

Mark Scheme (Results)

Summer 2013

GCE Chemistry 6CH04/01 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 <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 Number	Correct Answer	Reject	Mark
1(a)	С		1
(b)	Α		1

Question Number	Correct Answer	Reject	Mark
2	В		1

Question Number	Correct Answer	Reject	Mark
3	С		1

Question Number	Correct Answer	Reject	Mark
4(a)	В		1
(b)	D		1

Question Number	Correct Answer	Reject	Mark
5(a)	В		1
(b)	С		1
(c)	В		1

Question Number	Correct Answer	Reject	Mark
6	Α		1

Question Number	Correct Answer	Reject	Mark
7	A		1

Question Number	Correct Answer	Reject	Mark
8	С		1

Question Number	Correct Answer	Reject	Mark
9	Α		1

Question Number	Correct Answer	Reject	Mark
10	Α		1

Question Number	Correct Answer	Reject	Mark
11	D		1

Question Number	Correct Answer	Reject	Mark
12	В		1
Question Number	Correct Answer	Reject	Mark
13	В		1
Question Number	Correct Answer	Reject	Mark
14	С		1
Question Number	Correct Answer	Reject	Mark
15	D		1
Ouestion	Correct Answer	Reject	Mark

Question Number	Correct Answer	Reject	Mark
16	D		1

Total for Section A = 20 Marks

Section B

Question Number	Acceptable Answers	Reject	Mark
Number 17(a)	Units are not required in (a) or (c) but if used should be correct. Penalise incorrect units in (a), (b) & (c) once only IGNORE case of J and K order of units First mark: 65.3/130.6 and 69.9 (J mol ⁻¹ K ⁻¹) (1) Second mark: $\Delta S = 69.9 - (130.6 + 102.5)$ (1) Third mark: $\Delta S = -163.2 = -163$ (J mol ⁻¹ K ⁻¹) (1) Correct answer with no working scores 3 Ignore SF except 1 SF	+163 or any positive answer	3
	TE at each stage If 65.3 used instead of 130.6 penalize once (answer is then $\Delta S = -97.9$ (J mol ⁻¹ K ⁻¹)		

Question Number	Acceptable Answers	Reject	Mark
17(b)	$\Delta S_{\text{surroundings}} = -\Delta H / \text{T or just numbers (1)}$ = +285800/298 = +959.06 = +959 J mol ⁻¹ K ⁻¹ / +0.959 kJ mol ⁻¹ K ⁻¹		3
	Correct value to 3SF (1)		
	Correct units and positive sign (1)	answer with no sign	
	Correct answer with no working scores 3		

Question Number	Acceptable Answers	Reject	Mark
17(c)	$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} $ (1) Allow $\Delta S_{\text{reaction}}$ for ΔS_{system} $\Delta S_{\text{total}} = \text{answer} (a) + \text{answer} (b)$ = -163.2 + 959 $= (+)795.8 = (+)796 \text{ (J mol}^{-1} \text{ K}^{-1})$		2
	If $\Delta S_{\text{surroundings}} = +959.06$ then $\Delta S_{\text{total}} = +795.9$ (1)		
	Correct answer with no working scores 2		
	Ignore SF except 1 SF		
	TE on values in (a) & (b) no TE on incorrect equation		
	If answer to (a) = -97.9 (J mol ⁻¹ K ⁻¹) $\Delta S_{\text{total}} = (+)861.1 (J mol^{-1} K^{-1})$		

Question Number	Acceptable Answers		Reject	Mark
17(d)	A mixture of hydrogen and oxygen is thermodynamically unstable because ΔS_{total} is positive		Reference to the stability of individual elements	2
	OR Reaction between hydrogen and oxygen thermodynamically feasible because ΔS_{total} is positive	is		
	ALLOW ΔS for ΔS_{total}	(1)		
	No TE on negative ΔS_{total} from (c)			
	The mixture is kinetically inert /stable or reaction is (very) slow because the activation energy is (very) high	(1)		
	Mixture / reaction is kinetically inert / stable but thermodynamically unstable feasible scores 1 mark	e /		
	IGNORE References to spark / flame providing the (activation) energy for reaction	9		

Total for Question 17 = 10 Marks

Question Number	Acceptable Answers	Reject	Mark
18(a)(i)	$\begin{array}{l} HC_2O_4^{-}(aq) + H_2O(l) \ \Rightarrow C_2O_4^{2-}(aq) \ + H_3O^+(aq) \\ (or \rightarrow) \\ \end{array}$ $\begin{array}{l} ALLOW \ H_2O(aq) \\ Equation \ \textbf{(1)} \qquad states \ \textbf{(1)} \\ \end{array}$ $\begin{array}{l} ALLOW \ for \ 1 \ mark \\ HC_2O_4^{-}(aq) \ \Rightarrow C_2O_4^{2-}(aq) \ + \ H^+(aq) \\ \end{array}$ $\begin{array}{l} States \ mark \ is \ not \ stand \ alone \ but \ can \ be \ awarded \ if \ the \ equation \ has \ a \ minor \ error \ e.g. \ an \ incorrect \ charge \end{array}$		2

Question Number	Acceptable Answers	Reject	Mark
18(a)(ii)	$K_{a} = [C_{2}O_{4}^{2^{-}}] [H_{3}O^{+}] / [HC_{2}O_{4}^{-}]$	K _a =	1
	OR	$[H^+]^2 / [HC_2O_4^-]$	
	$K_a = [C_2O_4^{2^-}] [H^+] / [HC_2O_4^-]$ No TE on incorrect equation in (a)(i) Penalise incorrect charges in (i) and (ii) once only	[H ⁺][A ⁻]/ [HA]	

Question Number	Acceptable Answers	Reject	Mark
18 (a) (iii)	No TE on (a)(ii) $K_a = 10^{-4.28}$ OR 5.24807 x 10 ⁻⁵ (mol dm ⁻³) (1) $K_a = [H^+]^2 / [HC_2O_4^-]$ $K_a = [H^+]^2 / 0.050$ $[H^+] = \sqrt{(0.05 \times 10^{-4.28})} = 1.61988 \times 10^{-3} (mol dm^{-3})$ (1)		3
	TE on incorrect K_a value pH = $-\log 1.61988 \times 10^{-3} = 2.7905 = 2.8$ (1) For final mark TE on algebraic / arithmetical errors providing pH ≥ 1.3 Correct answer with no working scores 3 Ignore SF except 1 SF		

Question Number	Acceptable Answers	Reject	Mark
18(b)(i)	IGNORE explanationsFirst mark: $HC_2O_4^-/hydrogenethanedioate ion ionizationnegligibleALLOWAcid for HC_2O_4^-Slight / partial / incomplete / does not dissociatefor negligibleOR[HC_2O_4^-]_{equilibrium} = [HC_2O_4^-]_{initial} / 0.050 (mol dm^{-3})(1)Second mark:[H^+] due to ionization of water negligibleOR[H^+] only due to ionization of HC_2O_4^-/acidOR[C_2O_4^{2-}] = [H^+]IGNORE references to temperature and to HA andA^-Penalize omission of [] in discussion once only$	Use of NaHC ₂ O ₄ for HC ₂ O ₄ ⁻ OR sodium hydrogen- ethanedioate for hydrogen- ethanedioate ion throughout this item	2

Question Number	Acceptable Answers	Reject	Mark
18(b)(ii)	Ethanedioic acid is a (much) stronger acid (than hydrogenethanedioate ion / sodium hydrogenethanedioate) OR Ethanedioic acid has a (much) smaller pK_a (than hydrogenethanedioate) OR Ionization / dissociation of ethanedioic acid is (much) greater (than hydrogenethanedioate)	Ethanedioic acid is a strong acid / fully dissociated	2
	OR Reverse arguments (1)		
	IGNORE NaHC ₂ O ₄ ionization negligible		
	Approximation of negligible ionization invalid / incorrect OR $[H_2C_2O_4]_{equilibrium}$ not equal to $[H_2C_2O_4]_{initial}$ (1)	Just `approximation invalid'	
	No TE on 18(a)(iii) IGNORE Second ionization occurs		

Question Number	Acceptable Answers	Reject	Mark
18(c)(i)	Start pH at 2.8ALLOW2-4(1)		3
	Vertical section at 25 cm ³ within pH range 6-11 and 2.5-4 units long (1)	deviation from vertical	
	end pH (approaching) value in range 12-13 (asymptotically) (1)	maximum before final pH	

Question Number	Acceptable Answers	Reject	Mark
18(c)(ii)	First mark: Methyl yellow range = 2.9-4 and the phenolphthalein range = 8.2-10 ALLOW pK _{in} (methyl yellow) = 3.5 and pK _{in} (phenolphthalein) = 9.3 (1) Second mark: (The volumes are different) because ethanedioic acid is dibasic / diprotic / has two replaceable/acidic hydrogen atoms ALLOW dicarboxylic (acid) (therefore there are two stages to the neutralization) OR		2
	Methyl yellow range coincides with neutralization of first proton and phenolphthalein range coincides with neutralization of second proton (1)		

Total for Question 18 = 15 Marks

Question Number	Acceptable Answers	Reject	Mark
19(a)(i)	A chiral molecule is non-superimposable on its mirror image / 3D molecule with no plane of symmetry (1)	just `non- superimposable' just `no plane of symmetry'	3
	2-hydroxypropanoic acid has a carbon atom which is asymmetric / has four different groups attached (1)	Molecules for groups	
	Middle carbon labelled in any clear way (1) e.g. H OH O I I I III H OH O OH H I III IIII H OH OH OH H H OH OH H H H OH		
	ALLOW asymmetric C described but not labelled		
	IGNORE references to rotation of plane polarized light		

Question Number	Acceptable Answers	Reject	Mark
19(a)(ii)	2-hydroxypropanoic acid formed in muscles is a single (allow pure) enantiomer /(optical) isomer ALLOW Unequal mixture of enantiomers /(optical) isomers (1)	Just "not a racemic mixture"	2
	2-hydroxypropanoic acid formed in milk is a racemic mixture / equimolar mixture of the two enantiomers / racemate (1) If milk and muscles are reversed but the rest is correct, one mark is awarded	Just 'a mixture of enantiomers'	

Question Number	Acceptable Answers	Reject	Mark
19(b)(i)	First step NaOH(aq) / KOH(aq) or names(1)	OH ⁻ / alkali	2
	Second mark dependent on first being correct		
	Second step HCl(aq) / hydrochloric acid / $H_2SO_4(aq)$ / sulfuric acid	H ⁺ / H₃O ⁺ /acid	
	ALLOW HNO ₃ / nitric acid /dil HCl /(dil) H ₂ SO4 /(dil) HNO ₃ or any strong acid (name or formula) including HBr((aq)) and HI((aq)) (1)		
	IGNORE Omission of (aq) and references to temperature Ethanolic /alcoholic solutions		
	ALLOW One mark for correct two reagents in the wrong order One mark for 'alkali / OH^- followed by acid / H^+ / H_3O^+ '		

Question Number	Acceptable Answers	Reject	Mark
-	First mark (Stand alone) A racemic mixture is not formed OR More of one enantiomer /(optical) isomer is formed OR Only one enantiomer /(optical) isomer is formed (1) Second mark (Stand alone) (Some of the) reaction is S _N 2 (1) Third mark (Stand alone)		Mark 3
	Nucleophile / OH^- only attacks from one side of the molecule / from the opposite side to leaving group (1) ALLOW Use of 'intermediate' for 'transition state' in description of S_N2 Reverse argument based on S_N1 forming a racemic mixture	Carbocation (for molecule)	

Question Number	Acceptable Answers	Reject	Mark
19(c)(i)	Nucleophilic (1)		2
	Addition (1)	$S_N 1/S_N 2$	

Question Number	Acceptable Answers	Reject	Mark
19(c)(ii)	Cyanide (ion) / $CN^-/C \equiv N^-/ : C \equiv N^-/ ^-CN$	HCN/ C≡N	1

19 (c) (iii) H H H H Omission of charges (penalise once only) 2 H H H H H H C	Question Number	Acceptable Answers	Reject	Mark
Both Curly arrows (1) on ethanal Intermediate (1) -C-NC in intermediate ALLOW Omission of lone pair -curly arrow from anywhere on nucleophile including from charge or nitrogen Formation of charged canonical form followed by Formation of charged canonical form followed by Intermediate		$ \begin{array}{c c} H & H \\ H & G \\ H & G \\ H \\$	charges (penalise	2
ALLOW Omission of lone pair Curly arrow from anywhere on nucleophile including from charge or nitrogen Formation of charged canonical form followed by		Both curly arrows (1)		
IGNORE $\delta + /\delta$ - even if unbalanced		ALLOW Omission of lone pair Curly arrow from anywhere on nucleophile including from charge or nitrogen Formation of charged canonical form followed by attack of cyanide ion		

Question Number	Acceptable Answers	Reject	Mark
19 (c) (iv)	Racemic mixture / equal amounts of the two enantiomers / racemate formed(1)		3
	Stand alone mark		
	CHO / aldehyde group is (trigonal) planar (1)	Intermediate / carbonyl	
	ALLOW ethanal / molecule is (trigonal) planar	group /C_O is planar	
	Cyanide (ion) / CN^- /nucleophile attacks (equally) from above or below / either side (of the molecule) (1)	two positions Intermediate	
	Penalise use of intermediate / ion for aldehyde group once only		
	Third mark cannot be awarded if the reaction is described as a nucleophilic substitution		

Question Number	Acceptable Answers	Reject	Mark
19(d)(i)	Any value /range within the range $3750-2500$ cm ⁻¹ due to O-H / OH / -OH	Wavenumbers alone OH in alcohol	1
	IGNORE COOH / CO ₂ H / carboxylic acid		

Question Number	Acceptable Answers	Reject	Mark
19(d)(ii)	These three marks are stand alone Q is due to C=O (1) The (C=O) aldehyde range is 1740-1720 cm ⁻¹ and (C=O) carboxylic acid range is 1725-1700 cm ⁻¹ (1)	Carboxylic acid / COOH group	3
	So the peaks / absorptions cannot be used to distinguish these two compounds because they overlap. OR The (broad) absorption Q covers both the aldehyde and the carboxylic acid ranges (1) ALLOW 'too close'/'quite similar' for 'overlap'	Just 'cannot be used to distinguish the compounds'	

Question Number	Acceptable Answers			Reject	Mark
Question Number 19(e)	If reagent incorrect, obs awarded for a near miss Test positive for ethana Reagent (1) Tollens' Fehling's / Benedict's 2,4-DNP(H) / Brady's reagent Test positive for 2-hydre Reagent PCI ₅ / Phosphorus (V)chloride / phosphor pentachloride Named metal carbonat (solution) Sodium hydrogencarbonate (solution) Magnesium (& water) Ethanol & H ₂ SO ₄ /name strong acid Ethanoic acid & H ₂ SO ₄ /named strong a	s Obs Silve ppt Red Oral ALLO oxypr (1) us :e	Servation (1) er mirror / black / grey -brown ppt nge / red / yellow ppt OW brick-red ppt copanoic acid Observation (1) Steamy fumes* ALLOW gas evolved turns (blue) litmus / UI red Effervescence ALLOW gas / CO2 evolved turns lime water cloudy Effervescence ALLOW gas / CO2 evolved turns lime water cloudy Effervescence ALLOW gas / CO2 evolved turns lime water cloudy Effervescence Sweet / fruity / pear drops / glue smell Sweet / fruity / pear drops / glue smell	Reject Iodine in alkali / iodoform test Acidified potassium dichromate Smoke Just 'fumes' Any indicator as sole test incorrect formulae of reagents	Mark 4
	H_2SO_4 /named strong a	gas e oxypr ferves	drops / glue smell evolved pops with a opanoic acid scence bstance both must be		

Total for Question 19 = 26 Marks

Total for Section B = 51 Marks

Section C

Question Number	Acceptable Answers	Reject	Mark
20(a)(i)	(Sodium thiosulfate) (rapidly) reacts with / reduces the iodine (as it is formed) (1)	iodide / I⁻	2
	So prevents the starch-iodine colour appearing until a fixed amount of reaction has occurred		
	ALLOW (for second mark) So prevents the starch-iodine colour appearing until all the thiosulfate has reacted		
	OR		
	Moles of iodine reacted / thiosulfate ÷ time is (approximately) proportional to the (initial) rate of reaction (1)		
	ALLOW Use of `thio' for thiosulfate		

Question Number	Acceptable Answers	Reject	Mark
20(a)(ii)	(From 2 to 1) $[S_2O_8^{2^-}]$ doubles ($[I^-]$ unchanged) and rate doubles / time halves so order wrt $S_2O_8^{2^-} = 1$ (1) (From 3 to 1) $[I^-]$ doubles ($[S_2O_8^{2^-}]$ unchanged) and rate doubles / time halves so order wrt $I^- = 1$ OR (if first mark awarded) (From 3 to 2) $[I^-]$ doubles ($[S_2O_8^{2^-}]$ halved) and rate unchanged so order wrt $I^- = 1$ (1) Penalise omission of concentration/square brackets once only Rate = $k[S_2O_8^{2^-}][I^-]$ (1)	Rate equation =	3
	Third mark stand alone if no working & TE on incorrect orders IGNORE case of k		

Question Number	Acceptable Answers	Reject	Mark
20(b)(i)	First mark Colorimetry /Use a colorimeter Second mark Measure transmittance / absorbance (at various times) Third mark (Use a calibration curve to) convert transmittance / absorbance into concentration. OR transmittance / absorbance proportional to concentration ALLOW	Sampling methods calorimeter	3
	Colorimetry may be used because iodine (solution) is coloured (and other reagents are colourless) / to measure intensity of the iodine colour (1) ALLOW (for the same three marks) Electrical conductivity Measured at various times / (use a calibration curve to) convert conductivity into concentration. Conductivity reduces as reaction proceeds because 3 mol ions converted to 2 mol ions / fewer ions on right hand side	pH meter Just conductivity changes	

Question Number	Acceptable Answers	Reject	Mark
20(b)(ii)	[(NH ₄) ₂ S ₂ O ₈] / [S ₂ O ₈ ²⁻] / [peroxodisulfate] / [persulfate] remains (approximately) unchanged during the reaction. OR	$(NH_4)_2S_2O_8$ in excess. $[(NH_4)_2S_2O_8]$ etc does not affect the rate	1
	[KI] / $[I^-]$ is the only variable	Only [KI] / [I ⁻] affects the rate	

Question Number	Acceptable Answers	Reject	Mark
20(b)(iii)	Plot a graph of concentration (of iodine/ I_2) (on the y axis) against time (1) Measure the initial gradient / gradient at t=0 (1) 'Plot a graph and measure the initial gradient / gradient at t=0' alone scores second mark		2

Question Number	Acceptable Answers		Reject	Mark
20(b)(iv)	appropriate units $8.75 \times 10^{-5} = k \times 2.0 \times 0.025$ $k = 8.75 \times 10^{-5} / (2.0 \times 0.025)$ $= 1.75 \times 10^{-3}$	(1) (1)	1 SF	2



Question Number	Acceptable Answers	Reject	Mark
20(c)(ii)	Gradient = $-(-3.505.27) / (0.00333 - 0.00294)$ = $(-)4538 = (-)4500$ ALLOW		4
	values from (-)4300 to (-)4700 (1)		
	gradient value negative (1)		
	$E_{a} = -\text{gradient } x R = -4538 \times 8.31$ = (+)37700 J mol ⁻¹ (= (+)38 kJ mol ⁻¹) (1)		
	TE on value of gradient even if it is positive		
	-4300 gives 35.7; -4700 gives 39.1		
	Correct units (1)		
	Correct answer from the gradient calculation with units scores final 2 marks		
	BUT correct answer with units but no gradient calculation scores units mark only		

Total for Section C = 19 Marks

Total for Paper = 90 Marks

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