Assessment Schedule – 2008

Scholarship Chemistry (93102)

Evidence Statement

<table>
<tr><th>Question</th><th>Evidence</th><th>Mark Allocation</th></tr>
<tr><td>1(a)</td><td>
Fe^{3+} ions in solution are orange–brown.
Fe^{3+} with KI will give a red–brown precipitate.
$Fe^{3+} + KI \rightarrow I_2$ (dark red–brown) $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
E^o_{cell} for the reaction between Fe^{3+} and I^- is $E^o_{cell} = +0.77 - 0.54 = +0.23$ V and since this is positive the reaction is spontaneous. In contrast when the Fe^{3+} is added to the NaCl there is no reaction; $E^o_{cell} = +0.77 - 1.36 = -0.59$ V
Fe^{3+} + Na_2CO_3 and NaOH. → brown precipitates
$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$ and $2Fe^{3+} + 3CO_3^{2-} \rightarrow Fe_2(CO_3)_3$
To distinguish the remaining 4 ions use:
<table>
<tr><th></th><th>NaOH</th><th>Na_2CO_3</th></tr>
<tr><td>$Zn(NO_3)_2$</td><td>White precipitate dissolves in excess</td><td>White precipitate remains</td></tr>
<tr><td>NaCl</td><td>No reaction</td><td>No reaction</td></tr>
</table>
$Zn^{2+} + CO_3^{2-} \rightarrow ZnCO_3$
$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$ $Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$
OR Fe^{3+} is acidic so with Na_2CO_3 bubbles of gas will form
$[Fe(H_2O)_6]^{3+} + H_2O \rightarrow [Fe(H_2O)_5OH]^{2+} + H_3O^+$
$2H_3O^+ + CO_3^{2-} \rightarrow CO_2 + 3H_2O$
</td><td rowspan="2">
7–8 marks
Shows understanding of the principles of chemistry by:
(a) developing a procedure that would correctly identify the 6 solutions, justifying answers where appropriate, including equations
AND
(b) carrying out a correct calculation and showing understanding of the species present in solution.
5–6 marks
Shows understanding of principles of chemistry by:
(a) developing a procedure that would identify most of the ions
AND
(b) using a correct procedure for the calculation and recognising the nature of at least one of the species.
1–4 marks
Answers include:
• Correct identification of some of the solids.
• Some aspects of the procedure for the calculation correct.
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<tr><td>(b) (i)</td><td>
Acidic conditions: CrO_4^{2-} in acid becomes $Cr_2O_7^{2-}$ so reduces amount of indicator.
Basic conditions: Ag_2O (brown precipitate) may form – interferes with the formation of silver chloride (reducing the accuracy of the analysis).
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(b) (ii)	At end point: $n(\mathrm{Cl^-}) = n(\mathrm{Ag^+}) = 0.0500\ \mathrm{mol\ L^{-1}} \times 0.01835\ \mathrm{L} = 9.175 \times 10^{-4}\ \mathrm{mol}$ At end point: $V_{\mathrm{total}} = 41.35\ \mathrm{mL}$ $[\mathrm{Ag^+}][\mathrm{CrO_4^{2-}}] = 2.60 \times 10^{-12}$ $n(\mathrm{CrO_4^{2-}}) = 0.100\ \mathrm{mol\ L^{-1}} \times 0.00300\ \mathrm{L} = 3.00 \times 10^{-4}\ \mathrm{mol}$ $[\mathrm{CrO_4^{2-}}] = \frac{3 \times 10^{-4}\ \mathrm{mol}}{0.04135\ \mathrm{L}} = 0.007255\ \mathrm{mol\ L^{-1}}$ At end point $[\mathrm{Ag^+}] = \sqrt{\frac{2.6\times10^{-12}}{0.007255}} = 1.89 \times 10^{-5}$ And $[\mathrm{Ag^+}][\mathrm{Cl^-}] = 1.77 \times 10^{-10}$ So $[\mathrm{Cl^-}] = \frac{1.77\times10^{-10}}{1.89\times10^{-5}} = 9.36 \times 10^{-6}\ \mathrm{mol\ L^{-1}}$ Amount of $\mathrm{Cl^-}$ remaining in the solution (41.35 mL): $9.36 \times 10^{-6}\ \mathrm{mol\ L^{-1}} \times 0.04135\ \mathrm{L} = 3.872 \times 10^{-7}\ \mathrm{mol}$ which is 0.042% and is therefore less than 0.1% of the chloride that was originally present in the solution.	• Understanding of the nature of one of the species present.

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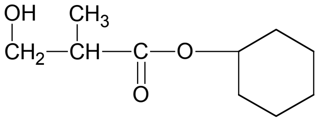
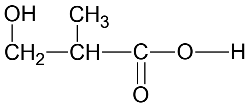
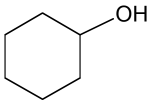
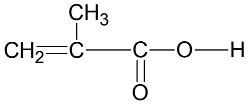
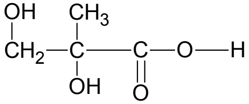
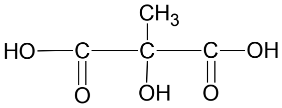
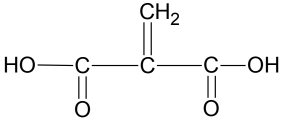
<tr>
<td>2(a)</td>
<td>

Compound A

$CH_2(OH)-CH(CH_3)-C(=O)-O-H$
Compound B

Compound C

$CH_2=C(CH_3)-C(=O)-O-H$
Compound D

$CH_2(OH)-C(CH_3)(OH)-C(=O)-O-H$
Compound E

$HO-C(=O)-C(CH_3)(OH)-C(=O)-OH$
Compound F

$HO-C(=O)-C(=CH_2)-C(=O)-OH$
Compound G
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<td rowspan="2">
7–8 marks
Shows understanding of the principles of organic chemistry by:
(a) correctly identifying Structures A to G
AND
(b) developing a reaction scheme with reasons for order.

5–6 marks
Shows understanding of principles of organic chemistry by:
(a) correctly identifying the structure of at least 5 of the compounds
AND
(b) developing a reaction scheme that provides a framework for Compound X although the order of reactions might be incorrect.

1–4 marks
Answers include:
• Correctly identifying some of the functional groups in Compounds A to G or some of the structures of Compounds A to G.
• Correctly identifying the reactants for up to 4 steps in the reaction scheme.
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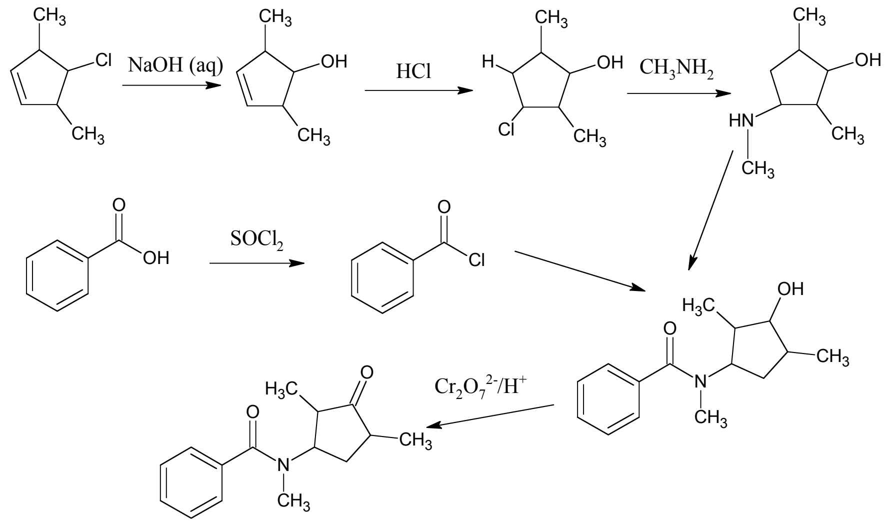
<tr>
<td>2(b)</td>
<td>


Compound X
Order: –Cl to –OH first so that later substitution will occur at the required –Cl.
– if MnO_4^-/H^+ is used then must be after addition to double bond.
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3(a) (i)	State reflects the strength of the intermolecular forces between the molecules. Instantaneous – induced dipoles (temporary) – largest in NI_3 since this has the biggest molar mass, and therefore the largest electron cloud giving the strongest instantaneous dipole forces of attraction. Similarly $NCl_3 > NF_3$ Dipole–dipole forces (permanent) – all three molecules are polar (trigonal pyramidal) but NI_3 and NF_3 are both more polar than NCl_3 (smaller difference in electronegativity between N and Cl). Overall NI_3 has the strongest temporary and permanent dipoles so has higher melting and boiling points (forms a solid at room temperature). Although NCl_3 is less polar than NF_3 the larger permanent dipole forces increase the forces of attraction between the molecules to a greater extent than the combined temporary and permanent dipoles of NF_3. Hence the melting/boiling points are higher and NCl_3 is a liquid at room temperature and NF_3 is a gas.	**7–8 marks** Shows understanding of the principles of chemistry by : (a) accounting for differences in the properties of the compounds given in terms of the structure and bonding in the molecules AND (b) developing a coherent and valid discussion of the two models proposed AND justification for the radii assigned. **5–6 marks** Shows understanding of the principles of chemistry by: (a) accounting for at least two of the differences in the properties of the compounds given in terms of the structure and bonding in the molecules AND (b) logically discussing the two models along with a coherent understanding of most of the factors that influence the radii of atoms and ions. **1–4 marks** Answers include: • Some correct reasons for the differences in the properties of the compounds. • Correct order of radii with some attempt at reasons. • Some correct reasons for the different models.
3(a) (ii)	$NF_3(g) \rightarrow \frac{1}{2}N_2(g) + 1\frac{1}{2}F_2(g)$ $\Delta_r H = \Sigma E_{bonds\ broken} - \Sigma E_{bonds\ made} = (3 \times 278) - (\frac{1}{2} \times 945 + 1.5 \times 159)$ $= 123\ \text{kJ mol}^{-1}$ $NI_3(g) \rightarrow \frac{1}{2}N_2(g) + 1\frac{1}{2}I_2(g)$ $\Delta_r H = \Sigma E_{bonds\ broken} - \Sigma E_{bonds\ made} - \Delta_{sub}(I_2)$ $= (3 \times 159) - (\frac{1}{2} \times 945 + 1.5 \times 151) - 62\ (93) = -284\ (-315)\ \text{kJ mol}^{-1}$ (-222 if Δ_{sub} not included) The decomposition of NF_3 is an endothermic reaction whereas the decomposition of NI_3 is exothermic. Exothermic is more likely to be spontaneous (if activation energy is low – the fact that it decomposes violently suggests that the activation energy is not large and is easily overcome).	
3(a)(iii)	Base = proton acceptor so must have large $\delta-$ on one atom N in NH_3 has greater electron density than N in NF_3 because: F atom is more electronegative than the N so in NF_3 it removes electron density from N atom which becomes more positive. But N atom is more electronegative than H so in NH_3 electron in the bond is more attracted to N which becomes more $\delta-$. Hence proton more likely to be attracted to NH_3, but not NF_3.	

3(b)(i)	Accepted model – expect ionisation energy (IE) of Li < He because in Li an electron is being removed from an energy level further from the nucleus so the electron is less strongly attracted to the nuclear charge (greater distance from nucleus + more shielding). Alternative model – expect IE of Li > He. The valence electron in He and Li are in the same energy level (similar shielding and distance) but the nucleus of Li has more protons so the electrons are more strongly held.	
3(b)(ii)	Expect Se^{2-} > Ga > Se > S > Ga^{3+} 198 135 122 103 62 Se^{2-} (198) largest because added electrons (e^-) cause more electron-electron repulsions so the electron cloud is expanded. Ga (135) > Se (122) because nuclear charge in Ga is smaller than in Se so valence e^- (which are in the same energy level) are less strongly held. Se > S (103) because S has one less energy level so the outer electrons are closer to the nucleus. S > Ga^{3+} (62) because although valence e^- for both species are in the same energy level, the nuclear charge for Ga is considerably greater than for S so the e^-.are held closer to the nucleu.s Ga > Ga^{3+} (62) because all electrons in the outer energy level of Ga are lost when the ion is formed, so the valence e^- in the ion are in an energy level closer to the nucleus (or there are fewer electron in Ga^{3+} than in Ga, so there are less e^- to e^- repulsions so the e^- are held closer to the nucleus).	

4(a)(i)	$Cl_2 + OH^- \rightarrow OCl^- + Cl^- + H^+$ $E° = E°_{red} - E°_{ox} = 1.36 - 0.42 > 0$ (0.94 V) So reaction is spontaneous. $2ClO_2^- \rightarrow OCl^- + ClO_3^-$ $E° = E°_{red} - E°_{ox} = 0.68 - 0.30 > 0$ (0.38 V) So reaction is spontaneous. First reaction proceeds further when the pH is high, as increased OH^- ions causes the reaction to move to the right. At low pH, high H^+ ions will reduce OH^- ions and the reaction will move to the left, meaning less Cl_2 will react.	**7–8 marks** Shows understanding of the principles of chemistry by: (a) correctly identifying disproportionation with reasons and equations which are used to discuss the effect of pH change OR (b) the effect of using HCl in the standardisation AND calculations in (a) and (b) are mostly correct. **5–6 marks** Shows understanding of the principles of chemistry by: (a) correctly identifying disproportionation with reasons AND (b) correct calculation. **1–4 marks** Answers include: • disproportionation identified • reasons for disproportionation given • one step in the calculations for hypochlorous acid correct • method for calculations related to quinine titration correct.
4(b)(i)	From the disproportionation reaction in (a)(i), it can be seen that if HCl is added to OCl^- then Cl_2 gas will be released, (which will make the standardisation dangerous and reduce the amount of OCl^- so that results are incorrect).	
4(a)(ii)	For 7.6% dissociation; $[OCl^-]$ = 7.6% and [HOCl] is 92.4%. At pH = 6.5 $K_a = \frac{[H_3O^+][OCl-]}{[HOCl]} = \frac{10^{-6.5} \times 7.6}{92.4} \cdot = 2.6 \times 10^{-8}$ $pK_a = -\log_{10}(2.6 \times 10^{-8}) = 7.58$	
	$n(OCl^-) = 2 \times \frac{40 \times 10^{-3}}{143.0} = 5.59 \times 10^{-4}$ $[H_3O^+] = \sqrt{\frac{10^{-7.58} \times 10^{-14}}{5.59 \times 10^{-4}}} = 6.92 \times 10^{-10}$ pH = 9.16 OR $K_b = \frac{\underline{[OH^-]^2}}{[ClO^-]} = 10^{-6.42}$ $[OH^-] = \sqrt{10^{-6.42} \times 5.59 \times 10^{-4}}$ = 1.46 x 10^{-5} mol L^{-1} $[H_3O^+]$ = 6.859 x 10^{-10} mol L^{-1}	
4(b)(ii)	Solubility = 5.77×10^{-1} g L^{-1} / 324.4 g mol^{-1} = 1.779×10^{-3} mol L^{-1} 100 mL contains 1.779×10^{-4} mol. V(HCl) = n/c = 1.779×10^{-4} / 0.0100 = 17.79 mL Total V = 117.79 mL	
	c = 1.779×10^{-4} / 117.79×10^{-3} = 1.51×10^{-3} mol L^{-1} $[H_3O^+] = \sqrt{10^{-8.9} \times 1.51 \times 10^{-3}} = 1.378 \times 10^{-6}$ pH = 5.86	

5(a)	$ZnSO_4(s) \rightarrow Zn^{2+}(aq) + SO_4^{2-}(aq)$ eqn 1 $\Delta T = 0.97\ ^{o}C$ for dissolution of 7.80 g $n(ZnSO_4) = 7.80\ g / 161.5\ g\ mol^{-1} = 0.0483\ mol$ For this reaction $q = 0.900\ kJ\ ^{o}C^{-1} \times 0.\ 97\ ^{o}C = 0.873\ kJ$ $\Delta_r H = -0.873\ kJ / 0.0483\ mol = -18.07\ kJ\ mol^{-1}$ $ZnSO_4 . 7H_2O(s) \rightarrow Zn^{2+}(aq) + SO_4^{2-}(aq) + 7H_2O(l)$ eqn 2 $\Delta T = 0.31\ ^{o}C$ for dissolution of 12.30 g $n(ZnSO_4 . 7H_2O) = 12.30\ g / 287.5\ g\ mol^{-1} = 0.04278\ mol$ For this reaction $q = 0.900\ kJ\ ^{o}C^{-1} \times 0.\ 31\ ^{o}C = 0.279\ kJ$ $\Delta_r H = +0.279\ kJ / 0.04278\ mol = +6.521\ kJ\ mol^{-1}$ Combining eqn 1 – 2 $ZnSO_4(s) + 7H_2O(l) \rightarrow ZnSO_4 . 7H_2O(s)$ **$\Delta_r H = -18.07\ kJ\ mol^{-1} - +6.521\ kJ\ mol^{-1} = -24.59\ kJ\ mol^{-1}$**	**7–8 marks** Shows understanding of the principles of chemistry by: (a) correctly calculating $\Delta_r H$ AND (b) providing a valid discussion of the dissolving process illustrated with the data given, including some indication as to why AgCl and $MgCl_2$ have differing solubilities. **5–6 marks** Shows understanding of the principles of chemistry by: (a) using a correct procedure to calculate $\Delta_r H$ (minor error allowed) AND (b) giving some valid points in the discussion of the dissolving process with reference to the data given. Recognises some factors contributing to the differing solubilities of $MgCl_2$ and AgCl. **1–4 marks** Answers include: • Some correct steps of the calculations for $\Delta_r H$ • Some valid points in the discussion of the dissolving process. • Data used to show steps in dissolving process.
5(b)	It is possible to dissolve ionic solids if the ion–dipole ‘bonds’ formed in the solution are stronger than the sum of the ionic bonds in the solid (lattice) and hydrogen bonds between the water molecules (OR more energy is released when the bonds in the aqueous solution form than is needed to break the bonds in the solid (lattice) and the water). AgCl has weaker bonds between its ions than $MgCl_2$’ as it has a lower melting point. Separating ions into the gaseous phase needs less energy for AgCl than for $MgCl_2$. However, less energy is released when the aqueous solution is formed, suggesting that the $Ag^+ - H_2O$ interactions are weaker than the $Mg^{2+} - H_2O$ interactions. Overall, this means that the dissolving reaction is less likely to proceed. Weaker forces of attraction between Ag^+ and H_2O compared to those between Mg^{2+} and water are due to the larger size of the ion and the smaller charge on the ion. Comparison of the enthalpies of solution**:** $\Delta_{sol}H(AgCl) = 915 - 835 = 80\ kJ\ mol^{-1}$ $\Delta_{sol}H(MgCl_2) = 2523 - 2653 = -130\ kJ\ mol^{-1}$ Since dissolving of AgCl is endothermic it is less likely to occur than the exothermic dissolving reaction of $MgCl_2$.	