

#### CHEMISTRY

9701/41 October/November 2017

Paper 4 A Level Structured Questions 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(b)	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					
	3 bonding pairs around N (in a structure involving NOBr)	1				
	rest of molecule correct	1				
1(c)(i)	the <b>power</b> to which a concentration of a reactant is raised in the <b>rate equation</b>	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 $[Br_2] 1^{st}$ 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 = <b>188.9</b>	1				
	mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup>	1				
1(c)(v)	k decreases (as rate decreases)	1				

Question	Answer	Marks	
1(d)	m = 2 <b>and</b> 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 <sub>3</sub> )	1
	as $[CO_3^{2-}]$ increases shifting equilibrium to the LHS (precipitating out MgCO <sub>3</sub> )	1
2(c)	solubility = $\sqrt{1.0 \times 10^{-5}} = 3.16 \times 10^{-3} \text{mol}\text{dm}^{-3}$	1
	solubility= $3.2 \times 10^{-3} \times 84.3 = 0.27 \text{ g dm}^{-3}$	1
2(d)(i)	Mg <sup>2+</sup> ion is smaller than Ba <sup>2+</sup> ion <b>or</b> ionic radii increase down group ora	1
	$(Mg^{2+})$ distorts/polarises/the anion/nitrate group/nitrate ion/NO <sub>3</sub> <sup>(1)-</sup> /NO <sub>3</sub> ion more easily (than Ba <sup>2+</sup> ) ora	1
2(d)(ii)	$Ba(NO_3)_2 \to BaO + 2NO_2 + \frac{1}{2}O_2$	1
2(d)(iii)	$BaO + H_2O \rightarrow Ba(OH)_2$	1
	$Ba(OH)_2 + H_2SO_4 \to BaSO_4 + 2H_2O$	1

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

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Question	Answer	Marks
3(c)(i)	Q = $0.4 \times 80 \times 60$ = <b>1920</b> C and use of 96500/193000 Moles of Pb = $1920/193000 = 9.95 \times 10^{-3}$ Mass of Pb = $207.2 \times 9.95 \times 10^{-3} = 2.1 \text{ g}$	
	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 × 0.01 = 2.1 g	
3(c)(ii)	$PbO_{2}(s) + SO_{4}^{2-}(aq) + \mathbf{4H}^{+} + \mathbf{2e}^{-} \rightarrow PbSO_{4}(s) + \mathbf{2H}_{2}\mathbf{O}$	1
3(d)	reagents/PbO <sub>2</sub> /H <sub>2</sub> SO <sub>4</sub> and used up/concentration decreases	1
	as fuel/hydrogen is being continuously supplied/fuel has not run out	1

Question	Answer				
4(a)	density is higher <b>and</b> melting point is higher				
	(density) due to <i>A</i> <sub>r</sub> being larger <b>and</b> smaller atomic radii <b>or</b> (Co) <b>atoms/ions</b> heavier <b>and</b> smaller				
	(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				
4(c)(i)	same number and type of atoms and different structural formula	1			

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Question		Answer		Marks
4(c)(ii)	octahedral <b>AND</b> 3D structure of $[Co(NH_3)_5Br]^{2+}$ e.g. $H_3N_{IIIIII}$ $H_3N_{IIIIIII}$ $H_3N_{IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII$	NH <sub>3</sub> NH <sub>3</sub> NH <sub>3</sub> NH <sub>3</sub>		1
4(c)(iii)	co-ordinate/dative covalent			1
4(c)(iv)	+3 for <b>both</b>			1
4(d)	(HNO <sub>3</sub> ) Ag <sup>+</sup> /AgNO <sub>3</sub> cream(–yellow) ppt. (of AgBr) <b>and</b> r	no reaction/white pp	t. for other isomer	1
	$Ba(OH)_2/Ba^{2+}(aq)/BaCl_2/Ba(NO_3)_2$ white ppt. (of BaSC	D <sub>4</sub> ) <b>and</b> no reaction f	or other isomer	1
4(e)	(d-d) energy gap / $\Delta E$ is different			1
	absorb different wavelength/frequency (of light)			1
4(f)		heterogeneous	homogeneous	2
	Fe in the Haber process	×		
	$Fe^{2+}$ in the $I^-/S_2O_8^{2-}$ reaction		~	
	NO <sub>2</sub> in the oxidation of SO <sub>2</sub>		~	
	V <sub>2</sub> O <sub>5</sub> in the Contact process	~		

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

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Question		Answer		
5(c)	reagent	structure of product	type of organic reaction	8
	excess Br₂(aq)		(electrophilic) addition	
	excess hot, conc. MnO₄⁻(aq)	С <sup><i>I</i></sup> но о с <sup><i>N</i></sup> с <sup><i>N</i></sup> с <sup><i>N</i></sup> с <sup><i>O</i></sup> о с <sup><i>N</i></sup> с <sup><i>O</i></sup> с <sup><i>N</i></sup> с <sup><i>N</i></sup> с <sup><i>O</i></sup> с <sup><i>N</i></sup> с <sup><i>N</i></sup> с <sup><i>O</i></sup> с <sup><i>N</i></sup> с <sup><i>O</i></sup> с <sup><i>N</i></sup> с <sup><i>O</i></sup> с <sup><i>N</i></sup> с <sup><i>N</i></sup> с <sup><i>O</i></sup> с <sup><i>N</i></sup> с <sup><i>N</i></sup> с <sup><i>O</i></sup> с <sup><i>N</i></sup> с	oxidation	
	excess hot, aqueous HC <i>l</i>		hydrolysis	
	excess H <sub>2</sub> /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)	NO <sub>2</sub>	1
6(a)(ii)	$HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$	1
6(a)(iii)	any three from:	3
	<ul> <li>Point 1: bonds/electrons are partially delocalised in T or delocalised/π system/π bonding extends over only five carbons</li> <li>Point 2: four π-electrons in the (delocalised system of T) or methylbenzene has (two) more π-electrons/(two) more delocalised electrons</li> <li>Point 3: contains a carbon that is sp<sup>3</sup> hybridised in T or (all the) carbons are sp<sup>2</sup> hybridised in methylbenzene</li> <li>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)</li> </ul>	
6(b)(i)	4-aminobenzoic acid	1
6(b)(ii)	step 1Sn + 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 4aqueous HCl and heat [1]step 5ethanol, H_2SO_4, concentrated/reflux/heat [1]	6

Question		Ansv			Ma	larks
6(c)	(benzocaine) is less (basic than ethylamine) AND lone pair (on N) is less available to accept a proton/H <sup>+</sup> since (lone pair on N) is delocalised over the ring <i>or</i> 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 <sup>+</sup>					:
	since ethyl/alkyl group is					
6(d)(i)	7 peaks					
6(d)(ii)	CDC <i>l</i> <sub>3</sub> will produce no signal in the spectrum or CHC <i>l</i> <sub>3</sub> would produce a signal/would be detected					
6(d)(iii)	δ/ppm	group responsible for the peak	number of H atoms responsible for the peak	splitting pattern		
	1.2	CH <sub>(3)</sub>	3	triplet		
	3.5	CH <sub>(2)</sub> O	2	quartet		
	5.5	NH <sub>2</sub>	2	singlet (broad)		
	7.1–7.4	H attached to aromatic/benzene ring	4	multiplet		
6(d)(iv)	neighbouring/adjacent carbon <b>atom</b> has two protons/H (attached to it) <b>or</b> there is an adjacent $CH_2(O)$ group					
6(d)(v)	peak at 5.5/NH <sub>2</sub> peak will disappear and NH <sub>2</sub> /protons exchange/swap with deuterium					1

Question	Answer	Marks
6(e)(i)	NaNO <sub>2</sub> + HC <i>l</i> or HNO <sub>2</sub>	1
6(e)(ii)	$ \begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & $	
l	structure of diazonium salt R	1
	structure of azo dye S	1

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Question	Answer	Marks
7(a)	Fe atom= $(1s^22s^22p^6)3s^23p^63d^64s^2$	1
	$Fe^{3+}$ ion= $(1s^22s^22p^6)3s^23p^63d^5$	
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) = <b>1.83</b>	1
7(c)(i)	$(K_{stab}$ is) the <b>equilibrium constant</b> 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)	$K_{\text{stab}} = \frac{[\text{Fe}(\text{ed})_2 C l_2^{3-}]}{[\text{Fe}(\text{H}_2 \text{O})_4 C l_2^{+}][\text{ed}]^2}$	1
	mol <sup>-2</sup> dm <sup>6</sup>	1
7(e)(i)	$Cl_{IIII} = Cl_{IIII} = Cl_{IIIII} = Cl_{IIII} = Cl_$	3
	cis cis trans	

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