

Mark Scheme (FINAL) Summer 2008

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.

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|---|-------------------------------------|------|
| 1 (a) | e.m.f. of a half cell relative/compared to a (standard) hydrogen electrode OR voltage produced from a half cell joined to a hydrogen electrode (1) | Potential (difference) /voltage for emf emf of a cell with standard hydrogen as the left electrode A description of the half cell e.g. a metal dipping into a solution of its ions | SHE | 2 |
| | (solutions at) 1 mol dm ⁻³ concentration, (gases at) 1 atm/100 kPa/10 ⁵ Pa/ 1 Bar pressure and stated temperature (1) | 101 kPa 298 K or 25 °C If any other | 'constant' pressure "STP" | |
| | all 3 conditions needed STAND ALONE | temperature is quoted it must be as an example of a stated | Room temperature Just "273 K" | |
| | | temperature | | |

| Question | Correct Answer | Acceptable | Reject | Mark |
|----------|---|------------|---|------|
| Number | | Answers | | |
| 1 (b) | Can only measure a potential difference/emf (if a reference electrode is present) OR | | Just "electron source and sink" | 1 |
| | voltmeter needs 2 connections OR Cannot measure the potential difference between a metal and a solution of its ions | | to make comparisons between half cells | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|-----------------------|--|------|
| 1 (c)(i) | 1st mark (simultaneous) oxidation and reduction of a (single) species/ substance/ reactant/compound/chemicalOr the oxidation state/number is both increased and decreased of a (single) species/ substance/ reactant/ compound/chemicalOr a (single) species/ substance/ | | oxidation and reduction occur at the same time oxidation state <u>s</u> are | 2 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|-----------------------|---|------|
| 1 (c)(ii) | $2H_2O_2 \rightarrow 2H_2O + O_2$ (1) $E_{cell} = (+) \ 1.09$ (V) (1) | | 2H ⁺ on both sides of equation | 3 |
| | E _{cell} is positive/greater than 0 so the reaction is feasible (1) 3 rd mark must be cq on sign of E _{cell} | | Greater than any other stated number | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|-----------------------|--|------|
| 1 (c)(iii) | activation energy of the reaction may be high OR reaction too slow to be observed | | Just "Not enough energy to overcome the activation energy" Conditions are non- standard Just "kinetically stable" | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|-----------------------|--------|------|
| 2 (a)(i) | second order (1) rate proportional to the square of the (partial) pressure of NO OR the rate doubles as the square of the (partial) pressure of NO doubles (1) Conditional on correct order | | | 2 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|--|--------|------|
| 2 (a)(ii) | as (partial) pressure (of O ₂) doubles rate doubles, so first order OR gradient of line is <i>k p</i> (O ₂) ^x so if this doubles the order (w.r.t. O ₂) must be 1 | Concentration of O ₂ instead of (partial) pressure | | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|--|--------------------------------|------|
| 2 (a)(iii) | rate = $k p(NO)^2 p(O_2)$ Cq on orders in (i) and (ii) | rate = <i>k</i> [NO] ² [O ₂] | Any equation without <i>k</i> | 1 |
| | | "R" for "rate" | rate = k $p[NO]^2 p[O_2]$ | |
| | | "K" for lower case "k" | | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|--|--------|------|
| 2 (a)(iv) | atm ⁻² s ⁻¹ ALLOW this mark, even if <i>p</i> [] used in (iii) Cq on (iii) [if overall second order, unit is atm ⁻¹ s ⁻¹ . If overall first order unit is s ⁻¹] | mol ⁻² dm ⁶ s ⁻¹ if concs used in (iii) | | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|---|---|------|
| 2 (a)(v) | partial pressure/concentration of NO is very small (so the collision frequency with O ₂ molecules is very low) | chance of a 3-body collision is slight | Equilibrium reaction Temp is too low | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|--|--------|------|
| 2 (b)(i) | plot In k vs 1/T (1) giving straight line of gradient - E_a/R OR E_a = -gradient x R (1) STAND ALONE MARKS [2 nd mark could be scored from (ii) if no reference to gradient here in (i) provided a clear expression is stated] | If plot 1/T vs In <i>k</i> and gradient is -R/ <i>E</i> _a (2) If plot In <i>k</i> vs 1/RT and gradient - <i>E</i> _a (2) | " log" | 2 |

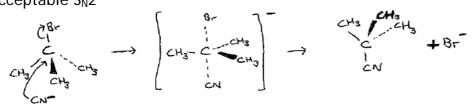
| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|----------------|--------------------|--------|------|
| 2 (b)(iii) | В | | | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---------------------------------------|-----------------------|--------|------|
| 3 (a) | (aqueous) ethanol /ethanolic solution | ethanol | | 1 |
| | | alcohol | | |
| | | propanone | | |

| Question | Correct Answer | Acceptable | Reject | Mark |
|----------|---|------------|--------|------|
| Number | | Answers | | |
| 3 (b)(i) | 1 st Mark | | | 2 |
| | S _N 1 | | | |
| | Or | | | |
| | must be (at least) two steps (1) | | | |
| | | | | |
| | 2 nd Mark | | | |
| | only the halogenoalkane is involved in the | | | |
| | r.d.s. | | | |
| | OR | | | |
| | CN ⁻ is not involved in rds (1) | | | |
| | | | | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|--|--------|------|
| 3 (b)(ii) | $\begin{array}{cccc} & & & & & & & \\ H_{3}C & & & & & \\ H_{3}C & & & & \\ $ | (CH₃)₃C-Br | | 3 |
| | $\begin{array}{c} \begin{array}{c} & & & \\ H_{3} & & \\ \hline \\ & & \\ & \\ & \\ & \\ & \\ & \\ & \\$ | | | |
| | structure of carbocation (1) Br ⁻ not essential attack by cyanide, arrow must start from C or -ve charge on C not N and -ve charge must be present somewhere on ion; lone pair not essential (1) IGNORE any references to rates of the steps | completely correct S _N 2 version scores (1) See below | | |

Acceptable $S_N 2$



| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|---|--|------|
| 3 (c) | yes, because the CN group will cause a different chemical shift (1) | no, because the proton/ H atom environment has not changed (so the nmr spectra will be the same) | Just 'No' any mention of more than one peak | 1 |

| Question | Correct Answer | Acceptable | Reject | Mark |
|--------------|---|--|--|------|
| Number | 1 st mark | Answers Names or formulae | | 4 |
| 3 (d) QWC | (heat with) NaOH / sodium hydroxide (solution) OR heat to red heat with sodium and drop into water (1) | can be used, but if both used both must be correct | | 4 |
| | 2 nd mark acidify / add excess / neutralise with nitric acid / HNO ₃ (1) If HCI is added here, only the 1 st mark can score 3 rd mark add silver nitrate (solution) /AgNO ₃ (1) 4 th mark | Dilute sulphuric acid for nitric | add HNO ₃ concentrated HNO ₃ | |
| | cream ppt (1) IGNORE reference to ammonia unless incorrect (e.g. soluble in dilute ammonia) | | Yellow /off- white ppt | |
| | Note: If no NaOH used only the 2^{nd} , 3^{rd} and 4^{th} marks can score If no acid is added, or if it is added before NaOH, only 3^{rd} and 4^{th} marks can score If order of addition is NaOH, AgNO ₃ , excess HNO ₃ , can score all marks If no NaOH and no HNO ₃ , can score 3^{rd} and 4^{th} marks If any reagent other than AgNO ₃ , including ammoniacal AgNO ₃ , is used, only 1^{st} and 2^{nd} marks can score. OR Mass spectroscopy (1) A doublet (1) of equal heights (1) in molecular ion peak (1) OR Mass spectroscopy (1) loss of m/e of 79 (1) | | | |
| | and 81 (1) from molecular ion (1) OR Infrared spectroscopy (1) Measure/record wavenumber (1) Absorption due to C-Br stretch (1) Compare wavenumber with data book (1) | | | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|--|---|------|
| 3 (e)(i) | dilute acid/(dilute) hydrochloric acid/dilute sulphuric acid / dilute nitric acid OR aqueous NaOH followed by dilute acid (1) | H ₃ O ⁺ (aq)/H ⁺ (aq) | concentrated acid OR Just "water" | 2 |
| | (CH ₃) ₃ CCOOH (1) STAND ALONE | (CH ₃) ₃ CCO ₂ H; displayed formulae | $C_3H_{10}O_2$ | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|---|------------------|------|
| 3 (e)(ii) | $(CH_3)_3CCOOH+CH_3CH_2OH \rightleftharpoons (CH_3)_3CCOOCH_2CH_3+H_2O$ | "-CO ₂ -" for "-COO-"; | CH₃CH₂ <u>HO</u> | 2 |
| | (1) for ethanol provided it is reacting with a carboxylic acid or acid chloride (1) for remainder of equation correct | "→" for " <i>⇒</i> " | | |
| | ALLOW $(CH_3)_3CCOCI+CH_3CH_2OH\rightarrow(CH_3)_3CCOOCH_2CH_3+HCI$ (2) if acid chloride is produced in first step | full structural formulae | | |
| | | $^{"}C_{2}H_{5}"$ for $^{"}CH_{3}CH_{2}"$ | | |

| Question | Correct Answer | Acceptable | Reject | Mark |
|----------|--------------------------------|-------------------------------------|--------|------|
| Number | | Answers | | |
| 4 (a)(i) | (anhydrous) aluminium chloride | Al ₂ Cl ₆ | Fe | 1 |
| | | AlBr ₃ FeBr ₃ | | |
| | [Name or formulae] | FeCl ₃ | | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|--|--------|------|
| 4 (a)(ii) | $CH_{3}CHCH_{3} + RICI_{3} \rightarrow CH_{3}CHCM_{3} + RICI_{3}Br^{-}(I)$ Br $CH_{3}CHCM_{3} + RICI_{3} \rightarrow CH_{3}CHCM_{3} + RICI_{3}Br^{-}(I)$ (I) $($ | either a delocalised or Kekule ring If CH ₃ CHBrCH ₃ → CH ₃ CH ⁺ CH ₃ + Br ⁻ loses 1 st mark but can score 2 nd , 3 rd and 4 th marks | | 4 |
| | OR $CH_{3}CHCH_{3}$ + AlCl ₃ \longrightarrow $CH_{3}CHCH_{3}$ + Br-AlCl ₃ \oplus H $CH_{3}CHCH_{3}$ + $Hr-AlCl_{3}$ \oplus H $CH_{3}CHCH_{3}$ + $Hr-AlCl_{3}$ | | | |
| | $ \begin{array}{c} & & & & & & \\ & & & & & \\ & & & & & $ | | | |
| | Equation for formation of electrophile (1) IGNORE if incorrect arrows added at this point | | | |
| | First arrow must be from C=C or from or within ring to C with + and can point to + (1) | | | |
| | Correct intermediate as shown in mechanism above (1) | | | |
| | Second arrow from C-H bond into ring (1) | | | |

| Question | Correct Answer | Acceptable | Reject | Mark |
|----------|------------------|----------------|------------------|------|
| Number | | Answers | | |
| 4 (b)(i) | $CH_3CH_2CH_2^+$ | $C_2H_5CH_2^+$ | $C_{3}H_{7}^{+}$ | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|-----------------------|---|------|
| 4 (b)(ii) | secondary carbocation is more stable than primary (1) primary carbocation $(CH_3CH_2CH_2^+)$ rearranges to produce a secondary carbocation OR primary carbocation $(CH_3CH_2CH_2^+)$ turns into a secondary carbocation OR a description of the rearrangement e.g. a hydrogen atom moves from the middle to the end (1) | | any reference to stability of intermediate /product | 2 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|-----------------------|--------------------------|------|
| 4 (c)(i) | First mark sodium nitrite /sodium nitrate(III)/NaNO ₂ (1) | | HNO ₂ | 2 |
| | Second mark hydrochloric acid / HCl(aq) (1) IGNORE concentration of acid 2 nd mark is conditional on NaNO ₂ or HNO ₂ | | HCI/hydrogen chloride | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|--------------------------------|--------|------|
| 4 (c)(ii) | below 0 °C reaction is too slow (1) | | | 2 |
| | above 10 °C the product/benzenediazonium ions decomposes /hydrolysed (1) | HNO ₂ decomposes | | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|--|---------|------|
| 4 (c)(iii) | N=N link, can be shown linear (1) IGNORE other atoms Remainder correct (1) | IGNORE position of OH group. —ONa or O ⁻ instead of OH | -N=N-O- | 2 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|-----------------------|--|------|
| 4 (c)(iv) | the bonds around the -N=N- bond are not linear (because of lone pairs) (1) Note: this could be shown on the diagram restricted rotation/no (free) rotation around the -N=N- (1) | | different groups on each N atom | 2 |

| Question | Correct Answer | Acceptable | Reject | Mark |
|-----------------|---|--|--|------|
| Number | | Answers | | |
| 4 (d)(i) QWC | First two marks add 2,4-dinitrophenylhydrazine/Brady's reagent (1) orange/yellow ppt (1) Allow this second mark if the name of the reagent is slightly incorrect e.g. 2,4-diphenylhydrazine | 2,4-dnp(h) Any combination of yellow and orange Must be ppt | Just "Red ppt" "solid" for "ppt" | 3 |
| | OR IR absorption due to C=O stretch (1) at 1700 cm ⁻¹ (1) Third mark Does not give a silver mirror with ammoniacal silver nitrate (or Tollens' reagent) | No change with Tollens' | | |
| | OR no red ppt/stays blue with Fehling's or Benedict's solution | | lodoform | |
| | OR H ⁺ /Cr ₂ O ₇ ²⁻ does not change from orange to green/stays orange | | | |
| | OR H ⁺ /MnO ₄ ⁻ does not change from purple to colourless/stays purple (1) | | | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|-----------------------|--------|------|
| 4 (d)(ii) | the C=O group is polar and the nucleophile attacks the $\delta^{\scriptscriptstyle +}$ carbon (1) | | | 2 |
| | whereas C=C is non-polar/electron-rich, the double bond/ π -bond is attacked by electrophiles (1) | | | |
| | OR C=O is polar and C=C is non-polar (1) | | | |
| | Nucleophile attacks the δ^+ carbon in C=O and electrophiles attack the π /double bond in C=C, which is electron rich/non-polar (1) | | | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|--|--------|------|
| 4 (d)(iii) | $H_{3}C$ H | | | 3 |
| | $H_{3C} \xrightarrow{O} H^{-CN} \xrightarrow{H_{3C} OH} H^{-CN} \xrightarrow{H_{3C} OH} H^{-CN} \xrightarrow{H_{3C} OH} H^{-CN}$ | curly arrow from O to H ⁺ | | |
| | both curly arrows in 1 st diagram, attack by cyanide, arrow must start from C or -ve charge on C not N and -ve charge must be present somewhere on ion; lone pair not essential. Arrow must start from bond between C and O and point towards the O (1) | | | |
| | Intermediate - Ione pair not essential but negative charge is essential (1) | | | |
| | Arrow from O (lone pair not needed) or negative charge to HCN or H ⁺ , this can be shown on the diagram of the intermediate (1) If HCN is used the arrow from H-CN bond is required | | | |
| | Any other ketone or aldehyde, max (2) | | | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|---|--------|------|
| 5 (a)(i) | Cr: [Ar] 3 <i>d</i> ⁶ 4 <i>s</i> ¹ Cu: [Ar] 3 <i>d</i> ¹⁰ 4 <i>s</i> ¹ Both needed for the mark | 4s ¹ 3d ⁵ 4s ¹ 3d ¹⁰ [Ar] written in full | | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|--|--|------|
| 5 (a)(ii) | all the others are 4s ² / have full 4s orbital (1) | Cr and Cu/they do not have a full 4s orbital | Just 'only have one electron in 4s' OR Have incomplete 4s orbital | 2 |
| | The d subshell is more stable when either half or fully filled OR A specific example of chromium having half-filled or copper having filled d sub-shell/set of d orbitals which is more stable (1) | sub-energy levels d shell | Half-filled or filled d- orbital(s) | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|---|--------|------|
| 5 (b)(i) | Octahedral drawn must be 3-D IGNORE any or no charge | -H ₂ O (bond to H) except on water molecules on left of Cr | | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|---|---|------|
| 5 (b)(ii) | Dative bond formed from electron pair/lone pair on oxygen (of the water molecule) to the ion This could be shown on a diagram | A clear description of the dative bond | 'dative' alone or from water Just "dative bond formed from oxygen" | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|--------------------|--------|------|
| 5 (b)(iii) | $[Cr(H_2O)_6]^{3+} + OH^- \rightarrow [Cr(H_2O)_5OH]^{2+} + H_2O$ OR $[Cr(H_2O)_6]^{3+} + 2OH^- \rightarrow [Cr(H_2O)_4(OH)_2]^+ + 2H_2O$ OR $[Cr(H_2O)_6]^{3+} + 3OH^- \rightarrow Cr(OH)_3 + 6H_2O$ OR $[Cr(H_2O)_6]^{3+} + 3OH^- \rightarrow [Cr(H_2O)_3(OH)_3] + 3H_2O$ First mark is for the correct Cr product Second mark is conditional on the first and is for the rest of the equation correct and balanced | | | 2 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|--|-----------------------|--------|------|
| 5 (b)(iv) | Forms a green precipitate (1) IGNORE initial colour of solution (which reacts or dissolves or changes to) a green solution (with excess reagent) (1) 2 nd mark is conditional on an initial ppt | any shade of green | | 2 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|----------------|--|---|------|
| 5 (b)(v) | acid / acidic | Amphoteric/able to be deprotonated | Coloured ions/ligand exchange/ deprotonation /partially filled d orbitals | 1 |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|-----------------------|--------|------|
| Number 5 (c)(i) | Check working - correct answer can be obtained by not dividing by 2 for 2^{nd} mark and not multiplying by 2 for 4^{th} mark amount thiosulphate in titre = 0.0372 dm ³ x 0.100 mol dm ⁻³ = 3.72 x 10 ⁻³ mol (1) amount $l_2 = \frac{3.72 \times 10^{-3}}{2}$ (1) =1.86 x10 ⁻³ mol 2^{nd} mark cq on amount thiosulphate amount dichromate in 25 cm ³ = $\frac{1.86 \times 10^{-3}}{3}$ (1) = 6.2 x10 ⁻⁴ mol 3^{rd} mark cq on amount l_2 Total mass Cr = 6.2 x10 ⁻⁴ mol x 2 x 10 x 52 g mol ⁻¹ (1) = 0.645 g 4 th mark cq on amount dichromate % of Cr = 64.5 % (1) IGNORE SF unless rounded to 1 SF cq on mass Cr, provided less than 1 g OR amount thiosulphate for whole sample = 0.0372 dm ³ x 0.100 mol dm ⁻³ x 10 = 3.72×10^{-2} mol (1) amount l_2 = 1.86 x10 ⁻² mol (1) amount dichromate = 6.2 x10 ⁻³ mol (1) mass Cr = 62 x 10 ⁻³ mol x 2 x 52 g mol ⁻¹ (1) = 0.645 g % of Cr = 64.5% (1) IGNORE SF unless rounded to 1 sf Mark consequentially, as above Note: | Answers 64.48 % | | 5 |
| | Correct answer with no working (3) | | | |

| Question Number | Correct Answer | Acceptable Answers | Reject | Mark |
|--------------------|---|--|---|------|
| 5 (c)(ii) | Colour at the end point would be green which would prevent the loss of iodine colour being seen OR colour change at end point would be disguised by the colour of Cr ³⁺ | Chromium instead of Cr ³⁺ | end point disguised by colour of Cr ₂ O ₇ ²⁻ /orange | 1 |