

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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# **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 <u>meaning</u> 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	Correct Answer	Reject	Mark
Number			
1	D		1
2	В		1
3 a	С		1
3 b	В		1
4	С		1
5	A		1
6 a	В		1
6 b	С		1
7	A		1
8 a	A		1
8 b	С		1
9	В		1
10	D		1
11 a	D		1
11 b	A		1
12 a	A		1
12 b	С		1
12 c	D		1
12 d	В		1
13	В		1
		Total for Section A	20 marks

## Section B

Question	Acceptable Answers	Reject	Mark
Number			
14	$Ka = [CH_3CO_2^{-}] [H^+]/[CH_3CO_2H]$	Numerator as	1
(a)(i)	OR	$[H^+]^2$	
	$Ka = [CH_3CO_2^{-}] [H_3O^{+}]/[CH_3CO_2H]$	Expressions	
	OR	in terms of	
	Use of $[CH_3COO^-]$ instead of $[CH_3CO_2^-]$	HA alone	
	and [CH <sub>3</sub> COOH] instead of [CH <sub>3</sub> CO <sub>2</sub> H]	Round/curved	
		brackets `()'	
	IGNORE state symbols even if wrong	Any other	
		carboxylic	
		acid	

Question Number	Acceptable Answers	Reject	Mark
14(a)(ii)	$\begin{array}{c} 1.7 \times 10^{-5} = [\text{H}^+]^2 / \ 0.5 \\ [\text{H}^+] = \sqrt{1.7 \times 10^{-5} \times 0.5} / \ 2.915(476) \times 10^{-3} \\ & 10^{-3} \end{array}$	4.77 or 4.8 from using pH = -log Ka loses both	2
	pH = (-log[H <sup>+</sup> ]) = 2.53529 OR = 2.54 OB	marks	
	= 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 pH = 2.53 if [H <sup>+</sup> ] is rounded to 2.92 x $10^{-3}$		
	IGNORE sf except 1		

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

Question Number	Acceptable Answers		Reject	Mark
14(a)(iv)	Moles of excess NaOH = $10/1000 \times 0^{-3}$	).50 (1)		4
	So $[NaOH/OH^{-}] = 5 \times 10^{-3} \times 1000/50$ 0.10 mol dm <sup>-3</sup>	= (1)		
	EITHER Kw route:			
	$[H^+] \times 0.1 = 1 \times 10^{-14}$	(1)		
	So pH = - log 1 x 10 <sup>-14</sup> / 0.1 = 13	(1)		
	OR pOH route:			
	pOH = 1 So pH = (14 - 1) = 13	(1) (1)		
	ALLOW TE throughout			
	Correct final answer scores (4)			

Question Number	Acceptable Answers	Reject	Mark
14(a)(v)	Starting at pH 2-3 AND finishing at pH between 12 and 13.7 inclusive (1	.)	3
	Vertical section at 20 cm <sup>3</sup> (1 S-shaped curve, with gradual rise and vertical section within the pH range 5.5 ar	L)	
	These are stand alone marks		
	2- 0- 0- 0- 0- 0- 0- 0- 0- 0- 0- 0- 0- 0-	5	

Question Number	Acceptable Answers		Reject	Mark
14(b)(i)	EITHER			4
	[base] = Ka [acid]/[H <sup>+</sup> ] Or			
	$[H+] = (10^{-pH4.70}) = 1.995 \times 10^{-5}$	(1)		
	[base] = 1.7 x 10 <sup>-5</sup> x 1/(1.995 x 10 <sup>-5</sup> ) = 0.85	2 (1)		
	moles base = $0.852 \times 0.5 = 0.426$ (mol)	(1)		
	mass base = 0.426 x 82 = 34.9 g	(1)		
	IGNORE sf except 1			
	Correct answer, with or without working (4)			
	OR			
	pH = pKa - log[acid]/[base]			
	4.70 = 4.8 - log [1/[base]]			
	Log[1/[base]] = 0.1	(1)		
	$[base] = 0.794(328) \pmod{4^{-3}}$	(1)		
	So in 500 cm <sup>3</sup> Moles = 0.794 x 0.5 = 0.397 mol	(1)		
	Mass = 0.397 x 82 = 32.554/32.6 g	(1)		
	(ALLOW using pKa = 4.77)			

Question Number	Acceptable Answers	Reject	Mark
14(b)(ii)	First markBuffer has large amount/ excess/ reservoir of CH3COOH (and CH3COO <sup>-</sup> )(1)		3
	Second mark $OH^-$ ions added react with $CH_3COOH$		
	OR CH <sub>3</sub> COOH + OH <sup>-</sup> $\rightarrow$ CH <sub>3</sub> COO <sup>-</sup> + H <sub>2</sub> O		
	$ \begin{array}{l} \text{OR} \\ \text{OH}^- + \ \text{H}^+ \rightarrow \text{H}_2\text{O} \ \textbf{and} \ \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- \\ & + \ \text{H}^+ \end{array} $		
	OR Equations described in words (1)		
	Third markRatio / values of [CH3COOH] to [CH3COO <sup>-</sup> ]remains (almost) unchanged(1)		
	IGNORE concentration of hydrogen ions remains constant		
	ALLOW answers in terms of HA and A <sup>-</sup>		

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

Question Number	Acceptable Answers		Reject	Mark
15(b)(i)	$CH_{3}C(CH_{3})=CHCH_{2}CH_{2}CH(CH_{3})CH_{2}OH OR CH_{3}C(CH_{3})CHCH_{2}CH_{2}CH(CH_{3})CH_{2}OH OR CH_{3}C(CH_{3})=CHCH_{2}CH_{2}C (CH_{3}) HCH_{2}OH ALLOW displayed or skeletal formulae$	(1)	C <sub>9</sub> H <sub>18</sub> O	3
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /name (oxidation state must be correct if given (VI)) This is a stand alone mark	(1)	KMnO₄ (0) for last 2 marks HCl (0) for	
	$H_2SO_4$ /name (ignore any references to concentration)	(1)	3 <sup>rd</sup> mark	
	ALLOW H <sup>+</sup> and $Cr_2O_7^{2-}$	(2)		
	'Acidified dichromate'	(1)		

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

Question Number	Acceptable Answers				Reject	Mark
15(c)			-			2
	Wavenumber range / cm <sup>-1</sup>	Bond	Functional group present in melonal			
	1740 - 1720 OR 2900 - 2820 /	C=0	(saturated) Aldehyde/CHO	(1)	Just carbonyl	
	2775 – 2700	C-H				
	1669 - 1645 OR 3095 - 3010	C=C C-H	Alkene ALLOW `carbon to carbon double bond'	(1)	Just C=C in 3 <sup>rd</sup> column	
	ALLOW any sing ranges above ALLOW one mat ranges and bon neither bond ide	gle value rk if bot d colum entified	e or range within h wavenumber ns are correct bu	the Jt		

Question Number	Acceptable Answers	Reject	Mark
15(d)	$\begin{array}{ccc} C_{3}H_{5}O^{+}/CH_{3}CHCHO^{+} & \textbf{(1)}\\ C_{6}H_{11}^{+} & \textbf{(1)}\\ [ALLOW Structural, skeletal or displayed formulae] & \\ Penalise omission of + charge once only \\ ALLOW any order of atoms if correct totals. \end{array}$	$C_4H_9^+$ $C_5H_7O^+$	2

Question Number	Acceptable Answers	Reject	Mark
15(e)(i)	$ \begin{array}{ c c c c c } H & H & H & H & H & H & H & H & H & H $	Circle around any other additional atoms	1

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

Question Number	Acceptable Answers	Reject	Mark
15(f)(i)	$ \begin{array}{c} H \\ R \\ R \\ \hline () \\ CN $		3
	Arrow from anywhere on the cyanide ion to the carbon of the carbonyl. Arrow to the O must come from the carbonyl bond(1)Formula of intermediate(1)	Starting from HCN/ CN <sup>∂-</sup>	
	Arrow from oxygen to H and from H-CN bond to CN(1)ALLOW arrow from $O^-$ to $H^+$ or to $H_2O$	Single headed arrows	

Question	Acceptable Answers	Reject	Mark
15(f)(ii)	These marks are stand alone EITHER No		3
	First mark: Reaction site/carbonyl/aldehyde/molecule is planar (1)	attack on a (planar) carbocation OR attack on a (planar) intermediate OR S <sub>N</sub> 1 OR S <sub>N</sub> 2 OR S <sub>N</sub> 2 OR "planar product"	
	Second mark: Attack (equally likely) from both sides OR Attack (equally likely) from above and below (1)	Any/either direction or any/either angle	
	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		

Question Number	Correct Answer	Reject	Mark
16	Sodium thiosulfate/Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Just	1
(a)(i)	ALLOW S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> or thiosulfate ions	thiosulfate	

Question Number	Acceptable Answers	Reject	Mark
16(a)(ii)	Add (excess) sodium hydrogencarbonate/ NaHCO $_3$ (1)	NaOH/ sodium hydroxide/ alkali	2
	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	just cold water	

Acceptable Answers	Reject	Mark
Suitable graph and scale (1)		3
Points plotted and line of best fit (1)		
0 order (with respect to iodine) (1)		
$\begin{cases} 9 \\ 4 \\ 6 \\ 6 \\ 6 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ $		
	Acceptable Answers Suitable graph and scale (1) Points plotted and line of best fit (1) 0 order (with respect to iodine) (1)	Acceptable Answers Suitable graph and scale (1) Points plotted and line of best fit (1) 0 order (with respect to iodine) (1)

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 <sub>3</sub> /titrate with alkali (to monitor change in [H <sup>+</sup> ])	C <b>a</b> lorimetry Use of starch/ Iodine clock reaction	1

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

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

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

### TOTAL FOR SECTION B = 52 MARKS

Question Number	Correct Answer	Reject	Mark
18(a)	First markEnthalpy change when 1 mol of gaseousions(1)ALLOW energy change/heatchange/energy evolved/released/ given	Energy required or energy taken in Atoms or molecules (0)	2
	out/exothermic 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)	1 mol of water	
	ALLOW Is dissolved to produce a solution of 1.0 mol dm <sup>-3</sup>		

Question Number	Acceptable Answers	Reject	Mark
18(b)(i)	K <sup>+</sup> (aq) (+) F <sup>-</sup> (aq)	K <sup>+</sup> F <sup>-</sup> (aq)	1

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

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

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

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

Question Number	Acceptable Answers		Reject	Mark
*18(c)(ii)	(The reaction is endothermic so)			4
	Entropy(change) of surroundings decreases OR ΔS <sub>sur</sub> is negative OR		S <sub>sur</sub> is negative	
	$-\Delta H/T$ is negative	(1)		
	But entropy (change)of system increases (as there is an increase in disorder) OR $\Delta S_{sys}$ is positive	(1)	S <sub>sys</sub> is positive	
	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 surrounding	r js <b>(1)</b>		
	Total entropy (change) is positive	(1)		
	All marks are stand alone			

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

## TOTAL FOR SECTION C = 18 MARKS

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