

GCE 2004
June Series



Mark Scheme

Chemistry – Advanced Extension Award *(Subject Code 6821)*

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

Advanced Extension Award (AEA)

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General Points

1. Mark in red.
2. Tick where mark is earned, not in margin.
3. Indicate errors which are penalised by underlining.
4. Ring errors which are not penalised.
5. Use a caret to indicate omission.
6. Write sub-totals in the margin at the end of each question.
7. Ring the total mark at the end of each question
8. Deduct one mark for an arithmetic error (AE) then mark consequentially (putting conseq in the margin.)
9. Wrong Chemistry (WC) or chemical error (CE) scores zero. (No consequential marking)
10. No marks for a contradiction.
11. Stick to the agreed mark scheme.
12. Do not make comments on the scripts.
13. Refer very difficult cases involving problems with several marks to the Senior Examiner.

Question 1

- (a) $\text{C}_6\text{H}_5\text{NO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + 2\text{H}_2\text{O}$ (1) **1**
- (b) $\text{SnCl}_2 + 4\text{HCl} \rightarrow [\text{SnCl}_6]^{2-} + 4\text{H}^+ + 2\text{e}^-$ species (1)
balance (1)
- or $\text{SnCl}_2 + 4\text{Cl}^- \rightarrow [\text{SnCl}_6]^{2-} + 2\text{e}^-$
- or $\text{Sn}^{2+} + 6\text{Cl}^- \rightarrow [\text{SnCl}_6]^{2-} + 2\text{e}^-$ **2**
- (c) $\text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^- \rightarrow \text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O}$ (1)
- $[\text{SnCl}_6]^{2-} + 6\text{OH}^- \rightarrow [\text{Sn}(\text{OH})_6]^{2-} (1) + 6\text{Cl}^-$ (1) **3**
- (d) pressure due to water = $100 - 8.0 = 92 \text{ kPa}$ (1)
- mole ratio $\text{H}_2\text{O} : \text{C}_6\text{H}_5\text{NH}_2 = 92 : 8.0$ (1)
- mass ratio $\text{H}_2\text{O} : \text{C}_6\text{H}_5\text{NH}_2 = 92 \times 18 : 8.0 \times 93$ (1)
- = $2.2(3) : 1$ (allow multiples) (1) **4**
- (e) dipole of water (1)
- attracted to high charge density on Ca^{2+} ion or Ca^{2+} hydrated (1) **2**
- or CaO reacts with water (1)
- to form $\text{Ca}(\text{OH})_2$ (1)
- (f) phenylamine has greater vdw (than water) (1)
- allow London forces or dispersion forces
- both phenylamine and water have hydrogen bonding (1)
- do not allow if hydrogen bonding, dipole-dipole and vdw all given
- larger vdw for phenylamine + one hydrogen bond >
smaller vdw + (2) hydrogen bonds for water (1) **3**
- allow total intermolecular forces greater for phenylamine

Question 2

- (a) (i) the ion from which the electron is removed has a greater net positive charge (1)
- the electron removed from Mg^+ is at a lower energy (*or attracted more*) (1) **2**
- OR* Mg^+ smaller than Mg (1)
- (*Outer electron nearer to*) attraction of nucleus (1)
- (ii) energy is released because there is a net attraction for the added electron by the oxygen nucleus (1)
- but the O^- ion has an overall negative charge or therefore electron repelled (1)
- energy must be supplied to add an electron (1) **3**
- (iii) method correct (1)
- correct numbers used (1)
- answer = 3888 (*ignore sign*) (1) **3**
- method marks; allow 496/2 used (1)*
- if both - 142 and +844 used allow (1)*
- NB 4136 scores (1)*
- (iv) *M1* (numerically) smaller (*must be linked to LE of formation or dissociation*) (1)
- M2* because Cl^- ion has only a single charge (1)
- M3* and Cl^- is larger than O^{2-} (1)
- M4* therefore weaker attraction between Cl^- and Mg^{2+} or converse (1) **4**
- allow (1) if surface density of charge stated rather than M2 and M3*

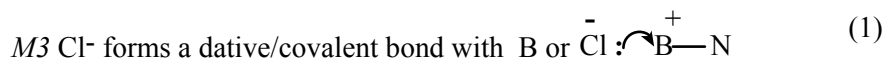
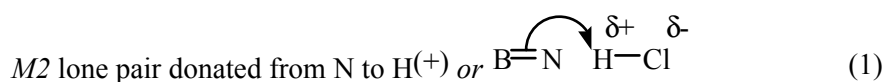
- (b) (i) $[\text{OH}^-]^2 = 1.1 \times 10^{-11}/[\text{Mg}^{2+}] = 5.5 \times 10^{-14}$ (1)
- $[\text{OH}^-] = 2.35 \times 10^{-4}$ (1)
- $K_{\text{w}} = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ (1)
- $[\text{H}^+] = K_{\text{w}} / [\text{OH}^-] = 4.26 \times 10^{-11}$ (1)
- pH = 10.37 *allow 10.36 to 10.38* (1) **5**
- equilibrium shifts to the left (1)
- concentration of Mg^{2+} reduced or $\text{Mg}(\text{OH})_2$ precipitates/ formed (1) **2**
- (ii) concentration of hydroxide ions is higher (1)
- therefore $\text{Ca}(\text{OH})_2$ is more soluble (*only allow if first mark given*) (1)
- add NaOH *allow OH^- or other suitable base* (1)
- keep pH below 12.3 *allow $12.3 > \text{pH} > 9.5$* (1)
- to prevent precipitation of $\text{Ca}(\text{OH})_2$ (1)
- allow; ions remain in solution or to keep $\text{Ca}(\text{OH})_2$ in solution*
- precipitate $\text{Mg}(\text{OH})_2$ (1) **6**
- allow addition of a buffer (1)*
- $12.3 > \text{pH} > 9.5$ (1)*
- (c) (i) uses only gaseous species in calculation (1)
- mole fractions correct (*mark consequentially*) (1)
- i.e. O_2 is 1/3 and Cl_2 is 2/3 if only gases used but
 O_2 is 0.25/1.75 and Cl_2 is 0.5/1.75 if solids included*
- partial pressures of Cl_2 and O_2 (*mark consequentially*) (1)
- $K_{\text{p}} = (\sqrt{33.3})/66.7 = 0.0866$ *Allow 0.086 - 0.087* (1)
- mark consequentially only to total moles = 1.75 then $K_{\text{p}} = 0.132$*
- units = $\text{kPa}^{-1/2}$ (1) **5**
- NB if candidates work in Pa then $K_{\text{p}} = 2.7(4) \times 10^{-3}$ (1) Units
 $\text{Pa}^{-1/2}$ (1)*

- (ii) total number of moles = 0.6 (*allow 1.6 if solids included*) (1)
- mole fraction correct (*mark consequentially even if total moles wrong*) (1)
- e.g. O₂ is 2/3 and Cl₂ is 1/3 if only gases used but
O₂ is 0.4/1.6 and Cl₂ is 0.2/1.6 if solids included*
- correct substitution into K_p relationship (1)
- $K_p = 790 - 820$ (1) **4**
- allow consequentially to K_p from above but only if total mole = 0.6
NB using given value, $K_p = 0.13$, answer in (ii) = 350 - 370 for full marks*
- (iii) M1 carbon removes O₂ (as CO₂ or CO) or reduces amount/concentration of O₂ (1)
- M2 equilibrium moves to the right (1)
- M3 ΔH for the reaction = $(2 \times -137) - (-395)$ data used correctly (1)
- = + 121 (kJ mol⁻¹) or - 121 for reverse reaction (1)
- M4 reaction endothermic (1)
- M5 (equilibrium shifts to right at high temperature hence) more CO (relative to CO₂) *allow the converse answer* (1) **6**
- only allow M4 and M5 if a value of ΔH has been calculated*

Question 3

- (a) (i) R1 $2\text{B}_2\text{O}_3 + 3\text{C} + 6\text{Cl}_2 \rightarrow 4\text{BCl}_3 + 3\text{CO}_2$ species (1)
balanced (1)
- or $\text{B}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \rightarrow 2\text{BCl}_3 + 3\text{CO}$
- R3 $\text{BCl}_3 + 6\text{NH}_3 \rightarrow \text{B}(\text{NH}_2)_3 + 3\text{NH}_4\text{Cl}$ species (1)
balanced (1)
- NB allow one for $\text{BCl}_3 + 3\text{NH}_3 \rightarrow \text{B}(\text{NH}_2)_3 + 3\text{HCl}$
- $\text{Cl}_2 =$ oxidising agent (1)
because $\text{Cl}^0 \rightarrow \text{Cl}^{-1}$ allow if shown with an equation (1)
- C = reducing agent (1)
because C gains oxygen or $\text{C}^0 \rightarrow \text{C}^{\text{II}}$ or C^{IV} (1) **8**
allow if shown with an equation
- (ii) M1 hexagonal rings with a minimum of 3 rings joined together correctly (1)
M2 alternate B and N (1)
M3 high temperature to overcome bond energy or E_a (1)
M4 high pressure to force layers together (to allow inter-layer bonds to form) (1)
M5 B - N bond stronger than C - C bond (must imply bonding is covalent) (1) **5**
allow a general explanation covering M3 and M4 (1)
- (iii) donation of electron pair from nitrogen (1)
to (electron deficient) B (1)
allow (1) if electrons stated to be delocalised as the only answer)
- P planar or flat (1)
Q puckered or not planar or not flat (1)
P bond angles $\sim 120^\circ$ or bond lengths different (1)
Q bond angles $\sim 109^\circ$ or bond lengths equal (1)
P; Trigonal planar bonding given as reason for planar structure (1)
Q; Pyramidal (or tetrahedral bonding) given as reason for puckered (1) **Max 6**

- (iv) M1 HCl is polar or a dipole shown on the molecule (1)



allow (1) if M2 and M3 not given but reaction stated to be an electrophilic addition

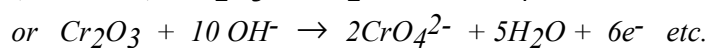
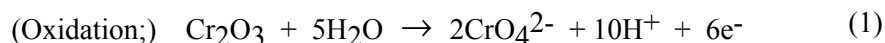
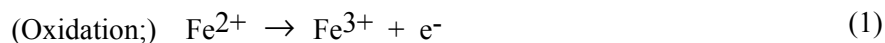
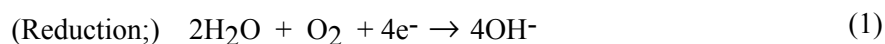
structure

ignore any charges included in this structure



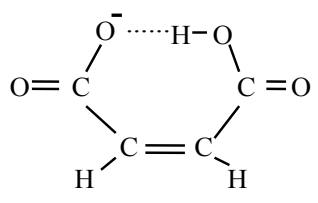
- (b) (i) brown precipitate of $\text{Fe}(\text{OH})_3$ or $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ where $x = 0 - 4$ (2)

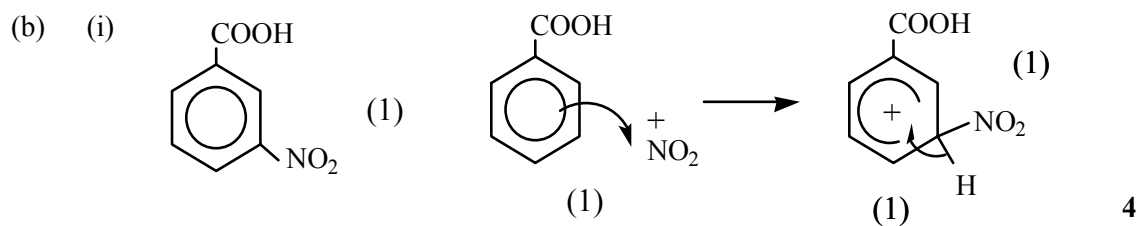
allow $\text{Fe}(\text{OH})_2$ (1)



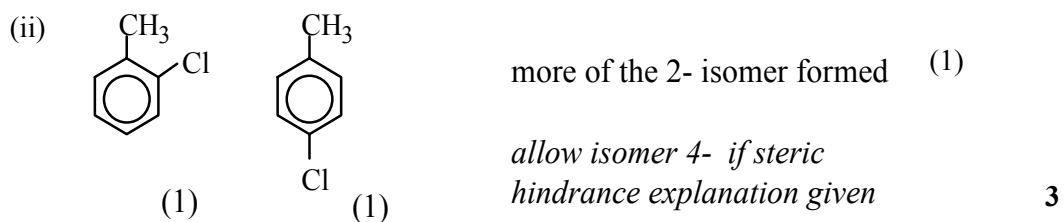
- (ii) empirical formula of $Z = \text{CrO}_2\text{Cl}_2$
- | | | | |
|--|--------|-----|--|
| | method | (1) | |
| | answer | (1) | |
- $pV = nRT$ (1)
- $n = pV/RT = 101000 \times 291 \times 10^{-6} / 8.31 \times 400 = 8.85 \times 10^{-3} \text{ mol}$ (1)
- $M_r = 1.37 / 8.85 \times 10^{-3} = 155$ allow 154 - 156 (1)
- empirical formula = molecular formula (1) **6**
- allow calculations based on GMV. Allow answers 154 - 156*
- structure = tetrahedral (1)
- bonding = $2 \times \text{Cr}=\text{O}$ and $2 \times \text{Cr}-\text{Cl}$ (1)
- $\text{Cr}_2\text{O}_7^{2-} + 4\text{Cl}^- + 6\text{H}^+ \rightarrow 2\text{CrO}_2\text{Cl}_2 + 3\text{H}_2\text{O}$
- | | | | |
|--|----------|-----|--|
| | species | (1) | |
| | balanced | (1) | |
- allow equations showing H_2SO_4 and HSO_4^- or SO_4^{2-} e.g.*
- $\text{Cr}_2\text{O}_7^{2-} + 4\text{Cl}^- + 6\text{H}_2\text{SO}_4 \rightarrow 2\text{CrO}_2\text{Cl}_2 + 6\text{HSO}_4^- + 3\text{H}_2\text{O}$
- $\text{CrO}_2\text{Cl}_2 + \text{Cl}^- + \text{H}_2\text{O} \rightarrow [\text{CrO}_3\text{Cl}^-] + 2\text{HCl}$ (1) **5**

Question 4

- (a) (i) $\text{CH}_3-\text{C} \begin{array}{l} \text{=O} \\ \text{O-H} \end{array} \rightleftharpoons \text{CH}_3-\text{C} \begin{array}{l} \text{=O} \\ \text{O}^- \end{array} + \text{H}^+$ (1)
- $\text{C}_2\text{H}_5-\text{O}-\text{H} \rightleftharpoons \text{C}_2\text{H}_5-\text{O}^- + \text{H}^+$ (1)
- inductive effects of C_2H_5 and CH_3CO compared (1)
- (effect of inductive effect on) strength of O - H bond compared (1)
- link to number of O - H bonds broken *or equilibrium position* (1)
- ability of anions to spread negative charge (1)
- effect on stability of CH_3COO^- and $\text{C}_2\text{H}_5\text{O}^-$ anions (1)
- linked to base strength of CH_3COO^- and $\text{C}_2\text{H}_5\text{O}^-$ anions *or equilibrium position* (1)
- hence $\text{C}_2\text{H}_5\text{OH}$ much less dissociated than CH_3COOH (1) **Max 6**
- (ii) the $\text{CH}_3\text{CH}_2 \rightarrow$ inductive effect (1)
- strengthens O - H *or makes $\text{CH}_3\text{CH}_2\text{COO}^-$ a stronger base* (1)
- $\text{Cl} \leftarrow$ inductive effect (1)
- weakens O - H *or makes RCOO^- a weaker base* (1)
- due to extra distance the effect of chlorine in 3 position is much less (1)
- F more electronegative than Cl (1) **6**
- (iii) in *cis*- isomer the COOH can interact *or are closer together* (1)
- interaction between COOH in *trans* - isomer not possible (1)
- cis*- anion stabilised by H bonding (1)
-  (1)
- no stabilisation for *trans*- anion therefore second H^+ lost more easily (1) **Max 2**

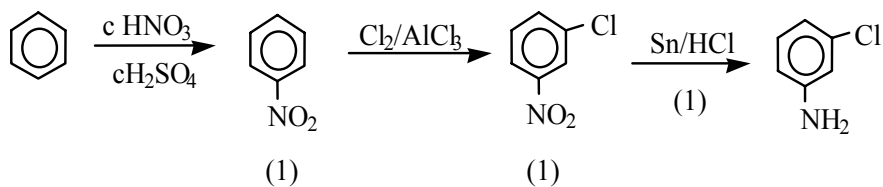
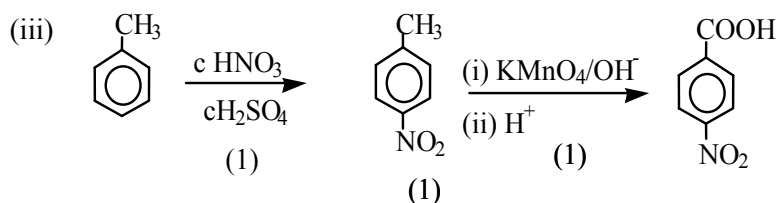


*allow arrow side of ring
if Kekule structure given
allow mechanism marks consequentially to an incorrect product*



more of the 2- isomer formed (1)

*allow isomer 4- if steric
hindrance explanation given*

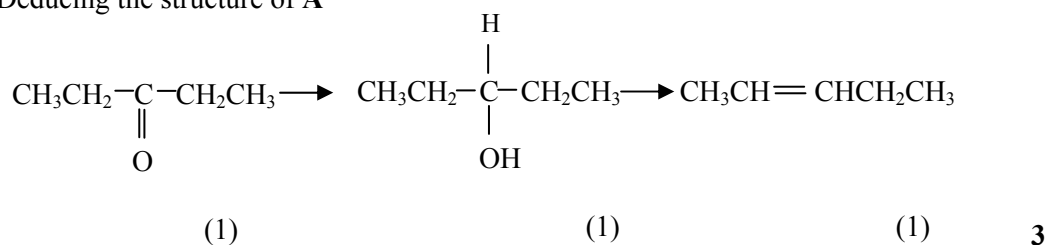


*allow an alternative oxidation e.g. by Cl₂ followed by NaOH and HCl
allow reduction by e.g. Sn/HCl even if reaction order incorrect in
second conversion*

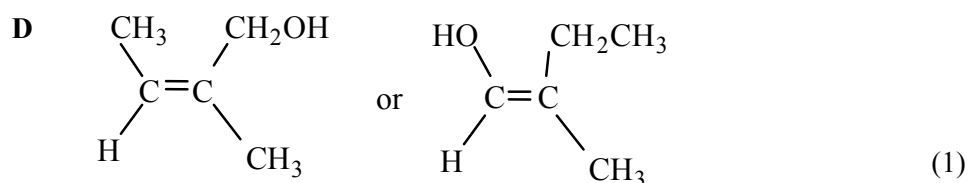
- (c) **A B C** contain C = O (1)
D E contain O - H in alcohols (1)
D contains C = C (1) **3**

allow each absorption once in any one correct structure

Deducing the structure of **A**



allow **B** as $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ if structure of **A** given incorrectly



allow any cyclic alcohol if no structure given for **E**, allow structure has an OH but no C = C (1)



allow any cyclic ether if no structure given for **F**, allow structure has no C = C, C = O or OH (1)

Total 13

Question 5(a)*allow answer given in relevant examples*

Rate

pressure/concentration

more particles collide (1)

more collisions with $E > E_a$ or more successful collisions (1)

increase in rate dependant on order of reaction (1)

rate $\propto [A]^n$ or Rate = $k[A]^m[B]^n$ or an example given (1)

rate constant unchanged (1)

surface area

more particles collide (1)

more successful collisions (1)

temperature

particles have more energy or greater velocity (1)

rate increases as temperature increase (1)

an exponential effect or rate increase rapidly (1)

small increase in number of collisions (1)

(large) increase in molecules with $E > E_a$ (1)

more successful collisions (1)

rate constant increases as temperature increases (1)

catalyst

alternative route (1)

lower activation energy (1)

more molecules with $E > E_{cat}$ (1)rate constant increases (1) **Max 15**

Equilibrium

effect predicted by Le Chatelier's Principle (1)

(total) pressure

effect depends on change in moles of gas, Δn (1)displace to right if $\Delta n =$ negative or converse (1)

equilibrium constant unchanged (1)

partial pressure/ concentration (1)

application of Le Chatelier's Principle to an example (1)

equilibrium constant unchanged (1)

temperature

depends on the sign of ΔH (1)displaced to right if ΔH is positive or converse (1)value of K_p increase if ΔH is positive or converse (1)

catalyst

rate of forward and back reactions increased equally (1)

equilibrium not displaced (1)

 K_p unchanged (1) **Max 10**

Question 5(b)

- (i)
- all examples given in part (i) must be real molecules*

Structural	(1)
same molecular formulae, different structures/ arrangement of atoms	(1)
a pair of molecules showing (<i>chain</i>) isomerism	(1)
a pair of molecules showing (<i>position</i>) isomerism	(1)
a pair of molecules showing (<i>functional group</i>) isomerism	(1)
Stereoisomers	(1)
same structural formula, atoms arranged differently in space	(1)
Geometrical or cis - trans	(1)
restricted or no rotation about a double bond	(1)
a pair of molecules showing <i>geometrical</i> isomerism	(1)
Optical	(1)
asymmetric carbon, or carbon with four different groups attached, or no plane/ centre/ axis of symmetry, or non-superimposable	(1)
a pair of mirror image molecules	(1)
rotate polarised light in opposite directions	(1)

Max 12

- (ii)
- in part (ii), ignore charges on all complexes and allow uncharged species*

Octahedral	
geometrical isomers can be formed	(1)
sketched structures of	
a complex with unidentate ligands, $[M(X)_2(Y)_4]^{(n+/-)}$ showing Xs at 90°	(1)
a complex with unidentate ligands, $[M(X)_2(Y)_4]^{(n+/-)}$ showing Xs at 180°	(1)
<i>if structures not given, allow complex written as $[M(X)_2(Y)_4]^{(n+/-)}$ (1)</i>	
a complex with bidentate ligands $[M(Z)_2(Y)_2]^{(n+/-)}$ showing bidentates's at 90°	(1)
a complex with bidentate ligands $[M(Z)_2(Y)_2]^{(n+/-)}$ showing bidentates's at 180°	(1)
<i>if structures not given, allow complex written as $[M(Z)_2(Y)_2]^{(n+/-)}$ (1)</i>	
optical isomers can be formed	(1)
sketched structures of	
an optically active complex	(1)
the mirror image of the complex	(1)
<i>if structures not given, allow a written complex with three bidentate ligands (1)</i>	

Tetrahedral

no geometrical isomers can be formed (1)

all isomers have a plane/ centre/ axis of symmetry, or are superimposable (1)

optical isomers can be formed (1)

sketched structures of a complex with four different ligands (1)

the mirror image of the complex (1)

if structures not given, allow a written complex with four different ligands (1)

NB Do not allow answers which refer to square planar complexes as the question asks for complexes with octahedral and tetrahedral shapes.

Max 15