

General Certificate of Education (A-level) June 2013

Chemistry

CHEM5

(Specification 2420)

Unit 5: Energetics, Redox and Inorganic Chemistry

Final

Mark Scheme

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Question	Marking Guidance	Mark	Comments
1(a)	Enthalpy change (to separate)1 mol of an (ionic) substance into its ions	1	If ionisation or hydration / solution, CE = 0 If atoms / molecules / elements mentioned, CE = 0
			Allow heat energy change but not energy change alone.
			If forms 1 mol ions, lose M1
	Forms ions in the gaseous state	1	If lattice formation not dissociation, allow M2 only.
			Ignore conditions.
			Allow enthalpy change for
			$MX(s) \rightarrow M^{+}(g) + X^{-}(g)$ (or similar) for M1 and M2
1(b)	Any one of:	1 max	If atoms / molecules mentioned, CE = 0
	lons are point charges		
	lons are perfect spheres		
	Only electrostatic attraction / bonds (between ions)		
	No covalent interaction / character		
	Only ionic bonding / no polarisation of ions		
1(c)	(Ionic) radius / distance between ions / size	1	Allow in any order.
			Do not allow charge / mass or mass / charge.
	(Ionic) charge / charge density	1	Do not allow 'atomic radius'.

1(d)	$\Delta H_{L} = \Delta H_{a}(\text{chlorine}) + \Delta H_{a}(\text{Ag}) + \text{I.E}(\text{Ag}) + \text{EA}(\text{CI}) - \Delta H_{f}^{\Theta}$	1	Or cycle If AgCl ₂ , CE=0/3
	= 121 + 289 + 732 -364 + 127	1	
	= (+) 905 (kJ mol ⁻¹)	1	Allow 1 for -905 Allow 1 for (+)844.5 (use of 121/2) Ignore units even if incorrect.
1(e)	 M1 Greater M2 (Born-Haber cycle method allows for additional) covalent interaction OR M1 Equal M2 AgCl is perfectly ionic / no covalent character 	1 1	Do not penalise AgCl ₂ Allow AgCl has covalent character. Only score M2 if M1 is correct.

Question	Marking Guidance	Mark	Comments
2(a)	Chlor <u>ide</u> (ions) are smaller (than brom <u>ide</u> ions)	1	Must state or imply ions. Allow chloride has greater charge density (than bromide).
	So the force of attraction between chloride ions and water is stronger	1	Penalise <u>chlorine ions</u> once only (max 2/3). This can be implied from M1 and M3 but do not allow intermolecular forces.
	Chloride \underline{ions} attract the $\delta+$ on H of water / electron deficient H on water	1	Allow attraction between ions and polar / dipole water. Penalise H ⁺ (ions) and mention of hydrogen bonding for M3 Ignore any reference to electronegativity. Note: If water not mentioned can score M1
2(b)	$\Delta H_{\text{solution}} = \Delta H_{\text{L}} + \Delta H_{\text{hyd}} \text{ K}^{+} \text{ ions} + \Delta H_{\text{hyd}} \text{ Br}^{-} \text{ ions} / = 670 - 322 - 335$	1	only. $ Allow \Delta H_{solution} = \Delta H_{L} + \Sigma \Delta H_{hyd} $
	= (+)13 (kJ mol ⁻¹)	1	Ignore units even if incorrect. +13 scores M1 and M2 -13 scores 0 -16 scores M2 only (transcription error).

2(c)(i)	The entropy change is positive / entropy increases	1	ΔS is negative loses M1 and M3
	Because 1 mol (solid) → 2 mol (aqueous ions) / no of particles increases	1	Allow the aqueous ions are more disordered (than the solid). Mention of atoms / molecules loses M2
		1	
	Therefore $\underline{T\Delta S} > \underline{\Delta H}$		
2(c)(ii)	Amount of KCI = $5/M_r = 5/74.6 = 0.067(0)$ mol	1	If moles of KCI not worked out can score M3, M4 only (answer to M4 likely to be 205.7 K)
	Heat absorbed = 17.2 × 0.0670 = 1.153 kJ	1	Process mark for M1 x 17.2
	Heat absorbed = mass × sp ht × ΔT (1.153 × 1000) = 20 × 4.18 × ΔT	1	If calculation uses 25 g not 20, lose M3 only
	$\Delta T = 1.153 \times 1000 / (20 \times 4.18) = 13.8 \text{ K}$	1	(M4 = 11.04, M5 = 287) If 1000 not used, can only score M1, M2, M3
			M4 is for a correct ΔT Note that 311.8 K scores 4 (M1, M2, M3, M4).
	T = 298 - 13.8 = 284(.2) K	1	If final temperature is negative, M5 = 0 Allow no units for final temp, penalise wrong units.

Question	Marking Guidance	Mark	Comments
3(a)(i)	(At 0 K) particles are stationary / not moving / not vibrating	1	Allow have zero energy. Ignore atoms / ions.
	No disorder / perfect order / maximum order	1	Mark independently.
3(a)(ii)	As T increases, particles start to move / vibrate	1	Ignore atoms / ions. Allow have more energy. If change in state, CE = 0
	<u>Disorder / randomness</u> increases / order decreases	1	
3(a)(iii)	Mark on temperature axis vertically below second 'step'	1	Must be marked as a line, an 'x', T_b or 'boiling point' on the temperature axis.
3(a)(iv)	$L_2 \ corresponds \ to \ boiling \ / \ evaporating \ / \ condensing \ / \ I \to g \ / \ g \to I$ And L_1 corresponds to melting \ / \ freezing \ / \ s \ \to I \ / \ I \ \to s	1	There must be a clear link between L_1 , L_2 and the change in state.
	Bigger change in disorder for L ₂ / boiling compared with L ₁ / melting	1	M2 answer must be in terms of changes in state and not absolute states eg must refer to change from liquid to gas not just gas. Ignore reference to atoms even if incorrect.

3(b)(i)	$\Delta G = \Delta H - T \Delta S$	1	
	$\Delta H = c$ and $(-)\Delta S = m/\Delta H$ and ΔS are constants (approx)	1	Allow ΔH is the intercept, and $(-)\Delta S$ is the slope / gradient. Can only score M2 if M1 is correct.
3(b)(ii)	Because the entropy change / ΔS is positive / $T\Delta S$ gets bigger	1	Allow - $T\Delta S$ gets more negative.
3(b)(iii)	Not feasible / unfeasible / not spontaneous	1	
3(c)(i)	+ 44.5 J K ⁻¹ mol ⁻¹	1	Allow answer without units but if units given they must be correct (including mol ⁻¹)
3(c)(ii)	At 5440 $\Delta H = T \Delta S$	1	
	= 5440 × 44.5 = 242 080 (<i>OR</i> using given value = 5440 × 98 = 533 120)	1	Mark is for answer to (c)(i) × 5440
	$\Delta H = 242 \text{ kJ mol}^{-1}$ (<i>OR</i> using given value $\Delta H = 533 \text{ kJ mol}^{-1}$)	1	Mark is for correct answer to M2 with correct units (J mol ⁻¹ or kJ mol ⁻¹) linked to answer. If answer consequentially correct based on (c)(i) except for incorrect sign (eg -242), max 1/3 provided units are correct.

Question	Marking Guidance	Mark	Comments
4(a)	MgO is ionic	1	If not ionic, CE = 0
	Melt it	1	If solution mentioned, cannot score M2 or M3
	(Molten oxide) conducts electricity	1	Allow acts as an electrolyte.
			Cannot score M3 unless M2 is correct.
4(b)	Macromolecular	1	CE = 0 if ionic, metallic or molecular. Allow giant molecule.
	Covalent bonding	1	Giant covalent scores M1 and M2
	Water cannot (supply enough energy to) break the covalent bonds / lattice	1	Hydration enthalpy < bond enthalpy.
4(c)	(Phosphorus pentoxide's melting point is) lower	1	If M1 is incorrect, can only score M2
	Molecular with covalent bonding	1	M2 can be awarded if molecular mentioned in M3
	Weak / easily broken / not much energy to break intermolecular forces OR weak vdW / dipole-dipole forces of attraction between molecules	1	Intermolecular / IMF means same as between molecules.

4(d)	Reagent (water or acid)	1	Can be awarded in the equation.
	Equation eg MgO + 2HCl → MgCl ₂ + H ₂ O	1	 MgO + H₂O → Mg(OH)₂ Equations can be ionic but must show all of the reagent eg H⁺ + Cl⁻ Simplified ionic equation without full reagent can score M2 only. Allow 6MgO + P₄O₁₀ → 2Mg₃(PO₄)₂
4(e)	$P_4O_{10} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O$	1	Allow P ₂ O ₅ and acid salts. Must be NaOH not just hydroxide ions.

Question	Marking Guidance	Mark	Comments
5(a)	It has mobile ions / ions can move through it / free ions	1	Do not allow movement of electrons. Allow specific ions provided they are moving but do not react.
5(b)	<u>Chloride</u> ions react with <u>copper ions</u> / <u>Cu²⁺</u> OR [CuCl ₄] ²⁻ formed	1	If incorrect chemistry, mark = 0
5(c)	The Cu ²⁺ ions / CuSO ₄ in the <u>left-hand</u> electrode more concentrated	1	Allow converse.
	So the reaction of Cu^{2+} with $2e^{-}$ will occur (in preference at) <u>left-hand</u> electrode / $Cu \rightarrow Cu^{2+}$ + electrons at <u>right-hand</u> electrode	1	Allow <u>left-hand</u> electrode positive / <u>right-hand</u> electrode negative. Also reduction at <u>left-hand</u> electrode / oxidation at <u>right-hand</u> electrode. Also <u>left-hand</u> electrode has oxidising agent / <u>right-hand</u> electrode has reducing agent. Allow <i>E</i> left-hand side > <i>E</i> right-hand side
5(d)	(Eventually) the copper ions / CuSO ₄ in each electrode will be at the same concentration	1	
5(e)(i)	-3.05 (V)	1	Must have minus sign3.05 only.

5(e)(ii)	LiMnO₂ → Li + MnO₂ correct equation	1	Allow 1 for reverse equation. Allow multiples.
	Correct direction	1	If Li+ not cancelled but otherwise correct, max = 1
			If electrons not cancelled, CE = 0
			LiMnO₂ → Li + MnO₂ scores 2
			$Li^+ + LiMnO_2 \rightarrow Li^+ + Li + MnO_2$ scores 1
			Li + MnO₂ → LiMnO₂ scores 1
5(e)(iii)	Electricity for recharging the cell may come from power stations burning (fossil) fuel	1	Allow any reference to <u>burning</u> (of carbon-containing) fuels.
			Note combustion = burning.

Question	Marking Guidance	Mark	Comments
6(a)	$\Delta E = h_V$	1	Allow = hf
	$v = \Delta E / h = 2.84 \times 10^{-19} / 6.63 \times 10^{-34} = 4.28 \times 10^{14} \text{ s}^{-1} / \text{Hz}$	1	Allow $4.3 \times 10^{14} \text{ s}^{-1} / \text{Hz}$ Answer must be in the range: $4.28 - 4.30 \times 10^{14}$
6(b)	(One colour of) light is absorbed (to excite the electron)	1	If light emitted, CE = 0
	The remaining colour / frequency / wavelength / energy is transmitted (through the solution)	1	Allow light reflected is the colour that we see.
6(c)	Bigger	1	
	Blue light would be absorbed \it{OR} light that has greater energy than red light would be absorbed \it{OR} higher frequency (of light absorbed / blue light) leads to higher ΔE	1	Can only score M2 if M1 is correct.

6(d)	Any three from:	3 max	
	(Identity of the) metal		
	Charge (on the metal) / oxidation state / charge on complex		
	(Identity of the) ligands		
	Co-ordination number / number of ligands		
	Shape		

Question	Marking Guidance	Mark	Comments
7(a)	Iron(II): green (solution) gives a green precipitate	1	Apply list principle throughout if extra colours and/or extra observations given. Ignore state symbols in equations.
			Not blue-green ppt.
	$[Fe(H_2O)_6]^{2+}$ + CO_3^{2-} → $FeCO_3$ + $6H_2O$	1	Must start from [Fe(H ₂ O) ₆] ²⁺
			Allow equations with Na ₂ CO ₃
	Iron(III):: yellow / purple / brown / lilac / violet (solution) gives a brown / rusty precipitate	1	
	Effervescence / gas / bubbles	1	Allow CO ₂ evolved but not just CO ₂
	$\frac{2[\text{Fe}(\text{H}_2\text{O})_6]^{3+}}{2[\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3] + 3\text{CO}_2 + 3\text{H}_2\text{O}}$	1	
7(b)	Copper(II): blue (solution) gives a green / yellow solution <i>OR</i> blue solution (turns) to green / yellow / olive green	1	Apply list principle throughout if extra colours and/or extra observations given. Ignore state symbols in equations.
	$[Cu(H_2O)_6]^{2+}$ + 4Cl ⁻ → $[CuCl_4]^{2-}$ + 6H ₂ O	1	Allow equations with HCI
	Cobalt(II): pink (solution) gives a blue solution <i>OR</i> pink solution turns blue	1	
	$\underline{[Co(H_2O)_6]^{2+}} + 4CI^{-} \rightarrow [CoCI_4]^{2-} + 6H_2O$	1	

7(-)	In a (II)		Analytic arise in the second of sectors and sectors
7(c)	Iron(II): green (solution) gives a green precipitate	1	Apply list principle throughout if extra colours and/or extra observations given. Ignore state symbols in equations.
		1	Allow equations with NaOH
	Chromium(III): green / ruby / purple / violet / red-violet (solution) gives a green solution <i>OR</i> green / ruby / purple / violet / red-violet solution turns green	1	Ignore green ppt.
	$\frac{[Cr(H_2O)_6]^{3+}}{[Cr(OH)_6]^{3-}} + 6OH^{-} \rightarrow [Cr(OH)_6]^{3-} + 6H_2O$	1	Allow also with 4 or 5 OH balanced with 2 or 1 waters.
			Also allow two correct equations showing $Cr(H_2O)_3(OH)_3$ as intermediate.
7(d)	AI: colourless (solution) gives a white ppt	1	Apply list principle throughout if extra colours and/or extra observations given. Ignore state symbols in equations.
	$[AI(H_2O)_6]^{3+} + 3NH_3 \rightarrow AI(H_2O)_3(OH)_3 + 3NH_4^+$	1	Allow + $3OH^{-} \rightarrow 3H_{2}O$ if
			$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ also
	Ag: colourless (solution) remains a colourless solution / no visible change	1	Ignore brown ppt.
	$[Ag(H_2O)_2]^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + 2H_2O$	1	Allow 2 / 3 equations involving Ag ₂ O or Ag(OH) ₂

Question	Marking Guidance	Mark	Comments
8(a)	Cobalt has variable oxidation states	1	Allow exists as Co(II) and Co(III)
	(It can act as an intermediate that) lowers the activation energy	1	Allow (alternative route with) lower E_a
	$CH_3CHO + 2Co^{3+} + H_2O \rightarrow CH_3COOH + 2Co^{2+} + 2H^+$	1	Allow multiples; allow molecular formulae Allow equations with H ₃ O ⁺
	$\frac{1}{2}O_2 + 2Co^{2+} + 2H^+ \rightarrow 2Co^{3+} + H_2O$	1	·
8(b)(i)	$ [Co(H_2O)_6]^{2+} + 3H_2NCH_2CH_2NH_2 \rightarrow [Co(H_2NCH_2CH_2NH_2)_3]^{2+} + 6H_2O $	1	Do not allow en in equation, allow C ₂ H ₈ N ₂
	The number of particles increases / changes from 4 to 7	1	Can score M2 and M3 even if equation incorrect or missing provided number of particles increases.
	So the entropy change is positive / disorder increases / entropy increases	1	
8(b)(ii)	Minimum for M1 is 3 bidentate ligands bonded to Co Ligands need not have any atoms shown but diagram must show 6 bonds from ligands to Co, 2 from each ligand	1	Ignore all charges for M1 and M3 but penalise charges on any ligand in M2
	Minimum for M2 is one ligand identified as H ₂ NNH ₂	1	Allow linkage as -C-C- or just a line.
	Minimum for M3 is one bidentate ligand showing two arrows from separate nitrogens to cobalt	1	

8(c)	Moles of cobalt = $(50 \times 0.203)/1000 = \underline{0.01015}$ mol	1	Allow 0.0101 to 0.0102
	Moles of AgCI = 4.22/143.4 = 0.0294	1	Allow 0.029 If not AgCl (eg AgCl ₂ or AgNO ₃), lose this mark and can only score M1 , M4 and M5
	Ratio = CI^{-} to $Co = 2.9 : 1$ [$Co(NH_3)_6$] CI_3 (square brackets not essential)	1	Do not allow 3: 1 if this is the only answer but if 2.9:1 seen somewhere in answer credit this as M3
	Difference due to incomplete oxidation in the preparation	1	Allow incomplete reaction. Allow formation [Co(NH ₃) ₅ Cl]Cl ₂ etc. Some chloride ions act as ligands / replace NH ₃ in complex. Do not allow 'impure sample' or reference to practical deficiencies.