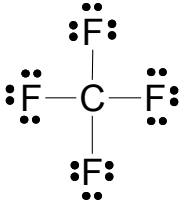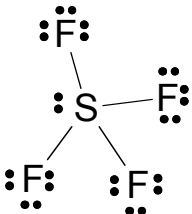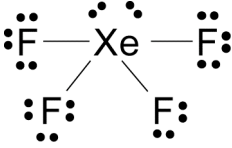## Assessment Schedule – 2005

## Scholarship Chemistry (93102)

A nine point marking scale (0-8) was used to assess Questions 1(b), 1(c), 2(a), 3(a)(ii), 3(b), 4(a)(i), 4(a)(ii), 5(b), 6(a), and 6(b).
A seven point marking scale (0-6) was used to assess Questions 1(a), 3(a)(i), 4(b), and 5(a).

### Evidence Statement

| Question | Evidence | 4 marks | 6 marks | 8 marks |
|---|---|---|---|---|
| 1(a) | $CH_3OH$<br>• Strongest intermolecular forces.<br>• Only molecules which can hydrogen bond (to each other).<br>• H bonds possible because (very electronegative) O bonded to H causing large $\sigma+$ on H (which is attracted to lone pair $e^-$s on O of neighbouring atoms).<br><br>$CH_3Br$ and $CH_3Cl$<br>• Cl is more electronegative than Br so $CH_3Cl$ is more polar than $CH_3Br$ so permanent dipoles are stronger.<br>• $CH_3Br$ molecule is larger than $CH_3Cl$ so has more $e^-$s so more polarisable, and temporary dipole attractions between molecules will be stronger.<br>• $CH_3Br$ has stronger overall forces of attraction between its molecules than $CH_3Cl$ (since boiling point is higher), so temporary dipoles have greater influence on boiling point than permanent dipoles. | Correctly discusses TWO forces.<br><br>**OR**<br><br>Recognises all THREE forces but some error in discussion | Correctly compares and discusses all THREE intermolecular forces. | |
| 1(b) | $[Cl^-]\quad \dfrac{3.65}{35.5} = 0.103$ mol $L^{-1}$<br>$n(AgNO_3) = \dfrac{5 \times 10^{-3}}{170} = 2.94 \times 10^{-5}$<br>$[AgCl] = \dfrac{2.94 \times 10^{-5}}{9} = 3.27 \times 10^{-6}$ mol $L^{-1}$<br>$n(Pb(NO_3)_2) = \dfrac{5 \times 10^{-3}}{331} = 1.52 \times 10^{-5}$<br>$[Pb(NO_3)_2] = \dfrac{1.52 \times 10^{-5}}{9} = 1.68 \times 10^{-6}$ mol $L^{-1}$<br>**For AgCl:** $K_s = 1.6 \times 10^{-10}$<br>$Q_s = [Ag^+][Cl^-]$<br>$\quad = 3.27 \times 10^{-6} \times 0.103$<br>$\quad = 3.37 \times 10^{-7} > K_s(1.6 \times 10^{-10})$ so precipitation will occur<br>**For PbCl$_2$:** $K_s = 2.4 \times 10^{-4}$<br>$Q_s = [Pb^{2+}][Cl^-]^2$<br>$\quad = 1.68 \times 10^{-6} \times (0.103)^2$<br>$\quad = 1.78 \times 10^{-8} < K_s (2.4 \times 10^{-4})$ so no precipitation<br>ie $Pb^{2+}$ stays in blood stream, AgCl is precipitated out. | Correct procedure and valid conclusion based on calculation.<br><br>**OR**<br><br>Correct conclusion, but two errors in calculation<br><br>**OR**<br><br>error plus lack of detail / coherence in answer. | Correct conclusion but one error in calculation.<br><br>**OR**<br><br>Calculation correct but conclusion inconclusive. | Correct answer and conclusion with coherent explanation. |
| 1(b) | Alternate calculation:<br>$K_s = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$<br>$[Ag^+] = \dfrac{1.6 \times 10^{-10}}{0.103} = 1.55 \times 10^{-9}$ = solubility of $AgNO_3$ $\quad (\times 9 = 1.40 \times 10^{-8}$ mol $= 1.51 \times 10^{-6}$ g$)$<br>Amount added $= \dfrac{2.94 \times 10^{-5}}{9} = 3.27 \times 10^{-6}$ mol $L^{-1}$ $\quad >$ solubility so only a small amount dissolves<br>$K_s = [Pb^{2+}][Cl^-]^2 = 12.4 \times 10^{-4}$<br>$[Pb^{2+}] = \dfrac{2.4 \times 10^{-4}}{} = 0.0227$ = solubility of $Pb(NO_3)_2$ $\quad (\times 9 = 0.2043$ mol $= 42.3$ g$)$ | | | |

| Question | Evidence | 4 marks | 6 marks | 8 marks |
|---|---|---|---|---|
| | Amount added $= \dfrac{0.103^2}{1.52 \times 10^{-5}} = 1.68 \times 10^{-6}$ mol L$^{-1}$ ($3.5 \times 10^{-4}$ g L$^{-1}$) $<$ solubility so all dissolves.<br><br>i.e. Pb$^{2+}$ stays in blood stream, AgCl is precipitated out. | | | |

| Question | Evidence | 4 marks | 6 marks | 8 marks |
|---|---|---|---|---|
| 1(c) | **Tetrahedral**<br>• need 4 bonded electron clouds, arranged tetrahedrally to minimise repulsion (no lone pairs)<br>• 4 valence $e^-$ on central atom (32 $e^-$ in total)<br>• atom from group 4, eg $CF_4$<br><br>*(Lewis structure of $CF_4$)*<br><br>**See-saw**<br>• need 5 $e^-$ clouds with one non-bonded $e^-$ pair,<br>• 6 valence $e^-$ on central atom (34 $e^-$ in total)<br>• atom from group 6<br>• 5 $e^-$ pairs on central atom so 5 $e^-$ clouds take a trigonal bipyramid arrangement. Only 4 bond $e^-$ pairs. Lone pair will be in equatorial position to minimise repulsion hence see-saw arrangement.<br>• eg $SF_4$<br><br>*(Lewis structure of $SF_4$)*<br><br>**Square planar**<br>• need 6 $e^-$ pairs on central atom with 2 non-bonded pairs<br>• 8 valence $e^-$ on central atom (36 $e^-$ in total)<br>• atom from Group 18<br>• 6 $e^-$ clouds arranged octahedrally. Two non-bonding pairs will take positions above and below the plane leaving a square planar arrangement.<br>• eg $XeF_4$<br><br>*(Lewis structure of $XeF_4$)*<br><br>Only $SF_4$ is non-polar because the other two molecules are symmetrical about the central atom so the dipoles caused by the polar *Z*-F bond will cancel. | Any TWO of<br>• THREE molecules correctly identified<br>• reasons for shapes related to electron distribution (discussion may lack coherence or some accuracy)<br>• reference to VSEPR<br>• polarity correctly identified with reasons<br>• a link to the no. of valence $e^-$ or the group in the periodic table. | TWO molecules correctly identified<br><br>**AND**<br><br>any TWO of<br>• reasons for shapes related to electron distribution (discussion may lack coherence or some accuracy)<br>• reference to VSEPR<br>• polarity of molecules correctly identified with reasons<br>• a link to the no. of valence $e^-$ or the group in the periodic table. | A logical coherent explanation which includes:<br><br>THREE correct molecules<br><br>Reference to VSEPR<br><br>A link to the no. of valence $e^-$ or the group in the periodic table<br><br>Polarity of molecules correctly identified with reasons. |

| Question | Evidence | 4 marks | 6 marks | 8 marks |
|---|---|---|---|---|
| 2(a) | $K_a = \dfrac{[base][H_3O^+]}{[acid]}$  $[H_3O^+] = \dfrac{K_a\,[acid]}{[base]}$<br><br>At pH = 7.4      $[H_3O^+] = 10^{-7.4} = 4 \times 10^{-8}$<br><br>**For $H_2CO_3/HCO_3^-$**<br><br>$\dfrac{[base]}{[acid]} = \dfrac{K_a}{[H_3O^+]}$      $\dfrac{[HCO_3^-]}{[H_2CO_3]} = \dfrac{4.2 \times 10^{-7}}{4 \times 10^{-8}} = 10.5$<br><br>• 10.5 times more $HCO_3^-$ than $H_2CO_3$<br>• more base available so buffer better at resisting acid.<br><br>**For $HCO_3^-/CO_3^{2-}$**<br><br>$\dfrac{[CO_3^-]}{[HCO_3^-]} = \dfrac{4.8 \times 10^{-11}}{4 \times 10^{-8}} = 1.2 \times 10^{-3}$<br><br>• very little $CO_3^{2-}$ present compared to $HCO_3^-$<br>• limited buffering action.<br><br>First acid-base conjugate pair is more important because both acid and conjugate base are present in significant amounts.<br><br>**OR**<br><br>$pH = pk_a + \log \dfrac{[base]}{[acid]}$<br><br>**For $H_2CO_3/HCO_3^-$**    $7.4 = 6.38 + \log \dfrac{[HCO_3^-]}{[H_2CO_3]} = 1.00$<br><br>$\log \dfrac{[HCO_3^-]}{[H_2CO_3]} = 1.02$ so $\dfrac{[HCO_3^-]}{[H_2CO_3]} = 10.5$<br><br>**For $HCO_3^-/CO_3^{2-}$**    $7.4 = 10.32 + \log \dfrac{[CO_3^{2-}]}{[HCO_3^-]}$<br><br>$\log \dfrac{[CO_3^{2-}]}{[HCO_3^-]} = -2.92$ so $\dfrac{[CO_3^{2-}]}{[HCO_3^-]} = 1.2 \times 10^{-3}$ | Correct procedure for calculation of [acid] / [base] ratio **AND** attempt at discussion. | Calculations are correct and are linked to choice of buffer present **OR** better resistance to acid. | Answer shows understanding of buffer systems and correctly links calculations to choice of buffer present **AND** better resistance to acid. |
| 2(b) | Possible individual acid reactions:<br><br>**1.** $Pt + 2H^+ \rightarrow Pt^{2+} + H_2$<br><br>$E_{rxn} = E_{red} - E_{ox} = 0.00 - 1.18$      $V < 0$ so not spontaneous<br><br>**2.** $3Pt + 2NO_3^- + 8H^+ \rightarrow 3Pt^{2+} + 2NO + 6H_2O$<br><br>$E_{rxn} = E_{red} - E_{ox} = 0.96 - 1.18$      $V < 0$ so not spontaneous<br><br>**3.** $Pt + 4Cl^- + 2H^+ \rightarrow H_2 + PtCl_4^{2-}$<br><br>$E_{rxn} = E_{red} - E_{ox} = 0.00 - 0.76$      $V < 0$ so not spontaneous<br><br>With aqua regia<br><br>**4.** $2NO_3^- + 3Pt + 12Cl^- + 8H^+ \rightarrow 3PtCl_4^{2-} + 2NO + 4H_2O$<br><br>$E_{rxn} = E_{red} - E_{ox} = 0.96 - 0.76$      $V > 0$ so reaction goes<br><br>Possible to further react to:<br><br>**5.** $2NO_3^- + 3PtCl_4^{2-} + 6Cl^- + 8H^+ \rightarrow 3PtCl_6^{2-} + 2NO + 4H_2O$<br><br>$E_{rxn} = E_{red} - E_{ox} = 0.96 - 0.68$      $V > 0$ so reaction goes<br><br>So acidic solution of nitrate ions and chloride ions will oxidise platinum metal to Pt(IV). Reaction product is $PtCl_6^{2-}$. | Correct procedure for calculation or discussion but some errors or inadequate discussion. At least THREE equations / reactions are used / discussed. | Discussion includes TWO equations out of **1, 2** and **3**, **AND** eqn. **4**, correctly linked to observations. |  |

| Question | Evidence | 4 marks | 6 marks | 8 marks |
|---|---|---|---|---|
| 3(a) (i) | $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$ <br><br> $n(MnO_4^-) = 0.0200 \times 0.0289 = 5.78 \times 10^{-4}$ <br><br> $n(Fe^{3+}) = 5 \times 5.78 \times 10^{-4} = 2.89 \times 10^{-3}$ <br><br> $n(hac) = \dfrac{1}{69.5} \times 0.1 = 1.44 \times 10^{-3}$ <br><br> $n(Fe^{3+}) : n(hac) = 2.89 \times 10^{-3} : 1.44 \times 10^{-3} = 2:1$ | Correct method with one error (eg 5:1 because miss dilution). | Correct mole ratio obtained from data. | |
| 3(a) (ii) <br><br><br><br> 3(b) | Oxidation Number (N) in hydroxylammonium chloride (hac) is $-1$. <br> Oxidation Number increases by 2 ($2e^-$ transferred) so product is $N_2O$ <br><br><br> $Fe^{3+} + e^- \rightarrow Fe^{2+}$ <br> $2\ ^+NH_3OHCl^- \rightarrow N_2O + H_2O + 6H^+ + 4e^- + 2Cl^-$ <br><br> $4Fe^{3+} + 2\ ^+NH_3OHCl^- \rightarrow 4Fe^{2+} + N_2O + H_2O + 6H^+ + 2Cl^-$ | Relates change in oxidation number to ratio and identity of product (ox. nos may be incorrect). <br><br> **OR** <br> Balanced equation written but no link to data. | Correctly identifies change in oxidation numbers **AND** writes a balanced equation (error may be introduced by wrong ox. nos). | Correct equation based on 3 (a) calculation. |

| Question | Evidence | 4 marks | 6 marks | 8 marks |
|---|---|---|---|---|
| 4(a) (i) | $Ba(OH)_2$:acid = 1:2 <br><br> $n(BaOH)_2 = 0.0940 \times 0.03074 = 2.89 \times 10^{-3}$ mol <br><br> n(acid) unused = $5.78 \times 10^{-3} \times 100 = 5.77 \times 10^{-1}$ mol <br><br> n(acid) used = $1.00 - 5.77 \times 10^{-1} = 0.423$ mol <br><br> _____ <br><br> $n(acid) = n(alcohol) = n(ester) = n(H_2O)$ <br><br> n(alcohol) equm = $0.500 - 0.423 = 0.077$ <br><br> $K = \frac{[ester][water]}{[acid][alcohol]} = \frac{0.423^2}{0.577 \times 0.077} = 4.03$ (3.95) <br><br> % yield = 0.423 / 0.5 × 100 = 84.4% | Correct yield. <br><br> **OR** <br><br> Correct method for calculation of $K$ and % yield. <br><br> **OR** <br><br> Correct discussion for (ii). | Correct calculation of $K$ and % yield. | 4(a) correct AND discussion or calculation for 4(b) is correct. |
| 4(a) (ii) | [Acid] is reduced so less ester and water formed (equilibrium shifts to the left) so less alcohol used up. So [acid] is less, [alcohol] is greater, [ester] and [water] both less (yield is lower since less ester formed). <br><br> **OR** <br><br> Let n(ester) = $x$ <br><br> $K = \frac{x^2}{(0.5 - x)^2} = 4.03$  $x = 0.33$ and % yield = 66% <br><br> ($x > 1$ not acceptable because more than starting conc.) | | | |
| 4(b) | <table><tr><th>Action</th><th>Reason</th></tr><tr><td>Dry flask</td><td>Water is a product of reaction so a wet flask will push equilibrium to the left and reduce the yield.</td></tr><tr><td>Conc $H_2SO_4$</td><td>Acts as a catalyst for the reaction so speeds up the rate at which equilibrium is achieved. **OR** Removes water from equilibrium so encourages more product.</td></tr><tr><td>Reflux</td><td>Allows heating to speed up the reaction without the loss of gaseous reactants products so yield maximized.</td></tr><tr><td>Distil</td><td>Separates ester from some impurities.</td></tr><tr><td>Sodium carbonate</td><td>Increases purity by removing excess acid.</td></tr><tr><td>$CaCl_2$</td><td>Increases purity by removing any excess water.</td></tr><tr><td>(Distil)</td><td>(As above)</td></tr></table> | Discussion correct for FOUR out of six correct discussion with at least TWO links to yield **OR** purity. | Discussion correct for FIVE out of six correct with at least THREE links made which show an understanding of **BOTH** increase yield **AND** increase in purity. | |

| Question | Evidence | 4 marks | 6 marks | 8 marks |
|---|---|---|---|---|
| 5(a) | <br><br>A = 2 methyl butan-1-ol<br>B = 3 methyl butan-1-ol<br>C = 2 methyl butan-2-ol<br>D = 3 methyl butan-2-ol<br>E = dimethyl propanol | One error permissible from the following:<br><br>• 1 structure missing<br><br>• 3 straight chains included<br><br>• 1 repeat<br><br>• 1 extra structure | ALL five structures correct with no repeats and no incorrect structures included. | |
| 5(b) | • Treat with $Cr_2O_7^{2-}/H^+$.<br>No colour change then **C (2 methyl butan-2-ol)** – 3° alcohol so not oxidized.<br><br>• Isolate products. Test with $NaHCO_3(aq)$. Product of reaction with **D (3 methyl butan-2-ol)** – 2° alcohol will be a ketone not carboxylic acid so no $CO_2$ evolved (nor reaction).<br><br>• React original sample with $SOCl_2$ followed by KOH(alc). Test product with $Br_2$. If no decolourisation then must be **E (dimethyl propanol)** (because no H on 3°), and $SOCl_2$ will form haloalkane with **E**.<br><br>• For **A** and **B (3 methyl butan-1-ol)** elimination to alkene will occur with KOH(alc) but not possible with **E**.<br><br>• To distinguish **A** and **B** – **A (2 methyl butan-1-ol)** can be identified because of stereocentre.<br><br>**OR**<br><br>• Treat with $Cr_2O_7^{2-}/H^+$.<br>No colour change then **C (2 methyl butan-1-ol)** –3° alocohol so not oxidized.<br><br>• Isolate products of oxidation. Test with $NaHCO_3(aq)$. Product of reaction with **D (3 methyl butan-1-ol)** –2° alcohol will be a ketone not carboxylic acid so no $CO_2$ evolved (nor reaction),<br><br>• React original sample with $SOCl_2$ followed by KOH (alc). Test product with $Br_2$. If no decolourisation then must be **E (dimethyl propanol)** (because no H to eliminate on 3°C) $SOCl_2$ will form haloalkane.<br><br>• For A and **B (3 methyl butan-2-ol)** elimination to alkene will occur with KOH (alc) but not possible with E.<br><br>• To distinguish A and B – **A (2 methyl butan-1-ol)** can be identified because of stereocentre. | THREE out of five actions correct with TWO adequate explanations. | FOUR out of five actions correct with adequate explanations.<br><br>**OR**<br><br>FIVE out of five but no links. | FIVE correct identifications with reasons. |

| Question | Evidence | 4 marks | 6 marks | 8 marks |
|---|---|---|---|---|
| 6 (a) | HCl with NaOH $\rightarrow$ NaCl + $H_2O$<br><br><table><tr><td></td><td>Concentration (relative)</td><td>Conductivity (relative)</td></tr><tr><td>Initial</td><td>1.00 $H_3O^+$, 1.00 $Cl^-$</td><td>5 1 = 6 (6)</td></tr><tr><td>½ way to equiv</td><td>0.333 $H_3O^+$ 0.333 $Na^+$ 0.667 $Cl^-$</td><td>1.67 0.333 0.667 = 2.7 (4)</td></tr><tr><td>Equivalence</td><td>0.5 $Na^+$ 0.5 $Cl^-$</td><td>0.5 0.5 = 1 (2)</td></tr><tr><td>2 × equivalence</td><td>0.67 $Na^+$ 0.33 $Cl^-$ 0.33 $OH^-$</td><td>0.67 0.33 1.00 = 2 (6)</td></tr></table><br>(Answers in brackets assume no dilution)<br><br><br><br>Initial conductivity is high because ions present are $H_3O^+$ and $Cl^-$ (combined relative conductivity = 6). As reaction proceeds $H_3O^+$ reacts to become $H_2O$ and $Na^+$ added to the solution. High conductivity ion replaced with a low conductivity ion and concentration reduced by dilution. Hence conductivity drops. After the equivalence point where only $Cl^-$ and $Na^+$ ions are present, $Na^+$ and $OH^-$ ions are added. Conductivity increases at a slower rate than the decrease before equivalence point because the ions are diluted and conductivity of $OH^-$ is less than for $H_3O^+$. | Basic shape (graph points) linked to most species in solutions.<br><br>(At least THREE points.) | 'V' shape with appropriate slopes, linked to accurate calculations<br><br>OR<br><br>Discussion which includes reference to species and relative conductance. | Correct shape with relevant discussion for before and after equivalence.<br><br>NOTE: If dilution not considered then a symmetrical V will result. Max marks for this is 6. |
| 6(b) | Starts close to 0 because only limited dissociation. Equivalence point the same as for HCl as species present have the same relative conductivity ($CH_3COO^-$ same as $Cl^-$). After equivalence point graph is the same as for (a) since change in conductivity only affected by addition of NaOH.<br><br>-------- on graph indicates difference in the conductivities of the two titrations. | Graph and reasoning correct either before or after equivalence point<br>**OR**<br>Graph correct but insufficient or incorrect reasons. | One error in graph or reasoning, either before or after equivalence point. | Explanation and correct graph, before and after equivalence point. |

## Judgement Statement

An aggregate mark of 94 from six questions was used in Chemistry.

In 2005, candidates who achieved 69 marks or better were awarded outstanding scholarship and candidates who achieved 46-68 marks were awarded scholarship.