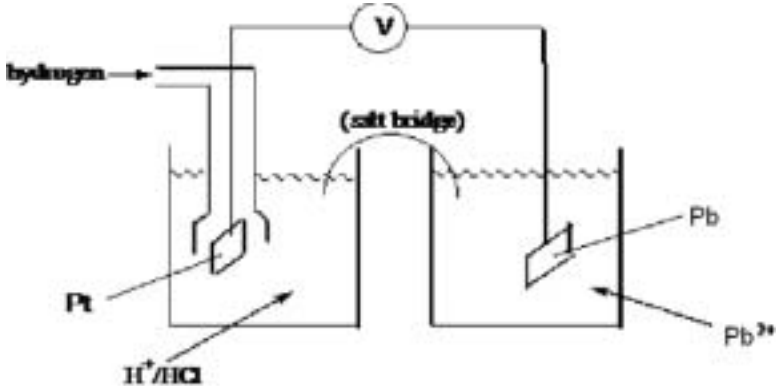
Question	Answer	Marks
1(a)	N $+2$ to $+3$ (and oxidised)	**1**
	Br_2 / Br 0 to -1 (and reduced)	**1**
1(b)		
	3 bonding pairs around N (in a structure involving NOBr)	**1**
	rest of molecule correct	**1**
1(c)(i)	the **power** to which a concentration of a reactant is raised in the **rate equation**	**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**
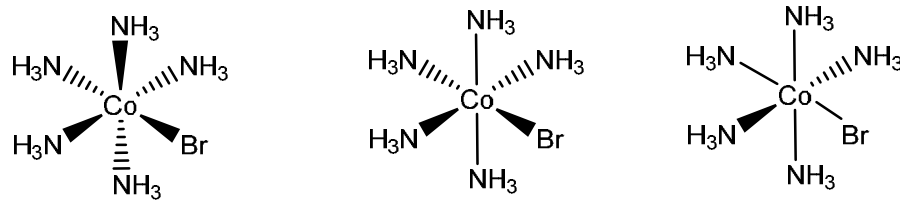
Question	Answer	Marks
1(d)	m = 2 **and** n = 0	**1**
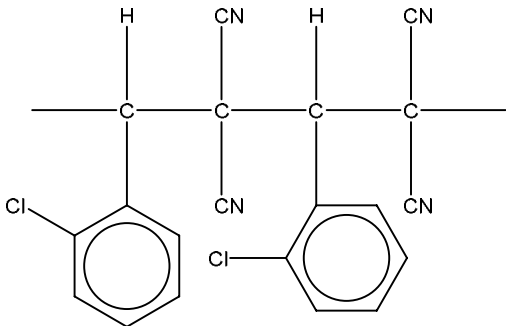
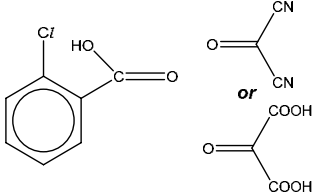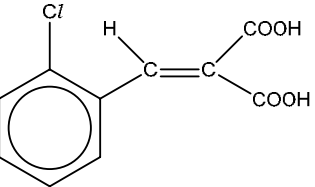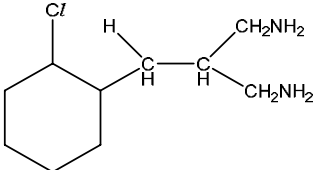| Question	Answer	Marks
2(a)	it / solubility **decreases** down the group **and** K_{sp} decreases	**1**
2(b)(i)	$MgCO_3\textbf{(s)} \rightleftharpoons Mg^{2+}\textbf{(aq)} + CO_3{}^{2-}\textbf{(aq)}$	**1**
2(b)(ii)	(white) solid appears / precipitation (of $MgCO_3$)	**1**
	as $[CO_3{}^{2-}]$ increases 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)	$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + \frac{1}{2}O_2$	**1**
2(d)(iii)	$BaO + H_2O \rightarrow Ba(OH)_2$	**1**
	$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$	**1**
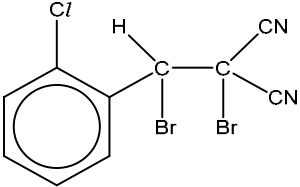
Question	Answer	Marks
3(a)	the potential **difference** between two half-cells / two electrodes (in a cell)	1
	under standard conditions of 1 atm., 298 K, (all) solutions being $1 \, mol \, dm^{-3}$	1
3(b)(i)	 8 marking points, any 2 points for each mark H_2 / hydrogen correct delivery system for H_2 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⁻) ⇌ Pb equilibrium / reaction to the left	1

Question	Answer	Marks
3(c)(i)	$Q = 0.4 \times 80 \times 60 = $ **1920** C **and** use of $96500/193000$ Moles of Pb $= 1920/193000 = 9.95 \times 10^{-3}$ Mass of Pb $= 207.2 \times 9.95 \times 10^{-3} = $ **2.1 g** **OR** $Q = 0.4 \times 80 \times 60 = $ **1920** C **and** use of $1.6 \times 10^{-19}/1.2 \times 10^{22}$ atoms Pb $= 6 \times 10^{21}$; moles of Pb $= 6 \times 10^{21}/6 \times 10^{23} = 0.01$ Mass of Pb $= 207.2 \times 0.01 = $ **2.1 g**	**2**
3(c)(ii)	$PbO_2(s) + SO_4^{2-}(aq) + $ **4H$^+$** $ + $ **2e$^-$** $\rightarrow PbSO_4(s) + $ **2H$_2$O**	**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**
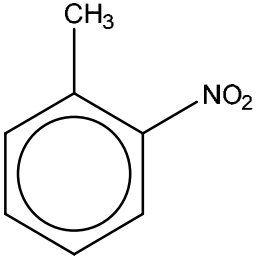
Question	Answer	Marks
4(a)	density is higher **and** melting point is higher	**1**
	(density) due to A_r being larger **and** smaller atomic radii **or** (Co) **atoms / ions** heavier **and** smaller	**1**
	(melting point) due to stronger attraction to cations as more delocalised electrons	**1**
4(b)	(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**

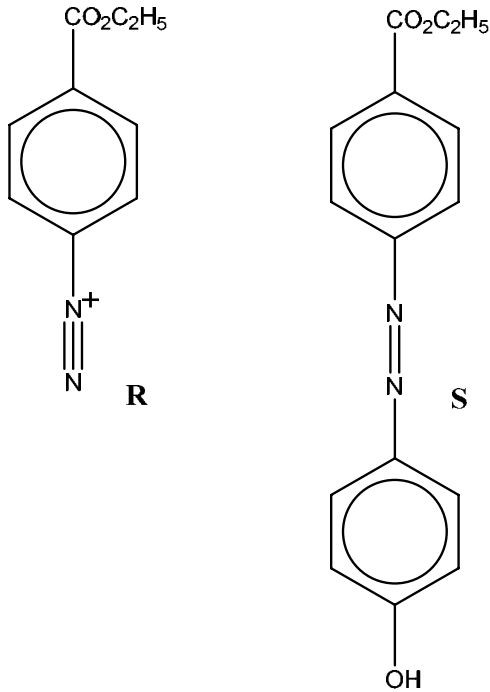| Question	Answer	Marks
4(c)(ii)	octahedral **AND** 3D structure of $[Co(NH_3)_5Br]^{2+}$ e.g. 	1
4(c)(iii)	co-ordinate / dative covalent	1
4(c)(iv)	+3 for **both**	1
4(d)	(HNO_3) Ag^+ / $AgNO_3$ cream(–yellow) ppt. (of AgBr) **and** no reaction / white ppt. for other isomer	1
	$Ba(OH)_2$ / Ba^{2+}(aq) / $BaCl_2$ / $Ba(NO_3)_2$ white ppt. (of $BaSO_4$) **and** no reaction for other isomer	1
4(e)	(d-d) energy gap / ΔE is different	1
	absorb different wavelength / frequency (of light)	1
4(f)	<table><thead><tr><th></th><th>heterogeneous</th><th>homogeneous</th></tr></thead><tbody><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></tbody></table>	2

Question	Answer	Marks
5(a)	nitrile; alkene; chloro; benzene / arene	**2**
5(b)		**1**
	addition (polymerisation)	**1**
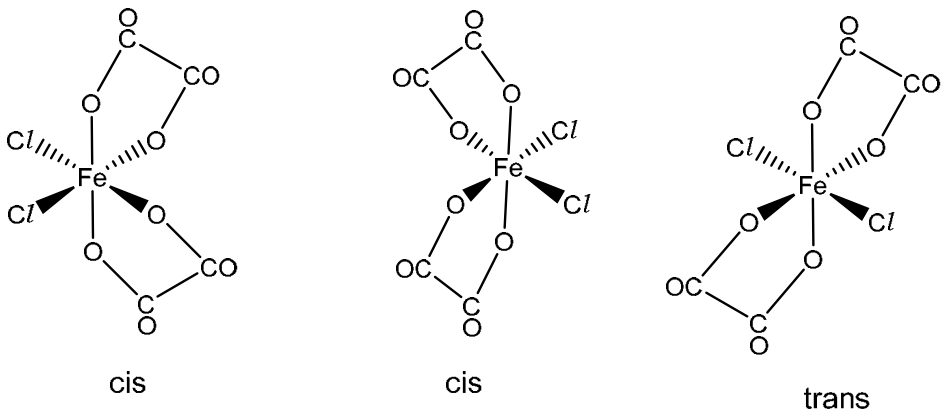
Question	Answer			Marks
5(c)				**8**

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]

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 $Sn + HCl$ [1] concentrated/reflux/heat [1] step 2 CH_3COCl [1] step 3 $KMnO_4$/manganate(<u>VII</u>)/MnO_4^- (acidified/alkaline) **and** heat [1] step 4 aqueous HCl **and** heat [1] step 5 ethanol, H_2SO_4, concentrated/reflux/heat [1]	6

Question	Answer	Marks
6(c)	(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	2
6(d)(i)	7 peaks	1
6(d)(ii)	CDCl_3 will produce no signal in the spectrum **or** CHCl_3 would produce a signal / would be detected	1
6(d)(iii)	(table below)	4

δ/ppm	group responsible for the peak	number of H atoms responsible for the peak	splitting pattern
1.2	CH$_{(3)}$	3	triplet
3.5	CH$_{(2)}$O	2	quartet
5.5	NH$_2$	2	singlet (broad)
7.1–7.4	H attached to aromatic / benzene ring	4	*multiplet*

Question	Answer	Marks
6(d)(iv)	neighbouring / adjacent carbon **atom** has two protons / H (attached to it) **or** there is an adjacent CH$_2$(O) group	1
6(d)(v)	peak at 5.5 / NH$_2$ peak will disappear **and** NH$_2$ / protons exchange / swap with deuterium	1

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)	$K_{stab} = \dfrac{[Fe(ed)_2 Cl_2^{3-}]}{[Fe(H_2O)_4 Cl_2^+][ed]^2}$	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**