



General Certificate of Education

Chemistry 6421

**CHM5 Thermodynamics and Further
Inorganic Chemistry**

Mark Scheme

2010 examination - January 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

Copyright © 2009 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.

Question	Part	Sub Part	Marking Guidance	Mark	Comments	
1	(a)		$\Delta H_r = \Sigma \Delta H_f \text{ products} - \Sigma \Delta H_f \text{ reactants}$ (or cycle)	1		
			$\Delta H_r = (0 + [2 \times -242]) - (4 \times -92)$	1		
			$= -484 + 368 = -116 \text{ (kJ mol}^{-1}\text{)}$	1		(+116 scores 1)
			$\Delta S = \Sigma S \text{ products} - \Sigma S \text{ reactants}$	1		
			$\Delta S = ([2 \times 223] + [2 \times 189]) - (205 + [4 \times 187])$	1		
			$= 824 - 953 = -129 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$	1		(+129 scores 1)
1	(b)		$\Delta G = \Delta H - T\Delta S$	1		
			Feasible when $\Delta G \leq 0$ or $T = \Delta H/\Delta S$	1		
			$T = 228 \times 1000/195$	1		
			$= 1169 \text{ K}$	1		

Question	Part	Sub Part	Marking Guidance	Mark	Comments
2	(a)		Fe ²⁺ OR Fe(II)	1	
2	(b)	(i)	(+) OR (VI)	1	
2	(b)	(ii)	(+) OR (III)	1	
2	(c)	(i)	MnO ₄ ⁻ /Mn ²⁺ has a more positive <i>E</i> ^o value than Cl ₂ /Cl ⁻ (or data used) and will oxidise Cl ⁻ (or change Cl ⁻ to Cl ₂)	1 1	Allow converse answers QoL mark must specify species
2	(c)	(ii)	NO ₃ ⁻ /HNO ₃ has a more positive <i>E</i> ^o value than Fe ³⁺ /Fe ²⁺ (or data used) and will oxidise Fe ²⁺ (or change Fe ²⁺ to Fe ³⁺)	1 1	QoL mark must specify species
2	(d)	(i)	0.5 V	1	
2	(d)	(ii)	2Mn ²⁺ + 8H ₂ O + 5S ₂ O ₈ ²⁻ → 10SO ₄ ²⁻ + 2MnO ₄ ⁻ + 16H ⁺ Both SO ₄ ²⁻ and MnO ₄ ⁻ on right Balanced	1 1	

Question	Part	Sub Part	Marking Guidance	Mark	Comments
3	(a)		A Cr(H ₂ O) ₃ (OH) ₃ or Cr(OH) ₃ or correct name	1	
			B CO ₂ or name	1	
			2[Cr(H ₂ O) ₆] ³⁺ + 3CO ₃ ²⁻ → 2Cr(H ₂ O) ₃ (OH) ₃ + 3CO ₂ + 3H ₂ O (or gives 2Cr(OH) ₃ + 3CO ₂ + 9H ₂ O)	1	
3	(b)	(i)	NaOH (or KOH) or correct name	1	
3	(b)	(ii)	H ₂ O ₂ (or Na ₂ O ₂ or BaO ₂) or correct name	1	
			[Cr(OH) ₆] ³⁻ + 2OH ⁻ → CrO ₄ ²⁻ + 4H ₂ O + 3e ⁻ (or [Cr(OH) ₆] ³⁻ → CrO ₄ ²⁻ + 2H ₂ O + 2H ⁺ + 3e ⁻)	1	
3	(c)	(i)	At least one H ₂ NCH ₂ CH ₂ NH ₂ with correct structure and bonding to Cr via N	1	Mark independently but must not have 6 monodentate ligands
			6 co-ordination with 3en	1	
			Correct 3+ charge	1	
3	(c)	(ii)	Same (or similar) types of bonds broken and made	1	
			Same number of bonds broken and made	1	
3	(c)	(iii)	Entropy change (or ΔS) is positive (or increase in disorder)	1	
			because there are more product particles than reactant particles	1	
3	(d)		[Cr(H ₂ O) ₆] ²⁺	1	Mark separately
			Reducing agent	1	
3	(e)	(i)	Ethanal (or CH ₃ CHO but not CH ₃ COH)	1	

3	(e)	(ii)	Ethanoic acid (or correct formula)	1	
---	-----	------	------------------------------------	---	--

Question	Part	Sub Part	Marking Guidance	Mark	Comments
4	(a)		A catalyst in the same phase/state as the reactants	1	
4	(b)	(i)	A reaction in which a product acts as a catalyst	1	
4	(b)	(ii)	Mn ²⁺ or Mn ³⁺	1	"Self-catalysing" not allowed.
4	(c)	(i)	$2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$ OR $4\text{CO} + 2\text{NO}_2 \rightarrow 4\text{CO}_2 + \text{N}_2$ Reducing agent CO	1 1	C not allowed as a product
4	(c)	(ii)	Pt, Pd or Rh Deposited on a ceramic honeycomb or matrix or mesh or sponge To increase the surface area of the catalyst	1 1 1	

Question	Part	Sub Part	Marking Guidance	Mark	Comments
5	(a)		A solution which resists change in pH	1	Do not allow pH remains constant
			when small amounts of acid or base are added / on dilution	1	
			NH ₄ Cl (allow other correct strong acid)	1	
5	(b)	(i)	$K_a = \frac{[H^+][A^-]}{[HA]}$	1	Allow pH conseq to [H ⁺] if 2 dp given) 3.96 Max 2
			$= \frac{[H^+][0.160 \times 4]}{1.00}$	1	
			$[H^+] = 1.74 \times 10^{-5} / 0.160 \times 4 = 2.72 \times 10^{-5}$	1	
			pH = $-\log_{10}[H^+] = 4.57$ (allow 4.55 to 4.58)	1	
5	(b)	(ii)	$H^+ + CH_3COO^- \rightarrow CH_3COOH$	1	Must be ionic

Question	Part	Sub Part	Marking Guidance	Mark	Comments
6	(a)	(i)	White precipitate formed	1	
			$3\text{AgNO}_3 + \text{AlCl}_3 \rightarrow 3\text{AgCl} + \text{Al}(\text{NO}_3)_3$ (or $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$)	1	
6	(a)	(ii)	$\text{Al}^{3+}(\text{aq})$ reacts with $\text{NH}_3(\text{aq})$ forming a white precipitate	1	
			hence cannot see if AgCl precipitate has dissolved	1	
6	(b)	(i)	White or steamy fumes	1	
6	(b)	(ii)	$2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ OR $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$	1	
6	(b)	(iii)	A proton donor (or an acid)	1	

SECTION B

Question	Part	Sub Part	Marking Guidance	Mark	Comments
7	(a)		An appropriate alkene; $\text{CH}_3\text{CH}_2\text{CHCH}_2$ or $(\text{CH}_3)_2\text{CCH}_2$ Isomer 1 Isomer 2 Position isomerism Mechanism Electrophilic attack and electron shift to Br Carbocation Reaction with carbocation	1 1 1 1 1 1 1	Allow mechanism marks for any alkene Allow one mark if mechanism for minor product given
7	(b)		$\text{CH}_3\text{CH}_2\text{CHO}$ Mechanism Nucleophilic attack and electron shift to O anion intermediate reaction with H^+ Correct isomer 1 Correct isomer 2 Optical isomerism	1 1 1 1 1 1	Allow mechanism marks for any carbonyl NB Isomer structure must be tetrahedral NB Penalise “stick” structure once. Independent

Question	Part	Sub Part	Marking Guidance	Mark	Comments
8	(a)		<p>FeCl₃ is Lewis acid</p> <p>Accepts an electron pair</p> <p>[Fe(H₂O)₆]³⁺ is a Bronsted-Lowry acid</p> <p>It donates protons</p>	<p>1</p> <p>1</p> <p>1</p> <p>1</p>	NB Mark separately
8	(b)		<p>$K_a = \frac{[\{\text{Fe}(\text{H}_2\text{O})_5(\text{OH})\}^{2+}][\text{H}^+]}{[\{\text{Fe}(\text{H}_2\text{O})_6\}^{3+}]}$</p> <p>$[\text{H}^+] = 1.35 \times 10^{-2}$</p> <p>$[\text{H}^+] = [\{\text{Fe}(\text{H}_2\text{O})_5(\text{OH})\}^{2+}]$</p> <p>$K_a = \frac{[\text{H}^+]^2}{[\{\text{Fe}(\text{H}_2\text{O})_6\}^{3+}]} = (1.35 \times 10^{-2})^2 / 0.125$</p> <p>$K_a = 1.46 \times 10^{-3}$</p> <p>$\text{p}K_a = 2.83 - 2.84$</p>	<p>1</p> <p>1</p> <p>1</p> <p>1</p> <p>1</p> <p>1</p>	Allow value of pK _a conseq to value of K _a
8	(c)		<p>Fe²⁺ has a smaller charge or larger size or smaller charge density</p> <p>Less polarising than Fe³⁺/less weakening effect on O-H bonds or hydrolysis equilibrium displaced more to the left</p>	<p>1</p> <p>1</p>	<p>Or converse</p> <p>Or converse</p>

Question	Part	Sub Part	Marking Guidance	Mark	Comments
9	(a)		MgCl ₂ is ionic	1	QoL mark for forces between molecules clearly indicated There must be a comparison of ionic and intermolecular forces to score this mark
			SiCl ₄ is molecular (or simple covalent)	1	
			<u>van der Waals'</u> (or <u>vdw</u>) forces <u>between molecules</u>	1	
			Ionic forces (or bonds) stronger than vdw	1	
			Therefore more energy required to separate the particles in MgCl ₂	1	
9	(b)		Charge on the oxide ion is bigger than that on the chloride ion (or oxide ion smaller than chloride ion)	1	QoL mark
			Therefore <u>electrostatic</u> attraction is stronger	1	
9	(c)		MgO (is a white solid that) forms a suspension (or slightly soluble)	1	Mark both pH values independently to equations
			MgO + H ₂ O → Mg(OH) ₂ (or MgO + H ₂ O → Mg ²⁺ + 2OH ⁻)	1	
			pH; between 8 and 10	1	
			SO ₂ dissolves or forms a solution	1	
			SO ₂ + H ₂ O → H ₂ SO ₃ (or SO ₂ + H ₂ O → H ⁺ + HSO ₃ ⁻ or → 2H ⁺ + SO ₃ ²⁻)	1	
pH; between 1 and 4	1				

9	(d)	$\text{Al(OH)}_3 + \text{OH}^- \rightarrow \text{Al(OH)}_4^-$ or $\text{Al(OH)}_3 + 3\text{OH}^- \rightarrow [\text{Al(OH)}_6]^{3-}$ Correct species formed Equation balanced	1 1	
		$\text{Al(OH)}_3 + 3\text{H}^+ + 3\text{H}_2\text{O} \rightarrow [\text{Al(H}_2\text{O)}_6]^{3+}$ Correct species formed Equation balanced	1 1	Allow other correct positive species

Question	Part	Sub Part	Marking Guidance	Mark	Comments
10	(a)		Iron has low reactivity Iron can be purified readily or used impure Pure titanium needed TiO ₂ reacts with C to form TiC Na more reactive than Ti Need to make TiCl ₄ /argon needed/Cl ₂ needed to make TiCl ₄ Na (or Mg have to be made and are) expensive / C is inexpensive Titanium is extracted by a batch process or iron is extracted by a continuous process	1 1 1 1 1 1 1 1	6 max
10	(b)	(i)	Moles MnO ₄ ⁻ = mv/1000 = 20.8 × 0.0210 × 10 ⁻³ = 4.368 × 10 ⁻⁴ Equation or ratio 5Fe ²⁺ : MnO ₄ ⁻ Moles Fe ²⁺ in 25 cm ² = 5 × 4.368 × 10 ⁻⁴ = 2.184 × 10 ⁻³ Moles Fe ²⁺ in 250 cm ² = 2.184 × 10 ⁻³ × 10 = 2.184 × 10 ⁻² Mass Fe ²⁺ = mole Fe ²⁺ × A _r = 2.184 × 10 ⁻² × 55.8 = 1.22 g Percentage, by mass, of iron in sample = 1.22 × 100/1.35 = 90.3 (to 90.7)	1 1 1 1 1 1	NB If M _r of FeSO ₄ used then last two marks lost
10	(b)	(ii)	Fe + H ₂ SO ₄ → FeSO ₄ + H ₂	1	
10	(b)	(iii)	PV = nRT V = nRT/P = 2.184 × 10 ⁻² × 8.31 × 298/101000 = 5.35 × 10 ⁻⁴ m ³ = 535 cm ³	1 1 1 1	NB Using 1.82 × 10 ⁻² mol Fe gives 446 cm ³