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CHEMISTRY

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Paper 4 A Level Structured Questions

October/November 2017

MARK SCHEME

Maximum Mark: 100

Published

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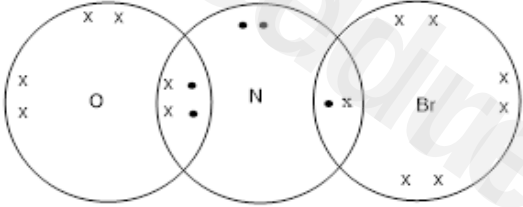
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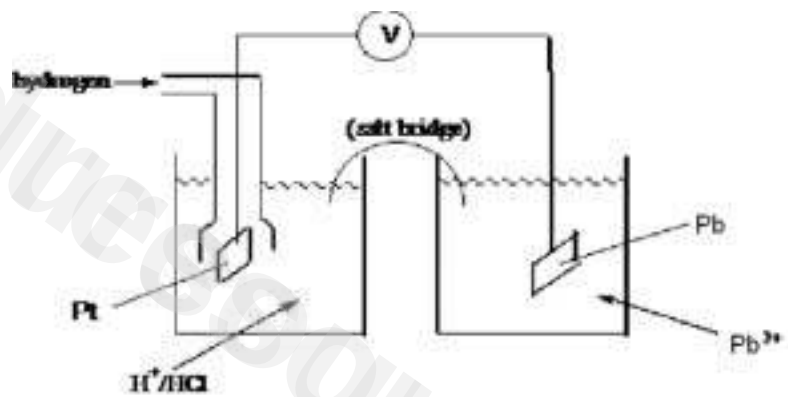
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This document consists of **13** printed pages.

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] 2 nd 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] 1 st 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

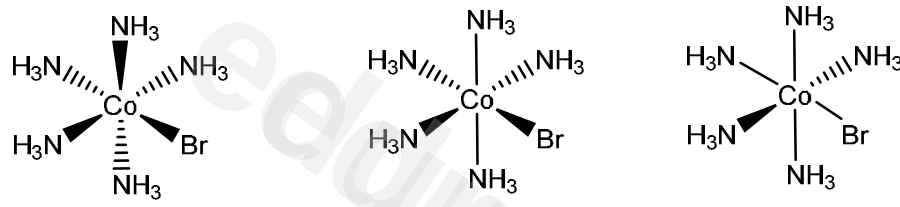
Question	Answer	Marks
1(d)	m = 2 and n = 0	1

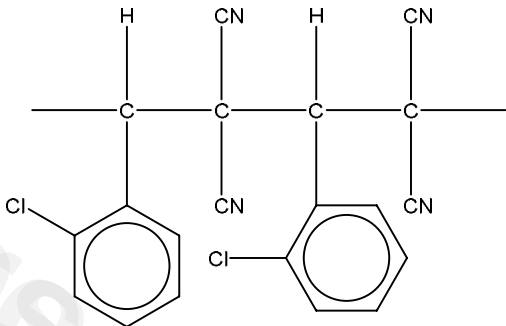
Question	Answer	Marks
2(a)	it / solubility decreases down the group and K_{sp} decreases	1
2(b)(i)	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	1
2(b)(ii)	(white) solid appears / precipitation (of $MgCO_3$)	1
	as $[CO_3^{2-}]$ increases shifting equilibrium to the LHS (precipitating out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

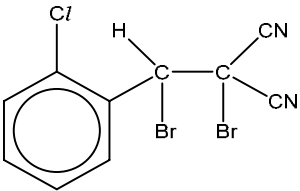
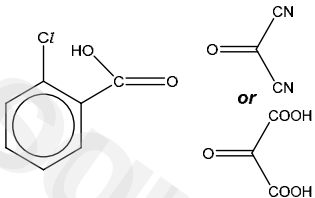
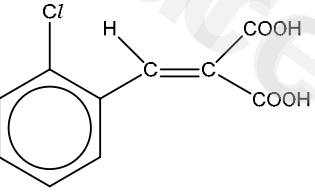
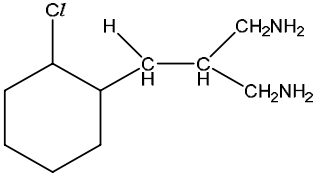
Question	Answer	Marks
3(a)	the potential difference between two half-cells / two electrodes (in a cell)	1
	under standard conditions of 1 atm., 298 K, (all) solutions being 1 mol dm ⁻³	1
3(b)(i)	 8 marking points, any 2 points for each mark H₂ / hydrogen correct delivery system for H₂ Pb²⁺ (aq) Pb electrode 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

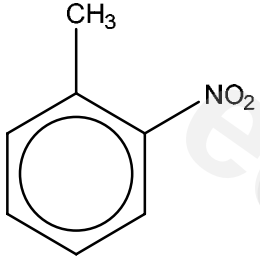
Question	Answer	Marks
3(c)(i)	$Q = 0.4 \times 80 \times 60 = \mathbf{1920\text{ C}}$ and use of 96500 / 193000 Moles of Pb = $1920 / 193000 = 9.95 \times 10^{-3}$ Mass of Pb = $207.2 \times 9.95 \times 10^{-3} = \mathbf{2.1\text{ g}}$ OR $Q = 0.4 \times 80 \times 60 = \mathbf{1920\text{ C}}$ and use of $1.6 \times 10^{-19} / 1.2 \times 10^{22}$ atoms Pb = 6×10^{21} ; moles of Pb = $6 \times 10^{21} / 6 \times 10^{23} = 0.01$ Mass of Pb = $207.2 \times 0.01 = \mathbf{2.1\text{ g}}$	2
3(c)(ii)	$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + \mathbf{4\text{H}^+ + 2\text{e}^-} \rightarrow \text{PbSO}_4(\text{s}) + \mathbf{2\text{H}_2\text{O}}$	1
3(d)	reagents / $\text{PbO}_2 / \text{H}_2\text{SO}_4$ 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

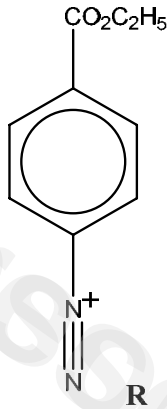
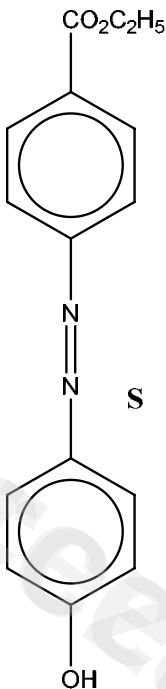
Question	Answer	Marks															
4(c)(ii)	octahedral AND 3D structure of $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ e.g. 	1															
4(c)(iii)	co-ordinate / dative covalent	1															
4(c)(iv)	+3 for both	1															
4(d)	(HNO_3) $\text{Ag}^+ / \text{AgNO}_3$ cream(–yellow) ppt. (of AgBr) and no reaction / white ppt. for other isomer	1															
	$\text{Ba}(\text{OH})_2 / \text{Ba}^{2+}(\text{aq}) / \text{BaCl}_2 / \text{Ba}(\text{NO}_3)_2$ 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 border="1"> <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 $\text{I}^- / \text{S}_2\text{O}_8^{2-}$ 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>		heterogeneous	homogeneous	Fe in the Haber process	✓		Fe^{2+} in the $\text{I}^- / \text{S}_2\text{O}_8^{2-}$ reaction		✓	NO_2 in the oxidation of SO_2		✓	V_2O_5 in the Contact process	✓		2
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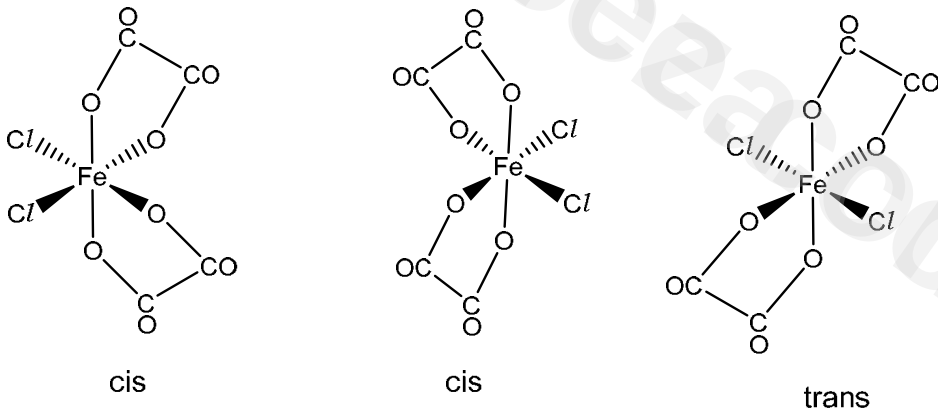
Question	Answer	Marks
5(a)	nitrile; alkene; chloro; benzene / arene	2
5(b)		1
	addition (polymerisation)	1

Question	Answer			Marks
5(c)	reagent	structure of product	type of organic reaction	8
	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 ₂ NH 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)	$\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{NO}_2^+ + 2\text{HSO}_4^-$	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 $\text{Sn} + \text{HCl}$ [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 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><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><i>multiplet</i></td></tr></table>	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	<i>multiplet</i>	4
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7.1–7.4	H attached to aromatic / benzene ring	4	<i>multiplet</i>																			
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)	$\text{NaNO}_2 + \text{HCl}$ 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)	$([H^+]^2 = 8.9 \times 10^{-4} \times 0.25 \text{ or } 2.225 \times 10^{-4})$ $[H^+] = 0.0149$	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)	$[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$ and $[\text{Hg}(\text{H}_2\text{O})_5\text{Cl}]^+$	1
7(d)	$K_{\text{stab}} = \frac{[\text{Fe}(\text{ed})_2\text{Cl}_2^{3-}]}{[\text{Fe}(\text{H}_2\text{O})_4\text{Cl}_2^+][\text{ed}]^2}$	1
	$\text{mol}^{-2} \text{dm}^6$	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