Assessment Schedule – 2010

Scholarship Chemistry (93102)

Evidence Statement

Q	Evidence	Mark Allocation
ONE (a)	Solubility of Tl_2S $\qquad$ $Tl_2S(s) \rightarrow 2Tl^{2+}(aq) + S^{2-}(aq)$ $K_s = [Tl^+]^2 \times [S^{2-}]$ $K_s = 4s^3 = 6 \times 10^{-22}$ $S = \sqrt[3]{\dfrac{6 \times 10^{-22}}{4}} = 5.31 \times 10^{-8} \text{ mol L}^{-1}$ $pK_a (HS^-) = 11.96$ so S^{2-} will be a weak base $S^{2-} + H_2O \rightleftharpoons HS^-(aq) + OH^-(aq)$ When acid is added $\quad$ [OH$^-$(aq)] is decreased $\quad$ $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O$ $\quad$ [S^{2-}(aq)] is decreased $\quad$ $S^{2-}(aq) + H_2O(\ell) \rightarrow HS^-(aq) + OH^-(aq)$ This causes more Tl_2S (s) to dissolve to restore [S^{2-}(aq)]. Therefore the solubility of Tl_2S increases as the pH decreases. Similarly, the solubility of Tl_2S decreases as the pH of the solution increases.	**7–8 marks** Shows an understanding of principles of Chemistry by: (a) Correctly calculating the solubility of Tl_2S AND identifying the S^{2-} as basic AND its increased solubility at low pH and decreased solubility at high pH AND (b) A full discussion of the contribution of bond types to the boiling points and dipole moments. An understanding of the reasons why a high dipole moment may not result in a high boiling point is shown.
(b)	• For all 5 compounds the size of the boiling point depends on the strength of the intermolecular forces • As all 5 compounds have similar masses (72–74) the instantaneous dipoles should have similar strength **Compound 1:** Despite not having a permanent dipole, the attractive force, due to temporary dipoles induced when the pentane molecules approach one another, is sufficiently strong that it is a liquid at room temperature. **Compound 2:** The oxygen in the chain in compound **2** results in a significant increase in the permanent dipole, due to the presence of two polar C–O bonds, but according to the data, this has little effect on the boiling point. This is most likely because the molecules can not pack as close together as for compound **1**. **Compound 3:** This compound has H–bonds between the polar N–H groups of neighbouring molecules. This compound has a lower dipole than compound **4** because N–H is less polar than O–H. It also has a lower boiling point because the attractive forces due to hydrogen bonds are not so strong for N–H as O–H, since this bond is not so polar. This is not compensated for by the fact that there can be more H bonds in the amine than in the alcohol. **Compound 4:** The higher boiling point for butan-1-ol must be due to the O–H bond and the hydrogen bonding between molecules. This is stronger than for the amine for the reasons given above because of the larger negativity of O compared to N.	**5–6 marks** Shows an understanding of principles of Chemistry by: (a) Correctly calculating the solubility of Tl_2S AND making some links between solubility and pH AND (b) Discussing the contribution of the attractive forces due to temporary dipoles / permanent dipoles and hydrogen bonding to the overall attractive force between the molecules. **1–4 marks** Answers include: • Correct calculation of the solubility of Tl_2S. • Identification of the sulfide ion as basic. • The effect of pH on the solubility of the sulfide ion. • Discussion of the bonds between molecules for 3 of the 5 compounds.

Compound 5:
The large increase in dipole moment indicates that the C=O bond is more polar than a C–O bond. The increased polarity means that the dipole-dipole contribution to the boiling point is higher than in compound **2**, but despite this increased contribution due to the polar bond, intermolecular attractive forces for this molecule are not as strong as for butan-1-ol, where hydrogen bonding is possible. The geometry around the carbonyl carbon is trigonal planar and differs from that around the other molecules which all contain tetrahedral carbon centres. The oxygen is no longer in the chain, but sticks out to one side which probably increases the distance between molecules which reduces the strength of the attraction.

TWO (a)	Trend from left to right across Period 4 shows steady increase in 2nd IE as it requires more energy to remove an electron with elements of greater nuclear charge. K has a very high 2nd IE, despite having the lowest nuclear charge, as the second electron is being removed from $3p$, which is much closer to the nucleus. • K has a higher 2nd IE than Kr despite it having almost twice the nuclear charge. • Ca [Ar] $4s^2$ has its second electron removed from the $4s$ orbital, requiring much less energy than K. • The transition elements Sc to Zn show increasing IE. Electrons are removed from $4s$ orbitals and the increase is due to increasing nuclear charge. • Cr [Ar] $3d^5\,4s^1$ needs more energy than expected, as the second electron is removed from the $3d$ orbital. • Mn [Ar] $3d^5\,4s^2$ needs less energy than Cr, as the second electron is removed from the $4s$ orbital. • Cu [Ar] $3d^{10}\,4s^1$ needs more energy than expected, as the second electron is removed from the $3d$ orbital. • Zn [Ar] $3d^{10}\,4s^2$ needs less energy, as the second electron is removed from the $4s$ orbital. • Ge [Ar] $3d^{10}\,4s^2\,4p^2$ needs less energy than Ga, as the second electron comes from $4p$, which is further from the nucleus than the $4s$ electron removed from Ga^+. • Br [Ar] $3d^{10}\,4s^2\,4p^5$ needs less energy than expected, as the electron removed is the last paired electron in $4p^5$. Paired electrons have repulsion in the orbital and it takes less energy to remove.	**7–8 marks** Shows an understanding of principles of Chemistry by: (a) Fully discussing the trend and providing an explanation for it as well as deviations, giving the electron configuration of the elements AND (b) Correctly calculating the % of NaCl. **5–6 marks** (a) Discussing the trend as well as some of the deviations AND (b) Using the correct procedure for partially calculating the % of NaCl. **1–4 marks** Answers include: • Discussing some of the deviations from the trend in IE. • Using the correct procedure for some steps in the calculation of the % of NaCl.
(b)	Na(K)Cl + AgNO$_3$ → AgCl + Na(K)NO$_3$ n (Cl$^-$) = 0.0256 × 0.0970 = 2.48 × 10^{-3} mol Concentration of Cl$^-$ = 0.04966 mol L^{-1} Mass Cl$^-$ in 250 mL = 0.4401 g 0.746 g of mixture of sodium chloride and potassium chloride contains 0.4401 g of Cl$^-$ Let mass of NaCl in mixture = x g. Then mass of KCl = 0.746 g – x g n(NaCl) = x g / 58.5 g mol^{-1} m(Cl$^-$) = x g / 58.5 g mol^{-1} × 35.5 g mol^{-1} n(KCl) = 0.746 – x g / 74.6 g mol^{-1} m(Cl$^-$) = 0.746 – x g / 74.6 g mol^{-1} × 35.5 g mol^{-1} Total mass of chlorine in mixture = [x g × 35.5 g mol^{-1} / 58.5 g mol^{-1}] + [(0.746 – x) g × 35.5 g mol^{-1} / 74.6 g mol^{-1}] = 0.441 g x = 0.655 g % NaCl in mixture = 0.65 g / 0.746 g × 100% = 87.8%	

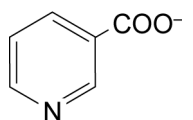| THREE (a)(i)	Nicotinic acid is a zwitterion in aqueous solution.	**7–8 marks** Shows an understanding of principles of Chemistry by:

THREE (a)(i)

Nicotinic acid is a zwitterion in aqueous solution.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$
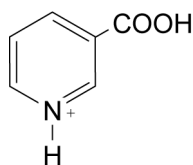
This structure is the conjugate acid of nicotinic acid
The pK_a (–COOH) = 3.0
The –COOH is the stronger acid and loses the H^+ more readily. Stronger acids have lower pK_a.

This structure is the conjugate base of nicotinic acid.

The conjugate acid of this base (the zwitterion) has the higher pK_a. **ie pK_a (–NH$^+$) = 4.9**

For the zwitterion to be the **major species** present in an aqueous solution the pH must be **between 3.0 and 4.9.**

When the zwitterion is the acid of the conjugate pair and is the major species in solution, the ratio $[A^-]$ / $[HA]$ is less than one. $[H_3O^+]$ will be greater than K_a and pH will be less than pK_a. ie pH < 4.9.
When the zwitterion is the base of the conjugate pair and is the major species in solution, the ratio $[A^-]$ / $[HA]$ is greater than one. $[H_3O^+]$ must be less than K_a and pH is more than pK_a. ie pH > 3.0

(ii)

pH 4.9
Nicotinic acid dissolved in water will be in the form of the zwitterion, and as the NaOH is added, the proton on the N will be removed / neutralised. When half of the acid is converted to its conjugate base the pH will be equal to pK_a associated with the –NH$^+$. This will be the centre of the buffer region.

(b)(i)
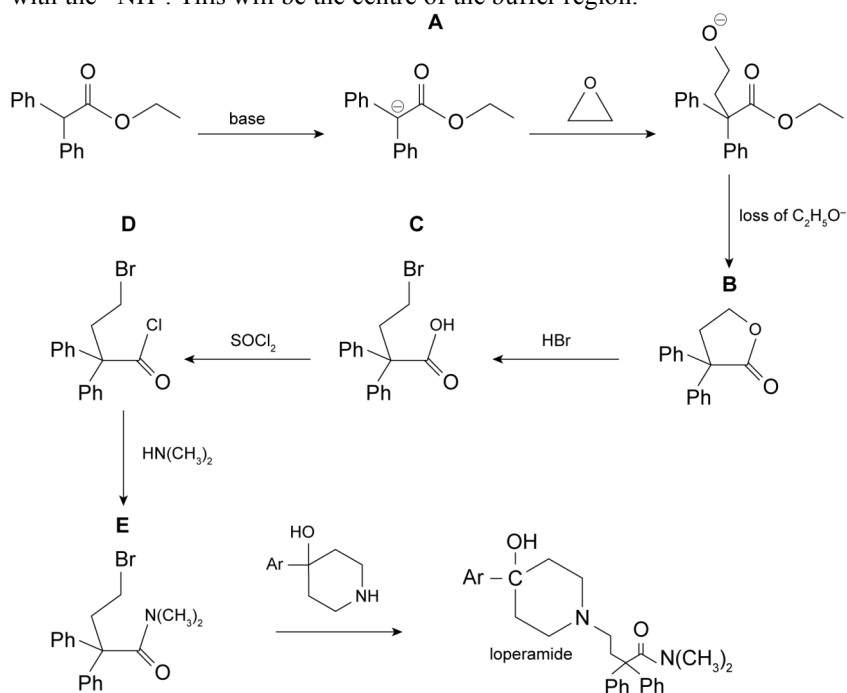
(ii)

Conversion to a salt increases the solubility in water and improves the absorption in the gut.

Loperamide is weakly basic, due to the amine group, so the salt preparation would be by reacting with an acid such as HCl (and crystalising the salt from solution).

Marking column:

7–8 marks
Shows an understanding of principles of Chemistry by:
(a) Drawing structural formulae for the conjugate acid and conjugate base of nicotinic acid AND assigning the pK_a to the correct groups AND explaining, with use of the expression for K_a, why the pH for nicotinic acid solution is between 3.0 and 4.9 AND explaining why the centre of the buffer region is pH 4.9 when a nicotinic acid solution is titrated with NaOH. AND
(b) Drawing correct structural formulae for compounds A to E AND recognising that salts are more soluble in water AND correctly describing salt preparation in general terms AND drawing the structural formula of the salt with the proton shown on the amine group (the amide group is not basic enough to be protonated).

5–6 marks
Shows an understanding of principles of Chemistry by:
(a) Drawing structural formulae for the conjugate acid and base of nicotinic acid as well as assigning the pK_a to the correct groups AND shows an understanding of which group acts as an acid when the solution is titrated with NaOH AND
(b) Drawing correct structural formulae for 3 compounds AND an incomplete discussion explaining the solubility of the salt of loperamide

1–4 marks
Answers include:
• A partial explanation of the pH of nicotinic acid solution
• Correct structural formulae of the conjugate acid and base of nicotinic acid
• Correct prediction of the pH at the centre of the buffer region when nicotinic acid is titrated with NaOH
• Correct structural formulae of 2 of compounds A to E
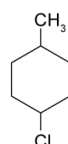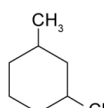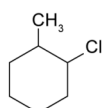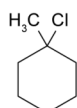• Correct structural formula of the salt of loperamide.
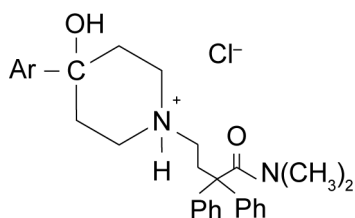
Structure must show charge on N of tertiary amine (not amide group).
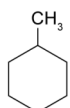
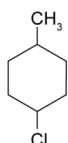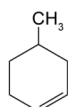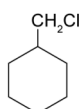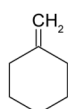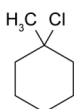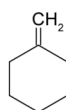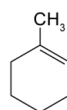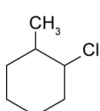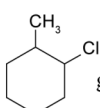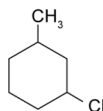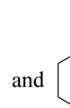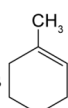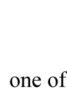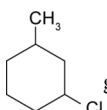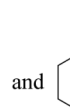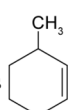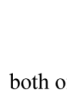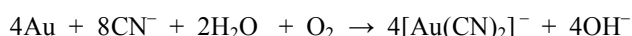|		
FOUR (a)	**R** would give five monochlorides The five monochlorides are: Following the reaction with KOH in ethanol, two of the monochlorides give one alkene isomer: gives which can exist as enantiomers, so this must be **Q**. gives which does not exist as enantiomers, so this must be **M**. One of the monochlorides does not exist as enantiomers, and gives two alkene isomers, this must be **N**. The alkenes formed are and which do not exist as enantiomers. Two of the monochlorides can exist as enantiomers and give two alkene isomers. and gives and one of which can exist as enantiomers, so this must be **O**. gives and both of which can exist as enantiomers, so this must be **P**. $4Au + 8CN^- + 2H_2O + O_2 \rightarrow 4[Au(CN)_2]^- + 4OH^-$	**7–8 marks** Shows an understanding of principles of Chemistry by: (a) Drawing correct structural formulae of compounds M to R with a concise and logical explanation AND (b) Calculating the $E°_{cell}$ value to show that cyanidation will occur spontaneously and that dissolving elemental Au in HCl will not occur spontaneously AND recognising that Ag does not need to be oxidised AND that the high pH is needed to maintain the maximum concentration of CN^- and not allow HCN formation. **5–6 marks** Shows an understanding of principles of Chemistry by: (a) Drawing correct structural formulae for 4 of the 6 compounds with concise and logical explanation OR all compounds correctly drawn with an explanation that is not logical and concise. AND (b) Calculating the $E°_{cell}$ to show that cyanidation will occur spontaneously AND that the Ag does not need to be oxidised OR that a highly basic pH is needed to maintain the high concentration of CN^-. **1–4 marks** Answers include: • Identifying R is methylcyclohexane and chlorination produces at least 2 alternate haloalkanes

(b)	$(\ Ag_2S + 4CN^- \rightarrow 2[Ag(CN)_2] + Na_2S\ )$ $Au + 2CN^- \rightarrow [Au(CN)_2]^- + e^- \qquad E^o = -0.60\ V$ $O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E^o = +0.40\ V$ $E^{\circ}_{cell} = +0.40 - (-0.60)\ V$ $\qquad\quad = +1.00\ V$ Positive E°_{cell} value shows this reaction will take place spontaneously in comparison with dissolving Au in HCl $Au \rightarrow Au^+ + e^- \qquad\qquad\qquad E^o = +1.83\ V$ $2H^+ + 2e^- \rightarrow H_2 \qquad\qquad\qquad E^o = 0\ V$ $E^{\circ}_{cell} = 0 - (+1.83)\ V$ $\qquad\quad = -1.83\ V$ Negative E°_{cell} value shows that this reaction will not proceed spontaneously. Also $E^{\circ}_{cell} = -1.52V$ for a reaction between acid and Au to form Au^{3+} so this is also negative and therefore reaction will not occur The reaction with gold is an oxidation–reduction reaction in combination with a complexation reaction requiring the presence of oxygen as an oxidant. The complex formation reaction with silver sulfide is not an oxidation-reduction reaction and does not need oxygen to proceed. The K_a (HCN) $= 6.17 \times 10^{-10}$. At a pH of less than 10.5, the $[H_3O^+]$ would be high enough to allow the formation of HCN. pH above 10.5 would maintain the maximum concentration of CN^- in solution and maximise the dicyanoaurate(I) complex formation.	• Identifies various alkenes as products of elimination • Correct calculation of E°_{cell} to show that cyanidation will occur spontaneously • Correct calculation of E°_{cell} to show that Au will not react with HCl • Balanced equations for the cyanidation reaction • Explanation that the recovery of Ag and Au differs as the Ag is already oxidised • Recognition that at below pH 10.5 the $[CN^-]$ will be lowered.

FIVE (a)	$\mathbf{V = H}$ • molar mass is 2.00 g mol^{-1} • has 1 valence e^-, same as Z (Na) • forms XV_3 with phosphorus • forms VW with fluorine • forms ZV with Na $\mathbf{W = F}$ • most reactive of its group, which contains only non-metals • ion has same number of electrons as Z • forms VW with hydrogen $\mathbf{X = P}$ • valence electrons in same shell as Y, sulfur, and Z, sodium • has higher first ionisation energy than Y, sulfur • forms gas, XV_3, with hydrogen $\mathbf{Y = S}$ • valence electrons in same shell as X, phosphorus, and Z, sodium • lower first ionisation energy than X, phosphorus • reacts with Z to form X_2Y, which is basic • has smaller atomic radius than X $\mathbf{Z = Na}$ • same number valence electrons as V, hydrogen • valence electrons in same shell as X, phosphorus, and Y, sulfur • reacts with Y to form Z_2Y, which is basic • ion has same number of electrons as W, fluorine • reacts with V to form an ionic solid Justification to be logical and clearly expressed.	**7–8 marks** Shows an understanding of principles of Chemistry by: (a) Correctly identifying elements V to Z with a justification that is clearly and concisely expressed AND (b) Correctly calculating the concentrations of Na_2CO_3 and $NaHCO_3$ AND commenting on the errors in back titrations compared to direct titrations AND discussing some of the criteria for selecting a primary standard **5–6 marks** Shows an understanding of principles of Chemistry by: (a) Correctly identifying elements V to Z but justification not clearly expressed or incomplete AND (b) Using the correct method for calculating the concentrations of Na_2CO_3 and $NaHCO_3$ AND commenting on the errors in a back titration AND discussing one criterium for selecting a primary standard
(b)(i)	Based on a pK_a for carbonic acid of **6.3** the first titration would involve complete neutralisation of the CO_3^{2-} and HCO_3^- Total n($HCO_3^- + CO_3^{2-}$) = n(HCl) = $0.143 \times 21.45 \times 10^{-3}$ mol $= 3.07 \times 10^{-3}$ mol **Determination of HCO_3^-** Add 10.00 mL of 0.128 mol L^{-1} NaOH $\qquad HCO_3^- + OH^- \rightarrow CO_3^{2-}$ n(NaOH) added $= 0.128 \times 10.00 \times 10^{-3}$ mol $= 1.28 \times 10^{-3}$ mol Remove CO_3^{2-} by precipitation with Ba^{2+} n(HCl) to titrate excess NaOH $= 0.143 \times 6.23 \times 10^{-3}$ mol $= 0.891 \times 10^{-3}$ mol n(NaOH) excess $= 0.891 \times 10^{-3}$ mol n(NaOH) used $= (1.28 \times 10^{-3}) - (0.891 \times 10^{-3})$ mol $= 0.389 \times 10^{-3}$ mol n(HCO_3^-) $= 0.389 \times 10^{-3}$ mol c(HCO_3^-) $= 0.389 \times 10^{-3}$ mol $/ 25.00 \times 10^{-3}$ L $= 0.0156$ mol L^{-1} **Determination of CO_3^{2-}**	**1–4 marks** Answers include:

	n(HCl) to react with CO_3^{2-} = $(3.07 \times 10^{-3}) - (0.389 \times 10^{-3})$ mol = 2.68×10^{-3} mol n(CO_3^{2-}) = 1.34×10^{-3} mol c(CO_3^{2-}) = 1.34×10^{-3} mol / 25.00×10^{-3} L = 0.0536 mol L^{-1} *Note that any valid calculation carried out using pK_a (H_2CO_3)= 3.6 provided in the question or assuming full neutralisation of the CO_3^{2-} and HCO_3^- was given full credit.*	• Correctly identifying 4 of the elements V to Z • Using the correct method to calculate the concentration of Na_2CO_3 or $NaHCO_3$ • Discussing the errors in comparing the two methods of analysis • Discussing the selection of a primary standard.
(ii)	First method involves a back titration, which increases the error due to measurement of NaOH and HCl for back titration. The errors are small and the method reliable. The second method involves a direct titration with reduced opportunity for volume measurement error, although the overall percentage error depends on the volume used in the titration. Any difficulty in the observation of the endpoint when using the methyl orange indicator is the same for both methods.	
(iii)	Possibilities include a metal carbonate or bicarbonate e.g. Na_2CO_3 Primary standard should: • Have high molar mass to minimise % error when weighing. $M(Na_2CO_3)$ = 106 g mol^{-1} is good. • Be stable. Na_2CO_3 absorbs water from air but this is easily removed by oven drying. • React quickly and completely with easily detected end point. Na_2CO_3 does this. • Be readily available in a pure form or easily purified. Na_2CO_3 is cheap and available.	