

Mark Scheme (Results)

Summer 2012

GCE Chemistry (6CH04) Paper 01

General Principles of Chemistry I
Rates, Equilibria and Further Organic
Chemistry
(Including synoptic assessment)

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Summer 2012

Publications Code UA031863

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General Marking Guidance

- All candidates must receive the same treatment. Examiners must mark the first candidate in exactly the same way as they mark the last.
- Mark schemes should be applied positively. Candidates must be rewarded for what they have shown they can do rather than penalised for omissions.
- Examiners should mark according to the mark scheme not according to their perception of where the grade boundaries may lie.
- There is no ceiling on achievement. All marks on the mark scheme should be used appropriately.
- All the marks on the mark scheme are designed to be awarded. Examiners should always award full marks if deserved, i.e. if the answer matches the mark scheme. Examiners should also be prepared to award zero marks if the candidate's response is not worthy of credit according to the mark scheme.
- Where some judgement is required, mark schemes will provide the principles by which marks will be awarded and exemplification may be limited.
- When examiners are in doubt regarding the application of the mark scheme to a candidate's response, the team leader must be consulted.
- Crossed out work should be marked UNLESS the candidate has replaced it with an alternative response.
- Mark schemes will indicate within the table where, and which strands of QWC, are being assessed. Questions labelled with an **asterix (*)** are ones where the quality of your written communication will be assessed.

Using the Mark Scheme

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.

The mark scheme gives examiners:

- 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.

/ means that the responses are alternatives and either answer should receive full credit.

() 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.

Phrases/words in **bold** indicate that the meaning of the phrase or the actual word is **essential** to the answer.

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.

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.

Quality of Written Communication

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

- write legibly, with accurate use of spelling, grammar and punctuation in order to make the meaning clear
- select and use a form and style of writing appropriate to purpose and to complex subject matter
- organise information clearly and coherently, using specialist vocabulary when appropriate.

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.

Section A (multiple choice)

Question Number	Correct Answer	Reject	Mark
1	D		1
2	B		1
3 a	C		1
3 b	B		1
4	C		1
5	A		1
6 a	B		1
6 b	C		1
7	A		1
8 a	A		1
8 b	C		1
9	B		1
10	D		1
11 a	D		1
11 b	A		1
12 a	A		1
12 b	C		1
12 c	D		1
12 d	B		1
13	B		1
		Total for Section A	20 marks

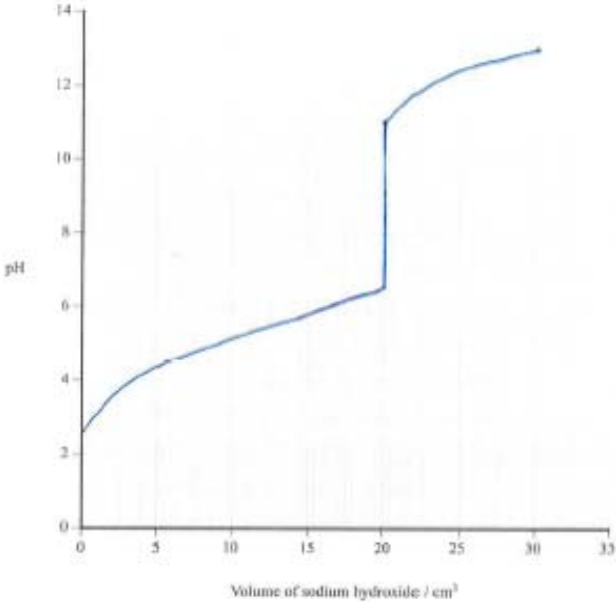
Section B

Question Number	Acceptable Answers	Reject	Mark
14 (a) (i)	$K_a = [\text{CH}_3\text{CO}_2^-] [\text{H}^+]/[\text{CH}_3\text{CO}_2\text{H}]$ OR $K_a = [\text{CH}_3\text{CO}_2^-] [\text{H}_3\text{O}^+]/[\text{CH}_3\text{CO}_2\text{H}]$ OR Use of $[\text{CH}_3\text{COO}^-]$ instead of $[\text{CH}_3\text{CO}_2^-]$ and $[\text{CH}_3\text{COOH}]$ instead of $[\text{CH}_3\text{CO}_2\text{H}]$ IGNORE state symbols even if wrong	Numerator as $[\text{H}^+]^2$ Expressions in terms of HA alone Round/curved brackets '()'' Any other carboxylic acid	1

Question Number	Acceptable Answers	Reject	Mark
14(a) (ii)	$1.7 \times 10^{-5} = [\text{H}^+]^2 / 0.5$ $[\text{H}^+] = \sqrt{1.7 \times 10^{-5} \times 0.5} / 2.915(476) \times 10^{-3}$ (1) $\text{pH} = (-\log[\text{H}^+]) = 2.53529$ OR = 2.54 OR = 2.5 (1) ALLOW TE for second mark from any hydrogen ion concentration as long as pH less than 7 Correct answer alone scores (2) ALLOW $\text{pH} = 2.53$ if $[\text{H}^+]$ is rounded to 2.92×10^{-3} IGNORE sf except 1	4.77 or 4.8 from using $\text{pH} = -\log K_a$ loses both marks	2

Question Number	Acceptable Answers	Reject	Mark
14(a) (iii)	20 (cm ³) IGNORE units OR 0.02 dm ³		1

Question Number	Acceptable Answers	Reject	Mark
14(a)(iv)	<p>Moles of excess NaOH = $10/1000 \times 0.50$ $= 5 \times 10^{-3}$ (1)</p> <p>So $[\text{NaOH}/\text{OH}^-] = 5 \times 10^{-3} \times 1000/50 =$ 0.10 mol dm^{-3} (1)</p> <p>EITHER</p> <p style="text-align: center;">Kw route:</p> <p>$[\text{H}^+] \times 0.1 = 1 \times 10^{-14}$ (1)</p> <p>So $\text{pH} = -\log 1 \times 10^{-14} / 0.1 = 13$ (1)</p> <p>OR</p> <p style="text-align: center;">pOH route:</p> <p>pOH = 1 (1) So pH = $(14 - 1) = 13$ (1)</p> <p>ALLOW TE throughout</p> <p>Correct final answer scores (4)</p>		4

Question Number	Acceptable Answers	Reject	Mark
<p>14(a)(v)</p>	<p>Starting at pH 2-3 AND finishing at pH between 12 and 13.7 inclusive (1)</p> <p>Vertical section at 20 cm³ (1)</p> <p>S-shaped curve, with gradual rise and vertical section within the pH range 5.5 and 11.5 and of 3 to 5 units in length (1)</p> <p>These are stand alone marks</p> 		<p>3</p>

Question Number	Acceptable Answers	Reject	Mark
14(b)(i)	<p>EITHER</p> <p>$[\text{base}] = K_a [\text{acid}]/[\text{H}^+]$ Or $[\text{H}^+] = (10^{-\text{pH}4.70}) = 1.995 \times 10^{-5}$ (1)</p> <p>$[\text{base}] = 1.7 \times 10^{-5} \times 1/(1.995 \times 10^{-5}) = 0.852$ (1)</p> <p>moles base = $0.852 \times 0.5 = 0.426$ (mol) (1)</p> <p>mass base = $0.426 \times 82 = 34.9$ g (1)</p> <p>IGNORE sf except 1</p> <p>Correct answer, with or without working (4)</p> <p>OR</p> <p>$\text{pH} = \text{p}K_a - \log[\text{acid}]/[\text{base}]$ $4.70 = 4.8 - \log [1/[\text{base}]]$</p> <p>$\text{Log}[1/[\text{base}]] = 0.1$ (1)</p> <p>$[\text{base}] = 0.794(328)$ (mol dm⁻³) (1)</p> <p>So in 500 cm³ Moles = $0.794 \times 0.5 = 0.397$ mol (1)</p> <p>Mass = $0.397 \times 82 = 32.554/32.6$ g (1)</p> <p>(ALLOW using pKa = 4.77)</p>		4

Question Number	Acceptable Answers	Reject	Mark
14(b)(ii)	<p>First mark Buffer has large amount/ excess/ reservoir of CH₃COOH (and CH₃COO⁻) (1)</p> <p>Second mark OH⁻ ions added react with CH₃COOH</p> <p>OR CH₃COOH + OH⁻ → CH₃COO⁻ + H₂O</p> <p>OR OH⁻ + H⁺ → H₂O and CH₃COOH → CH₃COO⁻ + H⁺</p> <p>OR Equations described in words (1)</p> <p>Third mark Ratio / values of [CH₃COOH] to [CH₃COO⁻] remains (almost) unchanged (1)</p> <p>IGNORE concentration of hydrogen ions remains constant</p> <p>ALLOW answers in terms of HA and A⁻</p>		3

Question Number	Acceptable Answers	Reject	Mark
15(a)	2,6-dimethylhept-5-enal (2) Either part scores (1) e.g. 2,6-dimethyl (1) hept-5-enal (1) IGNORE missing/misplaced/misused hyphens or commas ALLOW ene for en ALLOW methy or methly for methyl		2

Question Number	Acceptable Answers	Reject	Mark
15(b)(i)	$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ (1) OR $\text{CH}_3\text{C}(\text{CH}_3)\text{CHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ OR $\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{HCH}_2\text{OH}$ ALLOW displayed or skeletal formulae $\text{K}_2\text{Cr}_2\text{O}_7/\text{Na}_2\text{Cr}_2\text{O}_7/\text{name}$ (oxidation state must be correct if given (VI)) (1) This is a stand alone mark $\text{H}_2\text{SO}_4/\text{name}$ (ignore any references to concentration) (1) ALLOW H^+ and $\text{Cr}_2\text{O}_7^{2-}$ (2) 'Acidified dichromate' (1)	$\text{C}_9\text{H}_{18}\text{O}$ KMnO_4 (0) for last 2 marks HCl (0) for 3 rd mark	3

Question Number	Acceptable Answers	Reject	Mark
15(b)(ii)	(Steam) distil off melonal (as it forms) Allow add a limited amount of oxidizing agent/excess alcohol/excess X (1) To prevent further oxidation/To prevent carboxylic acid forming (1) Stand alone marks		2

Question Number	Acceptable Answers	Reject	Mark									
15(c)	<table border="1"> <thead> <tr> <th>Wavenumber range / cm^{-1}</th> <th>Bond</th> <th>Functional group present in melonal</th> </tr> </thead> <tbody> <tr> <td>1740 – 1720 OR 2900 – 2820 / 2775 – 2700</td> <td>C=O C-H</td> <td>(saturated) Aldehyde/CHO</td> </tr> <tr> <td>1669 – 1645 OR 3095 – 3010</td> <td>C=C C-H</td> <td>Alkene ALLOW 'carbon to carbon double bond'</td> </tr> </tbody> </table> <p>ALLOW any single value or range within the ranges above</p> <p>ALLOW one mark if both wavenumber ranges and bond columns are correct but neither bond identified</p>	Wavenumber range / cm^{-1}	Bond	Functional group present in melonal	1740 – 1720 OR 2900 – 2820 / 2775 – 2700	C=O C-H	(saturated) Aldehyde/CHO	1669 – 1645 OR 3095 – 3010	C=C C-H	Alkene ALLOW 'carbon to carbon double bond'	(1) (1) Just carbonyl Just C=C in 3 rd column	2
Wavenumber range / cm^{-1}	Bond	Functional group present in melonal										
1740 – 1720 OR 2900 – 2820 / 2775 – 2700	C=O C-H	(saturated) Aldehyde/CHO										
1669 – 1645 OR 3095 – 3010	C=C C-H	Alkene ALLOW 'carbon to carbon double bond'										

Question Number	Acceptable Answers	Reject	Mark
15(d)	$\text{C}_3\text{H}_5\text{O}^+$ / $\text{CH}_3\text{CHCHO}^+$ (1) $\text{C}_6\text{H}_{11}^+$ (1) [ALLOW Structural, skeletal or displayed formulae] Penalise omission of + charge once only ALLOW any order of atoms if correct totals.	C_4H_9^+ $\text{C}_5\text{H}_7\text{O}^+$	2

Question Number	Acceptable Answers	Reject	Mark
15(e)(i)		Circle around any other additional atoms	1

Question Number	Acceptable Answers	Reject	Mark
15(e)(ii)		Circle around any other additional atoms	1

Question Number	Acceptable Answers	Reject	Mark
15(f)(i)	<p>Arrow from anywhere on the cyanide ion to the carbon of the carbonyl. Arrow to the O must come from the carbonyl bond (1)</p> <p>Formula of intermediate (1)</p> <p>Arrow from oxygen to H and from H-CN bond to CN (1)</p> <p>ALLOW arrow from O⁻ to H⁺ or to H₂O</p>	Starting from HCN/ CN ^{δ-} Single headed arrows	3

Question Number	Acceptable Answers	Reject	Mark
15(f)(ii)	<p>These marks are stand alone EITHER No</p> <p>First mark: Reaction site/carbonyl/aldehyde/molecule is planar (1)</p> <p>Second mark: Attack (equally likely) from both sides OR Attack (equally likely) from above and below (1)</p> <p>Third mark: (gives) racemic mixture/(gives) equal amounts of each isomer/(gives) equal amounts of each enantiomer (1) OR Yes Melonal has a chiral carbon atom (1) Correct identification of chiral centre (1) This chiral centre unaffected by reaction (1)</p>	<p>attack on a (planar) carbocation OR attack on a (planar) intermediate OR S_N1 OR S_N2 OR "planar product"</p> <p>Any/either direction or any/either angle</p>	3

Question Number	Correct Answer	Reject	Mark
16 (a) (i)	Sodium thiosulfate/ $\text{Na}_2\text{S}_2\text{O}_3$ ALLOW $\text{S}_2\text{O}_3^{2-}$ or thiosulfate ions	Just thiosulfate	1

Question Number	Acceptable Answers	Reject	Mark
16 (a) (ii)	Add (excess) sodium hydrogencarbonate/ NaHCO_3 (1) To neutralize/remove/react with acid (catalyst) (1) Cool in ice (water) with no reference to neutralization – allow 1 mark but ignore if either of first two marks awarded	$\text{NaOH}/$ sodium hydroxide/ alkali just cold water	2

Question Number	Acceptable Answers	Reject	Mark														
16 (b) (i)	Suitable graph and scale (1) Points plotted and line of best fit (1) 0 order (with respect to iodine) (1)		3														
	<p>The graph shows a linear relationship between the concentration of aqueous iodine and time. The y-axis represents the concentration of $\text{I}_2(\text{aq})$ in $\text{mol dm}^{-3} \times 10^4$, ranging from 8.5 to 9.9. The x-axis represents time in minutes, ranging from 0 to 30. Six data points are plotted, and a straight line of best fit is drawn through them, indicating a zero-order reaction with respect to iodine.</p> <table border="1"> <caption>Data points from the graph</caption> <thead> <tr> <th>Time / minutes</th> <th>$[\text{I}_2(\text{aq})] / \text{mol dm}^{-3} \times 10^4$</th> </tr> </thead> <tbody> <tr><td>5</td><td>9.75</td></tr> <tr><td>10</td><td>9.5</td></tr> <tr><td>15</td><td>9.25</td></tr> <tr><td>20</td><td>9.0</td></tr> <tr><td>25</td><td>8.75</td></tr> <tr><td>30</td><td>8.5</td></tr> </tbody> </table>	Time / minutes	$[\text{I}_2(\text{aq})] / \text{mol dm}^{-3} \times 10^4$	5	9.75	10	9.5	15	9.25	20	9.0	25	8.75	30	8.5		
Time / minutes	$[\text{I}_2(\text{aq})] / \text{mol dm}^{-3} \times 10^4$																
5	9.75																
10	9.5																
15	9.25																
20	9.0																
25	8.75																
30	8.5																

Question Number	Acceptable Answers	Reject	Mark
16(b)(ii)	Graph is a straight line/Gradient is constant (1) Rate stays constant (as iodine used up)/ Concentration has no effect on rate (1) Stand alone marks	Half life is constant	2

Question Number	Acceptable Answers	Reject	Mark
16(c)	Colorimetry/use of pH meter/conductivity/titrate with AgNO_3 /titrate with alkali (to monitor change in $[\text{H}^+]$)	C olorimetry Use of starch/ Iodine clock reaction	1

Question Number	Correct Answer	Reject	Mark
17 (a) (i)	Methyl propanoate ALLOW methy or methly for methyl		1

Question Number	Acceptable Answers	Reject	Mark
17(a) (ii)	Toxic (steamy/misty) fumes/ toxic HCl(gas)/corrosive HCl(gas)/toxic propanoyl chloride/lachrymatory propanoyl chloride (1) So use in a fume cupboard (1) OR Corrosive Propanoyl chloride is (1) So wear gloves when handling (1)	HCl(aq)/hydrochloric acid Just harmful/irritant Just harmful/irritant	2

Question Number	Acceptable Answers	Reject	Mark
17(b)	Table 0.31, 0.16, 1.41 all 3 scores 2, 2 out of 3 scores 1, 1 or 0 out of 3 scores 0 (2) $K_c = \frac{(0.21/V) \times (1.41/V)}{(0.16/V) \times (0.31/V)}$ $K_c = 5.969758$ $K_c = 5.97$ (1) IGNORE sf except 1 IGNORE any units ALLOW TE from incorrect values in table.		3

TOTAL FOR SECTION B = 52 MARKS

Question Number	Correct Answer	Reject	Mark
18(a)	<p>First mark Enthalpy change when 1 mol of gaseous ions (1)</p> <p>ALLOW energy change/heat change/energy evolved/released/ given out/exothermic</p> <p>Second mark Is dissolved/hydrated/solvated such that further dilution causes no further heat change OR Is dissolved to produce an infinitely dilute solution/in excess water (1)</p> <p>ALLOW Is dissolved to produce a solution of 1.0 mol dm⁻³</p>	<p>Energy required or energy taken in</p> <p>Atoms or molecules (0)</p> <p>1 mol of water</p>	2

Question Number	Acceptable Answers	Reject	Mark
18(b) (i)	K ⁺ (aq) (+) F ⁻ (aq)	K ⁺ F ⁻ (aq)	1

Question Number	Acceptable Answers	Reject	Mark
18(b) (ii)	$\Delta H_{\text{sol}} = -\Delta H_1 + \Delta H_2$ OR $\Delta H_{\text{sol}} = \Delta H_2 - \Delta H_1$		1

Question Number	Acceptable Answers	Reject	Mark
18(b) (iii)	(Standard) Lattice(enthalpy/energy/ ΔH)	LE/Lat - Lattice	1

Question Number	Acceptable Answers	Reject	Mark
18(b) (iv)	<p>First mark Selection of (-)817 rather than (-)807 (1)</p> <p>Second mark $\Delta H_{\text{sol}} = 817 - 805 = (+)12 \text{ (kJ mol}^{-1}\text{)}$ (1)</p> <p>Just (+)12 (kJ mol⁻¹) (2)</p> <p>ALLOW TE for second mark e.g. for 807 gives (+) 2 (kJ mol⁻¹)</p> <p>ALLOW TE from incorrect b(ii)</p>	-12 (max 1)	2

Question Number	Acceptable Answers	Reject	Mark
18(c) (i)	<p>EITHER No change/no measurable change in temperature</p> <p>OR (Very small) decrease in temperature (1)</p> <p>Thermometer not sensitive/precise enough/precision of thermometer is + or - 0.5 °C/graduations too large (1)</p> <p>Amount of energy taken in is small /ΔH_{sol} is small/mass of sodium chloride is small/slightly endothermic (1)</p>	<p>Any reference to temp increase /exothermic</p> <p>Just accuracy +/- 1 °C</p>	3

Question Number	Acceptable Answers	Reject	Mark
* 18(c) (ii)	<p>(The reaction is endothermic so)</p> <p>Entropy(change) of surroundings decreases</p> <p>OR</p> <p>ΔS_{sur} is negative</p> <p>OR</p> <p>$-\Delta H/T$ is negative (1)</p> <p>But entropy (change)of system increases (as there is an increase in disorder)</p> <p>OR</p> <p>ΔS_{sys} is positive (1)</p> <p>Increase in entropy of system outweighs/greater than decrease in entropy of surroundings / value for entropy change of system is greater than entropy change of surroundings (1)</p> <p>Total entropy (change) is positive (1)</p> <p>All marks are stand alone</p>	<p>S_{sur} is negative</p> <p>S_{sys} is positive</p>	4

Question Number	Acceptable Answers	Reject	Mark
* 18(d)	<p>Any four from:</p> <p>The difference between Born Haber and theoretical LE is greater for LiI than for LiCl (1)</p> <p>(845 and 848 =) 3 for LiCl whereas (738 and 759 =) 21 for LiI (1)</p> <p>Iodide ion is larger than chloride ion/lower charge density on iodide ion (1)</p> <p>The iodide ion is more likely (than the chloride ion) to be polarized (by lithium ion) (1)</p> <p>LiI likely to have more covalent character than LiCl (1)</p>	<p>Reject values with +</p> <p>Iodine/Chlorine atoms or molecules</p> <p>Iodine/Chlorine atoms or molecules</p>	4

TOTAL FOR SECTION C = 18 MARKS

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Order Code UA031863 Summer 2012

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