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Mark Scheme (Final)

January 2009

GCE

GCE Chemistry (6245/01)

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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.

<table>
<tr><th>Question Number</th><th>Correct Answer</th><th>Acceptable Answers</th><th>Reject</th><th>Mark</th></tr>
<tr><td>1 (a)</td><td><table>
<tr><td></td><td colspan="5">3d</td><td>4s</td></tr>
<tr><td>Cu^{+}</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td></td></tr>
<tr><td>Cu^{2+}</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑</td><td></td></tr>
</table>1 mark for each row</td><td>Half arrows or just vertical lines</td><td></td><td>2</td></tr>
</table>

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (b)(i) **QWC**	**ligands** split *d* orbitals **(1)** This first mark is stand alone **absorb** light in (part) of visible region/all colours except blue**(1) Stand Alone** causes electron to jump / be promoted to a new level **(1)**	If sequence in wrong order eg jump **then** absorb Or any implication that this is an emission spectra then **only first mark** (orbitals splitting) available		**3**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (b)(ii)	No ligands to split (d) orbitals **(1)** Implication that all d orbitals the same	No complex ion /water ligand present	Full so cannot jump	**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (c)(i)	**X** $CuCl$ OR Cu_2Cl_2 OR copper(I) chloride**(1)** allow cuprous chloride $CuCl_2 + Cu \rightarrow 2CuCl$ or $CuCl_2 + Cu \rightarrow Cu_2Cl_2$**(1)**	Allow HCl on both sides		**2**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (c)(ii)	Redox **(1)**	Reduction		**1**

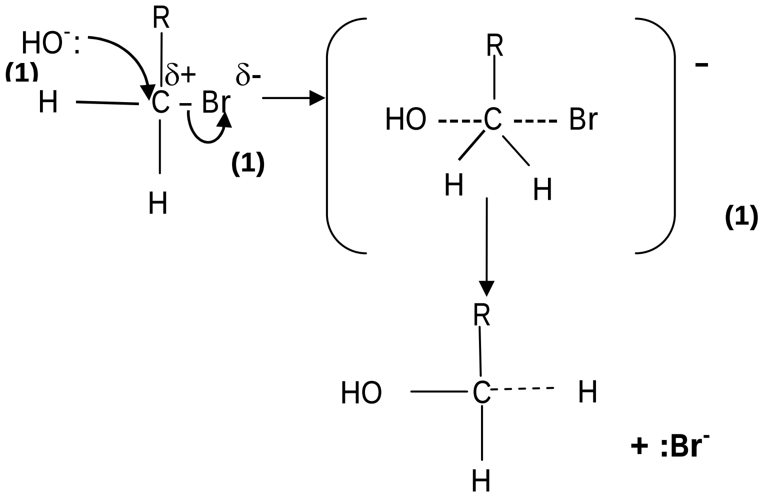
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (c)(iii)	$Cu(NH_3)_2^{+}$ **(1)**			**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (c)(iv)	The copper(I) ion has a full *d* (sub) shell/d^{10} OR All *d* orbitals are full **(1)** (so *d*-*d* transitions impossible) Or No partly filled d		*d* orbitals not splitting	**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
1 (c)(v)	$Cu(NH_3)_4^{2+}$ Or $[Cu(NH_3)_4(H_2O)_2]^{2+}$ **(1)** [ ] not essential		$Cu(NH_3)_6^{2+}$ And $Cu(NH_3)_2^{+}$	**1**

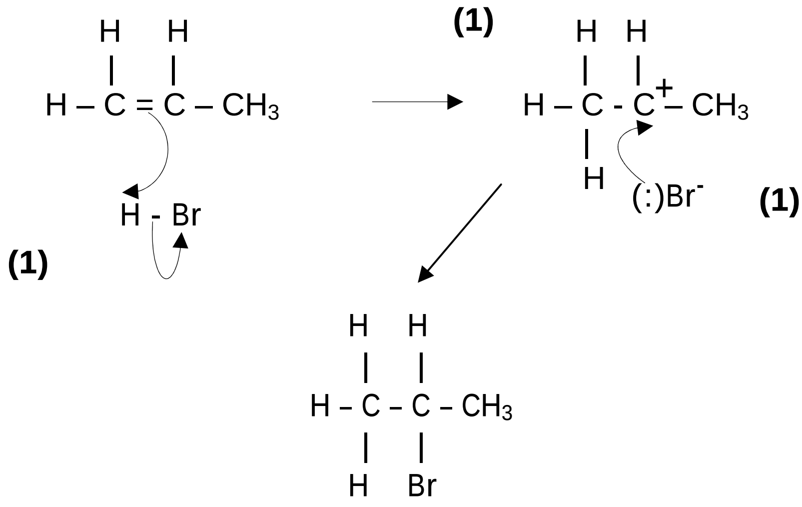
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (a)	Nucleophilic substitution **(1)**	Hydrolysis		**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(i)	Expt 1 and 2/concentration of 1-brombutane constant Concentration of hydroxide trebled, rate x3 First order with respect to OH^- **(1)** Expt 2 and 3/concentration of hydroxide constant. Concentration of 1-bromobutane x4, rate x4. First order with respect to 1-bromobutane.**(1)** *If both orders given with no explanation 1 (out of 2)* Rate = *k*[1-bromobutane] [hydroxide] **(1)** *mark rate equation consequently.*			**3**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (b)(ii)	 Both arrows must be in first step Allow S_N1 if rate equation in 2(b)(i) is zero order in OH^- and first order wrt. RBr Allow arrow from negative charge ignore $\delta+$ and $\delta-$ Lone pairs need not be shown	.		**3**

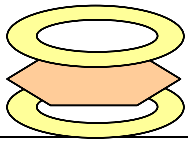
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)(i)	The S_N1 mechanism involves the production of a planar **intermediate (1)** which can be attacked from both sides(of the plane**)(1)** producing a racemic mixture/ equal amounts of both isomers/ both enantimorphs **(1)** **last mark stand alone** The S_N2 mechanism Either involves attack from opposite side to Br Or would produce a single (inverted) optical isomer or single enantiomorph Or Attack from one side only Or Intermediate not planar **(1)**			**4**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
2 (c)(ii)	The RDS is the slowest step (in a multi-step mechanism) **(1)** Breaking of bond between carbon and bromine/formation of carbocation / carbonium ion Or sketch to show this Or equation **(1)**	References to those species in the rate equation		**2**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (a)(i)	 If charge on wrong carbon leading to 1-bromoproduct only the 1st mark may be awarded.			**3**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (a)(ii)	Secondary intermediate/carbocation is the more stable **(1)** Or reverse argument Or drawings		Secondary bromopropane is more stable	**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (b)	**EITHER only consider changes** **Bonds broken** 3 x C = C = 3 x 612 = (+)1836 3 x H – H = 3 x 436 = <u>(+)1308</u> **(+)3144** **(1)** **Bonds formed** 3 x C – C = 3x 347 = (–)1041 6 x C – H = 6 x 413 = (–<u>)2478</u> **(–)3519 (1)** Enthalpy change = 3144 +(–3519) =–375 kJ mol^{-1}**(1)** **OR break and make all bonds** **Bonds broken** 3 x C – C = 3 x 347 = (+)1041 3 x C = C = 3 x 612 = (+)1836 6 x C – H = 6 x 413 = (+)2478 3 x H – H = 3 x 436 = <u>(+)1308</u> (+)**6663 (1)** **Bonds formed** 6 x C – C = 6x 347 = (–)2082 12 x C – H = 12 x 413 = (–<u>)4956</u> (–)**7038 (1)** Enthalpy change = 6663 +(–7038) =–375 (kJ mol^{-1})**(1)**	+375 is worth 2 marks since only one error. mark the third mark consequentially		**3**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (c)(i)	The unused p electron orbitals overlap (sidewayst to produce a π system that extends over the whole ring of carbon atoms) **(1)** Diagram **(1)** 		Any suggestion that sigma bond being formed	**2**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (c)(ii)	**Addition** would disrupt the delocalised π system **(1)** **Substitution** restores or retains the delocalised π system and this has greater (energetic) stability **(1)**	Allow reverse argument		**2**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(i)	One in which the solute shows high solubility in hot but low in cold **(1)**			**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(ii)	Firsthot filtration/ second step **(1)**			**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(iii)	Soluble impurities will not crystallise out after cooling OR Soluble impurities remain in solution after cooling OR Cold solution is not saturated with the impurities **(1)**			**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(iv)	To remove any impure solvent/solution on crystals **(1)** Must be idea of liquid not solid Allow remove any soluble impurities still in the solution			**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
3 (d)(v)	Minimum (volume) of hot solvent OR wash with (ice-)cold solvent OR I st filtration so that crystals not removed. **(1)**	"Bullets 1, 2 or 5"		**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
4	**Diagram Stand alone** Lozenge drawn **(1)** At least 2 horizontal and 2 vertical tie bars starting at 50/50 mixture **(1)** **Explanation - stand alone** Vapour richer in the more volatile component/ hexane **(1)** (Evaporates,)condenses and reboils**(1)** Pure hexane distilled off **(1)** *If say heat at 69 ^{o}C and boil off hexane NO marks for explanation*			**5**

<table>
<tr><th>Question Number</th><th>Correct Answer</th><th>Acceptable Answers</th><th>Reject</th><th>Mark</th></tr>
<tr><td>5(a)</td><td>
<table>
<tr><th>Carbon</th><th>Hydrogen</th><th>Oxygen</th></tr>
<tr><td>$\frac{81.82}{12}$
= 6.818</td><td>$\frac{6.06}{1}$
= 6.06</td><td>$\frac{12.12}{16}$ (1)
= 0.7575</td></tr>
<tr><td>$\frac{6.818}{0.7575}$
= 9</td><td>$\frac{6.06}{0.7575}$
= 8</td><td>$\frac{0.7575}{0.7575}$
=1 (1)</td></tr>
</table>

Empirical formula = C_9H_8O

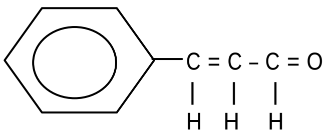
EF mass = 132
∴ Molecular formula = C_9H_8O (1)
Marking
1 mark for division by Ar
1 mark for division by smallest
1 mark for showing EF = MF by use of 132
Note the third mark is for showing that their EF adds up to 132
OR
% C = $\frac{9x12x100}{132}$ = 81.82 (1)
% H = $\frac{8x1x100}{132}$ = 6.06 (1)
% O = $\frac{16x100}{132}$ = 12.12
OR by difference for which ever one is not calculated(1)</td><td></td><td></td><td>3</td></tr>
</table>

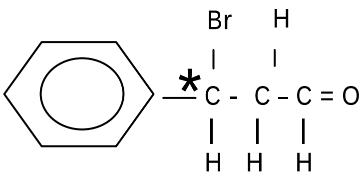
Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5 (b)(i)	Carbonyl group OR Aldehyde or ketone **(both needed)** OR C=O group **(1)**			**1**

Question	Correct Answer	Acceptable Answers	Reject	Mark

Number				
5 (b)(ii)	Aldehyde/CHO OR “Not a ketone” if mark awarded in (i) **(1)**			**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5 (b)(iii)	Must have (one) C=C **(1)**	Alkene Ignore unsaturated group		**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5 (c)(i)			Side chain EXCLUDED BY QUESTION	**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5 (c)(ii)	 **(1)** for correct structure or with the bromine on carbon 2 **(1)** mark for indentification of chiral centre	If give side chain in 5(c)(ii) allow marks here consequentially		**2**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
5 (c)(iii)	Substitution in the benzene ring **(1)** Addition to side chain **(1)** OR Substitution in the benzene ring **(1)** Different positions around the ring/multiple substitution **(1)**	Reacts by substitution and addition without clarification 1 mark only	Nucleophilic substitiution	**2**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
6 (a)	(dirty/grey) green ppt **(1)** (Then a dark) green solution **(1)** This mark does not depend on the colour of the ppt.	Any green		**2**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
6 (b)(i)	**1st mark** Both directions of change of position of equilibrium given **(1)** **2nd mark** Explanation involving H^+ in each case**(1)**			**2**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
6 (b)(ii)	Oxidation number of Cr in $Cr_2O_7^{2-}$ **and** CrO_4^{2-} is +6. **(1)** Actual oxidation number of Cr must be stated		No change in ON of Cr	**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
6 (c)(i)	$2Cr^{3+} + Zn \rightleftharpoons 2Cr^{2+} + Zn^{2+}$ **(1)** Ignore state symbols	Multiples		**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
6 (c)(ii)	$Cr^{2+} + Zn \rightleftharpoons Cr + Zn^{2+}$ **(1)** Ignore state symbols	Multiples		**1**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
6(c)(iii)	E^o for Zn reducing Cr^{3+} going to Cr^{2+} is+ 0.35 (V) **and** E^o for reducing Cr^{2+} to Cr = -0.14(V) **(1)** Both required for 1 mark because E^o for second reaction is negative / not feasible**(1)** Second mark consequential on figures in first part. Note If both E values correct final product is Cr^{2+} If E_1 and E_2 are both calculated as +ve - final product is Cr If E_1 and E_2 both calculated as negative final product is Cr^{3+}	Answers based on other use of the data eg. As cell diagrams and loss of electrons can score full marks Must be some reasoning for second mark		**2**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
6 (d)	Two possible routes ignore sig figs **1st mark** Amount of dichromate in used in titration $= \frac{19.00 \times 0.0136}{1000}$ **(1)** $= 2.584 \times 10^{-4}$ mol **2nd mark** Mols of iron = $\frac{\mathbf{6} \times 19.00 \times 0.0136}{1000}$ **(1)** = 0.00155 mol (1.550×10^{-3}) **3rd mark** Total amount in 250 cm^3 $= \frac{\mathbf{10} \times 6 \times 19.00 \times 0.0136}{1000}$ **(1)** = 0.0155 mol (1.55×10^{-2}) **OR** Conc of Fe^{2+} $= \frac{0.00155}{0.025}$ **(1)** = 0.0620 mol dm^{-3} **4th mark** Mass of iron(II) sulphate $= \frac{\mathbf{152} \times 10 \times 6 \times 19.00 \times 0.0136}{1000}$ **(1)** = 2.357 g **OR** Mass of $FeSO_4$ in 250 cm^3 $= \frac{0.0620 \times 152}{4}$ = 2.357 g dm^{-3} **5th mark** Percentage of iron sulphate $\frac{2.357 \times 100}{4.00}$ = 58.9% **(1)** allow 59	Alternative routes are possible for full marks Notes If use 56 (Fe) in place of 132 they get 21.7%.		**5**

Question Number	Correct Answer	Acceptable Answers	Reject	Mark
6 (e) **QWC**	**I[st] mark** Viable separation technique after reaction with heating with acidified potassium dichromate(VI) **(1)** **e.g.** If change in colour of dichromate from orange to green distil out product(as it is formed) **2[nd] mark** If no change in colour **tertiary** alcohol **(1)** **3[rd] mark** **Either** Test distillate of other two with Tollens' reagent If silver mirror aldehyde present and alcohol was primary **(1)** If no silver mirror ketone present and alcohol was secondary**(1)** **OR** Fehling's in place of Tollens' If answer just describes tests without chemical argument 1 out of the last two marks	If reflux to convert primary right through to acid and secondary to ketone. Allow dnp for ketone And a **positive** test for acid i.e not proof by elimination.		**4**