

**Assessment Schedule – 2016****Scholarship Chemistry (93102)****Evidence Statement**

Q	Evidence	Level 3	Scholarship	Outstanding
ONE (a)(i)	<p><math>4\text{Au} + 8\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4[\text{Au}(\text{CN})_2]^- + 4\text{OH}^-</math>  <math>E^\circ = +0.40 - (-0.06) = 1.00 \text{ V}</math></p> <p><b>Au is oxidised</b> to the +1 oxidation state with the formation of the complex ions. The oxidant is oxygen, which is reduced to <math>\text{OH}^-</math>, since the reaction conditions are basic.</p> <p>Addition of Zn metal reduces the Au(I) to Au(0) (metal). i.e. Zn metal reduces Au(I). This reaction is spontaneous, since <math>E^\circ</math> for the reaction is positive.</p> <p><math>\text{Zn} + 2[\text{Au}(\text{CN})_2]^- \rightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Au}</math>  <math>E^\circ = -0.60 - (-1.26) = 0.66 \text{ V}</math></p> <p>When there is a mixture of Au and Ag, Ag will react with nitric acid as it can be oxidised by <math>\text{NO}_3^-</math>, which oxidises Ag(s) to Ag(aq).</p> <p><b>Au does not react</b> with nitric acid.</p> <p><math>3\text{Ag}(s) + 4\text{H}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{NO}_2(g) + 3\text{Ag}^+(aq) + 2\text{H}_2\text{O}(l)</math>  <math>E^\circ = 0.94 - 0.80 \text{ V} = 0.14 \text{ V} (&gt; 0, \text{ so reaction has tendency to proceed}).</math></p> <p><math>3\text{Au}(s) + 4\text{H}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{NO}_2(g) + 3\text{Au}^+(aq) + 2\text{H}_2\text{O}(l)</math>  <math>E^\circ = 0.94 - 1.69 \text{ V} = -0.75 \text{ V} (&lt; 0, \text{ so reaction has tendency not to proceed})</math></p>	<ul style="list-style-type: none"> <li>• Correct use of <math>E^\circ</math> to predict spontaneity plus balanced equations.</li> <li>• Correct description of effect of pH on equilibrium.</li> </ul>	<ul style="list-style-type: none"> <li>• Equations linked to <math>E^\circ</math> and discussion.</li> <li>• Calculation of <math>[\text{CN}^-]</math>.</li> <li>• Discussion of pH appropriate for weak acid / base.</li> </ul>	<ul style="list-style-type: none"> <li>• Full complete discussion of all aspects of redox reactions.</li> </ul>

(ii)

$$99\% [\text{Au}(\text{CN})_2]^- \quad \text{so} \quad \frac{99}{100} = \frac{[\text{Au}(\text{CN})_2]^-}{[\text{Au}(\text{CN})_2]^- + [\text{Au}^+]}$$

$$\text{Therefore } [\text{Au}^+] = \frac{[\text{Au}(\text{CN})_2]^-}{99}$$

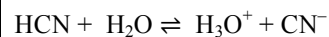
$$\text{Also } K_f = \frac{[\text{Au}(\text{CN})_2]^-}{[\text{Au}^+][\text{CN}^-]^2}$$

$$\text{Substituting for } [\text{Au}^+], \quad K_f = 4 \times 10^{28} = \frac{99}{[\text{CN}^-]^2}$$

$$[\text{CN}^-]^2 = \left( \frac{99}{4 \times 10^{28}} \right)^{\frac{1}{2}} = 4.97 \times 10^{-14} \text{ mol L}^{-1}$$

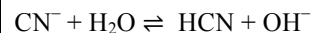
$$[\text{CN}^-] = 4.97 \times 10^{-14} \text{ mol L}^{-1}$$

HCN is a very weak acid, and  $\text{CN}^-$  is a weak base.



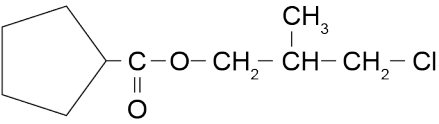
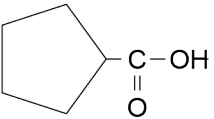
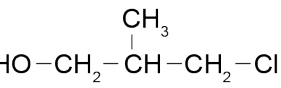
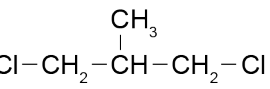
At low pH this equation will be reactant favoured, reducing the availability of  $\text{CN}^-$  in the mixture.

OR



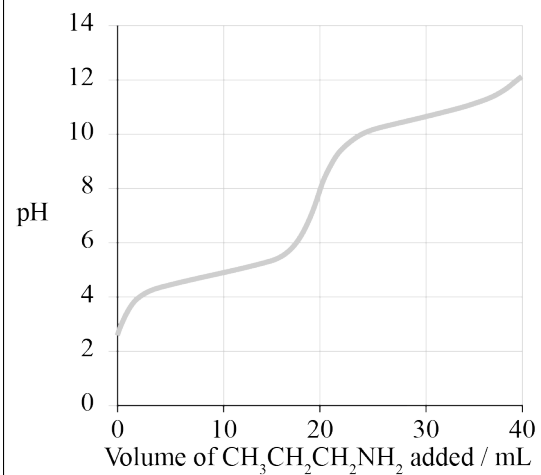
At high pH this equation will be reactant favoured, resulting in a decrease in HCN.

<p>(b)(i)</p>	<p>Concentration of the standard dichromate solution:</p> $n(\text{K}_2\text{Cr}_2\text{O}_7) = \frac{2.5077 \text{ g}}{294.2 \text{ g mol}^{-1}} = 8.524 \times 10^{-3} \text{ mol}$ $c(\text{K}_2\text{Cr}_2\text{O}_7) = \frac{8.524 \times 10^{-3} \text{ g}}{0.500 \text{ L}} = 0.017048 \text{ mol L}^{-1}$ <p>Titration reaction: <math>6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}</math></p> $n(\text{K}_2\text{Cr}_2\text{O}_7) = c \times V = 0.017048 \text{ mol L}^{-1} \times 0.01856 \text{ L} = 3.16403 \times 10^{-4}$ <p>From equation <math>n(\text{Fe}^{3+}) = 6 \times n(\text{K}_2\text{Cr}_2\text{O}_7) = 6 \times 3.16403 \times 10^{-4} = 1.898 \times 10^{-3} \text{ mol}</math></p> <p><math>(n(\text{Fe}^{3+}) = n(\text{Fe}^{2+})</math> since <math>\text{Fe}^{3+}</math> from ore sample was reduced to <math>\text{Fe}^{2+}</math> by reaction with <math>\text{Sn}^{2+}</math>.)</p> <p>In ore sample <math>n(\text{Fe}) = 1.898 \times 10^{-3} \text{ mol} \times \frac{250}{20} = 0.023731 \text{ mol} = 2n(\text{Fe}_2\text{O}_3)</math></p> $n(\text{Fe}_2\text{O}_3) = 0.011865 \text{ mol}$ $m(\text{Fe}_2\text{O}_3) = 0.011865 \text{ mol} \times 159.69 \text{ g mol}^{-1} = 1.895 \text{ g}$ $\% \text{Fe}_2\text{O}_3 = \frac{1.895 \text{ g}}{2.8351 \text{ g}} = 66.88\%$	<ul style="list-style-type: none"> <li>• Titration calculation.</li> <li>• Standard solution concentration.</li> <li>• Use of standard solution concentration.</li> <li>• Use of <math>E^\circ</math>.</li> </ul>	<ul style="list-style-type: none"> <li>• Correct answer for calculation (allow a minor error).</li> <li>• <math>\text{MnO}_4^-</math> discussion.</li> </ul>	<ul style="list-style-type: none"> <li>• Correct answer (no errors) AND <math>\text{MnO}_4^-</math> discussion.</li> </ul>
<p>(ii)</p>	<p>If permanganate is used <b>instead of dichromate</b>, it can oxidise chloride to chlorine (as well as <math>\text{Fe}^{2+}</math> to <math>\text{Fe}^{3+}</math>), so the titration results would be inaccurate, and chlorine gas, which is dangerous, could be released.</p> $2\text{MnO}_4^- + 10\text{Cl}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O} \quad E^\circ = 1.51 - 1.40 = 0.11 (> 0)$ <p style="text-align: right;">so spontaneous</p> <p>Dichromate will not oxidise chloride.</p> $6\text{Cl}^- + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 3\text{Cl}_2 + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E^\circ = 1.36 - 1.40 = -0.04 (< 0)$ <p style="text-align: right;">so not spontaneous</p>			

<p>TWO (a)</p>	<p>Compound A </p> <p>Compound B </p> <p>Compound C </p> <p>Compound D </p> <p>Compound <b>A</b>: Hydrolysis in acid reaction gives two products – could be ester reacting to produce carboxylic acid and alcohol. Ester functional group confirmed in <math>^{13}\text{C}</math> NMR, with peak downfield around 180 ppm. No double bond (no reaction with bromine), so possibly a cyclic compound.</p> <p>Compound <b>B</b>: From IR: <math>-\text{OH}</math> stretch at <math>3000\text{ s}^{-1}</math> and <math>\text{C}=\text{O}</math> at <math>1700\text{ s}^{-1}</math> and <math>\text{C}-\text{O}</math> at <math>1300\text{ s}^{-1}</math> identify the functional group as a carboxylic acid. This is confirmed in the carbon peak at <math>&gt; 180</math> ppm in the <math>^{13}\text{C}</math> NMR. From mass spec: M peak at <math>m/z</math> 114. 6 C atoms and molecular formula <math>\text{C}_6\text{H}_{10}\text{O}_2</math>. From NMR: The acid carbon peak is at 180 ppm, and there are only 3 other peaks. This is consistent with a 5-membered ring.</p> <p>Compound <b>C</b>: Contains an alcohol functional group (from the hydrolysis of the ester in <b>A</b>). Formula <math>\text{C}_4\text{H}_9\text{OCl}</math> (from the difference between the formula of Compound <b>A</b> and Compound <b>B</b>). Presence of Cl observed from mass spectrum data with M and M+2 peaks.</p> <p>Compound <b>D</b>: Has 4 carbon atoms, as it is formed from Compound <b>C</b>, but from <math>^{13}\text{C}</math> NMR there are only 3 carbon environments, so the molecule is symmetrical.</p>	<ul style="list-style-type: none"> <li>Recognises functional groups of all 4 molecules.</li> <li>Aspects of structural analysis.</li> </ul>	<ul style="list-style-type: none"> <li>All compounds correct, but discussion limited.</li> </ul>	<ul style="list-style-type: none"> <li>All compounds correct with most aspects of discussion.</li> </ul>
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<p>(b)(i)</p> <p>(ii)</p>	<p>Dimerisation equation: <math>2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})</math></p> <p>Enthalpy of reaction = <math>\Sigma\Delta H_{\text{products}} - \Sigma\Delta H_{\text{reactants}} = 9.2 - (2 \times -33.2) = -57.2 \text{ kJ mol}^{-1}</math></p> <p>So, forward reaction is favoured from an enthalpy point-of-view.</p> <p>However, it is unfavourable from an entropy point-of-view, because two molecules are more random than one.</p> <p>The combustion reaction equation is: <math>\text{N}_2\text{O}_4(\text{g}) + 2\text{N}_2\text{H}_4(\text{g}) \rightarrow 3\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})</math></p> <p><math>\Delta_r H = 4 \times -286 - (9.2 + 2 \times 50.6) = -1254 \text{ kJ mol}^{-1}</math>.</p> <p>OR</p> <p><math>\Delta_r H = \Sigma E_{\text{bonds broken}} - \Sigma E_{\text{bonds formed}} = [(57 + 4 \times 305) + 2(298 + 4 \times 391)] - [3(945) + 4(2 \times 499)]</math></p> <p><math>= 5001 - 6827</math></p> <p><math>= -1826 \text{ kJ mol}^{-1}</math></p> <p>The enthalpy of reaction is very negative, so there is a large amount of energy released making it useful as a fuel.</p> <p>The origin of this energy can be traced to the very strong N–N and O–H bonds in the products, meaning a large amount of energy is released when these form while much less energy is needed to break the weaker N–N bonds in the <math>\text{N}_2\text{O}_4</math> and <math>\text{N}_2\text{H}_4</math>.</p> <p>From an entropy viewpoint, more and smaller molecules are being produced, which makes the reaction favourable.</p> <p>(The reactants are liquids at ambient temperatures (or easily kept so), while one product is clearly a gas, and more and smaller molecules are being produced. Thus, the fuel will have a high density and the products can be thrown out backwards very quickly.)</p>	<ul style="list-style-type: none"> <li>• <math>\Delta H</math> calculations plus entropy changes.</li> </ul>	<ul style="list-style-type: none"> <li>• <math>\Delta H</math> calculations plus entropy changes linked to the reactions.</li> </ul>	<ul style="list-style-type: none"> <li>• <math>\Delta H</math> linked to reactions and structure, and combined with <math>\Delta S</math> for discussion.</li> </ul>
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THREE  
(a)(i)



(Graph should be recognised as a combination of the relevant sections of the two graphs given.)

- Graph combines aspects of graphs 1 and 2.

(ii)	<p>When the solutions are mixed, the following reaction takes place:  <math>\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \rightleftharpoons \text{CH}_3\text{COO}^- + \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+</math></p> <table border="1" data-bbox="286 245 1182 360"> <thead> <tr> <th>pH</th> <th>1</th> <th>8</th> <th>13</th> </tr> </thead> <tbody> <tr> <td>Dominant species</td> <td><math>\text{CH}_3\text{CH}_2\text{COOH}</math> and <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+</math></td> <td><math>\text{CH}_3\text{CH}_2\text{COO}^-</math> and <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+</math></td> <td><math>\text{CH}_3\text{CH}_2\text{COO}^-</math> and <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2</math></td> </tr> </tbody> </table> <p><b>If the pH of the solution is 1, then:</b>            From Graph One, we see that this is below the pH of <math>\text{CH}_3\text{CH}_2\text{COOH}</math> solution, so the equation for the acid dissociation will lie to the left OR at low pH, the dissociation equation lies to the left:  <math>\text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+</math>            From Graph Two, we see that this pH is past the equivalence point when all the propan-1-amine has been converted to the acid form.  <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{H}_3\text{O}^+ \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+ + \text{H}_2\text{O}</math>            OR at low pH, the hydrolysis reaction lies to the right.  <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+ + \text{OH}^-</math></p> <p><b>If the pH of the solution is 8, then:</b>            For all graphs, we are on the close-to vertical region, so the species present will be those expected at equivalence point, i.e. <math>\text{CH}_3\text{CH}_2\text{COO}^-</math> and <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+</math>.</p> <p><b>If the pH of the solution is 13, then:</b>            From Graph One, we see that this pH occurs past the equivalence point when all the propanoic acid has been converted to the conjugate base.  <math>\text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+</math>            OR at high pH, the hydrolysis reaction lies to the right.  <math>\text{CH}_3\text{CH}_2\text{COOH} + \text{OH}^- \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_2\text{O}</math>            From Graph Two, we see that this is above the pH of <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2</math> solution, so the dissociation will lie to the left OR at high pH, the dissociation equation lies to the left.  <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+ + \text{OH}^-</math></p>	pH	1	8	13	Dominant species	$\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$	$\text{CH}_3\text{CH}_2\text{COO}^-$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$	$\text{CH}_3\text{CH}_2\text{COO}^-$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	<ul style="list-style-type: none"> <li>Equations for acid / base hydrolysis and titrations. Titration curves.</li> </ul>	<ul style="list-style-type: none"> <li>Links species to reactions and graphs.</li> </ul>	<ul style="list-style-type: none"> <li>Links all aspects of species, pH, graphs, and equations.</li> </ul>
pH	1	8	13									
Dominant species	$\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$	$\text{CH}_3\text{CH}_2\text{COO}^-$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$	$\text{CH}_3\text{CH}_2\text{COO}^-$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$									





<p>FOUR (a)(i)</p> <p>(ii)</p> <p>(iii)</p>	<p><math>\text{SiH}_4 \rightarrow \text{PH}_3 \rightarrow \text{H}_2\text{S}</math></p> <p>Melting points are dependent on the strength of the intermolecular forces in the solids since energy is needed to separate the molecules from each other and allow them to move freely. All three of the compounds – <math>\text{SiH}_4</math>, <math>\text{PH}_3</math>, and <math>\text{H}_2\text{S}</math> – have the same number of electrons, so the instantaneous-induced dipole forces of attraction in each compound will be the same. The differences in the melting points reflect the different polarities of the molecules.</p> <p><math>\text{SiH}_4</math> is non-polar and hence the instantaneous induced dipoles are the only intermolecular forces present.</p> <p><math>\text{PH}_3</math> and <math>\text{H}_2\text{S}</math> are both polar molecules, which causes added dipole-dipole attractions to occur between the molecules. In both the <math>\text{PH}_3</math> and <math>\text{H}_2\text{S}</math> molecules, there are polar bonds unevenly arranged around the central atom, causing the molecules to be polar.</p> <p><math>\text{H}_2\text{S}</math> is a more polar molecule (has a larger dipole moment) since it has a greater electronegativity difference between the bonded atoms.</p> <p><math>\text{NH}_3 \rightarrow \text{PH}_3 \rightarrow \text{AsH}_3 \rightarrow \text{SbH}_3</math></p> <p>These molecules are all polar – they have a trigonal pyramid shape with polar bonds. Polarity of the molecules decreases down the group.</p> <p>However, apart from the first compound, <math>\text{NH}_3</math>, the trend is for the melting point to increase down the group. This follows the increase in the number of electrons in the molecule (size of the electron clouds), and hence the increase in the instantaneous induced dipoles. These intermolecular forces account for most of the attraction between the molecules.</p> <p>This is not the case for <math>\text{NH}_3</math>, where the high melting point indicates increasing intermolecular forces. These are hydrogen bonds formed between the small, electronegative N atoms of one molecule and the H atom of adjacent molecules.</p> <p>An acid is a proton donor: <math>\text{HA} \rightarrow \text{H}^+ + \text{A}^-</math></p> <p>The strength of an acid depends on the ease with which the HA bond can be broken.</p> <p><math>\text{CH}_4 \rightarrow \text{NH}_3 \rightarrow \text{H}_2\text{O} \rightarrow \text{HF}</math></p> <p>Going across the period from left to right, the electronegativity of the non-hydrogen atom increases. This increases the polarity of the H-X bond and so the charge on the H atom becomes more positive. The more electronegative the atom bonded to the H atom, the greater the positive charge on the H atom, making it easier for the bond to break.</p> <p><math>\text{H}_2\text{O} \rightarrow \text{H}_2\text{S} \rightarrow \text{H}_2\text{Se} \rightarrow \text{H}_2\text{Te}</math></p> <p>Going down the group the acid strength increases but the electronegativity decreases, so the H-X bond becomes less polar. However, the H-X bond will be more easily broken, as the increase in the size of the X atom will reduce the strength of the bond. As the H-X bond is easier to break, the strength of the acid increases.</p>	<ul style="list-style-type: none"> <li>Recognises intermolecular forces and links these to melting point trends.</li> <li>Recognises trends in electronegativity.</li> </ul>	<ul style="list-style-type: none"> <li>Discussions recognise and compare all relevant intermolecular forces.</li> <li>Recognises link between acid properties and strength of H-X bond with some trends correctly discussed.</li> </ul>	<ul style="list-style-type: none"> <li>All discussions are accurate, complete, concise, and logical.</li> </ul>
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(b)	<p>The metal hydrides are ionic solids with a strong ionic bond that must be broken for the solid to melt. The ionic bond strength is dependent on the size of the charge on the ions and the distance between them (size of the ion).</p> <p>Hence, the expectation is that down a group the ionic bonds will get weaker as the size of the cation gets bigger (the valence electrons are successively further from the nucleus).</p> <p>Across the group the expectation is that the ionic bond will get stronger as the charge on the cation increases (<math>\text{Mg}^{2+}</math> compared to <math>\text{Na}^+</math>)</p> <p>This pattern is reflected in the lattice enthalpy but not in the enthalpy of formation.</p> <p>Enthalpy of formation is the energy change for the reaction between metal and hydrogen gas. (e.g. <math>\text{Na}(s) + \frac{1}{2}\text{H}_2(g) \rightarrow \text{NaH}(s)</math>).</p> <p>The energy change is a comparison between the strength of the bonds broken and the bonds formed, so both the metallic and the ionic bond strengths contribute to the enthalpy change.</p> <p>The lattice enthalpy, however, is a direct measure of the strength of the ionic bond, as it indicates the energy released when the gaseous ions combine to form the lattice.</p>	<ul style="list-style-type: none"> <li>• Ionic bonding and trends in charge and size of ions.</li> </ul>	<ul style="list-style-type: none"> <li>• Recognises effect of charge and size of ions on LE.</li> </ul>	<ul style="list-style-type: none"> <li>• Compares and contrasts LE and <math>\Delta_f</math>.</li> </ul>
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