



## **General Certificate of Education**

# **Chemistry 6421**

**CHM5      Thermodynamics and Further  
Inorganic Chemistry**

## **Mark Scheme**

*2007 examination - June series*

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.

Further copies of this Mark Scheme are available to download from the AQA Website: [www.aqa.org.uk](http://www.aqa.org.uk)

Copyright © 2007 AQA and its licensors. All rights reserved.

#### COPYRIGHT

AQA retains the copyright on all its publications. However, registered centres for AQA are permitted to copy material from this booklet for their own internal use, with the following important exception: AQA cannot give permission to centres to photocopy any material that is acknowledged to a third party even for internal use within the centre.

Set and published by the Assessment and Qualifications Alliance.

**CHM 5****Question 1**

- (a)  $\text{Mg}^{2+}(\text{g}) + 2\text{e}^{-} + 2\text{Cl}(\text{g})$  (This is the only answer for the top line) (1)
- $\text{Mg}^{2+}(\text{g}) + 2\text{e}^{-} + \text{Cl}_2(\text{g})$  (1)
- $\text{Mg}^{+}(\text{g}) + \text{e}^{-} + \text{Cl}_2(\text{g})$  (1)
- $\text{Mg}(\text{g}) + \text{Cl}_2(\text{g})$  (state symbols and electrons essential) (1)  
(Note  $\text{Cl}_2$  to  $2\text{Cl}$  can be in any order but Mg must be in sequence)
- (b) I.E. + 642 + 150 + 736 + 2 × 121 = 2 × 364 + 2493 *numbers &* (1)  
*signs* (1)  
*Factors of 2*
- I.E. = (+)1451 ( $\text{kJ mol}^{-1}$ ) (Ignore units even if wrong) (1)
- (Note +1208, +1087, +1572 Each score one only)
- (c)  $\Delta H = -\Delta H(\text{lattice formation}) + \Sigma\Delta H(\text{hydration})$  (or cycle with state symbols, (1)  
*numbers or labels*)  
= 2493 – 1920 – 2 × 364 (1)  
= -155 (1)
- (Note MgCl score zero; +155 scores 1/3)
- (d) (i) Increase in disorder on dissolving or  $\Delta S$  positive (1)  
 $\Delta G$  negative or  $T\Delta S > \Delta H$  (1)
- (ii) Moles of  $\text{NH}_4\text{Cl} = 2/53.5 = 0.0374$  (Wrong compound loses first 2, (1)  
wrong  $M_r$  loses 1)  
Heat absorbed =  $15 \times 0.0374 = 0.561$  (mark is for × 15) (1)
- $Q = m c \Delta T$  (1)  
 $\Delta T = Q/mc = (0.561 \times 1000)/(50 \times 4.2) = 2.6$  ( $^{\circ}\text{C}$ ) (1)  
(allow 2.5 to 2.7)(can use 52) (ignore units, answer must be at least 2 sig figs)
- (Note; may not use moles (loses first 2 marks) so  $\Delta T = (15 \times 1000)/(50 \times 4.2)$   
So answers of 71.4 and 68.7 score last 2 out of first 4)
- Final temperature =  $20 - 2.6 = 17.4$   $^{\circ}\text{C}$  (Answer is for 20 – previous (1)  
ans; must be < 20)  
(allow no units for temperature, penalise wrong units)

**Total 17**

**Question 2**

- (a)  $\Delta H = \Sigma\Delta H(\text{formation products}) - \Sigma\Delta H(\text{formation reactants})$   
(or cycle with state symbols or numbers or labels and number of moles correct)
- =  $3 \times -111 - (-1669)$  (mark is for either these numbers or the above formula or cycle) (1)
- = +1336 (-1336 scores zero, ignore wrong units) (1)
- $\Delta S = \Sigma S(\text{products}) - \Sigma S(\text{reactants})$   
=  $2 \times 28 + 3 \times 198 - (51 + 3 \times 6)$  (mark is for either these numbers or the above formula) (1)
- = +581 (ignore wrong units) (1)
- $\Delta G = \Delta H - T\Delta S$  (1)
- =  $1336 - (298 \times 581)/1000$  (1)
- = 1163 (allow 1160 – 1170) (allow conseq but if 1000 omitted CE) (1)
- (allow no units, penalise wrong units)
- (if answer is 1163000 with no units award 3 marks)
- $\Delta G$  is positive (or free energy (G) increases) (mark independently) (1)
- (b) When  $\Delta G = 0$  OR  $T = \Delta H/\Delta S$  (1)
- =  $(1336 \times 1000)/581 = 2299$  K (allow 2300) (1)
- (given data produces same answer)
- (allow consequentially, Units of  $T$  must be present and correct)
- (negative value for  $T$  loses second mark)
- (c)  $E_a$  too high or reaction too slow (1)
- (d) Method: Electrolysis (zero if incorrect but if reduction stated lose this and mark on) (1)
- Conditions: Molten or high  $T$  or 500-1500 °C or dissolved (1)
- Cryolite (1)
- (ignore irrelevant conditions)

**Total 14****Question 3**

- (a) (i) None or No reaction (If wrong answer do not mark on) (1)
- $E(\text{Zn}^{2+}/\text{Zn})$  more negative than  $E(\text{Fe}^{2+}/\text{Fe})$  (allow converse) (1)
- (Allow  $E$  zinc (or zinc) more negative or  $E$  reaction negative or cell voltage = -0.32)
- (ii)  $\text{Fe}^{2+}$  (1)
- $\text{Cr}^{3+}$  (1)
- (apply list principle after looking at two answers, need one correct species to mark on)
- $E(\text{Fe}^{3+}/\text{Fe}^{2+})$  more positive than  $E(\text{Cr}^{3+}/\text{Cr}^{2+})$  (1)
- (Allow  $E$  iron (or iron) more positive or  $E$  reaction positive or cell voltage = 1.18)
- (b)  $\text{Emf} = -0.41 - (-0.76) = 0.35$  (1)
- $\text{Zn} + 2\text{Cr}^{3+} \rightarrow \text{Zn}^{2+} + 2\text{Cr}^{2+}$  (Ignore state symbols) (1)

- (c)  $K_a = \frac{[H^+][A^-]}{[HA]}$  or  $= \frac{[H^+]^2}{[HA]}$  (1)  
 $[H^+] = \sqrt{K_a[HA]} = \sqrt{(1.15 \times 10^{-4} \times 0.5)}$  (mark is for expression or numbers) (1)  
 $= 7.58 \times 10^{-3} \text{ mol dm}^{-3}$  (1)  
 $\text{pH} = -\log_{10}[H^+]$  (or log or lg) (allow last two marks consequential on wrong  $[H^+]$ ) (1)  
 $\text{pH} = 2.12$  (note that 4.24 will score last two marks) (1)
- (d) (i) Green solution (not blue-green or grey-green) (1)  
 $[\text{Cr}(\text{OH})_6]^{3-}$  (or  $\text{Cr}(\text{H}_2\text{O})(\text{OH})_5^{2-}$  or  $\text{Cr}(\text{H}_2\text{O})_2(\text{OH})_4^-$ ) (1)
- (ii) Green precipitate (allow grey-green) (1)  
 bubbles (or gas or fizzing or effervescence, not gives off  $\text{CO}_2$ ) (1)  
 $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3$  (or  $\text{Cr}(\text{OH})_3$ ) (1)

**Total 17****Question 4**

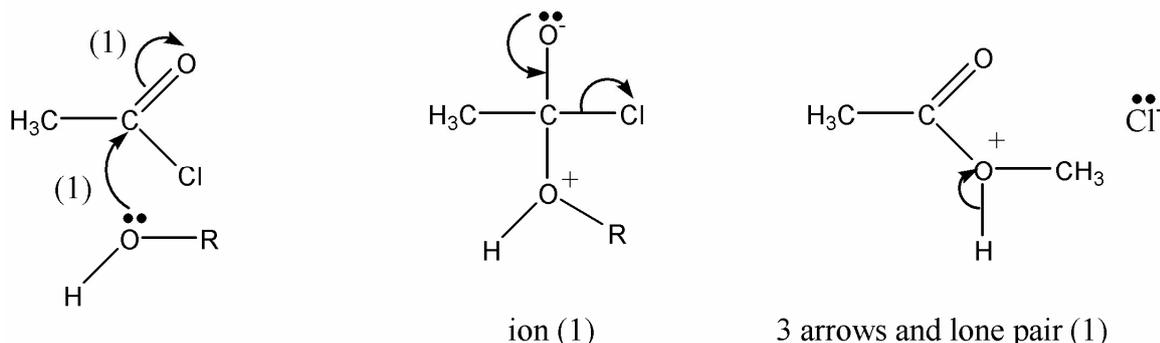
- (a) Ability of an atom or element to attract or withdraw electrons/electron density (1)  
 In a covalent bond (1)  
 (this mark consequential on a correct or sensible response to first mark e.g. when atom or element omitted lose first mark but gains second)
- (b) Trend; increases or stronger (Zero if this answer is wrong) (1)  
 Explanation: more protons or greater nuclear charge (1)  
 Similar/same shielding or electrons in same shell or similar radius or smaller radius (1)
- (c) (i)  $\text{MgO}$ : ionic (zero as a contradiction if mention of molecules) (1)  
 $\text{P}_4\text{O}_{10}$ : covalent (1)  
 (ignore information about structures unless there is a contradiction)
- (ii) Electronegativity difference small (1)  
 or electronegativities similar, NOT same  
 or converse: big difference in electronegativity leads to ionic bonding  
 This mark consequential on covalent for  $\text{P}_4\text{O}_{10}$
- (d)  $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^-$  (or  $2\text{NaOH}$ ) (1)  
 $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$  (or acid correctly ionised) (1)
- (e)  $\text{MgO} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O}$  (or  $\text{MgO} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2\text{O}$ ) (1)
- (f)  $\text{P}_4\text{O}_{10} + 12\text{NaOH} \rightarrow 4\text{Na}_3\text{PO}_4 + 6\text{H}_2\text{O}$  (or  $\text{P}_4\text{O}_{10} + 12\text{OH}^- \rightarrow 4\text{PO}_4^{3-} + 6\text{H}_2\text{O}$ ) (1)  
 (ignore state symbols)

**Total 12****Question 5**

- (a) H bonding in propanoic acid (1)  
 stronger than intermolecular forces in ester (mark is for a comparison) (1)  
 (not H bonding not ionic)

- (b)  $\text{---}\left(\text{OCH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{C}\right)_n\text{---}$  (brackets and n not essential)
- correct ester linkage (must show C=O) (1)
- correct formula and chain linkages (1)
- dipole-dipole intermolecular forces or attractions (1)
- stronger than van der Waals' forces in the poly(ethene) QWC mark (1)
- or more energy required to overcome than for vdw

(c)

(Cl<sup>-</sup> not essential)

(ignore partial charges on acid chloride even if wrong (circle them))

(penalise charges on acid chloride)

(4)

- (d) moles of ester = 0.5 – 0.35 = 0.15 (1)
- moles of water = 4 – 0.35 = 3.65 (1)
- moles of acid = moles of alcohol = 0.35 (1)
- (mark for equal moles of acid and alcohol can be gained from  $K_c$  expression)
- $K_c = \frac{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]} = \frac{(0.35/V)^2}{(0.15/V) \times (3.65/V)} = \frac{0.35^2}{0.15 \times 3.65}$  (mark for expression) (1)
- = 0.22 (allow 0.2 to 0.22, only this answer scores last mark) (1)

**Total 15****Question 6**

- (a) (i)  $\text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{V}_2\text{O}_4$  (allow  $2\text{VO}_2$ ) (1)
- $\text{V}_2\text{O}_4 + 1/2\text{O}_2 \rightarrow \text{V}_2\text{O}_5$  (1)
- V(IV) or 4 and V(V) or 5 (1)
- (ii)  $\text{MnO}_4^- + 8\text{H}^+ + 4\text{Mn}^{2+} \rightarrow 5\text{Mn}^{3+} + 4\text{H}_2\text{O}$  (1)
- $2\text{Mn}^{3+} + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 2\text{CO}_2$  (1)
- Mn(III) or 3 and Mn(II) or 2 (1)
- (b)  $[\text{Co}(\text{NH}_3)_6]^{2+}$  (formed) (1)
- Complex easy (easier) to oxidise (1)
- $\text{H}_2\text{O}_2$  (or air or oxygen) (1)
- (ignore additional reagents e.g. NaOH)

- (c) moles of dichromate =  $(29.2/1000) \times 0.04 = 0.001168$  or  $0.00117$  (1)  
 moles of  $Q^{2+} = (25/1000) \times 0.140 = 0.0035(0)$  (1)  
 each mole of dichromate needs 6 electrons or half equation with  $6 e^-$  (1)  
 moles of electrons =  $6 \times 0.001168 = 0.007008$  or moles  $Q^{2+}$ :moles (1)  
 dichromate = 3:1  
 Moles of electrons per mole of Q =  $0.007008/0.0035 = 2.002 = 2$  (gets previous (1)  
 mark also)  
 Q(IV) or  $Q^{4+}$  (1)

(If see this answer gets mark but need working to score other marks

If use  $MnO_4^-$  can score M1 and M2 only)

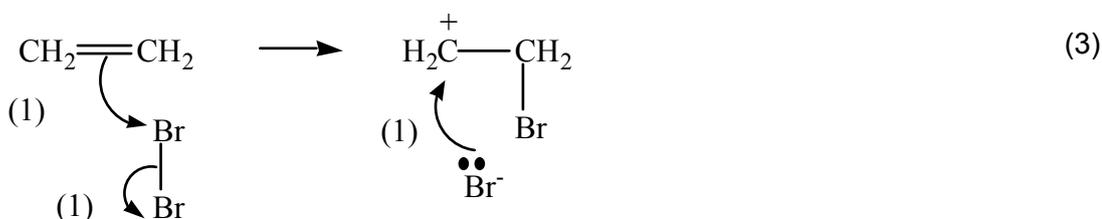
Can score full marks if M5 not given because M6 with workin implies M5

(Note,  $6 \times 0.001168 = 0.007008$  (M4) also score M3)

**Total 15**

### Question 7

- (a) Bromine (or  $Br_2$ ) (can score this mark from mechanism) (1)  
 (ignore solvents, ignore conditions)  
 electrophilic addition (1)

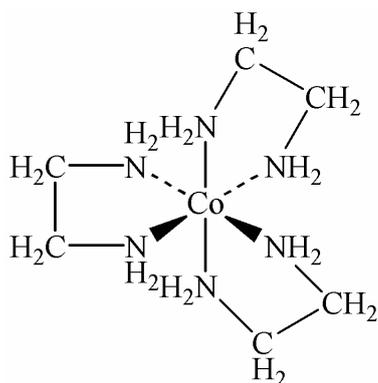


(arrow plus intermediate for last mark)

(ignore wrong partial charges on Br, penalise ionic charges one mark)

- (b) Ammonia or  $NH_3$  (apply list principle to multiple reagents)(can score this (1)  
 from equation)  
 nucleophilic substitution (1)  
 $4NH_3 + BrCH_2CH_2Br \rightarrow H_2NCH_2CH_2NH_2 + 2NH_4Br$  (can be two equations) (1)

(c)



(2+) (allow if charge not given, penalise wrong metal one mark)

6 co-ordination using N in three bidentate ligands (1)

All ligands correct (1)

(this mark consequential on gaining previous mark)

- (d) EDTA<sup>(4-)</sup> has 6 lone pairs to donate (1)  
 (or can for 6 co-ordinate bonds or has 6 donor atoms)  
 $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + \text{EDTA}^{4-} \rightarrow [\text{CoEDTA}]^{2-} + 6\text{H}_2\text{O}$  [] not essential (1)  
 Number of species increases 2 to 7) (1)  
 increase in disorder or positive entropy change (1)  
 Enthalpy change small (1)  
 hence negative free energy change or more stable ion or product or complex (1)
- max 5 marks  
**Total 15**

**Question 8**

- (a) CH<sub>3</sub>CH<sub>2</sub>Cl two peaks (zero if not two peaks) (1)  
 (mark for two peaks independent of wrong answer to next two marks)  
 integration ratio 3:2 (1)  
 split into triplet and quartet (allow if wrongly assigned, allow quad... etc) (1)
- CH<sub>3</sub>CHCl<sub>2</sub> two peaks (1)  
 (mark for two peaks independent of wrong answer to next two marks)  
 integration ratio 3:1 (1)  
 split into doublet and quartet (1)
- (b) (i) KBr orange-brown solution QWC (1)  
 (or orange or brown or yellow-brown) (fumes loses mark)  
 $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$  or equation with Cl<sub>2</sub> and I<sup>-</sup> one correct (1)  
 equation required  
 KI (red-) brown solution or black solid (mention of purple loses mark) (1)  
 $(\text{Cl}_2 + 2\text{I}^- \rightarrow 2\text{Cl}^- + \text{I}_2)$   
 (Note to score observation mark must be different from one with KBr)
- (ii) BaCl<sub>2</sub> white precipitate (apply list principle to incorrect observations) (1)  
 $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4$  ( or  $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + 2\text{HCl}$ ) (1)  
 MgCl<sub>2</sub> no precipitate or no change (ignore MgCl<sub>2</sub> equation) (1)  
 (do not allow nothing or no observation)
- (iii) CoCl<sub>2</sub> goes blue (not two colours) (1)  
 CuCl<sub>2</sub> goes green (or yellow) (1)  
 $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow \text{CoCl}_4^{2-} + 6\text{H}_2\text{O}$  (1)  
 or  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow \text{CuCl}_4^{2-} + 6\text{H}_2\text{O}$   
 (allow any balanced equation leading to CoCl<sub>4</sub><sup>2-</sup>)  
 (one correct equation required)

**Total 15**