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Mark Scheme (FINAL)
Summer 2008

GCE

GCE Chemistry Nuffield (6256/01)

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Registered Office: One90 High Holborn, London WC1V 7BH

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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 meaning 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.

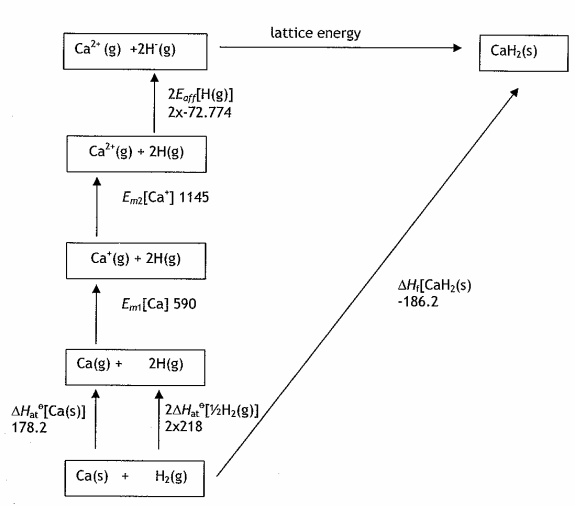
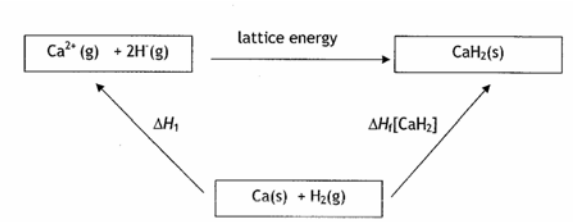
Quality of Written Communication

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)	**2 max for Cycle** **3 max for Calculation** **<u>CYCLE (Max 2)</u>**  …… **OR**  $\Delta H_1 = \Delta H_{at}[Ca(s)] + 2\Delta H_{at}[½H_2(g)] + E_{m1}[Ca(g)] + E_{m2}[Ca^+(g)] + 2E_{aff}[H(g)]$ Note: names or values of energy changes in ΔH_1 , and "lattice energy" and "ΔH_f" or value must be specified here …… Entities/formulae with state symbols **(1)** IGNORE multiples of ΔH_{at} and E_{aff} Energy changes, providing recognisable, can be numbers **(1)** IGNORE multiples	Do not penalise if state symbols and formulae of ions which do not feature in the triangular diagram are missing/wrong Minimum requirement is what is shown in triangular diagram Recognisable abbreviations for enthalpy changes in either diagram		5

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1(a) cont.	**CALCULATION (Max 3)** Lattice energy = -186.2–(178.2 + 2x218 + 590 + 1145 - 2x 72.774) **(1)** ALLOW TE from cycle labels = -186.2–2203.656 = **-2390 kJ (mol^{-1})** (4SF) **(2)** ie value, sign and unit **Errors (-1 mark for each error)** e.g. Incorrect significant figures **(2 max)** Arithmetic errors from correct Hess application **(2 max)** Wrong sign or unit **(2 max)** Only one ionisation energy for Ca **(2 max)** Only one E_{aff} for hydrogen gives –2463 **(2 max)** Only one ΔH_{at} for hydrogen gives –2172 **(2 max)** Only one E_{aff} & one ΔH_{at} for hydrogen gives –2245 **(1 max)** Using data for chlorine (121.7 and –348.8) gives –1645 **(1 max)** Using 1st ionisation of hydrogen (1312) gives –5159 **(2 max)** Based on CaH gives -1816 **(1 max)**	Correct answer without working **(3)** -2389.8 kJ (mol^{-1}) **(2)** ie -1 for incorrect SF		

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (b) **QWC**	Closer for CaH_2, as in AlH_3 H^- more distorted/polarised OR Closer for CaH_2, as in AlH_3 bond partially covalent/ bond has (more) covalent character/tendency **(1)** Al^{3+} has greater charge density OR is small**er** OR is more charged/is highly charged (or reverse statements for Ca) **(1)** For 2nd mark values must have been identified as closer for CaH_2. IGNORE comments on charge on hydride ion	More covalent bond**ing** in AlH_3 Diagram as in *Students Book* p389 to explain polarisation/ covalency	More covalent bonds in AlH_3 Fewer covalent bonds in CaH_2 Quotation of Fajans' rules if not applied to the compounds in question Any reference to molecules for the 1st mark Al^{3+} is small	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (c) **QWC**	KH: smaller charge on K^+ / potassium ions **so** weaker forces (in lattice) **(1)** [must be clear KH is ionic] HBr: (small) molecules/no lattice, **so** weaker forces (van der Waals'/dipole) **(1)** Same reason given for both having lower melting point can score 1 mark if either correct	K^+ bigger than Ca^{2+} **so** weaker forces (in lattice) Ca^{2+} has greater charge density than K^+ **so** stronger forces	Reference to forces between molecules of KH	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (d)(i)	$H^- + H_2O \rightarrow H_2 + OH^-$ ALLOW multiples IGNORE state symbols	$2H^- + 2H_2O + Ca^{2+} \rightarrow 2H_2 + 2OH^- + Ca^{2+}$	$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (d)(ii)	Water is an acid/reaction is acid-base as water donates protons/ H^+ (to H^-) OR acid-base reaction as H^- accepts proton **(1)**	Water identified as acid and oxidising agent OR reactions identified as acid-base and redox without reason **(max 1)**	Water is an acid and a base Water is a base as OH^- forms	2
	Water is oxidising agent / is reduced / reaction is redox as water accepts electrons (from H^-) / increases oxidation number of hydrogen (from –1 to 0) **(1)** OR reverse argument	H^- is oxidised with reason	Water is a reducing agent and an oxidising agent Just "Hydride ion is oxidised by the water" Type = Disproportionation	

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (a)(i)	One spot on chromatogram/no separation/poor separation/overlap of spots **(1)** R_f values very similar OR R_f values are 0.26 and 0.27 **(1)** IGNORE all references to colour with locating agent	Diagram of **ONE** spot on chromatogram	Chromatogram with spots run separately, not in mixture Two spots very close together but not touching	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (a)(ii)	Try different solvent IGNORE comments about turning through 90° unless solvent is different.	Use longer paper OR run chromatogram for longer (provided movement of solvent front is still possible)	Run at 90° with same solvent	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(i)	Only serine goes green/blue (with potassium dichromate(VI)) **(1)** Serine has alcohol/OH group (on side chain) which can be oxidised/reduces $Cr_2O_7^{2-}$ **(1)**	No change with glycine, green/ blue with serine OR glycine stays orange, green/ blue with serine **(1)** Serine can be oxidised to an aldehyde/carbonyl/carboxylic acid	Serine has keto group Serine has carboxylate group Just "Glycine cannot be oxidised"	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(ii)	**Only** serine rotates plane of polarisation/allows light through crossed polaroids **(1)** Glycine has no chiral carbon/no carbon attached to 4 different groups / is achiral /no enantiomers OR Serine has a carbon attached to 4 different groups /is chiral/asymmetric carbon **(1)** Note: ACCEPT recognisable spelling of chiral	Only serine rotates/twists polarised light	..changes the path of… …bends…. ..affects… Just "Serine is optically active"	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(iii)	Glycine 3 peaks **(1)** Serine 5 peaks **(1)** Different numbers of hydrogen/proton environments **(1)**	Different numbers of hydrogen/proton situations OR Different numbers of molecular environments for hydrogen OR list of 5 environments N**H**$_2$, O**H**, CO_2**H**, C**H**$_2$, **H** in serine OR list of 3 environments N**H**$_2$, CO_2**H**, **H** in glycine	Hydrogen types (Different) number of hydrogen atoms Different numbers of hydrogen **and** carbon environments	3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)	H_2NCH_2–C–N–CH(CH_2OH) CO_2H ‖ | O H OR $H_2NCH(CH_2OH)$–C–N–CH_2CO_2H ‖ | O H –C–N– to be displayed ‖ | O H (CH_2OH) to be in brackets or attached to chain as in diagrams on p 436 ie H_2NCH–C–N–$CHCO_2H$ | ‖ | | H O H CH_2OH	Amine group at left can be written NH_2 rather than H_2N Look for displayed peptide bond ACCEPT fully displayed		1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (a)	Electrophilic substitution **(1)** IGNORE extras eg Friedel Craft, alkylation UNLESS contradictory 1-chloro–(2)-methylpropane **(1)** IGNORE punctuation <u>Catalyst</u> $AlCl_3$/aluminium chloride **(1)**	(2)-methyl-1-chloropropane $CH_3CH(CH_3)CH_2Cl$/ $CH(CH_3)_2CH_2Cl$ "Bromo"/"iodo" for "chloro" Al_2Cl_6, $AlBr_3$, $FeBr_3$	1-methyl-2-chloropropane missing "1" from position of Cl in name	3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (b)	$LiAlH_4$ is a source of H^- / hydride ion **(1)** Hydrogen might reduce/attack benzene ring/ H^- won't attack region of negative charge/ H^- can attack (δ^+) C in keto group **(1)**		Comments on conditions or safety eg temperature, pressure $LiAlH_4$/H^- is a more powerful reducing agent H^- is a nucleophile/a stronger nucleophile Any mention of attack on carboxylate ion (for 2nd mark)	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (c)	**Note:** although many candidates have calculated the empirical formula, this is not required. Molecular formula of ibuprofen = $C_{13}H_{18}O_2$ **(1)** Allow marks for masses and number of moles if answers are rounded to 2 SF in "OR" but method is correct. **EITHER** M_r = 206 **(1)** 1 g = $\frac{1}{206}$ mol = 4.854 x10^{-3}mol mass CO_2 produced from 13 C = 13 x 44 x 4.854 x 10^{-3} = 2.78 g **(1)** mass H_2O from 18 H = 9 x 18 x 4.854 x10^{-3}= 0.787 g **(1)** **OR** Mass C = $\frac{(2.78 \times 12)}{44}$ = 0.758g Mass H = $\frac{(0.786)}{9}$ = 0.0873g **(1)** Moles C = $\frac{(0.758)}{12}$ = 0.0632 Moles H = 0.0873 **(1)** Ratio C:H = 0.0632: 0.0873 = 13:18 **(1)**	Allow if given at end		4

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(i)	(Aspirin and ibuprofen) both contain same (types of) **bond(s)**(so absorb at same frequency/wavenumber)	List of at least 4 bonds which are present in both	"groups" for "bonds"	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(ii)	Data is required for mark **Y =** paracetamol Peak at 3500–3300 (N-H) IGNORE mention of amine OR 3500–3140 (N-H or amide) OR 3750–3200 ((phenolic) O–H) OR Only **Y** has peaks above 3000 cm^{-1} (so must contain different type of bond to X and Z)		C–H in arene = 3030 as present in both 1700-1630 (amide)	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(iii)	<u>57 in Ibuprofen</u> $C_4H_9^+$ / $CH_3CH(CH_3)CH_2^+$ / $CH(CH_3)_2CH_2^+$ OR $C_2O_2H^+$ / CCO_2H^+ **(1)** <u>Aspirin</u> 59 **(1)** $OCOCH_3^+$ / $C_2H_3O_2^+$ **(1)** OR 121 **(1)** $C_6H_4CO_2H^+$ **(1)** OR 180 **(1)** $C_9H_8O_4^+$ (parent ion) **(1)** OR 137 **(1)** $C_6H_4(CO_2H)O^+$ **(1)** Penalise no/wrong charges once only	Structural or displayed formulae	Do not allow lines at 15 (CH_3^+) 76 ($C_6H_4^+$) 43 ($C_3H_7^+$ or CH_3CO^+) 45 ($COOH^+$) as present in both	3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(i)	**Delocalisation** (in carboxylate group/ COO^-) makes bond lengths the same	Resonance between C=O and C-O	Answers based on ethanedioic acid not the ion	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (a)(ii) QWC	3 electron clouds would give triangular/ trigonal (planar) structure round each C **(1)** Electron density in delocalised COO^- /in carboxylate ion/in C=O increases repulsion so bond above 120 ° **(1)** Must relate to 120 ° or triangular/trigonal structure for 2nd mark	3 bonds repelling…… Answers based on ethanedioic acid not the ion	Atoms repelling Lone pairs on O repelling	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (b)(i)	(One) lone pair on each carboxylate/ COO^- group OR lone pair on an oxygen at each end of ion **(1)** Form (dative covalent/co-ordinate) bond to (transition) metal (ion) **(1)**	5-membered ring can form with transition metal ion **(1)** OR diagram showing arrows from lone pairs on either oxygen at each end of ion/molecule to metal ion **(2)**	Bonds from both oxygens attached to same carbon loses both marks Ion/molecule bonded to two separate metal ions	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (b)(ii)	$[Cr(C_2O_4)_3]^{3-}$ /$[Cr((CO_2)_2)_3]^{3-}$ Formula **(1)** Charge **(1)** - 2nd mark dependent on 1st mark	[ ] optional	$[Cr(CO_2)_6]^{3-}$ $[Cr^{3+}((CO_2^-)_2)_3]$ $[Cr^{3+}(C_2O_4^{2-})_3]$	2

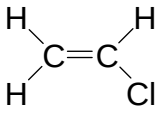
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (c)(i)	….. :: (2)CO_2(g), $C_2O_4^{2-}$(aq) | Pt OR ….. :: (2)CO_2(g), $(CO_2)_2^{2-}$(aq) | Pt Order must be correct	…2CO_2(aq)… ALLOW one missing state sign IGNORE solid line(s)	$(CO_2^{-})_2$	1

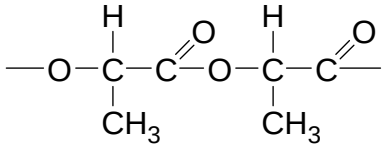
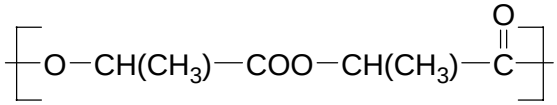
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (c)(ii)	Maximum (+) 1.51 (V) Minimum – 0.76 (V)			1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (d)(i)	$Fe^{2+} \rightarrow Fe^{3+} + e^{(-)}$ **(1)** $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^{(-)}$ **(1)** ALLOW multiples ALLOW electrons subtracted on LHS ALLOW $(CO_2)_2^{2-}$		$(CO_2^{-})_2$	2

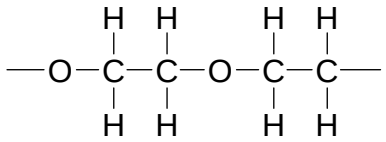
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (d)(ii)	Mol MnO_4^{-} =(16.80 x 0.0200 ÷ 1000) = 3.36×10^{-4} **(1)** (Mass 1 mol FeC_2O_4 = 56 + 24 + 64 = 144 g) Moles FeC_2O_4 =(0.0804 ÷ 144) = 5.583×10^{-4} mol **(1)** IGNORE SF Ratio ethanedioate : MnO_4^{-} (= 5.583 : 3.36) = 1.66 : 1 OR = 1.7 : 1 OR = 5 : 3 **(1)** ALLOW TE to here only Each FeC_2O_4 produces $3e^{(-)}$ so 5 FeC_2O_4 produce $15e^{(-)}$ required by 3 MnO_4^{-} OR answers based on increase and decrease of oxidation number **(1)**	Answers working backwards from reacting ratios from half-equations can be shown to be consistent with numerical data can gain full marks Full balanced equation		4

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4 (d)(iii)	Rate of decolorisation (of MnO_4^{-}) increases as titration proceeds OR It changes colour faster	Rate of production of gas increases as titration proceeds	Answers which are not observations Wrong colours	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5 (a)	 **(1)** Stronger van der Waals' forces because more electrons (in repeat unit) OR Stronger forces due to dipoles/polar chlorine /electronegativity of chlorine OR bigger Cl make chain less flexible **(1)**	**Cl** prevents strands/chains sliding past one another	References to chloride ions Explanations about intramolecular forces Chains are more tangled	2

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5 (b)	<u>Section of polymer chain</u> –O–CH(CH_3)–COO–CH(CH_3)–CO– [must have 4x O and 6x C atoms, but only continuation bonds need be shown] OR  OR  IGNORE "n" after bracket **(1)** <u>Type</u> Condensation polymerisation **(1)** <u>Type of link</u> Ester **(1)**	Different starting points in chain More than two monomer units	Dimer, rather than part of polymer ie no continuation bonds at each end Covalent bond/ esterification	3

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5 (c)(i) QWC	Bonds in rings are 60^{o} (but not $109(.5)^{o}$) so repel OR Bonds in ring are close together and (electrons) repel OR bond angles are very small/tight/very acute so repel/strain occurs OR Bonding round carbon is distorted as not tetrahedral *OWTTE*		Answers based on lone pair on oxygen causing attack by electrophiles	1

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5 (c)(ii)	$-CH_2-CH_2-O-CH_2-CH_2-O-$ OR $-CH_2-O-CH_2-CH_2-O-CH_2-$ OR  O can be LHS or RHS but not both Only continuation bonds need be shown Can be shown with brackets and "n"	More than two monomer units	-O-O- bond in chain	1