Mark Scheme (Final)

Summer 2008

GCE

GCE Chemistry (6246/02)

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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.

Using the mark scheme

1. / means that the responses are alternatives and either answer should receive full credit.
2. ( ) 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.
3. [ ] words inside square brackets are instructions or guidance for examiners.
4. Phrases/words in **bold** indicate that the <u>meaning</u> of the phrase or the actual word is **essential** to the answer.
5. 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.

Quality of Written Communication

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

- show clarity of expression
- construct and present coherent arguments
- demonstrate an effective use of grammar, punctuation and spelling.

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.

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (a)	Heat/enthalpy/energy change (for a reaction) is independent of the path/route taken (depending only on the initial and final states) OR Heat/enthalpy/energy change (for a reaction) depends only on the initial and final states.	Enthalpy change for a direct path is the same as that of an indirect path.	enthalpy change for the reaction is the same as the sum of the values for each step.	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (b)	heat change (= mC$\Delta\theta$) = 30g x 4.18 J $^{o}C^{-1}g^{-1}$ x(30.1–23.7) ^{o}C for this expression **or** the answer = (+)803 (J). **(1)** Units do not have to be in the calculation. If candidate believes that 803 or - 803 is the value of ΔH next two marks are lost. ΔH_1 = - 803 J ÷ 0.0187 mol = — 43 for sign and value (rounded or unrounded) **(1)** **to 2sf only** and kJ mol^{-1} **(1)** if value and units do not agree loses both second and third marks Correct answer plus some working **(3)**	(+) 802.56 or – 803 or – 802.56 - 802.56 ÷ 0.0187 —43000 J mol^{-1} **(2)**		3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (c)(i)	Multiplies the $KHCO_3$ equation by 2 **(1)** and subtracts the K_2CO_3 equation from it **(1)** This can come from a cycle. $\Delta H = 2\Delta H_2 - \Delta H_1$ scores these first two marks if $\Delta H = \Delta H_1 - 2\Delta H_2$ loses second and third marks if $\Delta H = \Delta H_1 + 2\Delta H_2$ loses second and third marks $\Delta H = 2\Delta H_2 - \Delta H_1$ = (+ 29.3 x 2) – (– 43) kJ mol^{-1} = (+)101.6 (kJ mol^{-1}) **(1)** IGNORE SF Correct answer plus some working **(3)** Failing to multiply by 2 loses first mark above, but can then score max 2 as follows: $\Delta H = \Delta H_2 - \Delta H_1$ **(1)** = +29.3 - (- 43) kJ mol^{-1} = (+)72.3 kJ mol^{-1} **(1).** Third mark is consequential on candidate answer in 1(b), e.g. if 1(b) equals + 43 kJ mol^{-1} the answer will be (+)15.6/15.7 kJ mol^{-1}	(+)101.5 if candidates uses – 42.9 from (b).		3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (c)(ii) QWC	reaction in solution produces $H_2O(l)$ whereas thermal decomposition produces $H_2O(g)$ OR water produced in the decomposition is gaseous which is not the standard state OR **energy** is required to vapourise (liquid) water		heat required to vapourise water must be taken into account	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (d)	**First mark:** K_c is smaller **as forward reaction is endothermic (1)** **Second mark:** The second mark can only be awarded if the amount of reactant/product changes **because** of a change in K_c. Increases the amount of $KHCO_3$ /reactants OR decreases amount K_2CO_3 /products **(1).** If K_c is said to be larger, then the second mark can be awarded consequentially for saying that the amount of $KHCO_3$ decreases, etc.	equilibrium shifts to the left	Equilibrium moves to left **and so K falls** scores (0) more $KHCO_3$ than K_2CO_3	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (a)(i)	Ignore any conditions (other than the need for aqueous acid) and ignore mechanisms whether correct or not.			5
	$CH_2{=}CH_2$ + HBr $\rightarrow$ CH_3CH_2Br **(1)** mark being for whole equation;	HCl or HI in place of HBr to give the appropriate product C_2H_5 instead of CH_3CH_2		
	OR			
	$H_2C{=}CH_2$ + H_2 $\rightarrow$ CH_3CH_3 *and* CH_3CH_3 + Cl_2 $\rightarrow$ CH_3CH_2Cl (+ HCl) **(1)**	+ Br_2 to give bromoethane	+ I_2	
	Then Mg **(1)** CH_3CH_2Br $\rightarrow$ CH_3CH_2MgBr **(1)** mark for the Grignard structure. Halogen must agree with the halogenoalkane used.	C_2H_5 instead of CH_3CH_2	CH_3CH_2BrMg	
	(CH_3CH_2MgBr) + CO_2 **(1)**	dry ice for CO_2		
	followed by H^+(aq) **(1)** Any acid acceptable but it must be clear that it is dilute or aqueous. **Note:** CO_2 + H^+(aq) scores **(1)** only.	hydrochloric acid	e.g. HCl, conc HCl	
	An equivalent answer in words can score full marks but the halogenoalkane must be identified and the **formula** of the Grignard reagent must be included			
	OR for the last two marks: Grignard + HCHO **and** hydrolysis (to give propan-1-ol) **(1)** followed by oxidation of product with dichromate(VI) + acid *or* manganate(VII) + acid **(1)**			
	This last mark can be awarded however the propan-1-ol is obtained.	dichromate or permanganate	HCl with MnO_4^-	

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (a)(ii)	Nucleophile/nucleophilic reagent **(1)** attack by $CH_3CH_2^{\delta -}$ of the Grignard on $C^{\delta +}$ (of C=O) **(1)**	$CH_3CH_2^-$ C_2H_5 for CH_3CH_2		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(i)	$CH_3CH_2COCl + CH_3CH_2OH \rightarrow CH_3CH_2COOCH_2CH_3 + HCl$ **(1)** $CH_3CH_2COOH + CH_3CH_2OH \rightleftharpoons CH_3CH_2COOCH_2CH_3 + H_2O$ **(1)** Allow $CH_3CH_2OCOCH_2CH_3$ or $CH_3CH_2OC(O)CH_2CH_3$ for the ester since it is symmetrical.	C_2H_5 instead of CH_3CH_2 $-CO_2-$ instead of -COO- $\rightarrow$ instead of $\rightleftharpoons$ or vice versa		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(ii)	Reaction with the acid chloride since it is not an equilibrium/not reversible/goes to completion (so the yield is higher) There must be a reason as to **why** the acid chloride reaction is better for the mark.	loss of HCl **as a gas** pulls equilibrium to the r.h.s.	Reaction faster HCl is a gas **alone** Just 'HCl pulls eqm to the right'	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)(i)	Solution maintaining an almost constant pH **(1)** for a **small** addition of acid or alkali/base **(1)** Ignore any reference to the composition of the buffer, whether correct or not. Ignore references to 'contaminated with' acid or alkali.	resists change in pH withstands changes in pH	resists small changes in pH maintains pH	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)(ii)	Correct answer with unit and some working scores **(4)**. Correct answer with unit but no working scores **(3)**. $[H^+] = 10^{-5.06} = 8.71 \times 10^{-6}$ mol dm^{-3} **(1)** [HA] = 0.10 mol dm^{-3}, so $[A^-] = \frac{1.3 \times 10^{-5} \times 0.10}{8.71 \times 10^{-6}}$ **(1)** (= 0.149 mol dm^{-3}) amount of A^- = 0.149 x 0.125 (= 0.0187 mol) **(1)** mass NaA = 0.0187 mol x 96 g mol^{-1} = **1.79 g (1)** MUST INCLUDE UNIT BUT IGNORE SF UNLESS ROUNDED TO 1 SF IN WORKING OR ANSWER. OR pH - pK_a = log([A^-] ÷ [HA]) = 5.06 – 4.886 = 0.174 **(1)** ([A^-] ÷ [HA]) = 1.49 so [A^-] = 0.149 x 0.0125 = 0.0187 mol **(1)** mass NaA =0.0187 mol x 96 g mol^{-1} = **1.79 g (1)** MUST INCLUDE UNIT BUT IGNORE SF OR Candidates who round the value of pK_a will get: pH = pK_a + log([A^-] ÷ [HA]) **(1)** pH - pK_a = log([A^-] ÷ [HA]) = 5.06 - 4.89 = 0.17 **(1)** ([A^-] ÷ [HA]) = 1.48 so [A^-] = 0.148 x 0.0125 = 0.0185 mol **(1)** mass NaA =0.0185 mol x 96 g mol^{-1} = **1.77/1.78 g (1)** MUST INCLUDE UNIT BUT IGNORE SF	1.8g 1.8g 1.8g	2g 2g 2g	4

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)(iii)	($[OH^-] = K_w / [H^+]$) (=) 1.0×10^{-14} mol^2 dm^{-6} ÷ 8.71×10^{-6} mol dm^{-3} **(1)** no need for units in calculation = 1.15×10^{-9} (mol dm^{-3}) **(1)** Ignore units even if wrong The answer is consequential on their value of $[H^+]$ in (ii) **provided that** the final answer is smaller than 10^{-7} mol dm^{-3}, i.e. the solution must be acidic. OR pOH = 14 – pH = 8.94 **(1)** $[OH^-]$ = 1.15×10^{-9} (mol dm^{-3}) **(1)** Ignore units even if wrong	1.148×10^{-9}	1.14×10^{-9}	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)(iv) QWC	H^+ and OH^- can be removed by reaction with HA or with A^- **(1)** but since $[A^-]$ is small the ratio $[A^-]$÷[HA] changes significantly and so does the pH **(1)** OR $[A^-]$÷ [HA] must remain nearly constant on addition of H^+ or OH^- **(1)** but this is possibly only if large reserves of both are present **(1)** For **(1)** only: If H^+ is added no/very little A^- available to react **so the pH will alter (1)**			2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (a)(i)	V-shape drawn **(1)** Ignore the bond angle (except for linear) and ignore the number of lone pairs. (justified on the basis of) **2 bond pairs and 2 lone pairs** repelling as far apart as possible/to minimum repulsion/to maximum separation **(1)** **Note:** The numbers of electron pairs can come from the diagram, the drawing of the bond being equivalent to the bond pair. If the diagram shows one lone pair but two are mentioned here ignore the diagram.		linear structure any double bonds O-H-O any argument based on three pairs of electrons maximum repulsion lp-lp>bp-bp **alone**	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (a)(ii)	For the first two marks: $\mathbf{H^{\delta+}}$ attracted to **lone pair** on (small) **O** on **different molecule (1)** but S atom is too large/not sufficiently electronegative for H-bonding **(1)** stand alone For third mark: boiling temperature of H_2O higher than that of H_2S **or** melting temperature of H_2O higher than that of H_2S **or** heat capacity of H_2O higher than that of H_2S **or** density of ice less than that of liquid water but solid H_2S denser than liquid H_2S (must give the states) **or** water is a liquid but H_2S a gas (at room temperature) **(1)**			3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (b)(i)	Ligand (water) lost from the copper(II) ions **or** no ligands in the product **(1)** so no splitting of *d*-subshell/*d*-orbitals **or** all *d*-orbitals are degenerate **(1)** so no electron **transitions**/*d*-*d* **transitions** (and so no colour) **(1)** Any mention of emission loses this mark. Any suggestion that copper has full *d*-subshell or changes its oxidation state after heating loses the last two marks.	no electrons promoted	no light absorbed **alone**	3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (b)(ii)	Bonds formed between ligand/water and the copper(II) ion/copper/copper sulphate **(1)** There is no need to mention the nature of this bond. and bond **formation** is exothermic/gives out heat/gives out energy **(1)**		**reaction** is exothermic	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (c) QWC	Solubility increases from Be to Ba because: hydration enthalpy (of the cation) becomes less exothermic (from Be^{2+} to Ba^{2+}) **(1)** lattice energy becomes less exothermic (from $Be(OH)_2$ to $Ba(OH)_2$) **(1)** but the change in lattice energy is dominant so the enthalpy of solution is more exothermic (and the compound is more soluble) **(1)** OR Hydration enthalpy (of cation) and lattice energy both exothermic **(1)** both decrease but lattice energy decreases more **(1)** enthalpy of solution is more exothermic (so compound is more soluble) **(1)** OR lattice energy and the hydration enthalpy (of the cation) both decrease/fall **(1)** but lattice energy decreases/falls more (than hydration enthalpy) **(1)** enthalpy of solution is more exothermic (so compound is more soluble) **(1)**	lattice enthalpy for lattice energy	'more endothermic' for 'less exothermic' atom or molecule for cation loses first mark only	3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(i) QWC	silicon has (energetically available) **3***d*-orbitals **(1)** for the **lone pair** on water to attack **(1)** whereas carbon has no energetically accessible/available *d*-orbitals **or** has no 2*d* orbitals **(1)** so a strong C-Cl bond would need to break first/ the small C atom is obstructed by the large Cl atoms so the water cannot get close enough to form a bond **(1)** **OR** (small) C atom surrounded by large Cl atoms **(1)** leads to obstruction/steric hindrance **(1)** so the water cannot get close enough to form a bond via its lone pairs **(1)** whereas the larger silicon atom will allow attack since the chlorine atoms are further apart **(1)** The marks are for four ideas that are relevant to the steric hindrance argument, the *d*-orbital argument, or a mixture of these.	converse for CCl_4 converse for $SiCl_4$	no *d*-orbitals/CCl_4 has no *d*-orbitals anything based on C-Cl bond being stronger than Si-Cl Cl^- ions for Cl atoms Cl^- ions for Cl atoms	4

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(ii)	**First mark:** NaCl dissolves to give ions which do not react further with water/are only solvated OR $NaCl(s) + aq \rightarrow Na^{+}(aq) + Cl^{-}(aq)$ **(1)** **Second mark:** $CH_3CH_2COO^{-} + H_2O \rightarrow CH_3CH_2COOH + OH^{-}$ OR $CH_3CH_2COONa + H_2O \rightarrow CH_3CH_2COOH + NaOH$ **(1)** OR propanoate ions react with water to give propanoic acid and hydroxide ions OR sodium propanoate reacts with water to give propanoic acid and sodium hydroxide **(1)** **Third mark:** (stand-alone) so $[H_3O^{+}] < [OH^{-}]$ as a result of reaction (and the solution is alkaline) OR hydroxide **ions** are formed/produced in the reaction which makes the solution alkaline **(1)**		Any reaction to give equal amounts of HCl and NaOH	3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(i)	The activation energy for the reaction is high **or** to ensure that more molecules have $E \geq E_a$.	$E > E_a$	to overcome E_a **alone** reactants kinetically stable; reactants thermodynamically stable	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(ii)	protonates the alcohol **(1)** providing H_2O as the leaving group which is more easily displaced by the bromide ion/is a better leaving group than hydroxide **(1)** OR reacts with NaBr **(1)** to give HBr (which is the attacking reagent) **(1)**		'as a catalyst' alone	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(iii)	H-bonding between water and the alcohol not strong enough to overcome hydrophobic interactions /effect of alkyl group **(1)** acid and alcohol form ionic species/$C_4H_9OH_2^+$ which is more soluble **(1)**	butyl group		2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(iv)	Removes acid	neutralises HCl /HBr neutralises acid		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(v)	Removes water	Absorbs water Dries the product		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(vi)	Electric heating mantle **or** sand bath **or** oil bath**(1)** because the alcohol/reaction mixture/bromobutane is flammable **or** because the heating is uniform and less likely to crack the flask **(1)** This mark is conditional on the first being scored.	Water bath	heat under reflux no naked flame fume cupboard 'volatile' for 'flammable'	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (b) QWC	**EITHER** Intermediate (ion) in S_N1 is planar **(1)** equal attack (by hydroxide ions) from either side **(1)** produces a racemic mixture **(1)** **Note:** Statement that the S_N2 mechanism is consistent with the information cannot score any marks. **OR** S_N2 involves attack from one side **(1)** so configuration of the product would be inverted **(1)** leading to retention of optical activity **so must be S_N1 (1)** Statement that the reaction is S_N1 alone scores zero.	Intermediate carbocation is a planar molecule forms one optical isomer only	intermediate **molecule alone** loses this mark attack by bromide ions	3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (c)(i)	Orange → green			1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (c)(ii)	$Cr_2O_7^{2-}$ + $6e^-$ + $14H^+$ → $2Cr^{3+}$ + $7H_2O$ **(1)** ($3CH_3CH(OH)CH_2CH_3$ → $3CH_3COCH_2CH_3$ + $6H^+$ + $6e^-$) $Cr_2O_7^{2-}$ + $3CH_3CH(OH)CH_2CH_3$ + $8H^+$ → $2Cr^{3+}$ + $7H_2O$ + $3CH_3COCH_2CH_3$ **(1)** No consequential marking on incorrect equations.	C_4H_9OH and C_4H_8O equation having non-cancelled H^+ ions	equation having non-cancelled electrons	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (c)(iii)	The broad peak/absorption/trough around 3400 cm^{-1} due to –OH **(1)** has disappeared in the product to be replaced by C=O at 1700 cm^{-1} **(1)** If no reference to both groups responsible for the peaks then max **(1)** OR If no reference to both wavenumbers responsible for the peaks then max **(1)**	3230 – 3550 1680 - 1750	broad transmission	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (d)(i)	Addition of barium ions pulls equilibrium to r.h.s. **(1)** increases $[H^+]$ **and** so lower pH/the pH falls **(1)** stand-alone mark		'..so gets more acidic'	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (d)(ii)	lower pH/pH falls		'mixture is more acidic' for 'lower pH'	1