

Mark Scheme (Results)

Summer 2007

GCE

GCE Chemistry (6246) Paper 02

General Guidance on Marking

Examiners should look for qualities to reward rather than faults to penalise. This does NOT mean giving credit for incorrect or inadequate answers, but it does mean allowing candidates to be rewarded for answers showing correct application of principles and knowledge.

Examiners should therefore read carefully and consider every response: even if it is not what is expected it may be worthy of credit.

Crossed out work should be marked **UNLESS** the candidate has replaced it with an alternative response.

Using the mark scheme

The mark scheme gives you:

- an idea of the types of response expected
- how individual marks are to be awarded
- the total mark for each question
- examples of responses that should NOT receive credit.

Candidates must make their meaning clear to the examiner to gain the mark. Make sure that the answer makes sense. Do not give credit for correct words/phrases which are put together in a meaningless manner. Answers must be in the correct context.

- 1 / means that the responses are alternatives and either answer should receive full credit.
- 2 () means that a phrase/word is not essential for the award of the mark, but helps the examiner to get the sense of the expected answer.
- 3 [] words inside square brackets are instructions or guidance for examiners.
- 4 Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.
- 5 ecf/TE/cq (error carried forward) means that a wrong answer given in an earlier part of a question is used correctly in answer to a later part of the same question.

Quality of Written Communication

Questions which involve the writing of continuous prose will expect candidates to:

- show clarity of expression
- construct and present coherent arguments
- demonstrate an effective use of grammar, punctuation and spelling.

Full marks will be awarded if the candidate has demonstrated the above abilities.

Questions where QWC is likely to be particularly important are indicated (QWC*) in the mark scheme BUT this does not preclude others.

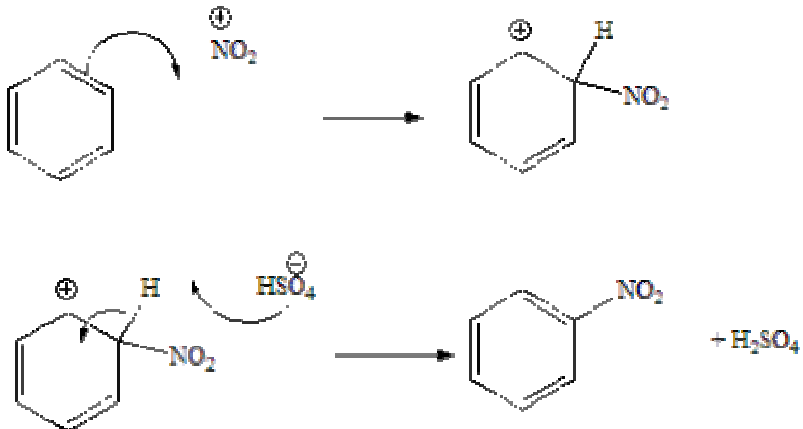
	EXPECTED ANSWER	ACCEPT	REJECT	MARK
1	(a) The amount of a solid present is immaterial since K_c does not depend on this OR solids do not appear in expression for equilibrium constants IGNORE any references to solid in excess.			(1)
	(b) $\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}$ IGNORE state symbols			(1)
	(c) Correct answer with some working and correct units scores full marks. Otherwise steps in calculation must make it reasonably clear to examiner what is being calculated (QWC). (initial amount) $\text{I}^- = 0.100 \text{ mol dm}^{-3} \times 0.050 \text{ dm}^3 = 5 \times 10^{-3} \text{ mol}$ (1) Amount $\text{Ag}^+ = 0.100 \text{ mol dm}^{-3} \times 0.031 \text{ dm}^3 = 3.1 \times 10^{-3} \text{ mol}$ (1) \therefore equilibrium amount $\text{I}^- = 3.1 \times 10^{-3} \text{ mol}$ (1) I^- reacted = $(5 - 3.1) \times 10^{-3} \text{ mol} = 1.9 \times 10^{-3} \text{ mol}$ (1) If this subtraction is not carried out then the next mark (for calculating amount of sulphate) can not be awarded. Thus amount of sulphate = $\frac{1}{2} \times 1.9 \times 10^{-3} (= 9.5 \times 10^{-4} \text{ mol})$ (1) conc iodide = $\frac{3.1 \times 10^{-3} \text{ mol}}{0.05 \text{ dm}^3} (= 0.062 \text{ mol dm}^{-3})$ AND conc sulphate = $\frac{0.95 \times 10^{-3} \text{ mol}}{0.05 \text{ dm}^3} (= 0.019 \text{ mol dm}^{-3})$ (1) The mark is for the process of dividing by 0.05 dm^3 $K_c = 0.019/0.062^2 = 4.94$ (1) Answer must be to 2 or more S.F. Value consequential on dividing their moles by a volume. $\text{mol}^{-1} \text{ dm}^3$ (1) Stand alone			(8)
Total 10 marks				

	EXPECTED ANSWER		ACCEPT	REJECT	MARK	
2	(a)	(i)	Pairs: acid NH_4^+ / ammonium ion and base NH_3 / ammonia acid H_3O^+ / hydronium ion and base H_2O / water	Hydroxonium ion		(1)
		(ii)	$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$ ignore lower case k	$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$	Answers including $[\text{H}_2\text{O}]$	(1)
		(iii)	$[\text{H}_3\text{O}^+] = 10^{-5} \text{ mol dm}^{-3}$ (1) Assumption ionization of NH_4^+ (negligibly) small (1) Assumption $[\text{NH}_3] = [\text{H}_3\text{O}^+]$ (1) thus $[\text{NH}_4\text{Cl}] = (1 \times 10^{-5})^2 / 5.62 \times 10^{-10}$ $= 0.178 \text{ mol dm}^{-3}$ (1) Answer to 2 or more S.F.	$[\text{NH}_4^+] = [\text{NH}_4\text{Cl}]$ or NH_4Cl totally ionized		(4)
		(iv)	methyl red (1) Q W C* indicator constant or $\text{p}K_{\text{in}}$ must be near the endpoint pH OR indicator constant or $\text{p}K_{\text{in}}$ must be near 5 (1) 2 nd mark conditional on correct indicator	$\text{p}K_{\text{in}}$ in the steep part of the graph or it is a weak base-strong acid titration		(2)
	(b)		$\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$ IGNORE state symbols	Accept " \rightarrow " instead of " \rightleftharpoons "		(1)

	EXPECTED ANSWER		ACCEPT	REJECT	MARK
(c)	(i)	nucleophilic addition			(1)
	(ii)	<p>(1) for both arrows</p> <p>(1) for intermediate</p> <p>(1)</p> <p>OR for second step</p> <p>(1)</p>		Fish hook arrows (penalise once)	(3)
		<ul style="list-style-type: none"> •Ignore the groups attached to the carbonyl carbon throughout •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 $\text{C}=\text{O}$ bond must not go past the O atom •Lone pairs not essential •Single step addition of HCN or initial attack by H^+/HCN scores zero •Autoionisation of $\text{C}=\text{O}$ can only score the last two marks ie max 2 			

		EXPECTED ANSWER	ACCEPT	REJECT	MARK
	(iii) Q W C*	if too acidic too small a concentration of cyanide ions (1) if too alkaline too little HCN to donate the proton in the last step OR H ⁺ ion concentration too low (1)	Not enough / too little CN ⁻		(2)
(d)	(i)	rate = $k[\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}][\text{CN}^-]$ Must be an equation Must be [] NOT () Ignore upper case K	'R' or 'r' for rate C ₃ H ₇ Cl / [1-chloropropane] / [chloropropane] [cyanide ion] / [cyanide]	[KCN]	(1)
	(ii)	<p>Curly arrow (1)</p> <p>Curly arrow (1) Transition state (1)</p> <ul style="list-style-type: none"> • Must have partial bonds in transition state • CN and Cl must be on opposite sides of central C in the transition state • Accept negative charge on N of cyanide ion 		Mechanism based on S _N 1 scores 0 Fish hook arrows (penalise once) Arrow from N of CN	(3)
(e)		Useful for extending the carbon chain/skeleton	for ascending a homologous series	Just 'Increasing the number of carbon atoms in the molecule'	(1)
Total 20 marks					

	EXPECTED ANSWER		ACCEPT	REJECT	MARK
3	(a) Q W C*	Heat/enthalpy/energy change per mole for formation of a compound/substance (1) IGNORE any mention of standard conditions or temperature (in a stated physical state) from its elements in their standard states (1)	"Normal" OR "stable" instead of "standard"	Energy required OR Energy given out	(2)
	(b)	(i) $\Delta H = (+90.2 \times 4) + (-242 \times 6) - (-46.1 \times 4)$ $= -907 \text{ (kJ mol}^{-1}\text{)}$ (2) IGNORE sf Correct answer with no working scores (2) One mark for correct use of all three coefficients One mark for correct use of signs throughout			(2)
		(ii) $-1268 \text{ (kJ mol}^{-1}\text{)}$ IGNORE sf			(1)
	(c)	(i) Because it is the more exothermic			(1)
		(ii) changes the activation energy for a reaction by changing the mechanism/route (1) Q W C* lowers it for Reaction I more than for Reaction II OR catalyst specific for Reaction I (1) [Comparison is essential]			(2)

		EXPECTED ANSWER	ACCEPT	REJECT	MARK
(d)	(i)	<p>To protonate the nitric acid OR to generate NO_2^+ OR increases the concentration of NO_2^+ compared with nitric acid alone (1) IGNORE comments concerning H_2SO_4 being a catalyst</p> <p>$2\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{H}_3\text{O}^+ + \text{NO}_2^+ + 2\text{HSO}_4^-$ or $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_2^+ + \text{HSO}_4^-$ (1) or both of: $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$ then $\text{H}_2\text{NO}_3^+ \rightarrow \text{H}_2\text{O} + \text{NO}_2^+$ OR $\text{H}_2\text{NO}_3^+ + \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{O}^+ + \text{NO}_2^+ + \text{HSO}_4^-$</p>	If candidate says to generate the electrophile, the mark can be awarded if NO_2^+ is shown in the equation		(2)
	(ii)	<p>sulphuric acid protonates nitric acid OR nitric acid accepts a proton / H^+ from the sulphuric acid (1)</p> <p>Answer may refer to the equation forming H_2NO_3^+</p>		Just " H_2SO_4 is dibasic and HNO_3 is monobasic" or similar arguments	(1)
	(iii)	 <p>Curly arrow from double bond/ circle towards N of electrophile (1) Correct intermediate. (if a broken ring is used for the delocalised electrons it must extend over the other 5 carbons) (1) Curly arrow from C-H bond back into ring (1)</p>	<p>allow equivalent using the circled symbol for benzene;</p> <p>allow loss of H^+ in the last step</p>		(3)
	(iv)	Any dinitrobenzene isomer OR any trinitrobenzene			(1)

	EXPECTED ANSWER		ACCEPT	REJECT	MARK
	(v) Q W C*	delocalised (π) electrons over the benzene ring (1) substitution regains/retains the stabilisation energy (1) which would be lost if addition occurred (1)	Delocalised pi system Stability for stabilisation energy	Just 'Delocalised ring' Just 'Delocalised bonds'	(3)
	(e)	Alkaline (potassium) manganate(VII) (1) any named acid (1) consequential on correct answer or near miss for first mark.	"permanganate" instead of "manganate(VII)" OR Formulae Formula e.g. HCl etc.	Just "Alkaline manganate" KMnO ₄ + dilute acid scores neither mark Concentrated sulphuric acid	(2)
Total 20 marks					

	EXPECTED ANSWER		ACCEPT	REJECT	MARK
4	(a)	$3d^{10}4s^1$ and $3d^{10}$	$4s^13d^{10}$		(1)
	(b)	(i) the (3) <i>d</i> sub-shell is full (1) Q W so no d-d transitions are possible C OR no transitions in the right energy range are possible (1) * (and no light is absorbed) Any mention of light emission loses 2 nd mark	Orbitals (it must be plural) for sub-shell	Comments on partially filled sub-shell	(2)
		(ii) combine the half-reactions to get $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$ (1) IGNORE state symbols and show that E° for this is (+) 0.37 (V) (and as it is positive it is feasible) (1) conditional on correct reaction		Just '> 0.3 (V)'	(2)
		(iii) activation energy (for the disproportionation) is high OR Cu^+ is kinetically stable		Activation energy for one of the half-equations is too high	(1)
	(c)	(i) divides each by atomic mass (1) divides by smallest to obtain $\text{Cu}_2\text{SO}_6\text{H}_2$ (1)		Division by atomic number scores zero	(2)
		(ii) $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$ (2) If formula wrong but sulphate/ SO_4 is present scores 1 (out of 2)	$\text{Cu}_2\text{SO}_4(\text{OH})_2$ $\text{Cu}_2(\text{OH})_2\text{SO}_4$ $(\text{CuOH})_2\text{SO}_4$	HSO_4 instead of SO_4	(2)
		(iii) $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	$[\text{Cu}(\text{NH}_3)_6]^{2+}$	(1)
		(iv) ligand exchange / ligand substitution			(1)

		EXPECTED ANSWER	ACCEPT	REJECT	MARK
	(d)	(i) (add aldehyde to 2,4-DNP) to obtain precipitate/ppt/solid/crystals (1) Q W C* recrystallise derivative (1) determine melting temperature of derivative (1) compare with data tables (1) 4 th mark conditional on melting temperature of a derivative being measured		Any identification method based on IR, NMR or mass for last 2 marks	(4)
		(ii) the aldehyde is distilled off as it is formed		Any mention of reflux Just 'the aldehyde is distilled off'	(1)
		(iii) propanoic acid OR CH ₃ CH ₂ COOH OR CH ₃ CH ₂ CO ₂ H	C ₂ H ₅ for CH ₃ CH ₂		(1)
		(iv) No (extra) oxygen present OR catalyst specific to formation of aldehyde / only lowers E _a of first oxidation OR presence of hydrogen gives reducing conditions OR copper is not an oxidising agent OR aldehydes rapidly leave catalyst surface			(1)
		(v) (At high pressure) all active sites are occupied/full OR (At higher pressures) rate controlled by availability of sites.	Reverse argument for low pressure		(1)
			Total 20 marks		