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CHEMISTRY

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Paper 4 A Level Structured Questions

March 2017

MARK SCHEME

Maximum Mark: 100

Published

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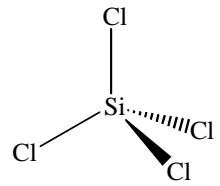
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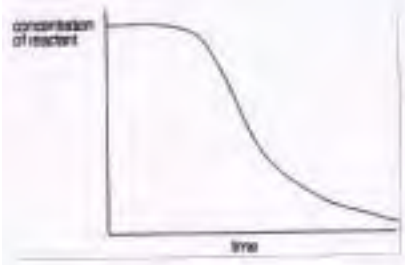
This document consists of **12** printed pages.

Question	Answer	Marks
1(a)(i)	$(28 \times 0.922) + (29 \times 0.047) + (30 \times 0.031) = 28.11$	1
1(a)(ii)	$\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_4 + 4\text{HCl}$	1
1(a)(iii)	 <p>diagram</p>	1
	bond angle = 109.5	1
1(a)(iv)	SiO_2	1
	SiO_2 is giant covalent/molecular but SiCl_4 is simple molecular/covalent	1
1(b)(i)	$2\text{A}(\text{NO}_3)_2 \rightarrow 2\text{AO} + 4\text{NO}_2 + \text{O}_2$ correct formula balanced equation	2 1 1
1(b)(ii)	giant ionic	1

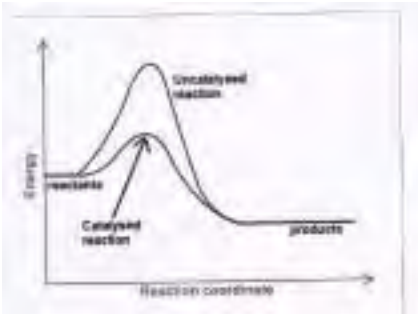
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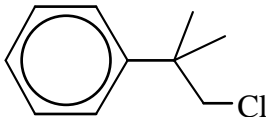
Question	Answer	Marks																				
2(a)	<table border="1" style="width: 100%; text-align: center;"> <tr> <td data-bbox="542 217 1052 316">enthalpy change</td> <td data-bbox="1052 217 1279 316">positive</td> <td data-bbox="1279 217 1505 316">negative</td> <td data-bbox="1505 217 1731 316">either positive or negative</td> </tr> <tr> <td data-bbox="542 316 1052 383">electron affinity</td> <td data-bbox="1052 316 1279 383"></td> <td data-bbox="1279 316 1505 383"></td> <td data-bbox="1505 316 1731 383">✓</td> </tr> <tr> <td data-bbox="542 383 1052 450">enthalpy change of atomisation</td> <td data-bbox="1052 383 1279 450">✓</td> <td data-bbox="1279 383 1505 450"></td> <td data-bbox="1505 383 1731 450"></td> </tr> <tr> <td data-bbox="542 450 1052 517">enthalpy change of ionisation</td> <td data-bbox="1052 450 1279 517">✓</td> <td data-bbox="1279 450 1505 517"></td> <td data-bbox="1505 450 1731 517"></td> </tr> <tr> <td data-bbox="542 517 1052 584">lattice enthalpy</td> <td data-bbox="1052 517 1279 584"></td> <td data-bbox="1279 517 1505 584">✓</td> <td data-bbox="1505 517 1731 584"></td> </tr> </table>	enthalpy change	positive	negative	either positive or negative	electron affinity			✓	enthalpy change of atomisation	✓			enthalpy change of ionisation	✓			lattice enthalpy		✓		2
enthalpy change	positive	negative	either positive or negative																			
electron affinity			✓																			
enthalpy change of atomisation	✓																					
enthalpy change of ionisation	✓																					
lattice enthalpy		✓																				
2(b)(i)	the second electron is removed from a (more) positively charged ion	1																				
2(b)(ii)	ΔH_6 is lattice (energy/enthalpy) AND ΔH_7 is (energy/enthalpy of) formation	1																				
2(c)	the electron affinity becomes less exothermic/negative down the Group 17	1																				
	electron affinity depends (mainly) on the electron-nucleus distance which increases down Group 17	1																				
2(d)	M1 correct use of $\Delta G = \Delta H - T\Delta S$	1																				
	M2 $\Delta S = 26.9 - (32.7 + 102.5) = -108.3 \text{ JK}^{-1} \text{ mol}^{-1}$ OR $-0.1083 \text{ kJK}^{-1} \text{ mol}^{-1}$	1																				
	M3 $\Delta G = -602 - (298 \times (-0.1083)) = -570$	1																				
	M4 units: kJ mol^{-1}	1																				

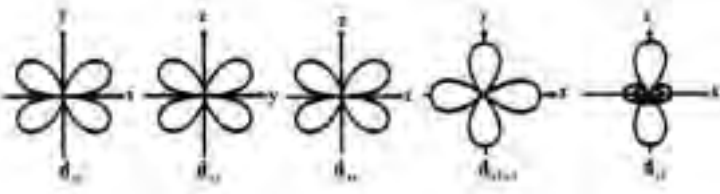
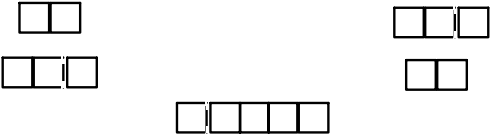
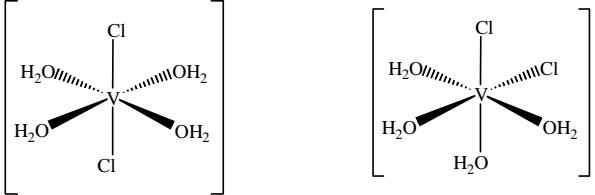
Question	Answer	Marks
3(a)(i)	A – H ₂ , 1 atm B – platinum C – 1 mol dm ⁻³ H ⁺ /HCl etc. D – salt bridge/KNO ₃ etc. E – platinum F – 1 mol dm ⁻³ Fe ²⁺ AND 1 mol dm ⁻³ Fe ³⁺	3
3(a)(ii)	positive electrode is (Pt) on RHS AND electrons flow clockwise	1
3(b)	cell potential is 0.77 – 0.34 = (+) 0.43 (V)	1
3(c)(i)	electrode potential would become more negative as equilibrium shifts to left/ explanation in terms of the Nernst equation	1
3(c)(ii)	$E = -0.41 + (0.059/1)\log[\text{Cr}^{3+}]/[\text{Cr}^{2+}]$ $= -0.41 + 0.059 \log 4.0$	1
	= -0.37 (V)	1


Question	Answer	Marks												
4(a)(i)	experiments 1 and 2: doubling $[\text{ClO}_2]$ quadruples the rate, so second order	1												
	experiments 2 and 3: doubling $[\text{OH}^-]$ doubles the rate, so first order	1												
	rate equation = $k[\text{ClO}_2]^2[\text{OH}^-]$	1												
4(a)(ii)	from experiment t 2: $9.34 \times 10^{-4} = k(2.50 \times 10^{-2})^2 \times 1.30 \times 10^{-3}$ $k = 1.15 \times 10^3$	1												
	units: $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$	1												
4(b)(i)	heterogeneous catalysts are in different physical state from the reactants AND homogeneous catalysts are in the same physical state as the reactants	1												
4(b)(ii)	<table border="1"> <thead> <tr> <th>catalysed reaction</th> <th>heterogeneous</th> <th>homogeneous</th> </tr> </thead> <tbody> <tr> <td>manufacture of ammonia in the Haber process</td> <td>✓</td> <td></td> </tr> <tr> <td>removal of nitrogen oxides from car exhausts</td> <td>✓</td> <td></td> </tr> <tr> <td>oxidation of sulfur dioxide in the atmosphere</td> <td></td> <td>✓</td> </tr> </tbody> </table>	catalysed reaction	heterogeneous	homogeneous	manufacture of ammonia in the Haber process	✓		removal of nitrogen oxides from car exhausts	✓		oxidation of sulfur dioxide in the atmosphere		✓	2
catalysed reaction	heterogeneous	homogeneous												
manufacture of ammonia in the Haber process	✓													
removal of nitrogen oxides from car exhausts	✓													
oxidation of sulfur dioxide in the atmosphere		✓												
4(c)(i)	$2\text{MnO}_4^- + 6\text{H}^+ + 5(\text{CO}_2\text{H})_2 \rightarrow 2\text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$ correct Mn : $(\text{CO}_2\text{H})_2$ ratio rest of equation	2 1 1												
4(c)(ii)	<p>first section: flatter second section: steeper, before flattening</p> 	2 1 1												

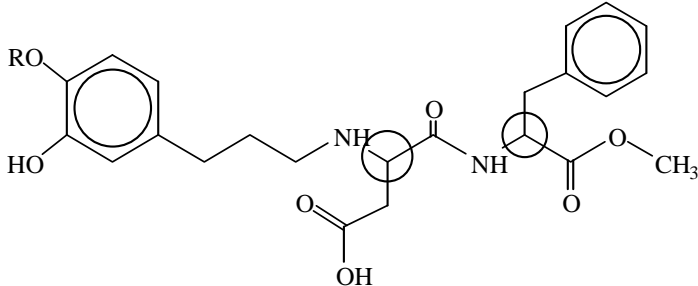
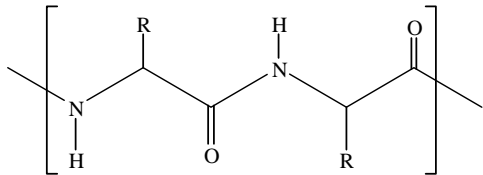
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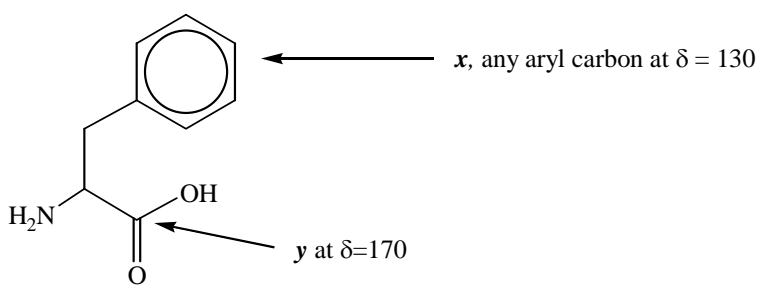
Question	Answer	Marks
,4(d)(i)	 <p>diagram catalyst lowers E_a for both the forward and reverse reactions so the process requires less energy/can occur at a lower temperature</p>	3 1 1 1
4(d)(ii)	$K_p = \frac{(p\text{NH}_3)^2}{(p\text{N}_2)(p\text{H}_2)^3}$ $1.45 \times 10^{-5} = \frac{(p\text{NH}_3)^2}{20 \times 60 \times 60 \times 60}$	1
	$p\text{NH}_3 = 7.91$	1

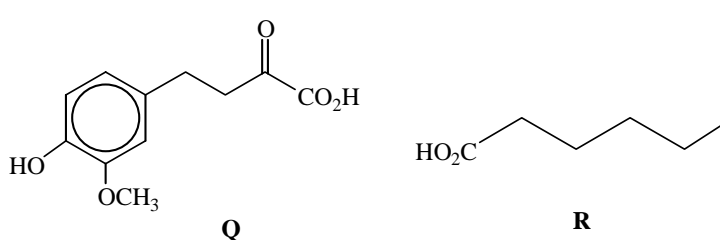
Question	Answer	Marks
5(a)(i)	$(\text{CH}_3)_3\text{C-Cl} / (\text{CH}_3)_2\text{C} = \text{CH}_2$	1
	$\text{AlCl}_3 + \text{heat}$	1
5(a)(ii)	(UV) light	1
5(a)(iii)		1
5(a)(iv)	ammonia/ NH_3	1
	heat in sealed tube/heat under pressure	1
5(b)	$\text{C}_{10}\text{H}_{13}\text{NH}_2 + \text{H}_3\text{O}^+ \rightleftharpoons \text{C}_{10}\text{H}_{13}\text{NH}_3^+ + \text{H}_2\text{O}$	1
5(c)	in compound H , the alkyl groups are electron donating/have a positive inductive effect, so it is more basic than NH_3	1
	in phenylamine, the lone pair (of N) is delocalised over the aryl group/benzene ring, so phenylamine is less basic than NH_3	1

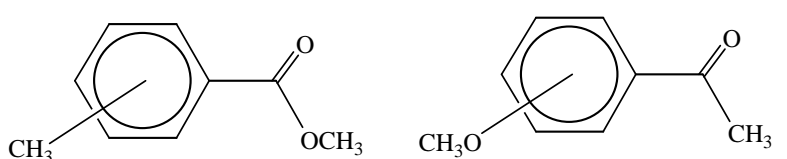
Question	Answer	Marks
6(a)(i)		1
6(a)(ii)	Ni : $[1s^2 2s^2 2p^6 3s^2 3p^6] 3d^8 4s^2$ Ni ³⁺ : $[1s^2 2s^2 2p^6 3s^2 3p^6] 3d^7$	1
6(b)(i)	 <p>octahedral complex isolated ion tetrahedral complex</p>	1
6(b)(ii)	energy / photon is absorbed in the visible region / light	1
	electron jumps from the lower to the upper energy level / is excited	1
6(b)(iii)	different frequency / wavelength of light are absorbed by the two complexes OR different size of energy gap	1
6(c)	colour of solution: green	1
	explanation: because the solution absorbs most strongly in the blue AND red regions	1
6(d)(i)		2

Question	Answer	Marks
6(d)(ii)	cis-trans / geometrical	1
6(e)(i)		2
6(e)(ii)	optical	1
6(f)(i)	$K_{\text{stab}} = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}]}{[\text{Ni}(\text{H}_2\text{O})_6^{2+}][\text{NH}_3]^6}$	1
6(f)(ii)	[Ni(en) ₃] ²⁺ would be formed because it is much more stable / K_{stab} is much greater OR in the presence of both ligands the overall equilibrium $[\text{Ni}(\text{NH}_3)_6]^{2+} \rightleftharpoons [\text{Ni}(\text{H}_2\text{O})_6]^{2+} \rightleftharpoons [\text{Ni}(\text{en})_3]^{2+}$ would shift right	1
6(f)(iii)	cis-trans isomers identified	1
	two cis isomers identified	1

Question	Answer	Marks
7(a)		1
7(b)(i)	$\text{H}^+(\text{aq}) + \text{heat}$	1
7(b)(ii)	hydrolysis	1
7(b)(iii)	CH_3OH	1
7(c)(i)	white precipitate	1
7(c)(ii)	$\text{C}_{14}\text{H}_{19}\text{O}_6\text{N} + 3\text{NaOH} \rightarrow \text{C}_{14}\text{H}_{16}\text{O}_6\text{NNa}_3 + 3\text{H}_2\text{O}$	2
7(d)(i)	no change / colour remains orange	1
7(d)(ii)	 <p>amide bond displayed two repeat units</p>	2 1 1
7(e)(i)	seven	1

Question	Answer	Marks
7(e)(ii)		1

Question	Answer	Marks
8(a)	oxidation of -OH / alcohol to C=O / ketone / carbonyl	1
8(b)(i)	dehydration / elimination	1
8(b)(ii)	heat with Al_2O_3 OR heat with $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$	1
8(b)(iii)		2
8(c)	phenol	1
	ketone	1

Question	Answer	Marks
9(a)(i)	$n = 100 \times (M+1)/(1.1 \times M) = 100 \times 3.4/(1.1 \times 33.9) = 9.1$	1
	hence <u>9</u> carbons atoms	1
9(a)(ii)	$C_9H_{10}O_2$	1
9(a)(iii)	(150 – 119 = 31), hence fragment is CH_3O	1
9(b)	V is C=O AND W is C–O	1
9(c)(i)	δ 3.9 is CH or alkyl/ CH_3 next to oxygen AND δ 7.2–7.9 is CH/aryl hydrogens	1
9(c)(ii)	alkyl H next to C=O AND alkyl H next to aryl ring	1
9(c)(iii)	none of the functional groups in T contains a labile proton/ T does not contain –OH or –NH groups.	1
9(d)		2