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ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry 6421

CHM5 Thermodynamics and Further Inorganic Chemistry

Mark Scheme

2007 examination - June series

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CHM 5

Question 1

(a) $Mg^{2+}(g) + 2e^- + 2Cl(g)$ (This is the only answer for the top line) (1)

$Mg^{2+}(g) + 2e^- + Cl_2(g)$ (1)

$Mg^{+}(g) + e^- + Cl_2(g)$ (1)

$Mg(g) + Cl_2(g)$ (state symbols and electrons essential) (1)
(Note Cl_2 to 2Cl 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 (kJ mol^{-1}) (Ignore units even if wrong) (1)

(Note +1208, +1087, +1572 Each score one only)

(c) ΔH = -ΔH*(lattice formation)* + $\Sigma\Delta H$*(hydration) (or cycle with state symbols, numbers or labels)* (1)
= 2493 – 1920 – 2 × 364 (1)
= -155 (1)

(Note MgCl score zero; +155 scores 1/3)

(d) (i) Increase in disorder on dissolving or ΔS positive (1)
ΔG negative or $T\Delta S > \Delta H$ (1)

(ii) Moles of NH_4Cl = 2/53.5 = 0.0374 (Wrong compound loses first 2, wrong M_r loses 1) (1)
Heat absorbed = 15 × 0.0374 = 0.561 (mark is for × 15) (1)

Q = $m\ c\ \Delta T$ (1)
$\Delta T = Q/mc$ = (0.561×1000)/(50×4.2) = 2.6 (^oC) (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 ΔT = (15×1000)/(50×4.2)
So answers of 71.4 and 68.7 score last 2 out of first 4)

Final temperature = 20 – 2.6 = 17.4 ^oC (Answer is for 20 – previous ans; must be < 20) (1)
(allow no units for temperature, penalise wrong units)

Total 17

Question 2

(a) $\Delta H = \Sigma\Delta H$(formation products) - $\Sigma\Delta H$(formation reactants)
(or cycle with state symbols or numbers or labels and number of moles correct)

= 3×-111 –(-1669) (mark is for either these numbers or the above formula or cycle) (1)
= +1336 (-1336 scores zero, ignore wrong units) (1)
$\Delta S = \Sigma S(products) - \Sigma S(reactants)$
= 2×28 + 3×198 –(51 + 3×6) (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 – (298×581)/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)
ΔG is positive (or free energy (G) increases) (mark independently) (1)

(b) When $\Delta G = 0$ OR $T = \Delta H/\Delta S$ (1)
= (1336×1000)/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 ^{o}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)
$E(Zn^{2+}/Zn)$ more negative than $E(Fe^{2+}/Fe)$ (allow converse) (1)
(Allow *E* zinc (or zinc) more negative or *E* reaction negative or cell voltage = -0.32)

(ii) Fe^{2+} (1)
Cr^{3+} (1)
(apply list principle after looking at two answers, need one correct species to mark on)

$E(Fe^{3+}/Fe^{2+})$ more positive than $E(Cr^{3+}/Cr^{2+})$ (1)
(Allow *E* iron (or iron) more positive or *E* reaction positive or cell voltage = 1.18)

(b) Emf = -0.41 –(-0.76) = 0.35 (1)
$Zn + 2Cr^{3+} \rightarrow Zn^{2+} + 2Cr^{2+}$ (Ignore state symbols) (1)

(c) $K_a = [H^+][A^-]/[HA]$ or $= [H^+]^2/[HA]$ (1)
$[H^+] = \sqrt{K_a}[HA] = \sqrt{(1.15\times10^{-4}\times0.5)}$ (mark is for expression or numbers) (1)
$=7.58\times10^{-3}$ mol dm^{-3} (1)
$pH = -\log_{10}[H^+]$ (or log or lg) (allow last two marks consequential on wrong $[H^+]$) (1)
pH = 2.12 (note that 4.24 will score last two marks) (1)

(d) (i) Green solution (not blue-green or grey-green) (1)
$[Cr(OH)_6]^{3-}$ (or $Cr(H_2O)(OH)_5]^{2-}$ or $Cr(H_2O)_2(OH)_4]^-$) (1)

(ii) Green precipitate (allow grey-green) (1)
bubbles (or gas or fizzing or effervescence, not gives off CO_2) (1)
$Cr(H_2O)_3(OH)_3$ (or $Cr(OH)_3$) (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) MgO: ionic (zero as a contradiction if mention of molecules) (1)
P_4O_{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 P_4O_{10}

(d) $Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$ (or 2NaOH) (1)
$SO_2 + H_2O \rightarrow H_2SO_3$ (or acid correctly ionised) (1)

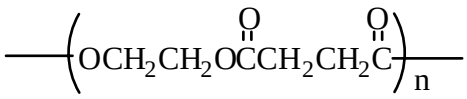
(e) $MgO + 2HCl \rightarrow MgCl_2 + H_2O$ (or $MgO + 2H^+ \rightarrow Mg^{2+} + H_2O$) (1)

(f) $P_4O_{10} + 12NaOH \rightarrow 4Na_3PO_4 + 6H_2O$ (or $P_4O_{10} + 12OH^- \rightarrow 4PO_4^{3-} + 6H_2O$) (1)
(ignore state symbols)

Total 12

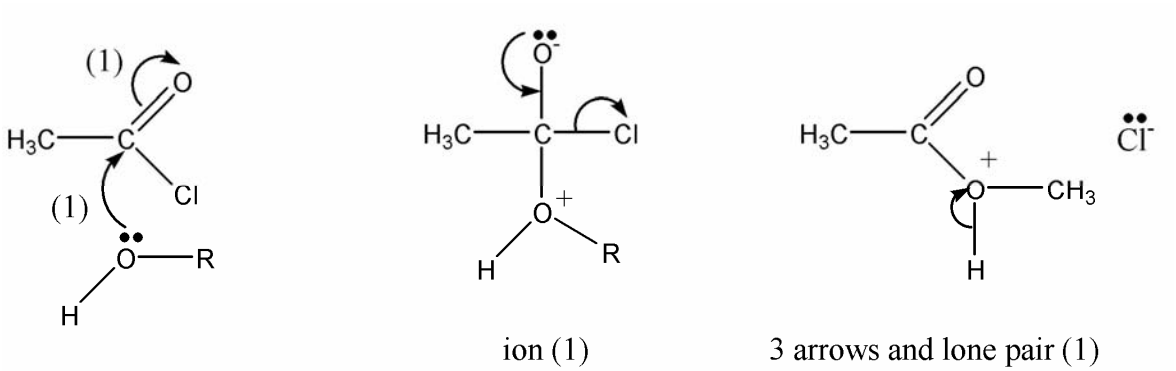
Question 5

(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)  (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^- 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)
$K_c = \frac{[CH_3COOH][CH_3CH_2OH]}{[CH_3COOC_2H_5][H_2O]} = \frac{(0.35/V)^2}{(0.15/V)\times(3.65/V)} = \frac{0.35^2}{0.15\times3.65}$ (mark is for expression) (1) (any of these can score)
= 0.22 (allow 0.2 to 0.22, only this answer scores last mark) (1)

Total 15

Question 6

(a) (i) $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$ (allow $2VO_2$) (1)
$V_2O_4 + 1/2O_2 \rightarrow V_2O_5$ (1)
V(IV) or 4 and V(V) or 5 (1)

(ii) $MnO_4^- + 8H^+ + 4Mn^{2+} \rightarrow 5Mn^{3+} + 4H_2O$ (1)
$2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2CO_2$ (1)
Mn(III) or 3 and Mn(II) or 2 (1)

(b) $[Co(NH_3)_6]^{2+}$ (formed) (1)
Complex easy (easier) to oxidise (1)
H_2O_2 (or air or oxygen) (1)
(ignore additional reagents e.g.NaOH)

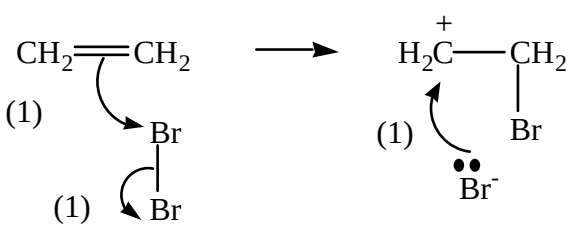
(c) moles of dichromate = (29.2/1000)×0.04 = 0.001168 or 0.00117 (1)
moles of Q^{2+} = (25/1000)×0.140 = 0.0035(0) (1)
each mole of dichromate needs 6 electrons or half equation with 6 e^- (1)
moles of electrons = 6×0.001168 = 0.007008 or moles Q^{2+}:moles dichromate = 3:1 (1)
Moles of electrons per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

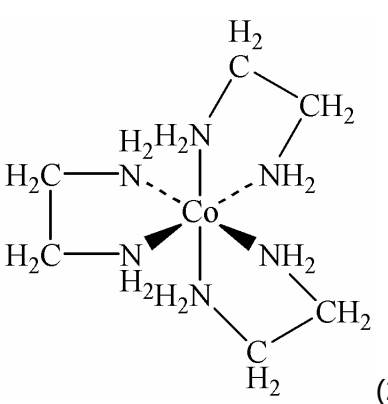


(3)

(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 from equation) (1)
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) $EDTA^{(4-)}$ has 6 lone pairs to donate (1)
(or can for 6 co-ordinate bonds or has 6 donor atoms)
$[Co(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [CoEDTA]^{2-} + 6H_2O$ [] 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_3CH_2Cl 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_3CHCl_2 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)
$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$ or equation with Cl_2 and I^- one correct equation required (1)
KI (red-) brown solution or black solid (mention of purple loses mark) (1)
($Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$)
(Note to score observation mark must be different from one with KBr)

(ii) $BaCl_2$ white precipitate (apply list principle to incorrect observations) (1)
$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$ (or $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$) (1)
$MgCl_2$ no precipitate or no change (ignore $MgCl_2$ equation) (1)
(do not allow nothing or no observation)

(iii) $CoCl_2$ goes blue (not two colours) (1)
$CuCl_2$ goes green (or yellow) (1)
$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow CoCl_4^{2-} + 6H_2O$ (1)
or $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow CuCl_4^{2-} + 6H_2O$
(allow any balanced equation leading to $CoCl_4^{2-}$)
(one correct equation required)

Total 15