

Assessment Schedule – 2019

Scholarship Chemistry (93102)

Evidence Statement

Q	Evidence	Scholarship Not Awarded	Scholarship	Outstanding Scholarship
ONE (a)(i)	$\Delta_{\text{soln}}H(\text{NH}_4\text{NO}_3) = -307 \text{ kJ mol}^{-1} + -314 \text{ kJ mol}^{-1} + 646 \text{ kJ mol}^{-1}$ $= +25 \text{ kJ mol}^{-1}$ $m(\text{NH}_4\text{NO}_3) = 39 \text{ g}$ $n(\text{NH}_4\text{NO}_3) = \frac{39 \text{ g}}{80 \text{ g mol}^{-1}} = 0.4875 \text{ mol}$ $q_{\text{system}} = \Delta_{\text{soln}}H \times n = 25 \text{ kJ mol}^{-1} \times 0.4875 \text{ mol} = 12.19 \text{ kJ (12190 J)}$ $\Delta T_{\text{solution}} = \frac{-q_{\text{system}}}{c(\text{H}_2\text{O}) \times m(\text{solution})} = \frac{-12190 \text{ J}}{4.18 \text{ J } ^\circ\text{C}^{-1} \times 154 \text{ g}} = -18.94 ^\circ\text{C}$ Final Temp = $25 ^\circ\text{C} - 18.94 ^\circ\text{C} = \mathbf{6.07 ^\circ\text{C}}$	Any of the following: <ul style="list-style-type: none"> • correct $\Delta_{\text{soln}}H$ value • identifies process as endothermic • enthalpy changes described • entropy changes described • understanding of thermodynamic favourability (spontaneity) shown • description of attractive forces in molecules given • melting point of any one molecule explained. 	Calculates a final temperature for the cool pack with minor error. AND Explanation of the enthalpy and entropy changes occurring in hot and cold packs but does not fully justify the favourability in terms of overall increases in entropy of the processes. AND Explanation given for the different factors contributing to the melting points of the three substances but has not fully justified the melting points of all three substances.	Correctly calculates the final temperature for the cool pack. AND Comprehensive discussion of the enthalpy and entropy changes occurring in hot and cold packs, leading to them both to be thermodynamically favoured. AND Comprehensive discussion of the factors affecting the melting points of the three substances.

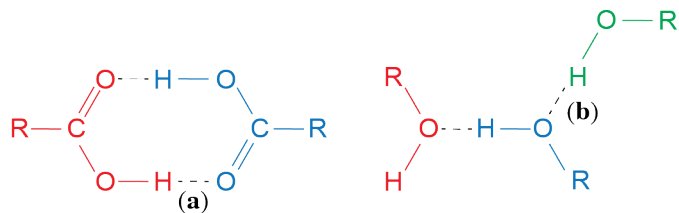
(ii)	<p>Any process that occurs spontaneously at a given temperature is thermodynamically favoured.</p> <p>For a process to be spontaneous there must be an overall increase in the total entropy of the system and the surroundings ($\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$). Changes to the entropy of the surroundings occurs with the gain or loss of heat (kinetic energy) in the surrounding particles, as a result of exothermic or endothermic enthalpy changes in the system. Exothermic reactions increase entropy of the surroundings, while endothermic reactions decrease the entropy of the surroundings. Changes to the entropy of the system occurs as a result of the increase or decrease of random motion of the particles within the system.</p> <p>In both hot and cold packs, the dissolution processes result in an increase in the entropy of the system. As the ionic solids dissolve, the ions are separated from their lattice structure and form hydrated ions within the solution. The entropy of the hydrated ions is higher than the ionic solid due to the greater random motion of the particles within the solution, compared to the lattice.</p> <p>In hot packs, the process is also exothermic ($\Delta H < 0$), and the heat transfer to the surroundings increases the entropy of the surroundings. Since the entropy is increasing in both the system and the surroundings, the process will be spontaneous.</p> <p>In cold packs, the process is endothermic ($\Delta H > 0$), and heat loss from the surroundings decreases the entropy of the surroundings. However, as the process is spontaneous, the increase in the entropy of the system (due to the dissolution) must outweigh the decrease in entropy of the surroundings, leading to an overall increase in the total entropy of the process, and the process being thermodynamically favoured.</p>			
(b)	<p><i>The discussion must give a clear account of the attractive forces responsible for the melting points of the substances. The grade awarded will be dependent on the quality of the justifications made.</i></p> <p>The melting point of molecular substances are related to the strength of the attractions between the particles. The key attractive forces involved in these structures are temporary dipole forces, permanent dipole forces, and hydrogen bonding.</p> <p>The random movement of electrons in all three molecules results in temporary dipole forces. These forces are strongest in acetylsalicylic acid, followed by methyl salicylate, followed by salicylic acid. An increase in molar mass means a greater number of electrons, which increases the size of the temporary dipole, so intermolecular forces increase. These forces are weak, however become stronger with shorter bonding distance, and therefore have the greatest impact within</p>			

salicylic acid, where the molecules are able to pack closest together.

All three molecules contain permanent dipoles as a result of the presence of C–O, C=O, and O–H bonds. The presence of ester groups in the side chains of methyl salicylate and acetylsalicylic acid, however, reduces the overall net dipoles of the molecules due to the addition of non-polar –CH₃ groups.

Hydrogen bonds form between the lone pairs of electrons on O atoms and the nearby positively charged H atoms. These H atoms are positively charged as the O atoms to which they are covalently bonded have a high electronegativity, resulting in the withdrawal of electron density from the atoms. Salicylic acid has the highest melting point, as it has the greatest capacity to form hydrogen bonds, with two positions able to form such attractions – the –OH hydroxyl group, and –COOH carboxyl group. In methyl salicylate the –COOH group is replaced with an ester group, limiting the ability for the molecule to form hydrogen bonds, therefore lowering the melting point compared to salicylic acid. Similarly, in acetylsalicylic acid, the –OH group is replaced with an ester group, again limiting the formation of hydrogen bonds and lowering the melting point.

The carboxyl –COOH group is able to form a greater number of hydrogen bonds due to the presence of both carbonyl C=O and hydroxyl –OH groups **(a)**, compared to the hydroxyl –OH groups **(b)**. The esterification of the carboxyl functional group in the formation of methyl salicylate appears to have a much greater impact than the esterification of the hydroxyl functional group in the formation of acetylsalicylic acid, therefore the melting point drops more significantly. The significantly lowered melting point of methyl salicylate may also be due to internal hydrogen bonding occurring within the molecules, reducing the capacity for the molecules to form attractions with other nearby molecules. Dimerisation may also occur between molecules with the –COOH groups, and the dimer units will have greater temporary dipole forces and therefore higher melting points.



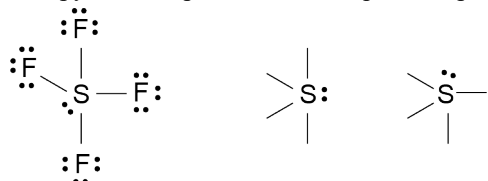
Q	Evidence	Scholarship Not Awarded	Scholarship	Outstanding Scholarship
TWO (a)(i)	$5\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 5\text{O}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$ $5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$ $n(\text{C}_2\text{O}_4^{2-}) = \frac{1.756 \text{ g}}{134 \text{ g mol}^{-1}} = 1.3104 \times 10^{-2} \text{ mol}$ $n(\text{C}_2\text{O}_4^{2-})_{\text{aliquot}} = \frac{0.013104 \text{ mol} \times 0.02500 \text{ L}}{0.2500 \text{ L}} = 1.3104 \times 10^{-3} \text{ mol}$ $n(\text{MnO}_4^-) = 0.0013104 \text{ mol} \times \frac{2}{5} = 5.2418 \times 10^{-4} \text{ mol}$ $c(\text{MnO}_4^-) = \frac{5.2418 \times 10^{-4} \text{ mol}}{0.01785 \text{ L}} = 2.9365 \times 10^{-2} \text{ mol L}^{-1}$ $n(\text{MnO}_4) = 2.9365 \times 10^{-2} \text{ mol L}^{-1} \times 0.01343 \text{ L} = 3.9438 \times 10^{-4} \text{ mol}$ <p>In 10 mL aliquot, $n(\text{H}_2\text{O}_2) = 3.9438 \times 10^{-4} \text{ mol} \times \frac{5}{2} = 9.8595 \times 10^{-4} \text{ mol}$</p> <p>In 100 mL vol. flask, $n(\text{H}_2\text{O}_2) = 9.8595 \times 10^{-4} \text{ mol} \times \frac{100}{10} = 9.8595 \times 10^{-3} \text{ mol}$</p> <p>In the original 10 mL sample of H_2O_2, $m(\text{H}_2\text{O}_2) = 9.8595 \times 10^{-3} \text{ mol} \times 34.01 \text{ g mol}^{-1} = 0.3352 \text{ g}$</p> <p>In a 100 mL sample of H_2O_2, $m(\text{H}_2\text{O}_2) = 10 \times 0.3352 \text{ g} = \mathbf{3.353 \text{ g}}$</p> <p>The expected concentration was 6 g per 100 mL, so since manufacture the hydrogen peroxide has decomposed by:</p> $\% \text{ decomposition} = \frac{6 \text{ g} - 3.352 \text{ g}}{6 \text{ g}} \times 100 = \mathbf{44.11\%}$	<p>Any of the following:</p> <ul style="list-style-type: none"> calculation of the concentration of permanganate calculation of the mass of peroxide correct process for titration calculation reasons given for any of the steps shapes for SF_4 and XeF_4 drawn polarity described with reasons for molecules correct shape determined for either compound with reasons. 	<p>Balanced chemical equations written, and correct process for determining the mass of H_2O_2 followed.</p> <p>AND</p> <p>Reasons given for the three steps, but with limited justification.</p> <p>AND</p> <p>Draws the possible shapes, identifies the correct shape, and provides bond angles, justification of polarity, and limited justification of the shape.</p>	<p>Correct mass and % decomposition determined for the H_2O_2 solution.</p> <p>AND</p> <p>Reasons given for the three steps with comprehensive justification.</p> <p>AND</p> <p>Comprehensive justification of the correct shape, polarity, bond angles for SF_4 and XeF_4, with reference to repulsion of bonding v non-bonding electron pairs.</p>

(ii)	<p>Standardisation of the KMnO_4 solution.</p> <ul style="list-style-type: none"> • KMnO_4 is not appropriate for use as a primary standard. It cannot be obtained in a sufficiently pure form. • The concentration cannot be reliably calculated from the mass of solid used. • $[\text{MnO}_4^-]$ therefore has to be determined using an appropriate primary standard. In this investigation, sodium oxalate is a more reliable primary standard and is used to standardise the permanganate solution prior to use. • This improves the accuracy of the investigation by determining an accurate $[\text{MnO}_4^-]$ to then derive $[\text{H}_2\text{O}_2]$ from. <p>Addition of H_2SO_4 solution to the reaction mixture.</p> <ul style="list-style-type: none"> • MnO_4^- ions in the solution can react to form a variety of products depending on the pH of the solution. If the solution is neutral or alkaline then insoluble brown / black MnO_2 forms. If the solution is acidic then a colourless solution of Mn^{2+} ions form. • The mol ratio of $\text{MnO}_4^- : \text{H}_2\text{O}_2$ changes when the reaction conditions and subsequent products change. Using an incorrect balanced equation will result in incorrect calculations. • The formation of brown / black MnO_2 would prevent an accurate end point of the titration being detected. • This improves the accuracy of the investigation by ensuring the end point can be clearly observed, giving accurate titres. <p>Heating the $\text{Na}_2\text{C}_2\text{O}_4$ solution prior to titration with the KMnO_4 solution.</p> <ul style="list-style-type: none"> • The rate of reaction between the $\text{C}_2\text{O}_4^{2-}$ ions and MnO_4^- ions must be slow if it is necessary to heat it. • Since the titration end point is based on the presence of excess unreacted purple MnO_4^- ions, if the reaction mixture is not heated, then the end point would be difficult to determine based on whether excess ions were present, or they had simply not yet reacted due to the slow rate. • Heating the solution decreases the time needed to carry out the titration. • This improves the accuracy of the investigation by ensuring that the end point is not misjudged. 			
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(b)(i)

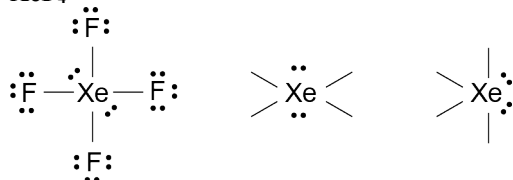
SF₄

Based on the Lewis diagram there is one lone pair of electrons. This lone pair could theoretically occupy an axial position, or an equatorial position.



Lone pair equatorial: Shape is see-saw (distorted tetrahedral). Molecule would be polar.

Lone pair axial: Shape is trigonal pyramidal. Molecule would be polar.

XeF₄

Two lone pair both axial (180° apart): Shape is square planar. Molecule would be non-polar.

Two lone pairs both equatorial (90° apart): Shape is see-saw. Molecule would be polar.

(ii)	<p>Repulsion between lone pair and bonding pair electrons is greater than between bonding pair electrons since lone pair electrons occupy more space than bonding pair electrons/are closer to the nucleus than bonding pair electrons. Hence, to minimise repulsion, lone pairs will tend to occupy equatorial positions where bond angles are 120° rather than axial positions where the bond angles are smaller (90°).</p> <p>For SF_4, there are two possible arrangements. In the triangle-based pyramid, the lone pair of electrons is just 90° away from 3 of the bonding pairs of electrons. In the see-saw arrangement, the lone pair of electrons is around 120° away from two of the bonding pairs of electrons. Since lone pair electrons occupy more space than bond pair electrons, the see-saw arrangement minimises repulsion between electrons to a greater extent, and so is more favourable. This minimises repulsion between electrons to a greater extent. The arrangement of the bonds in both these structures does not allow for the cancellation of the bond dipoles and hence the molecules will be polar.</p> <p>Therefore, the correct shape is see-saw. SF_4 will be polar. The S-F bond angles are $\sim 120^\circ$ in the equatorial plane, and $\sim 90^\circ / 180^\circ$ in the axial plane. Due to the increased repulsion of the lone pair of electrons, the F atoms will be pushed closer together, so the bond angles will be slightly less than $120^\circ / 90^\circ / 180^\circ$.</p> <p>For XeF_4, there are two possible arrangements. The see-saw arrangement has the lone pairs closer to each other than the square planar arrangement, and so will be less favorable – the square planar arrangement minimises repulsion between electrons to a greater extent. The see-saw arrangement will be polar as the shape of the molecule means that the bond dipoles do not cancel. In the square planar arrangement, the lone pairs are opposite each other, as are the polar bonds and so the bond dipoles cancel cause the molecule to be non-polar.</p> <p>Therefore, the correct shape is square planar. XeF_4 will be non-polar. The Xe-F bond angles are 90°.</p>			
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Q	Evidence	Scholarship Not Awarded	Scholarship	Outstanding Scholarship
THREE (a)	$\text{HClO} \rightarrow \text{ClO}_2$ AND $\text{HClO}_2 \rightarrow \text{HCl}$ $4\text{HClO} + 3\text{HClO}_2 \rightarrow 4\text{ClO}_2 + 3\text{HCl} + 2\text{H}_2\text{O}$ $E^\circ_{\text{cell}} = 1.58 \text{ V} - 1.51 \text{ V} = +0.07 \text{ V}$ $\text{HClO} \rightarrow \text{HCl}$ AND $\text{HClO}_2 \rightarrow \text{ClO}_2$ $\text{HClO} + 2\text{HClO}_2 \rightarrow 2\text{ClO}_2 + \text{HCl} + \text{H}_2\text{O}$ $E^\circ_{\text{cell}} = 1.50 \text{ V} - 1.18 \text{ V} = +0.32 \text{ V}$ Larger $E^\circ_{\text{cell}} = +0.32 \text{ V}$, therefore the second equation represents the reaction that is thermodynamically favoured.			
THREE (b)(i)	<div><div>A: 5-chloro-4-methylpentan-1-ol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{Cl}$</div><div>C: 4-methylpentan-1-ol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_3$</div><div>E: 4-methylpentan-1,4-diol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\overset{\text{OH}}{\text{C}}}}-\text{CH}_3$</div><div>G: 4-hydroxy-4-methylpentanoic acid $\text{HO}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\overset{\text{OH}}{\text{C}}}}-\text{CH}_3$</div></div> <div><div>B: 4-methylpent-4-en-1-ol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}_2$</div><div>D: 4-methylpentan-1,5-diol $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{OH}$</div><div>F: 4-methylpentan-1,5-dioic acid $\text{HO}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\overset{\text{O}}{\text{C}}}}-\text{OH}$</div><div>H: methyl 4-chloro-4-methylpentanoate $\text{H}_3\text{C}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_2-\underset{\text{CH}_3}{\underset{ }{\overset{\text{Cl}}{\text{C}}}}-\text{CH}_3$</div></div> <div>Any of the following:<ul style="list-style-type: none">identifies some of the Compounds A – Hidentifies Compound Kpartial explanation of spectroscopic databalanced half equations writtenspontaneous reaction justified with use of reduction potentials.</div> <div>Six of Compounds A – H are correctly identified. AND Identifies Compound K with limited integration of spectroscopic data. AND Writes balanced redox equations for the two different ways the reaction can proceed, but limited justification of spontaneity.</div> <div>All of Compounds A – H are correctly identified. AND Identifies Compound K with comprehensive integration of spectroscopic data. AND Identifies the thermodynamically favoured reaction with use of E° calculations and balanced redox equations.</div>			

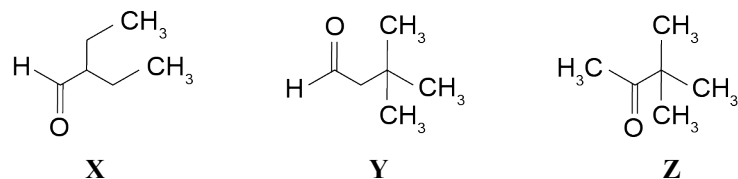
- (ii) *The discussion must integrate spectral data from all three spectra to identify Compound K. The grade awarded will be dependent on the quality of the argument made, and the amount of data integrated, in the identification of Compound K.*

The molecular formula for **B** is $C_6H_{12}O$, which has a matching molar mass of 100 g mol^{-1} . Assuming **K** is indeed a structural isomer, it will also have the molecular formula $C_6H_{12}O$.

There is no broad O-H peak in the IR spectra, and there is no peak shifted to $\sim 50\text{--}60 \text{ ppm}$ on the ^{13}C NMR spectra, indicating there is no $-\text{OH}$ functional group present in **K**. The O atom is therefore likely to be present in a $\text{C}=\text{O}$ group. This is confirmed with the presence of a sharp $\text{C}=\text{O}$ peak in the IR spectra at $\sim 1700 \text{ cm}^{-1}$, and the peak at 213 ppm on the ^{13}C NMR spectra. The fact that the peak on the ^{13}C NMR spectra is shifted downfield beyond 200 ppm indicates the $\text{C}=\text{O}$ is either an aldehyde group, or ketone group, and is not part of an ester or carboxylic acid functional group.

There are only four peaks on the ^{13}C NMR spectra, indicating four unique carbon bonding environments. As only one carbon environment is shifted downfield, and three are not, the remaining carbons are not part of a functional group.

As the molecular formula is $C_6H_{12}O$, then there must be one $\text{C}=\text{O}$ group and some form of symmetry within the compound. There are three possible isomers for $C_6H_{12}O$ which contain a $\text{C}=\text{O}$ functional group and four carbon bonding environments. These are:



The base peak in the MS spectra is found at 57 m/z , indicating the formation of a fragment of molar mass 57 g mol^{-1} . The only fragment that satisfies this molar mass is $\text{C}(\text{CH}_3)_3^+$, which can only be formed from fragmentation of two of the possible isomers (**Y** and **Z**).

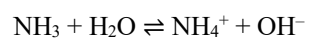
Compound **K** could be either **Z** or **Y**. To narrow these two isomers down further, a test for the functional group could be carried out. Any coloured oxidising agent (Tollens, Benedicts, $\text{H}^+/\text{MnO}_4^-$, $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$) could be used to identify the presence or absence of an aldehyde functional group. Based on a positive or negative result, Compound **K** could be identified.

Q	Evidence	Scholarship Not Awarded	Scholarship	Outstanding Scholarship
FOUR (a)	$s(\text{Ag}_3\text{PO}_4) = \frac{0.007381 \text{ g L}^{-1}}{418.6 \text{ g mol}^{-1}}$ $= 1.763 \times 10^{-5} \text{ mol L}^{-1}$ $K_s(\text{Ag}_3\text{PO}_4) = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$ $= (3 \times 1.763 \times 10^{-5})^3 \times (1.763 \times 10^{-5})$ $= 2.609 \times 10^{-18}$ $K_s(\text{Ag}_3\text{PO}_4) = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$ $2.609 \times 10^{-18} = (5.017 \times 10^{-5})^3 \times [\text{PO}_4^{3-}]$ $[\text{PO}_4^{3-}] = 2.066 \times 10^{-5} \text{ mol L}^{-1}$ $n(\text{PO}_4^{3-})_{\text{solution}} = 2.066 \times 10^{-5} \text{ mol L}^{-1} \times 0.4713 \text{ L}$ $= 9.740 \times 10^{-6} \text{ mol}$ $n(\text{PO}_4^{3-})_{\text{precipitated}} = \frac{17.32 \text{ g}}{418.6 \text{ g mol}^{-1}}$ $= 0.04137 \text{ mol}$ $n(\text{PO}_4^{3-})_{\text{total}} = 9.740 \times 10^{-6} \text{ mol} + 0.04137 \text{ mol}$ $= 0.04138 \text{ mol}$ $\%(\text{PO}_4^{3-})_{\text{solution}} = \frac{9.750 \times 10^{-6} \text{ mol}}{0.04138} \times 100$ $= 0.02356 \%$ <p>This indicates that 99.98% of the PO_4^{3-} is captured by the procedure, so it can be considered fairly efficient.</p>	<p>Any of the following:</p> <ul style="list-style-type: none"> calculated $\text{p}K_a(\text{NH}_4^+)$ calculated pH at 0 mL calculated pH at 35 mL titration curve similar to expected curve explains formation and loss of complex ions explains formation and loss of $\text{Zn}(\text{OH})_2$ precipitate uses correct procedure to determine $K_s(\text{Ag}_3\text{PO}_4)$ partial calculation completed for PO_4^{3-} ion concentration. 	<p>Correct process followed for calculating $\text{p}K_a(\text{NH}_4^+)$ and the pH at 0 mL, 3 mL, 35 mL, and sketched an approximate curve.</p> <p>AND</p> <p>Explains the changes in solution composition with reference to the species present at different pH values.</p> <p>AND</p> <p>Correct process followed for the calculation of K_s and concentration of phosphate ions in solution.</p>	<p>Calculated the expected pH values and used these, plus additional values, to sketch an accurate curve.</p> <p>AND</p> <p>Comprehensively discussed the changes in the solution composition with reference to correct species, balanced equations, and equilibrium principles.</p> <p>AND</p> <p>Correctly determined the percentage of PO_4^{3-} remaining in solution.</p>

(b)(i)	<p>Acid-base reaction:</p> $n(\text{HBr}) = cV = 1.150 \text{ mol L}^{-1} \times 0.021 \text{ L} = 2.415 \times 10^{-2} \text{ mol}$ $n(\text{NH}_3) = 2.415 \times 10^{-2} \text{ mol}$ $[\text{NH}_3]_{\text{initial}} = \frac{n}{V} = \frac{2.415 \times 10^{-2} \text{ mol}}{0.015 \text{ L}} = 1.610 \text{ mol L}^{-1}$ <p>$\text{p}K_{\text{a}}$ based on $\text{pH} = 4.70$ at equivalence point:</p> $[\text{H}_3\text{O}^+] = 10^{-4.70} = 1.995 \times 10^{-5} \text{ mol L}^{-1}$ $[\text{NH}_4^+] = [\text{NH}_3]_{\text{initial}} \times \frac{15 \text{ mL}}{36 \text{ mL}} = 0.6708 \text{ mol L}^{-1}$ $K_{\text{a}} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{NH}_4^+]} = \frac{(1.995 \times 10^{-5})^2}{0.6708} = 5.934 \times 10^{-10}$ $\text{p}K_{\text{a}} = -\log(K_{\text{a}}) = -\log(5.934 \times 10^{-10}) = \mathbf{9.23}$			
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pH at 0 mL HBr:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$



$$[\text{NH}_4^+] = [\text{OH}^-] = \frac{[K_w]}{[\text{H}_3\text{O}^+]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[K_w]} \bigg/ [\text{H}_3\text{O}^+]$$

$$K_a = \frac{[\text{H}_3\text{O}^+]^2[\text{NH}_3]}{[K_w]}$$

$$\frac{K_a \times K_w}{[\text{NH}_3]} = [\text{H}_3\text{O}^+]^2$$

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_a \times K_w}{[\text{NH}_3]}}$$

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{10^{-14} \times 5.934 \times 10^{-10}}{1.610}} \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = 1.919 \times 10^{-12} \text{ mol L}^{-1}$$

$$\text{pH} = -\log(1.919 \times 10^{-12}) = \mathbf{11.72}$$

<p>OR</p> $pK_b = 14 - pK_a = 14 - 9.23 = 4.77$ $K_b = 10^{-pK_b} = 1.698 \times 10^{-5}$ $K_b = \frac{[\text{OH}^-]^2}{[\text{NH}_3]_{\text{initial}}}$ $1.698 \times 10^{-5} = \frac{[\text{OH}^-]^2}{1.610 \text{ mol L}^{-1}}$ $[\text{OH}^-] = \sqrt{1.698 \times 10^{-5} \times 1.610 \text{ mol L}^{-1}} = 5.228 \times 10^{-3} \text{ mol L}^{-1}$ $p\text{OH} = -\log(5.228 \times 10^{-3}) = 2.28$ $p\text{H} = 14 - 2.28 = \mathbf{11.72}$			
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pH at 3 mL HBr:

$$n(\text{NH}_3)_{0 \text{ mL}} = [\text{NH}_3]_{\text{initial}} \times V(\text{NH}_3)_{0 \text{ mL}}$$

$$= 1.61 \text{ mol L}^{-1} \times 0.015 \text{ L}$$

$$= 2.415 \times 10^{-2} \text{ mol}$$

$$n(\text{HBr})_{\text{added}} = 0.003 \text{ L} \times 1.15 \text{ mol L}^{-1} = 3.450 \times 10^{-3} \text{ mol}$$

$$n(\text{NH}_3)_{3 \text{ mL}} = n(\text{NH}_3)_{0 \text{ mL}} - 3.450 \times 10^{-3} \text{ mol}$$

$$= 2.415 \times 10^{-2} \text{ mol} - 3.450 \times 10^{-3} \text{ mol}$$

$$= 2.070 \times 10^{-2} \text{ mol}$$

$$n(\text{NH}_4^+)_{3 \text{ mL}} = n(\text{HBr})_{\text{added}}$$

$$= 3.450 \times 10^{-3} \text{ mol}$$

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{n(\text{NH}_3)}{n(\text{NH}_4^+)}$$

$$= 9.23 + \log \frac{2.070 \times 10^{-2} \text{ mol}}{3.450 \times 10^{-3} \text{ mol}} = \mathbf{10.00}$$

OR

$$[\text{NH}_3] = \frac{2.070 \times 10^{-2} \text{ mol}}{0.018 \text{ L}} = 1.150 \times 10^{-3} \text{ mol L}^{-1}$$

$$[\text{NH}_4^+] = \frac{3.450 \times 10^{-3} \text{ mol}}{0.018 \text{ L}} = 1.916 \times 10^{-4} \text{ mol L}^{-1}$$

$$K_{\text{a}} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$[\text{H}_3\text{O}^+] = K_{\text{a}} \times \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$= \frac{5.934 \times 10^{-10} \text{ mol L}^{-1} \times 1.916 \times 10^{-4} \text{ mol L}^{-1}}{1.150 \times 10^{-3} \text{ mol L}^{-1}}$$

$$= 9.887 \times 10^{-11} \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$= -\log (9.887 \times 10^{-11} \text{ mol L}^{-1}) = \mathbf{10.00}$$

pH at 35 mL HBr:

$$n(\text{H}_3\text{O}^+) = n(\text{HBr})_{\text{excess}} = c \times V_{\text{excess}} = 1.15 \text{ mol L}^{-1} \times 0.014 \text{ L} = 1.61 \times 10^{-2} \text{ mol}$$

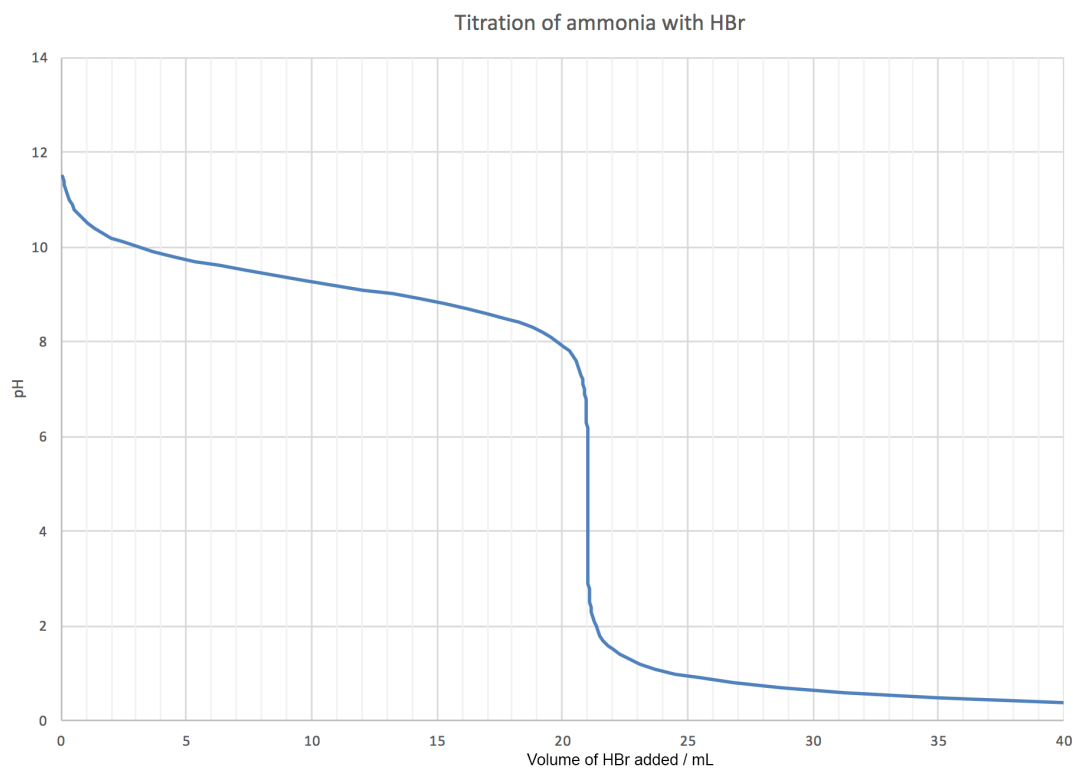
$$[\text{H}_3\text{O}^+] = \frac{n}{V} = \frac{1.61 \times 10^{-2} \text{ mol}}{0.050 \text{ L}} = 0.322 \text{ mol L}^{-1}$$

$$\text{pH} = -\log(0.322) = \mathbf{0.49}$$

pH at halfway to equivalence point:

$$\text{pH} = \text{p}K_{\text{a}} = 9.23$$

A computer modelled titration curve is plotted below. Provided the student has calculated the variety of pH values expected, they should have been able to sketch the curve provided.



(ii)	<p>Initially the zinc bromide dissolves into the NH_3 solution.</p> $\text{ZnBr}_2(s) \rightarrow \text{Zn}^{2+}(aq) + 2\text{Br}^-(aq)$ <p>The Zn^{2+} ions then form complex ions with the high concentration of NH_3 molecules in solution.</p> $\text{Zn}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons [\text{Zn}(\text{NH}_3)_4]^{2+}(aq)$ <p>On addition of $\text{HBr}(aq)$ an acid-base reaction occurred, reacting NH_3 molecules into NH_4^+ ions.</p> $\text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{NH}_4^+(aq) + \text{H}_2\text{O}(\ell)$ <p>As the acid was slowly added, the concentration of NH_3 molecules in the solution gradually decreased, resulting in the release of Zn^{2+} ions due to the equilibrium given below shifting in favour of the products.</p> $[\text{Zn}(\text{NH}_3)_4]^{2+}(aq) \rightleftharpoons \text{Zn}^{2+}(aq) + 4\text{NH}_3(aq)$ <p>The pH at this point was above 7, with a high $[\text{OH}^-]$. As the Zn^{2+} ions were released they then reacted with the hydroxide ions in the solution forming $\text{Zn}(\text{OH})_2$, a white precipitate as $[\text{Zn}^{2+}][\text{OH}^-]^2 > K_s(\text{Zn}(\text{OH})_2)$.</p> $\text{Zn}^{2+}(aq) + 2\text{OH}^-(aq) \rightleftharpoons \text{Zn}(\text{OH})_2(s)$ <p>At the 10–15 mL mark, a majority of the NH_3 molecules had been reacted, reducing the concentration of NH_3 molecules in solution, while still maintaining a pH above 7. At this point, the amount of $\text{Zn}(\text{OH})_2$ solid formed is in greatest quantity, giving the cloudiest solution.</p> <p>As further $\text{HBr}(aq)$ was added, the pH steadily dropped as the titration approached the equivalence point. As the pH lowered, $[\text{OH}^-]$ lowered, causing the $\text{Zn}(\text{OH})_2$ to dissolve.</p> $\text{Zn}(\text{OH})_2(s) \rightleftharpoons \text{Zn}^{2+}(aq) + 2\text{OH}^-(aq)$ <p>Once 15 mL of $\text{HBr}(aq)$ had been added, the remaining NH_3 had completely reacted into NH_4^+ ions. At this point the pH was below 7 due to the dissociation of NH_4^+ ions.</p> $\text{NH}_4^+(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)$ <p>At this point $[\text{Zn}^{2+}][\text{OH}^-]^2 < K_s(\text{Zn}(\text{OH})_2)$ and all the precipitate has dissolved, forming a colourless solution.</p>			
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Cut Scores

Scholarship	Outstanding Scholarship
17 – 24	25 – 32