

# General Certificate of Education

## Chemistry 6421

### *CHM5 Thermodynamics and Further Inorganic Chemistry*

## Mark Scheme

### *2005 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.

**Question 1**

(a)	oxidation state of N in $\text{Cu}(\text{NO}_3)_2$ :	+5;	1
	oxidation state of N in $\text{NO}_2$ :	+4;	1
	oxidation product:	oxygen;	1
			Total 3
(b)	copper-containing species:	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ;	1
	shape:	octahedral;	1
			Total 2
(c)	(i) precipitate B: $\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2$ or $\text{Cu}(\text{OH})_2$ or name;		1
	equation: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 2\text{NH}_3 \rightarrow \text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2 + 2\text{NH}_4^+$		
	OR		
		$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$	
	and		
		$[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 2\text{OH}^- \rightarrow \text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2 + 2\text{H}_2\text{O}$ ;	1
	(ii) $\text{NH}_3$ accepts a proton;		1
			Total 3
(d)	(i) identity: $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ ;		1
	colour: deep blue;		1
	equation: $\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2 + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 2\text{H}_2\text{O} + 2\text{OH}^-$ ;		1
	(ii) $\text{NH}_3$ is an electron pair donor;		1
			Total 4
(e)	identity: $[\text{CuCl}_4]^{2-}$ ;		1
	colour: yellow-green;		1
	shape: tetrahedral;		1
(f)	(i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ ;		1
	(ii) role of Cu: a reducing agent;		1
			Total 2
			<b>Total 17</b>

**Question 2**

(a) Concentration of acid:  $m_1v_1 = m_2v_2$  hence  $25 \times m_1 = 18.2 \times 0.150$

OR

moles NaOH =  $2.73 \times 10^{-3}$ ; 1

$m_1 = 18.2 \times 0.150 / 25 = 0.109$ ; 1

Total 2

(b) (i)  $K_a = [H^+][A^-] / [HA]$  not  $K_a = [H^+]^2 / [HA]$ ; 1

(ii)  $pK_a = -\log K_a$ ; 1

(iii)  $\{A^-] = [HA]$ ; 1

hence  $K_a = [H^+][A^-] / [HA] = [H^+]$   
and  $-\log K_a = -\log [H^+]$ ; 1

Total 4

(c) ratio  $[A^-] : [HA]$  remains constant; 1

hence as  $[H^+] = K_a [HA] / [A^-]$ ;  $[H^+]$  remains constant; 1

Total 2

(d) (i) pH of  $0.250 \text{ mol dm}^{-3}$  HCl = 0.60 and  
pH of  $0.150 \text{ mol dm}^{-3}$  HCl = 0.82; 1  
pH change = 0.22; 1

(ii) moles HCl =  $30 \times 0.250 \times 10^{-3} = v \times 0.150 \times 10^{-3} = 7.50 \times 10^{-3}$

OR

$v = 30 \times 0.250 \times 10^{-3} / 0.150 \times 10^{-3} = 50$ ; 1

water added =  $50 - 30 = 20 \text{ cm}^3$ ; 1

Total 4

**Total 12**

**Question 3**

(a) (i)

	The addition of AgNO <sub>3</sub>	followed by	the addition of concentrated NH <sub>3</sub> (aq)
Observation with NaBr(aq)	Cream or off white precipitate or solid (1)		Precipitate dissolves (1)
Observation with NaI(aq)	Yellow precipitate or solid (1)		Precipitate insoluble or no change (1)

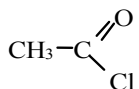
(ii) Ag F is soluble; 1

Total 5

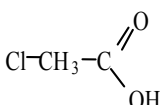
(b) (i) identity: [Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>3-</sup>; 1(ii) equation:  $\text{AgI} + 2\text{S}_2\text{O}_3^{2-} \rightarrow [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} + \text{I}^-$ ; 1

(iii) use: in photography or as a fixer; 1

Total 3

(c) (i) Structure:  1

Observation: Vigorous or violent or exothermic reaction or fumes or white precipitate formed immediately; 1

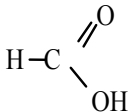
(ii) Structure:  1

Observation: No immediate precipitate or reaction

OR

white precipitate formed very slowly; 1

Total 4

- (d) (i) Silver-containing complex:  $[\text{Ag}(\text{NH}_3)_2]^+$ ; 1  
Shape: Linear; 1
- (ii) Structure  1  
Explanation: Methanoic acid contains an aldehyde group; 1
- (iii)  $\text{H}_2\text{CO}_3$  or  $\text{CO}_2$  or  $\text{OC}(\text{OH})\text{NH}_2$  or  $(\text{NH}_2)_2\text{CO}$  or  $(\text{NH}_4)_2\text{CO}_3$   
OR  
 $\text{HCOONH}_4$ ; 1

Total 5

**Total 17**

**Question 4**

(a) most powerful reducing agent: Zn; 1

Total 1

(b) (i) reducing species:  $\text{Fe}^{2+}$ ; 1

(ii) oxidising species:  $\text{Cl}_2$ ; 1

Total 2

(c) (i) standard electrode potential 1.25 V; 1

(ii) equation:  $\text{Tl}^{3+} + 2 \text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{Tl}^{+}$  balanced; 1  
correct direction; 1

Total 3

(d) (i) moles  $\text{KMnO}_4 = 16.2 \times 0.0200 \times 10^{-3} = 3.24 \times 10^{-4}$ ; 1

moles  $\text{H}_2\text{O}_2 = \text{Moles KMnO}_4 \times 5 / 2 = 8.10 \times 10^{-4}$ ; 1

$8.10 \times 10^{-4}$  moles  $\text{H}_2\text{O}_2$  in  $25 \text{ cm}^3$

$8.10 \times 10^{-4} \times 1000 / 25$  in  $1000 \text{ cm}^3 = 0.0324 \text{ mol dm}^{-3}$ ; 1

hence  $\text{g dm}^{-3} = \text{mol dm}^{-3} \times M_r = 0.0324 \times 34 = 1.10$ ; 1

*(penalise use of an incorrect  $\text{H}_2\text{O}_2$  to  $\text{KMnO}_4$  ratio by two marks)*

(ii)  $PV = nRT$ ; 1

hence  $V = nRT / P$

$= 8.10 \times 10^{-4} \times 8.31 \times 298 / 98000$ ; 1

$= 2.05 \times 10^{-5}$ ; 1

units  $\text{m}^3$ ; 1

Total 8

*(mark consequentially to answers in (c)(i))*

*(allow correct answers with other units)*

*(answers to (c)(i) and (ii) must be to 3 significant figures; penalise once only)*

**Total 14**

**Question 5**

- (a) effect on reaction rate: catalyst provides an alternative reaction route.; 1  
 with a lower  $E_a$ ; 1  
 more molecules able to react or rate increased; 1
- equilibrium: forward and backward rates changes by the same amount; 1  
 hence concentration of reactants and products constant or 1  
 yield unchanged;

Total 5

- (b) heterogeneous: catalyst in a different phase or state to that of the reactants; 1
- active site: place where reactants adsorbed or attached or bond etc.; 1  
 reaction occurs or an explanation of what happens; 1  
 (*allow absorbed*)
- reasons: large surface area; 1  
 reduce cost or amount of catalyst; 1
- catalyst poison: lead adsorbed; 1  
 lead not desorbed or site blocked; 1  
 (*lead adsorbed irreversibly scores both of these marks*)

Total 7

- (c) reaction slow as: both ions negatively charged or ions repel; 1
- $2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$  Species; 1  
 Balanced; 1
- $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$  Species ; 1  
 Balanced; 1

Total 5

**Total 17**

**Question 6**

- (a) aluminium chloride is covalent; 1  
 aluminium chloride does not conduct electricity; 1  
 aluminium chloride sublimes when heated; 1  
 aluminium chloride does not occur naturally; 1  
 manufacture of  $\text{AlCl}_3$  involves expensive chlorine; 1  
*(allow any two correct statements but not  $\text{AlCl}_3$  is expensive without justification)*
- Total 2 max
- (b)  $\Delta H_{\text{r}} = \Sigma \Delta H_{\text{f}} \text{ products} - \Sigma \Delta H_{\text{f}} \text{ reactants}$   
 $= (-111 \times 3) - (-1676);$  1  
 $= 1340 \text{ to } 1343 \text{ kJ mol}^{-1};$  1
- $\Delta S_{\text{r}} = \Sigma S \text{ products} - \Sigma S \text{ reactants}$   
 $= [(3 \times 198) + (2 \times 28)] - [51 + (3 \times 6)];$  1  
 $= 581 \text{ J K mol}^{-1};$  1
- $\Delta G = \Delta H - T \Delta S;$  1
- Minimum temperature when  $\Delta G \leq 0;$  1  
*(either  $T = \Delta H / \Delta S$  or  $0 = \Delta H - T \Delta S$  scores these two marks)*
- $= 1343 \times 1000(1) / 581$   
 $= 2310 \text{ to } 2314 \text{ K};$  1
- (K not required but penalise if incorrect)*  
*(mark consequentially to incorrect values of  $\Delta H$  and  $\Delta S$ )*
- Total 8
- (c) fluorine:
- (i) fluorine is the most reactive halogen ;  
 or the strongest oxidising agent; 1  
*(do not allow F for fluorine and penalise  $\text{Fl}_2$  once)*
- (ii) a stated product is HF or  $\text{NaHF}_2;$  1  
 $\text{NaF} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HF};$  1
- Total 3



**Question 7**

- (a) magnesium chloride: lattice; 1  
ionic; 1

Q of L: strong electrostatic attraction or forces between oppositely charged ions; 1  
(CE = 0 if there is any reference to molecules or atoms or delocalised electrons or metallic bonding)

- silicon tetrachloride: molecular or molecules; 1  
covalent; 1

Q of L: van der Waals or London or Dispersion or Temporary dipole-dipole forces between molecules; 1  
(CE = 0 if there is any reference to ions or delocalised electrons or metallic bonding) (do not allow vdw)  
(penalise 'permanent dipole-dipole' as a contradiction to vdw)  
(penalise 'Si - Cl bonds broken' by lost of the Q of L mark)  
(max 1, for 'covalent bonding' if there is any reference to a macromolecule)

Total 6

- (b) Na<sub>2</sub>O: vigorous or violent or exothermic reaction; or forms a colourless solution; 1  
pH of solution formed = 13 or 14; 1  
Na<sub>2</sub>O + H<sub>2</sub>O → 2NaOH; 1  
(allow ionic equations)

P<sub>4</sub>O<sub>10</sub> or P<sub>2</sub>O<sub>5</sub>: vigorous or violent or exothermic reaction; or forms a colourless solution; 1  
pH of solution formed = 0 or 1; 1  
P<sub>4</sub>O<sub>10</sub> + 6H<sub>2</sub>O → 4H<sub>3</sub>PO<sub>4</sub>; 1  
(Allow equations with P<sub>2</sub>O<sub>5</sub>)  
(mark on following an incorrect observation)  
(penalise the observation mark if contradictory observations given)  
(ignore equilibrium signs in equations)

Total 6

**Total 12**

**Question 8**

(a) nucleophile (*this must be stated and must be a reagent*)

HCN or KCN or NaCN or KCN/H<sup>+</sup> or NaCN/H<sup>+</sup> ; 1  
 (not KCN/OH<sup>-</sup> or CN<sup>-</sup>)

Equation: CH<sub>3</sub>CHO + HCN → CH<sub>3</sub>CH(OH)CN; 1

Explanation: a racemic mixture has equal amounts of two optical isomers; 1  
 the CHO or aldehyde (group) is planar; 1  
 attacked from each side (with equal probability); 1  
 (2 max)

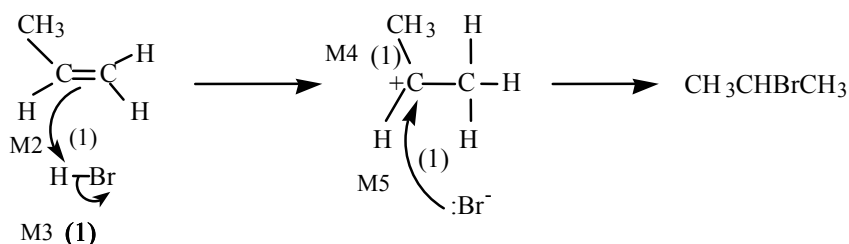
(mark independently)  
 (do not allow 'Molecule is planar')

Total 4

(b) electrophile;

M1 HBr or H<sub>2</sub>SO<sub>4</sub> or Br<sub>2</sub>; 1  
 (not HCl or HI or H<sup>+</sup> or Cl<sub>2</sub> but mark on)

mechanism:



4

(if a nucleophile is given mark CE =0)  
 (if a wrong alkene is given penalise carbocation, M4)  
 (allow either isomer formed in the mechanism)  
 (penalise use of 'half arrows' once)  
 (penalise initial ionisation of H-Br by loss of M3)

Isomers: With HBr and H<sub>2</sub>SO<sub>4</sub>

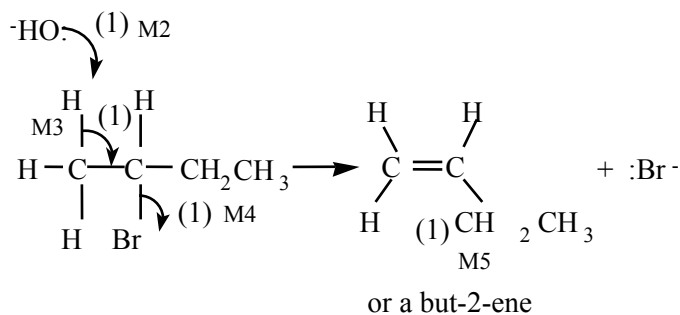
Propene stated to be unsymmetrical; 1  
 Attack can occur on different C atoms which can be shown by two different products, named or in a mechanism; 1  
 Different carbocation intermediates can be formed; 1  
 (allow marks when correct attack shown on TWO different C atoms and formation of TWO different carbocations correctly shown in a mechanism) (2 max)

If Br<sub>2</sub> given as the electrophile:  
 product has an asymmetric carbon atom ; 1  
 hence two optical isomers formed; 1

Total 7

(c) Reagent: M1 KOH or NaOH or RONa; 1

Mechanism



4

*(loss of Br must be in the first step either as above or by the formation of a carbocation)*

*(this mechanism can also score full marks. M4 is marked independently)*

*(if initial removal of H<sup>+</sup> by HO<sup>-</sup> shown, allow only M1, M2 and product marks)*

*(penalise M2 if a covalent bond shown between O and K or Na)*

*(penalise M2 and M3 if attack by HO<sup>-</sup> not on a H adjacent to C bonded to Br)*

*(if reagent given as CN<sup>-</sup> or NH<sub>3</sub>, penalise M1 and M2 but then mark on)*

Drawn structures of other isomers

M6 *cis* but-2-ene; 1

M7 and *trans* but-2-ene; 1

or

but-1-ene if not given above

*(allow M5, M6 and M7 if isomers correct even when an incorrect reagent and mechanism are given above)*

**Total 7**

**Total 18**