

GCE 2005
January Series



Mark Scheme

Chemistry

CHM4 Further Physical and Organic Chemistry

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

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Dr Michael Cresswell Director General

Guidance on the award of the mark for Quality of Written Communication

Quality of Written Communication assessment requires candidates to:

- select and use a form and style of writing appropriate to purpose and complex subject matter;
- organise relevant information clearly and coherently, using specialist vocabulary when appropriate; and
- ensure text is legible, and spelling, grammar and punctuation are accurate, so that meaning is clear.

For a candidate to be awarded 1 mark for quality of written communication on the question identified as assessing QWC in a unit test, the minimum acceptable standard of performance should be:

- the longer parts (worth 4 marks or more) should be structured in a reasonably logical way, appropriate and relevant to the question asked;
- ideas and concepts should be explained sufficiently clearly to be readily understood. Continuous prose should be used and sentences should be generally be complete and constructed grammatically. However, minor errors of punctuation or style should not disqualify;
- appropriate AS/A level terminology should be used. Candidates should not use such phrases as ‘fighting disease’, ‘messages passing along nerves’, ‘enzymes being killed’ etc, but a single lapse would not necessarily disqualify. Technical terms should be spelled correctly, especially where confusion might occur, e.g. mitosis/meiosis, glycogen/glucagon.

The Quality of Written Communication mark is intended as a recognition of competence in written English. Award of the mark should be based on overall impression of performance on the question identified on the paper as assessing QWC. Perfection is not required, and typical slips resulting from exam pressure such as ‘of’ for ‘off’ should not be penalised. Good performance in one area may outweigh poorer performance in another. Care should be taken not to disqualify candidates whose lack of knowledge relating to certain parts of a question hampers their ability to write a clear and coherent answer; in such cases positive achievement on other questions might still be creditworthy. No allowance should be made in the award of this mark for candidates who appear to suffer from dyslexia or for whom English is a second language. Other procedures will be used by the Board for such candidates.

Examiners should record 1 or 0 at the end of the paper in the Quality of Written Communication lozenge. This mark should then be transferred to the designated box on the cover of the script.

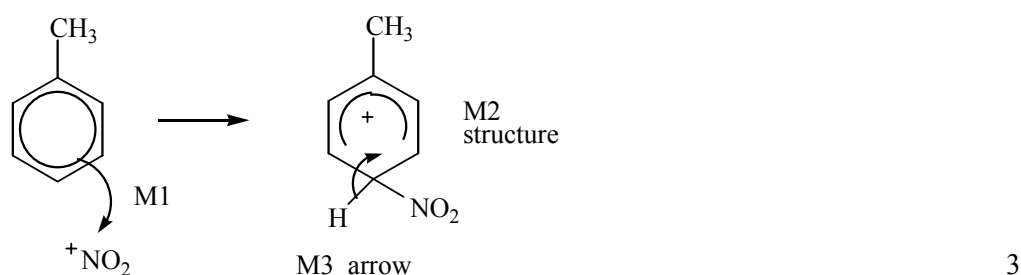
CHM 4 Further Physical and Organic Chemistry

SECTION A

Question 1

- (a) (i) conc HNO₃ 1
 conc H₂SO₄ 1
 allow 1 for both acids if either conc missing
 $\text{HNO}_3 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$ 1
 or $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^-$

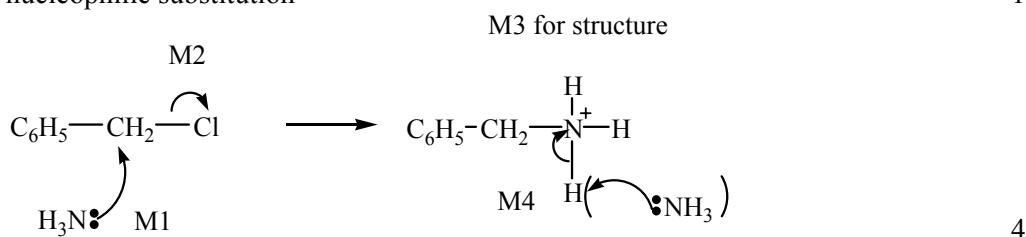
- (ii) electrophilic substitution 1



horseshoe must not extend beyond C2 to C6 but can be smaller
 + must not be too close to C1

- (b) Sn or Fe / HCl (conc or dil or neither) 1
 or Ni / H₂ not NaBH₄/ LiAlH₄

- (c) (i) NH₃ 1
 Use an excess of ammonia 1
 (ii) nucleophilic substitution 1



- (d) lone pair on N less available (in correct context) 1
delocalised into the ring (Q of L) 1

- (e) ignore Br⁻ 1
 + must be on N or outside a square bracket

- (f) 1

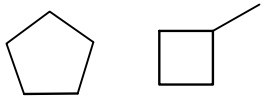
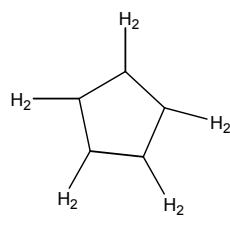
Total 19

Question 2

- (a) (i)
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{N}^+ - \text{C} - \text{COO}^- \\ | \\ \text{H} \end{array}$$
 penalise $^+\text{NH}_3$ or $+$ on H once per paper 1
- zwitterion 1
- (ii)
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{N}^+ - \text{C} - \text{COOH} \\ | \\ \text{H} \end{array}$$
 1
- (b)
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{---N---C---C---} \\ | \quad | \quad || \\ \text{H} \quad \text{H} \quad \text{O} \end{array}$$
 ignore n, but allow **one** drawn out repeating unit only 1
- condensation or (nucleophilic) addition-elimination 1
- (c) 3-methylpent-2-ene 1

Total 6

Question 3

- (a) **A** any C₅ alkene 1
- B**  etc 1
- penalise  1
- (b) **C**
$$\begin{array}{c} \text{O} \\ // \\ \text{H}_3\text{C}-\text{C} \\ \backslash \\ \text{OH} \end{array} \quad \text{or} \quad \begin{array}{c} \text{O} \\ // \\ \text{H}-\text{C} \\ \backslash \\ \text{O}-\text{CH}_3 \end{array}$$
 1
- or CH₃COOH or HCOOCH₃
- D**
$$\begin{array}{c} \text{H} \\ | \\ \text{H}_2\text{C}-\text{C} \\ | \quad // \\ \text{OH} \quad \text{O} \end{array} \quad \text{or} \quad \text{HOCH}_2\text{CHO}$$
 1
- (c) **E**
$$\begin{array}{c} \text{O} \\ // \\ \text{H}-\text{C} \\ \backslash \\ \text{O}-\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
 1

F	$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_3$ (allow C_2H_5)	1
(d) G	$\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2\text{Cl} \\ \\ \text{Cl} \end{array}$	1
H	$\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CHCl}_2 \\ \\ \text{H} \end{array}$ or $\text{ClH}_2\text{C}-\begin{array}{c} \text{H} \\ \\ \text{C}-\text{CH}_2\text{Cl} \\ \\ \text{H} \end{array}$ or $\begin{array}{c} \text{Cl} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{Cl} \end{array}$	1
(e) I	$\begin{array}{c} \text{H}_3\text{C} \quad \quad \text{CH}_3 \\ \quad \quad \diagdown \quad \diagup \\ \quad \quad \text{C}=\text{C} \\ \quad \quad \diagup \quad \diagdown \\ \text{H}_3\text{C} \quad \quad \text{CH}_3 \end{array}$	1
J	$\begin{array}{c} \text{H} \quad \quad \quad \text{CH}_2\text{CH}_3 \\ \quad \quad \diagdown \quad \diagup \\ \quad \quad \text{C}=\text{C} \\ \quad \quad \diagup \quad \diagdown \\ \text{H} \quad \quad \quad \text{CH}_2\text{CH}_3 \end{array}$ (allow C_2H_5)	1
	NOT hex-3-ene	
		Total 10

Question 4

(a)	order with respect to P is 2	1
	order with respect to Q is 1	1
(b) (i)	rate = $k[\mathbf{R}][\mathbf{S}]^2$ (if wrong expression, no further marks)	1
	rate = $(4.2 \times 10^{-4}) \times 0.16 \times 0.84^2$	1
	= 4.7×10^{-5} ($\text{mol dm}^{-3} \text{ s}^{-1}$) ignore units even if wrong	1
(ii)	$k = \frac{\text{rate}}{[\mathbf{R}][\mathbf{S}]^2} = \frac{8.1 \times 10^{-5}}{0.76 \times 0.98^2}$	1
	= 1.1×10^{-4} *	1
(iii)	T_1	1
	* If calculated value for $k > 4.2 \times 10^{-4}$, then answer to (iii) is T_2	

Total 8

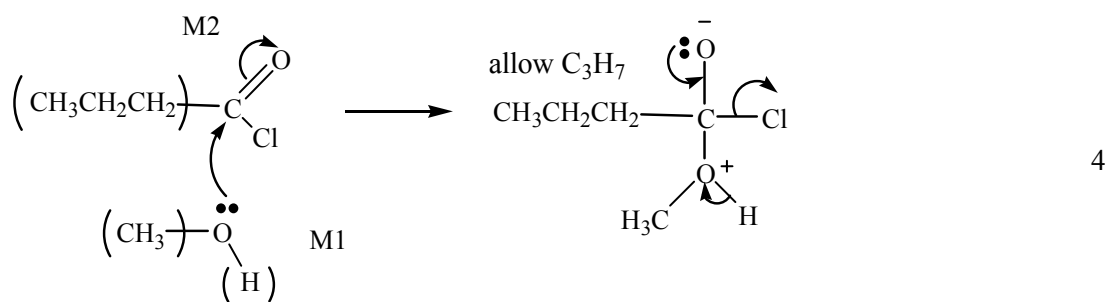
Question 5

- (a) (i) moles of $C_2F_2 = 0.40$ mark independently from HCl 1
 moles of HCl = 0.80 **not** consequential 1
- (ii) $K_c = \frac{[C_2F_4][HCl]^2}{[CHClF_2]^2}$ wrong K_c means they can only score for 1
 units in (iii) consequ on their K_c
- (iii) $K_c = \frac{(0.40/18.5)(0.80/18.5)^2}{(0.20/18.5)^2}$ 1
 $= 0.35$ 1
 mol dm^{-3} 1
- (b) (i) increase 1
 (ii) decrease 1
- (c) addition or radical 1

Total 9

Question 6

- (a) butanoyl chloride 1
- (b) (i) Cl has (two) isotopes or ^{35}Cl and ^{37}Cl 1
 (ii) 106 **and** 108 1
- (c) (nucleophilic) addition-elimination, penalise electrophilic ... not esterification 1



M3 for structure
 M4 for 3 arrows and lone pair
 (only allow for correct M3 or close)

M2 not allowed independent of M1,
 but allow M1 for correct attack on C^+ if M2 shown as independent first.

Total 8

Question 8

- (a) $\text{pH} = -\log[\text{H}^+]$ 1
 $K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]}$ or $[\text{H}^+] = [\text{A}^-]$ 1
 $[\text{H}^+] = \sqrt{1.74 \times 10^{-5} \times 0.15}$ (or 1.62×10^{-3}) 1
 $\text{pH} = 2.79$ (penalise 1 dp or more than 2dp once in the qu) 1
- (b) (i) Solution which resists change in pH /maintains pH 1
 despite the addition of (small amounts of) acid/base (or dilution) 1
- (ii) $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH}$ 1
 must show an equation full or ionic in which ethanoate ions are converted to ethanoic acid
- (c) (i) $[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$ if rearrangement incorrect, no further marks 1
 $= 1.74 \times 10^{-5} \times \frac{0.15}{0.10}$ 1
 (= 2.61×10^{-5})
 $\text{pH} = 4.58$ 1
- (ii) M1 moles H^+ added = $10 \times 10^{-3} \times 1.0 = 0.01$ 1
 M2 moles ethanoic acid after addition = $0.15 + 0.01 = 0.16$ 1
 M3 moles ethanoate ions after addition = $0.10 - 0.01 = 0.09$ 1
- M4 $[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 1.74 \times 10^{-5} \times \frac{0.16/V}{0.09/V}$ 1
 (= 3.09×10^{-5})
- M5 $\text{pH} = 4.51$ 1

The essential part of this calculation is addition/subtraction of 0.01 moles to gain marks M2 and M3. If both of these are missing, only mark M1 is available. Thereafter treat each mark independently, except if the expression in M4 is wrong, in which case both M4 and M5 are lost.

Total 15

alternative scheme for part (c)(i)

$$\text{pH} = \text{p}K_a - \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad 1$$

$$\text{p}K_a = 4.76 \quad 1$$

$$\text{pH} = (4.76 - \log \frac{0.15}{0.10}) = 4.58 \quad 1$$

alternative for penultimate mark of part (c)(ii)

$$\text{pH} = 4.76 - \log \frac{0.16}{0.09} \quad 1$$

GENERAL ORGANIC POINTS FOR MARKING CHM4

1. Curly arrows

These must show the movement of a pair of electrons, i.e.

from a bond or a lone pair

either to an atom (example 1) or to the space between two atoms (example 2)

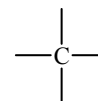
Example 1 correct	Example 2 correct

Curly arrows never start at an atom e.g. the right hand arrow in example 3 is wrong

Example 3 wrong

2. Incorrect Structures which are generally penalised once per paper:

a) Sticks, i.e. bonds without (hydrogen) atoms on their ends, e.g.



b) Incorrectly bonded functional groups e.g.

correct	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{HO}-\text{C}-\text{R} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{H} \\ \\ \text{OH} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{R} \\ \\ \text{H} \end{array}$
wrong	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{HO} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{OH}-\text{C}-\text{R} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{H} \\ \\ \text{OH} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{NH}_2-\text{C}-\text{R} \\ \\ \text{H} \end{array}$

Alkyl groups, however, can be written in several different ways

The following alkyl group arrangements are allowed as correct.:

CH ₃ —	H ₃ C—	—CH ₃	$\begin{array}{c} \text{CH}_3 \\ \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \end{array}$
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c) cyclohexane for benzene **penalised once per paper**

d) -NH₃⁺ or ⁺H₃N- penalised once per paper