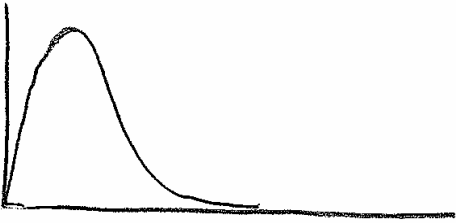
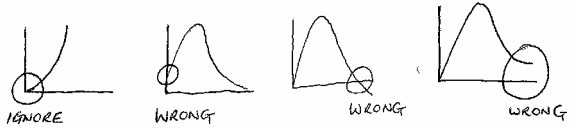


Mark Scheme (Results) January 2007

GCE

GCE Chemistry (6245/01)

		EXPECTED ANSWER	ACCEPT	REJECT	MARK	
1.	(a)	(i)	The sum of the powers to which the concentrations are raised in the rate equation <i>Note if candidates choose to define order with respect to one species or give complete rate equation in terms of powers of 'x' and 'y' and explain that the order is x or y or x+ y 1 mark</i>	"The sum of the partial/individual orders" if exemplified by a rate equation OR number of species/reactants involved in (up to and including) the rate determining step	The sum of the partial/individual orders" on its own	(1 mark)
		(ii)	1 st order because rate halves as [A] halves in expt. 1 → 2 or [B] constant (1) 2 nd order because rate quadruples / increases by 2 ² as [B] doubles in expt. 2 → 3 or [A] constant (1) 1 (out of 2) if incomplete or no reasons given rate = $k[A][B]^2$ (1) <i>consequential on their orders</i>			(3 marks)
		(iii)	$k = 0.0080$ (1) $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$ (1) <i>both marks consequential on rate equation</i> <i>IGNORE SF</i>			(2 marks)
		(iv)	(k) increases		Any reference to endothermic reaction scores zero	(1 mark)

	EXPECTED ANSWER	ACCEPT	REJECT	MARK
(b)	(i)  Shape i.e. start at origin skewed and asymptotic to x-axis 			(1 mark)
	(ii) E_{cat} to left of E_{uncat} and both to the right of hump	If draw energy profile could get this mark if the E_s are correct and clearly marked on the profile		(1 mark)
	(iii) Peak (more) to the right (1) Peak lower (1) <i>OR shown on diagram</i>		Any reference to increase in area under graph deduct 1 mark	(2 marks)
	(iv) Manufacture of ammonia (1) Iron (1) <i>MUST be a metal not a compound</i> <i>OR</i> e.g. Hydrogenation of oils (1) Ni/Pt/Pd (1) Manufacture of H_2 from CH_4 (1) Ni (1) Explanation uses d orbitals to bond with reactants(at active sites) (1) - <i>stand alone</i>	Variable /more than 1/several oxidation states	"Haber process" on its own Sulphuric acid manufacture with V_2O_5 Must have a least three oxidation states	(3 marks)

	EXPECTED ANSWER	ACCEPT	REJECT	MARK
	(v) Catalysed k bigger/Higher <i>OR</i> uncatalysed k lower			(1 mark)
	Total 15 marks			

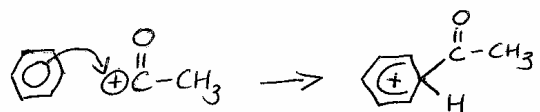
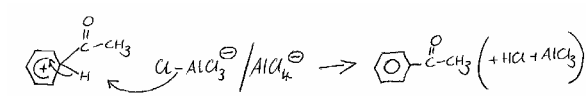
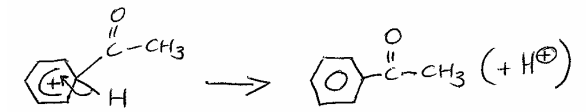
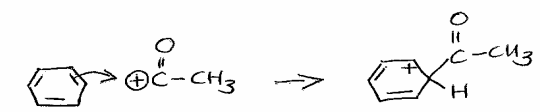
	EXPECTED ANSWER	ACCEPT	REJECT	MARK
2	(a) Pt electrode (1) chlorine gas at 1 atm (1) chloride ions at 1.0 mol dm ⁻³ (1) <i>IGNORE references to temperature</i>	101 kPa		(3 marks)
	(b) (i) $2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq})$ <i>IGNORE state symbols</i>			(1 mark)
	(ii) $E_{\text{cell}} = +0.37 \text{ V}$ OR E^\ominus for $\text{Cu}^+/\text{Cu} > E^\ominus$ for $\text{Cu}^{2+}/\text{Cu}^+$ (1) Is positive (and thus feasible) (1)	<i>Could argue reverses reaction is not feasible because.....</i>		(2 marks)
	(iii) (Copper) oxidised from +1 to +2 (1) and also reduced to zero (1) OR The Cu^+ is oxidised to Cu^{2+} (1) and Cu^+ also reduced to Cu (1)		A definition of disproportionation alone does not score	(2 marks)

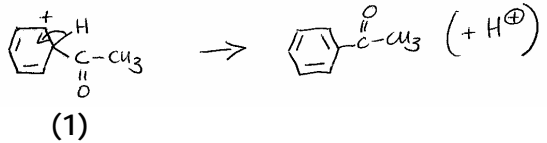
	EXPECTED ANSWER	ACCEPT	REJECT	MARK
(c)	$(1s^2) 2s^2 2p^6 3s^2 3p^6 3d^{10}$ OR $(1s^2) 2s^2 2p^6 3s^2 3p^6 4s^0 3d^{10}$ OR $(1s^2) 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^0$ Ignore spaces between items Ignore punctuation			(1 mark)
(d)	(i) ligand exchange OR ligand substitution (1) deep/dark blue (1)	“Nucleophilic substitution” Any type of blue that is darker than hydrated Cu(II) ions	“Substitution” on its own OR “deprotonation”	(2 marks)
	(ii) d-orbitals split (in energy) by ligands / become non-degenerate in presence of ligands (1) absorbs energy(light in visible region) (1) electron is promoted OR electron moves to a higher energy level (1) <i>Any mention of emission of light can only score 1st mark</i> <i>Any implication of electron promotion before absorption of light can only score 1st mark</i>	d-sublevel The first mark may be awarded provided at some point in the answer it is clear that there are <i>d</i> - orbitals of different energy	“UV light”	(3 marks)
	(iii) full d subshell / all d orbitals full (1) Therefore d-d transitions impossible / a clear idea that promotion of electrons by absorbing energy is not possible(1) No <i>d</i> orbital splitting max 1 mark			(2 marks)

	EXPECTED ANSWER	ACCEPT	REJECT	MARK
	(e) tetrahedral (1) range 109 - 110° (1) 4 (bonding) pairs of electrons repel to a position of maximum separation/minimum repulsion (1) Accept diagram to show shape(ignore charges)	OR Sq planar (1) 90° (1) with comparison with Ni or Pt complex (1) if say square planar and then argue that 4 pairs of electrons repel as far as possible max 1	Bonds/atoms repelling	(3 marks)
	Total 19 marks			

	EXPECTED ANSWER		ACCEPT	REJECT	MARK
3	(a)	All hydrogen nuclei / hydrogens atoms/ protons in same (chemical) environment			(1 mark)
	(b)	(i)	<u>reagent (1)</u> ethanoyl chloride / CH ₃ COCl <u>catalyst (1)</u> (anhydrous) aluminium chloride / AlCl ₃ /Al ₂ Cl ₆	AlBr ₃ FeBr ₃ , FeCl ₃	Fe (2 marks))
		(ii)	electrophilic substitution (1)	acylation Friedel-Crafts	(1 mark)

	EXPECTED ANSWER	ACCEPT	REJECT	MARK
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	<p>(iii)</p> $AlCl_3 + CH_3COCl \rightarrow CH_3C(=O)^+ + AlCl_4^-$ <p>(1) this could be shown as part of the mechanism</p> <p>.....</p>  <p>(1) for arrow (1) for intermediate- needs +ve charge</p> <p>.....</p> <p>Either:</p>  <p>(1) for arrow from C-H bond</p> <p>OR:</p>  <p>(1) for arrow</p> <p>.....</p> <p>ALTERNATIVE Kekulé</p>  <p>(1) (1)</p>		<p>Any arrows to C of CH₃ rather than of CO</p>	
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	EXPECTED ANSWER	ACCEPT	REJECT	MARK
	 <p>(1)</p> <p>Notes:</p> <p>1st curved arrow from benzene ring of electrons towards C of COCH₃ (1) <i>ALLOW the "+" anywhere on COCH₃</i></p> <p>Curved arrow from C-H bond back into benzene ring (1) <i>IGNORE if towards the "+"</i></p>			(4 marks)
(c)	(i) HCN (1) + KCN (1) OR KCN (1) + Acid (1) <i>EXCEPT</i> conc H ₂ SO ₄ OR HCN (1) + Base / alkali(1) OR HCN/KCN (1) pH 5 - 9 (1) <i>Names or formulae can be given</i>	CN ⁻ for KCN If KCN, HCN and acid max1		(2 marks)
	(ii) nucleophilic addition <i>Both needed</i>			(1 mark)

EXPECTED ANSWER

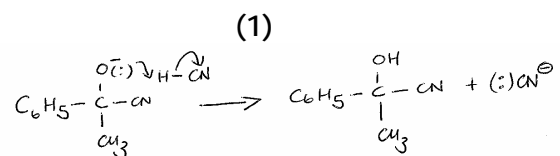
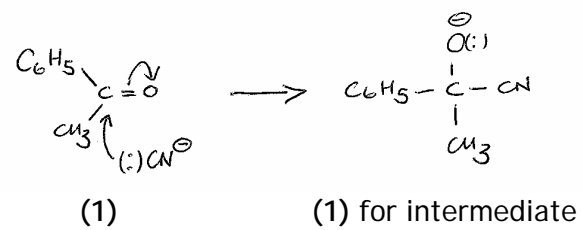
ACCEPT

REJECT

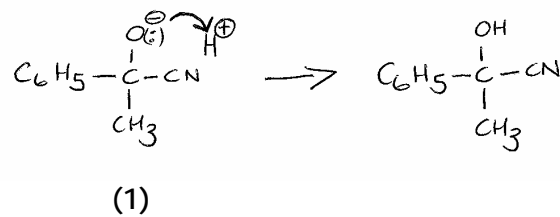
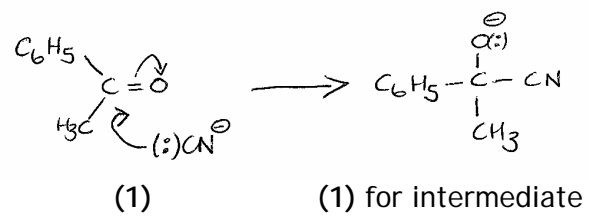
MARK

(iii)

EITHER



OR



		EXPECTED ANSWER	ACCEPT	REJECT	MARK
		<ul style="list-style-type: none"> The intermediate is not consequential on their first step The minus of the cyanide ion can be on either the C or the N The arrow can start from the minus of ^-CN in step 1 (but not from the minus of CN^-) and can start from the minus of O^- in step 2 The arrow from the bond must not go past the O atom Lone pairs not essential Single step addition of HCN scores zero Autoionisation of $\text{C}=\text{O}$ can only score the last two marks ie max 2 			(3 marks)
(d)	(i)	2 enantiomers drawn 			(1 mark)
	(ii)	(No effect) as ketone planar (1) Attack possible from top or bottom (1) Producing racemic/50:50 mixture (of enantiomers) / rotations cancel out (1) no effect could appear here in the answer			(3 marks)
(e)		No absorption corresponding to $\text{C}=\text{O}$ / carbonyl <i>OR</i> No absorption around 1700 cm^{-1}	Peak / band	Ketone group	(1 mark)
					Total 19 marks

	EXPECTED ANSWER			ACCEPT	REJECT	MARK
4	(a)	(i)	(free) radical substitution	phonetic spelling e.g. radicle	"radical nucleophilic substitution"	(1 mark)
		(ii)	UV radiation OR sunlight OR ultraviolet radiation OR UV OR UV light OR white light OR heat		"light" on its own NOT hv NOT strong light	(1 mark)
	(b)	<p>Diagram labelled axes, lozenge and b.pt. values (1)</p> <p>At least 2 horizontal + 2 vertical tie lines from anywhere except 100% (1)</p> <p>Explanation Vapour richer in more volatile/chloropropane (1)</p> <p>Condense and then reboil (1)</p> <p>Pure chloropropane distilled off / bromopropane left as residue (1)</p> <p>If heat to 46 (or when at 46) all chloropropane boils off then..... scores (0) for explanation</p>			The curve must not noticeably go above or below the boiling points indicating a max or min on the curve	(5 marks)

	EXPECTED ANSWER	ACCEPT	REJECT	MARK
	<p>(c) heat with NaOH (1)</p> <p>add excess HNO₃ <i>OR</i> acidify with HNO₃ (1)</p> <p>add AgNO₃ (1)</p> <p>chloro gives white <u>and</u> bromo gives cream ppt (1)</p> <p>white/off white/ pale yellow ppt soluble in dil NH₃, cream ppt slightly/partially soluble in dil NH₃, (or soluble in conc NH₃) (1)</p> <p><i>If fail to add NaOH or fail to add HNO₃ 3 max</i></p>		Methods based on displacement	(5 marks)
	<p>(d) MS shows different <i>m/e</i> values for molecular ion (1)</p> <p>Because molar masses different / or reason why different(1)</p> <p>Nmr give same number/3 peaks with both (1)</p> <p><i>OR</i></p> <p>Nmr shows different chemical shifts (1)</p> <p>Due to different halides (1)</p> <p>In MS molecular ion peak often absent (1)</p> <p><i>Must be a statement about both MS and NMR to score 3 marks</i></p>	Hydrogens in same environment in both molecules		(3 marks)
	Total 15 marks			

	EXPECTED ANSWER	ACCEPT	REJECT	MARK
5	(a) Moles manganate = 0.0239×0.2 (1) = 0.00478 Moles bromide = $\frac{2.46}{103}$ (1) = 0.0239 ratio $\text{MnO}_4^- : \text{Br}^- = 1:5$ OR ratio $\text{Br}^- : \text{MnO}_4^- = 5:1$ (1) $\text{MnO}_4^- + 5\text{Br}^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 2.5\text{Br}_2$ species (1) balance (1) <i>If no calculation allow correct equation marks</i> <i>If calculation wrong equation must be consequential on the ratio calculated for balance mark</i>	Multiples	Answers that start from the equation and then use it to derive ratio	(5 marks)
	(b) (i) Not oxidised by manganate(VII)/ does not react with oxidising agents OR Not hydrolysed by acid	Cannot be oxidised	unreactive	(1 mark)
	(ii) non-biodegradable therefore fills landfill sites	Non-biodegradable therefore persists in environment	toxic gas if burned	(1 mark)
				Total 7 marks