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Mark Scheme (Results)

Summer 2013

GCE Chemistry 6CH04/01R
General Principles of Chemistry I

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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. The strands are as follows:

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

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

Question Number	Correct Answer	Reject	Mark
2	D		1

Question Number	Correct Answer	Reject	Mark
3 (a)	A		1

Question Number	Correct Answer	Reject	Mark
(b)	D		1

Question Number	Correct Answer	Reject	Mark
(c)	A		1

Question Number	Correct Answer	Reject	Mark
(d)	D		1

Question Number	Correct Answer	Reject	Mark
4(a)	B		1

Question Number	Correct Answer	Reject	Mark
(b)	C		1

Question Number	Correct Answer	Reject	Mark
(c)	C		1

Question Number	Correct Answer	Reject	Mark
(d)	B		1

Question Number	Correct Answer	Reject	Mark
5(a)	D		1

Question Number	Correct Answer	Reject	Mark
(b)	C		1

Question Number	Correct Answer	Reject	Mark
(c)	C		1

Question Number	Correct Answer	Reject	Mark
(d)	C		1

Question Number	Correct Answer	Reject	Mark
(e)	D		1

Question Number	Correct Answer	Reject	Mark
6	A		1

Question Number	Correct Answer	Reject	Mark
7	C		1

Question Number	Correct Answer	Reject	Mark
8	C		1

Question Number	Correct Answer	Reject	Mark
9	B		1

Question Number	Correct Answer	Reject	Mark
10	B		1

SECTION A = 20 MARKS

Section B

Question Number	Acceptable Answers	Reject	Mark
* 11(a)	(A green solution) forms a yellow / orange / brown (solution) ALLOW reddish-brown (1) A grey / black precipitate ALLOW silver ppt ALLOW solid / crystals for precipitate (1)	 Red 'Green(ish)' with any other colour Silver mirror silver compound	2

Question Number	Acceptable Answers	Reject	Mark
11(b)(i)	0.05(00) (mol dm^{-3})		1

Question Number	Acceptable Answers	Reject	Mark
11(b)(ii)	Amount of silver ion in 10 cm^3 = amount of thiocyanate = $\frac{5.6 \times 0.0200}{1000}$ = $0.000112/1.12 \times 10^{-4}$ (mol) (1) So concentration of silver ion = $0.000112 \times \frac{1000}{10}$ = $0.0112/1.12 \times 10^{-2}$ (mol dm^{-3}) (1)		2

Question Number	Acceptable Answers	Reject	Mark
11(b)(iii)	$0.0112/1.12 \times 10^{-2}$ (mol dm^{-3}) Accept TE = answer to (ii)		1

Question Number	Acceptable Answers	Reject	Mark
11(b)(iv)	$0.0500 - 0.0112 = 0.0388/3.88 \times 10^{-2}$ (mol dm^{-3}) Accept TE = 0.05 - answer to (iii) Accept answer to (i) – answer to (iii)		1

Question Number	Acceptable Answers	Reject	Mark
11(b)(v)	$K_c = \frac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)]\,[Ag^{+}(aq)]}$ ALLOW $K_c = \frac{[Fe^{3+}]}{[Fe^{2+}]\,[Ag^{+}]}$ (1) $= \frac{0.0388}{0.0112^2}$ $= 309.311 = 309\ dm^3\ mol^{-1}$ Value (1) Unit (any order) (1) Three SF (1) Accept TE from (iii) and (iv): (use of 0.1 from (i) gives 708 $dm^3\ mol^{-1}$) If [Ag] is included in the numerator and taken as =$[Fe^{3+}(aq)]$, then allow unit and SF marks ONLY, but must either state 'no units' or show working	[Ag] in numerator	4

Question Number	Acceptable Answers	Reject	Mark
11(c)(i)	$\Delta S^{\ominus}_{total} = 8.31 \times \ln 309$ $= +47.6(4) / +47.6(5) J\ mol^{-1}\ K^{-1}$ OR $= 8.31 \times \ln 309.311 = +47.6(5)\ J\ mol^{-1}\ K^{-1}$ Accept TE : 8.31 x ln(answer from b(v)) Value (1) Sign and Unit (any order) (1) IGNORE sf except 1		2

Question Number	Acceptable Answers	Reject	Mark
11(c)(ii)	First Mark: One of the products is a solid OR Two moles going to two moles but one of them is a solid OR Two moles of solution react to form one mole of solution / liquid and one mole of solid (1) Second Mark (Hence) RHS more ordered / LHS less ordered (1)		2

Question Number	Acceptable Answers	Reject	Mark
11(c)(iii)	$\Delta S^{\ominus}_{surroundings} = \Delta S^{\ominus}_{total} - \Delta S^{\ominus}_{system}$ = +47.6 – (-208.3) = (+)255.9 (J mol^{-1} K^{-1}) Accept TE on c(i) IGNORE sf except 1		1

Question Number	Acceptable Answers	Reject	Mark
11(c)(iv)	Because $\Delta S^{\ominus}_{surroundings} = \frac{-\Delta H^{\ominus}}{T}$ (1) ΔH= -298 x 255.9 = -76258 (J mol^{-1}) = -76.258 (kJ mol^{-1}) (1) Units if given must be correct Correct answer with or without working scores 2 marks IGNORE SF except 1 As T increases $\Delta S^{\ominus}_{surroundings}$ becomes less positive / decreases therefore ΔS_{total} becomes less positive / decreases ALLOW more negative for less positive (1)	$\Delta S^{\ominus}_{total} = \frac{-\Delta H^{\ominus}}{T}$	3

Question Number	Acceptable Answers	Reject	Mark
11* (d)	No change in the titre ALLOW No significant change Stand alone mark (1) (though silver solid was removed the equilibrium constant remains the same so) the equilibrium concentration(s) would remain the same (1) Second mark dependent on first IGNORE references to temperature		2

Total for Question 11 = 21 Marks

Question Number	Acceptable Answers	Reject	Mark
12(a)(i)	Aldehydes often contain (carboxylic) acid formed by oxidation (by the oxygen in air)		1

Question Number	Acceptable Answers	Reject	Mark
12(a)(ii)	A larger volume of sodium carbonate solution is neutralized / a larger volume of carbon dioxide forms / faster reaction / more effervescence / more vigorous ALLOW reverse argument for impure aldehyde	(The old stock of) aldehyde does not react	1

Question Number	Acceptable Answers	Reject	Mark
12(a)(iii)	$Na_2CO_3(aq) + 2C_3H_7COOH(aq) \rightarrow$ $2C_3H_7COO^{(-)}Na^{(+)}(aq) + CO_2(g) + H_2O(l)$ Correct balanced equation (1) Correct state symbols on correct species (1) ALLOW $H_2O(aq)$ $C_3H_7COO^{(-)}Na^{(+)}(s)$ $C_3H_7COOH(l)$	$NaCO_3$	2

Question Number	Acceptable Answers	Reject	Mark
12(a)*(iv)	3300 -2500 (cm^{-1}) AND O-H (stretching) (1) 1725 – 1700 (cm^{-1}) AND C=O (stretching) (1) ALLOW single numbers or ranges within these ranges ALLOW 1300-1250 (cm^{-1}) AND C-O in COOH Very broad (O-H) due to hydrogen bonding (1)	COOH (group) COOH (group) Hydrogen Bonding in C=O	3

Question Number	Acceptable Answers	Reject	Mark
12(a)(v)	First mark (stand alone) 4 peaks OR 4 hydrogen environments ALLOW 4 chemical shifts (1) Second and Third Marks Splitting pattern: ($CH_3CH_2CH_2COO\underline{H}$) singlet /1 line ($CH_3CH_2C\underline{H_2}COOH$) triplet / three lines ($CH_3C\underline{H_2}CH_2COOH$) sextuplet / sextet / six lines ($C\underline{H_3}CH_2CH_2COOH$) triplet / three lines All four correct (2) any three (1) ALLOW No splits, 2 splits, five splits, 2 splits scores 2 1,3,6,3 'splits' scores 1 mark	 1 split 3 splits 6 splits 3 splits	3

Question Number	Acceptable Answers	Reject	Mark
12(b)	Start pH at 2.9 ALLOW 2—4 (1) Initial sharp rise to buffer region then vertical section at 25 cm^3 ALLOW Gradual rise to vertical section at 25 cm^3 (1) Vertical within pH range 6-11 and 2.5-4 units long (1) End pH value in range 12-13 (1)	 Horizontal from start deviation from vertical maximum before final pH Graph ending before 50cm^3	4

Question Number	Acceptable Answers	Reject	Mark
12(c)(i)	White / steamy / misty fumes ALLOW 'gas' for fumes IGNORE correct indicator test on product	White smoke Effervescence Just 'fumes' Just 'gas'	1

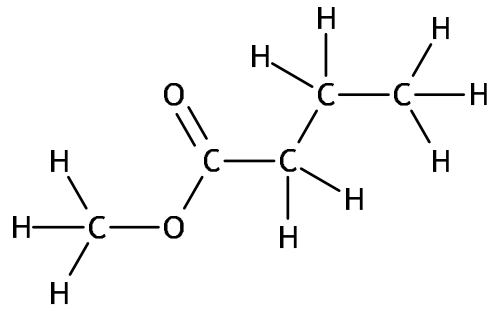
Question Number	Acceptable Answers	Reject	Mark
12(c)(ii)	$CH_3CH_2CH_2COCl$ (1) ALLOW displayed formula butanoyl chloride (1) ALLOW Butanyl chloride No TE on incorrect structure	C_3H_7COCL Butyl Chloride Buthyl Chloride	2

Question Number	Acceptable Answers	Reject	Mark
12(d)(i)	Butan-1-ol OR $CH_3CH_2CH_2CH_2OH$ If 2 answers are given both must be correct	Butanol Butanal C_4H_9OH	1

Question Number	Acceptable Answers	Reject	Mark
12(d)(ii)	(Dry) Ethoxyethane / diethylether / Ether OR $C_2H_5OC_2H_5$ / $CH_3CH_2OCH_2CH_3$ If 2 answers are given they must both be correct		1

Question Number	Acceptable Answers	Reject	Mark
12(d)(iii)	The responses are in pairs: a type (1) and an associated justification (1) Reduction (of butanoic acid) (1) By addition of hydrogen / loss of oxygen (1) OR Oxidation of lithium tetrahydroidaluminate / aluminium hydride / $LiAlH_4$ (1) By addition of oxygen (1) OR (Nucleophilic) addition (1) of hydride / H^- (1) OR Redox (1) Because butanoic acid has been reduced AND $LiAlH_4$ has been oxidised (1)	Any substitution Electrophilic addition	2

Question Number	Acceptable Answers	Reject	Mark
12(e)(i)	(Concentrated / dilute) sulfuric / hydrochloric acid ALLOW any strong acid ALLOW 'acid (catalyst)' (1) (heat or boil under) reflux ALLOW Heat / warm (1) Elevated temp$\leq 65^0$C	Just 'catalyst' Just H^+ Just 'boil' Just 'distil' High temperature Increased concentration	2

Question Number	Acceptable Answers	Reject	Mark
12(e)(ii)	 All bonds must be shown except ALLOW CH_3 at either end of molecule.	Omitted Hydrogen / sticks	1

Question Number	Acceptable Answers	Reject	Mark
12(e)(iii)	Butanoyl chloride / $CH_3CH_2CH_2COCl$ ALLOW Butanyl chloride OR Butanoic anhydride / ($CH_3CH_2CH_2CO)_2O$ OR Specified alkyl butanoate (not methyl butanoate) If name and structure are both given they must both be correct	Butyl Chloride Buthyl Chloride	1

Question Number	Acceptable Answers	Reject	Mark
12(e)(iv)	Advantage marks are dependent on correct reagent (or near miss e.g. propanoyl chloride) in (iii). No TE on random answer to (iii) eg H_2SO_4 Advantages – any two from: Higher yield / goes to completion/ not an equilibrium reaction / not reversible No heat / no refluxing / less energy needed No catalyst needed / faster By-product is a gas (so easier to separate) (2) Disadvantage (marked independently of (e)(iii)) any one of: (Acyl chloride is) more expensive / corrosive IGNORE Acyl chloride is toxic / hazardous / harmful / difficult to store OR toxic /corrosive and HCl /gas / fumes evolved IGNORE harmful/ hazardous/ dangerous OR has lower atom economy (1)	Good yield	3

Total for Question 12 = 28 Marks

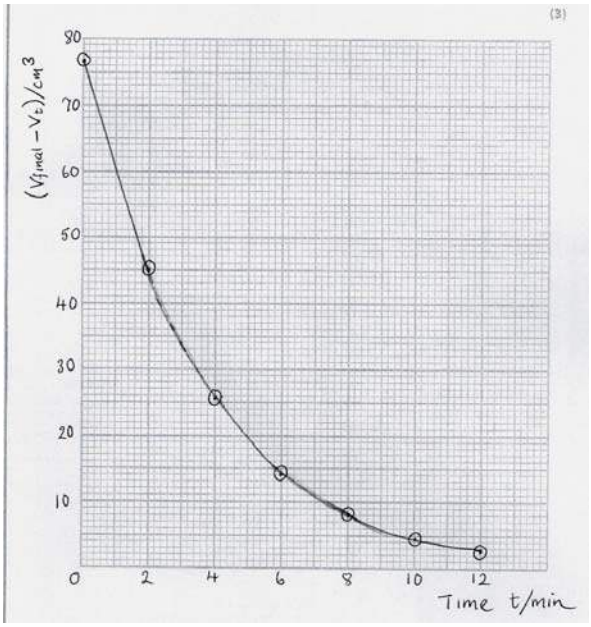
Total for Section B = 49 Marks

Section C

Question Number	Acceptable Answers	Reject	Mark
13(a)(i)	Mass of bromobutane = 0.6 x 1.276 (=0.7656 (g)) (1) Amount of bromobutane = $\frac{0.6 \times 1.276}{137.0}$ = 5.5883×10^{-3} = 5.59×10^{-3} / 0.00559 (mol) OR Amount of bromobutane = $\frac{0.6 \times 1.276}{136.9}$ = 5.5924×10^{-3} = 5.59×10^{-3} / 0.00559 (mol) TE on incorrect mass ALLOW 6×10^{-3} (mol) (1) Correct answer with no working scores 2 marks		2

Question Number	Acceptable Answers	Reject	Mark
13(a)(ii)	$5.5883 \times 10^{-3} \times 24\,000$ = 134.12 (134.22 from 136.9)=134 cm^3 (1) ALLOW answer from (i) x 24000 IGNORE SF except 1 Any two from: Formation of butan-1-ol / other / side reactions Incomplete reaction Some but-1-ene may remain in solution (2) IGNORE Reaches equilibrium / reaction reversible But-1-ene reacts with ethanol/ solvent	Transfer losses Gas escapes Gas reacts with water But-1-ene condenses	3

Question Number	Acceptable Answers	Reject	Mark
13(b)(i)	So $[OH^-]$ remains (effectively) constant OR [1-bromobutane] is the only variable IGNORE So $[OH^-]$ is not the limiting factor	Ensure that all C_4H_9Br reacts $[OH^-]$ is in excess $[OH^-]$ does not affect the rate Just 'Only [1-bromobutane] affects the rate'	1

Question Number	Acceptable Answer	Reject	Mark
13 (b)(ii)	 Axes correct with sensible scales to use at least half of graph paper on both axes (1) Labels ((V_{final} - V_t) and t) fully correct with units (1) All 7 points correctly plotted and smooth curve drawn (1)	Axes plotted wrong way round 'Volume'	3

Question Number	Acceptable Answers	Reject	Mark
13(b)(iii)	(V_{final} - V_t) is proportional to the concentration of 1-bromobutane		1

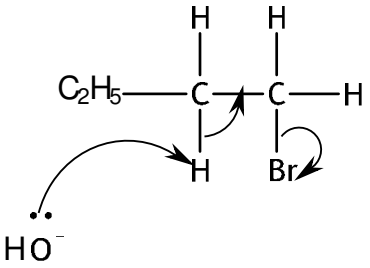
Question Number	Acceptable Answers	Reject	Mark
13(b)(iv)	Two values 2.5 ± 0.3 (min) (each scores one mark) (2)		2

Question Number	Acceptable Answers	Reject	Mark
13(b)(v)	Answer must be consistent with values in (iv) Because half lives are constant / similar (1) The reaction is first order... (1) If values in (iv) are 2.5 and 5, then: Reaction is 2nd order because half lives are increasing scores both marks. Reaction is 1st order because half lives are constant scores 1 mark		2

Question Number	Acceptable Answers	Reject	Mark
13(c)(i)	Order one (1) Any one of: (Exp 1 and 2) $[OH^-]$ halves and rate halves. (Exp 1 and 3) $[OH^-]$ 1/5 and rate 1/5 (Exp 2 and 3) $[OH^-]$ 2/5 and rate 2/5 ALLOW reverse logic (1)		2

Question Number	Acceptable Answers	Reject	Mark
13(c)(ii)	Rate = $k[C_4H_9Br][OH^-]$ IGNORE case of K/k TE on b(v) and c(i)		1

Question Number	Acceptable Answers	Reject	Mark
13(c)(iii)	$dm^3\ mol^{-1}\ min^{-1}$ ALLOW $dm^3\ mol^{-1}\ s^{-1}$ any sequence of units TE on (ii)		1

Question Number	Acceptable Answers	Reject	Mark
13(c)*(iv)	 Arrows from OH-to H and from C-H bond to make additional bond between carbons (1) Third arrow from bond between carbon and bromine to bromine (1) (Because) both 1–bromobutane and hydroxide ion appear in the RDS ALLOW Attack of OH- on H is slow, therefore this is the RDS (Because) both 1–bromobutane and hydroxide ion appear in the slow step (1) IGNORE mention of rate equation	Both are involved in the reaction Mechanism described as S_N2	3

Total for Section C = 21 Marks

Total for Paper = 90 Marks

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