

Assessment Schedule – 2018

Scholarship Chemistry (93102)

Evidence Statement

Q	Evidence	1–4	5–6	7–8
ONE (a)	$2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \quad \times 5$ $2\text{NH}_4^+ \rightarrow \text{N}_2 + 8\text{H}^+ + 6\text{e}^-$ $16\text{e}^- + 18\text{H}^+ + 2\text{ClO}_4^- \rightarrow 2\text{HCl} + 8\text{H}_2\text{O} \quad \left. \vphantom{\begin{matrix} 2\text{Al} + 3\text{H}_2\text{O} \\ 2\text{NH}_4^+ \end{matrix}} \right\} \times 3$ <hr style="width: 25%; margin-left: 0;"/> $6\text{NH}_4\text{ClO}_4 + 10\text{Al} \rightarrow 5\text{Al}_2\text{O}_3 + 3\text{N}_2 + 6\text{HCl} + 9\text{H}_2\text{O}$ $6\text{HCl} + \text{Al}_2\text{O}_3 \rightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}$ <hr style="width: 25%; margin-left: 0;"/> $6\text{NH}_4\text{ClO}_4 + 10\text{Al} \rightarrow 4\text{Al}_2\text{O}_3 + 3\text{N}_2 + 2\text{AlCl}_3 + 12\text{H}_2\text{O}$ <p>NH₄⁺ and Al are reductants – both lose electrons so are oxidised ClO₄⁻ is the oxidant – gains electrons Al is being oxidised from an oxidation state of 0 in Al to +3 in Al₂O₃ N is being oxidised from an oxidation state of –3 in NH₄ClO₄ to 0 in N₂ Cl is being reduced from an oxidation state of +7 in NH₄ClO₄ to –1 in HCl</p>	<p>Any of the following:</p> <ul style="list-style-type: none"> • correct equation • some of oxidants and reductants identified • discussion of redox process in terms of electron transfer • discussion of redox process in terms of oxidation state • enthalpy calculations • determination of formulae for ionic compounds • explanation for differences in melting points of ionic solids. 	<p>Balanced equation or redox process are omitted or not all oxidants / reductants identified.</p> <p>AND</p> <p>Process for calculation is correct but some aspects of incorrect / omitted e.g. limiting reagent.</p> <p>AND</p> <p>Formula for oxides determined but discussion of difference in melting points lacks detail.</p>	<p>Balanced equation AND discussion of redox process identifies all oxidants and reductants and electron transfers.</p> <p>AND</p> <p>Calculation for the energy includes determination of limiting reagent.</p> <p>AND</p> <p>Comprehensive discussion of difference in melting points of the two ionic solids.</p>

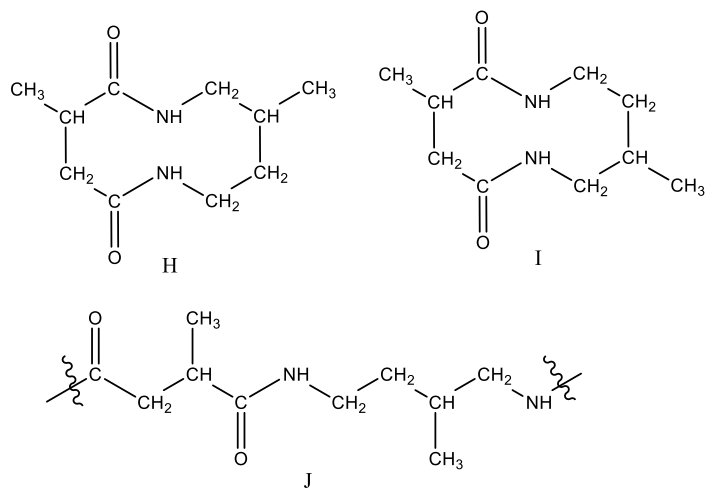
(b)	<p>Conversion of enthalpy values.</p> $\frac{3}{4} \text{O}_2(\text{g}) + \text{Al}(\text{s}) \rightarrow \frac{1}{2} \text{Al}_2\text{O}_3(\text{s}) \quad \Delta_{\text{c}}H(\text{Al}(\text{s})) = -838.0 \text{ kJ mol}^{-1}$ $\frac{3}{2} \text{O}_2(\text{g}) + 2\text{Al}(\text{s}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) \quad \Delta_{\text{f}}H(\text{Al}_2\text{O}_3(\text{s})) = -1676 \text{ kJ mol}^{-1}$ $\Delta_{\text{f}}H(\text{H}_2\text{O}(\text{g})) = \Delta_{\text{c}}H(\text{H}_2(\text{g})) + \Delta_{\text{vap}}H(\text{H}_2\text{O}(\ell)) = -241.8 \text{ kJ mol}^{-1}$ $3\text{NH}_4\text{ClO}_4(\text{s}) + 3\text{Al}(\text{s}) \rightarrow 2\text{Al}_2\text{O}_3(\text{s}) + 3\text{NO}(\text{g}) + \text{AlCl}_3(\text{s}) + 6\text{H}_2\text{O}(\text{g})$ $\Delta_{\text{r}}H = \Sigma\Delta_{\text{f}}H(\text{products}) - \Sigma\Delta_{\text{f}}H(\text{reactants})$ $= (-1676) + 3(90.3) + (-704.0) + 6(-241.8) - 3(-295.3)$ $= -2674 \text{ kJ mol}^{-1}$ $\Delta_{\text{r}}H_{(\text{per mol Al})} = -2674 / 3$ $= -891.3 \text{ kJ mol}^{-1}$ $m(\text{Al}) = 0.11 \times 590\,000 = 64\,900\,000 \text{ g}$ $n(\text{Al}) = 64\,900\,000 \text{ g} / 26.98 \text{ g mol}^{-1}$ $= 2\,405\,486 \text{ mol}$ $m(\text{NH}_4\text{ClO}_4) = 0.74 \times 590\,000 = 436\,600\,000 \text{ g}$ $n(\text{NH}_4\text{ClO}_4) = 436\,600\,000 \text{ g} / 117.46 \text{ g mol}^{-1}$ $= 3\,717\,010 \text{ mol}$ <p>Since there is more than sufficient NH_4ClO_4, this reagent is present in excess and the Al is the limiting reagent.</p> $\text{Heat released} = 891.3 \text{ kJ mol}^{-1} \times 2\,405\,486 \text{ mol}$ $= 2\,144\,000\,000 \text{ kJ}$ $= 2.14 \times 10^9 \text{ kJ}$			
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(c)		<i>n</i>(Tl)	<i>n</i>(o)	<i>n</i>(Tl) : <i>n</i>(O)			
	I	$\frac{89.49}{204.38} = 0.438$	$\frac{10.51}{16.00} = 0.657$	1 : 1.5			
	II	$\frac{96.23}{204.38} = 0.471$	$\frac{3.77}{16.00} = 0.236$	2 : 1			

Compound I: Formula is Tl_2O_3 made of Tl^{3+} and O^{2-} ions
 Compound II: Formula is Tl_2O made of Tl^+ and O^{2-} ions
 The strength of the ionic bonds broken when the solid melts is proportional to the size of the charge on the ions and inversely proportional to the distance between the ions (based on the ionic radii).
 Tl is in Group 13 of the periodic table so the valence electrons will be s^2p^1 . Since it is in Row 6 it will be $6s^26p^1$.
 Tl^{3+} has lost all the outer shell electrons from the Tl atom and so the valence electrons will be in the 5th shell.
 Tl^+ has the outer shell electron configuration $6s^2$. I.e. valence electrons are in the 6th shell.
 This means that the Tl^{3+} ion will be smaller than the Tl^+ ion, as its outer shell electrons are closer to the nucleus, and there is less shielding from inner shell core electrons.
 The higher charge on the Tl^{3+} ions and the smaller radii of the Tl^{3+} ions combine to give Tl_2O_3 the higher melting point.

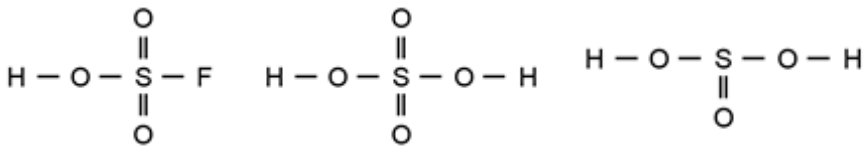
Q	Evidence	1-4 marks	5-6 marks	7-8 marks
TWO (a)		<p>Any of the following:</p> <ul style="list-style-type: none"> Some isomers of $C_5H_{10}O$ are given. Recognises some of the organic reactions described in terms of functional group changes. Some of the Compounds A to G are determined. Compound J is recognised as a polyamide. 	All 5 isomers are given and Compounds A to G are identified.	All 5 isomers are given. AND Compounds A to G are correctly identified (including enantiomers for B). AND Compounds H, I, and J are correctly identified with explanation for the effect of the two different sets of conditions.
(b)				

(c)



The concentrations of the reactants are much lower in Method One than in Method Two. This means that once the initial amine / acid chloride product has formed, there is more likelihood, in Method One, of an intramolecular condensation reaction to form a ring compound. In Method Two, the larger concentration of reactants means that there is more likelihood of collisions between reactants, resulting in intermolecular condensations and the formation of a polymer chain.

Q	Evidence	1-4 marks	5-6 marks	7-8 marks
THREE (a)(i)	<p><u>Thiosulfate solution</u></p> $n(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) = \frac{2.456 \text{ g}}{248.2 \text{ g mol}^{-1}}$ $n(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) = 0.009895 \text{ mol}$ $c(\text{S}_2\text{O}_3^{2-}) = \frac{9.895 \times 10^{-3} \text{ mol}}{0.1000 \text{ L}}$ $c(\text{S}_2\text{O}_3^{2-}) = 9.895 \times 10^{-2} \text{ mol L}^{-1}$ <p><u>Diluted thiosulfate solution</u></p> $c(\text{S}_2\text{O}_3^{2-}) = \frac{0.09895 \text{ mol L}^{-1} \times 5.00 \text{ mL}}{250 \text{ mL}}$ $c(\text{S}_2\text{O}_3^{2-}) = 0.001979 \text{ mol L}^{-1}$ <p><u>25 mg/kg of iodine</u> Per kg</p> $n(\text{I}) = \frac{0.025 \text{ g}}{126.9 \text{ g mol}^{-1}}$ $n(\text{I}) = 1.970 \times 10^{-4} \text{ mol}$ $n(\text{IO}_3^-) = 1.970 \times 10^{-4} \text{ mol}$ <p><u>In 50 g sample</u></p> $n(\text{IO}_3^-) = \frac{1.970 \times 10^{-4} \text{ mol} \times 50 \text{ g}}{1000 \text{ g}} = 9.850 \times 10^{-6} \text{ mol}$ <p><u>In 50 mL sample</u></p> $n(\text{IO}_3^-) = 9.850 \times 10^{-6} \text{ mol} \times 0.2$ $= 1.970 \times 10^{-6} \text{ mol}$ $n(\text{I}_2) = 3 \times n(\text{IO}_3^-) = 3 \times 1.970 \times 10^{-6} \text{ mol} (\text{I}_2) = 5.910 \times 10^{-6} \text{ mol}$ $n(\text{S}_2\text{O}_3^{2-}) = 2 \times n(\text{I}_2) = 2 \times 5.910 \times 10^{-6} \text{ mol} = 1.182 \times 10^{-5} \text{ mol}$ $V = \frac{n}{c} = \frac{1.1820 \times 10^{-5} \text{ mol}}{0.001979 \text{ mol L}^{-1}} = 0.005973 \text{ L} = 5.97 \text{ mL}$ <p>The titre volume should be above 5.97 mL for the salt sample to contain more than 25 mg / kg of iodine.</p>	<p>Any of the following:</p> <ul style="list-style-type: none"> • calculation of concentration of the thiosulfate solution • correct process for titration calculation • spontaneity linked to E°_{cell} • discussion of factors that affect the strength of acids, e.g. strength of O–H bond, change in electronegativity of ‘X’, addition of more = O bonds. 	<p>Correct process for calculating the titre value and one aspect of accuracy of results discussed in relation to the electrode potentials.</p> <p>AND</p> <p>Discussion of trends in acidity recognises factors that affect the strength of O–H bond including electronegativity of ‘X’, and the presence of = O, but lacks clarity.</p>	<p>Correct titre value AND discussion of accuracy of results in relation to the electrode potentials provided.</p> <p>AND</p> <p>Comprehensive discussion for relationship between the trends in acidity and the structure of the molecules, and correctly ranks the three acids with reasons related to the molecular structure and bonding.</p>

(ii)	<p>Using the electrode potentials it can be seen that I^- can be oxidised to I_2 by oxygen from the air. This means that vigorous mixing of the titration reaction could cause the $[\text{I}^-]$ to decrease, thus reducing the accuracy of the titration (since less $\text{S}_2\text{O}_3^{2-}$ is needed to reach equivalence point).</p> $4\text{I}^- + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} + 2\text{I}_2$ <p>$E^\circ_{\text{cell}} = 1.23 \text{ V} - 0.53 \text{ V} > 0$ so reaction is spontaneous in standard conditions.</p> <p>There is also the potential for $\text{S}_2\text{O}_3^{2-}$ to be oxidised to $\text{S}_4\text{O}_6^{2-}$ by O_2. This means that if the $\text{S}_2\text{O}_3^{2-}$ solution is not freshly prepared, its concentration would be lower than expected.</p> $4\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} + 2\text{S}_4\text{O}_6^{2-}$ <p>$E^\circ_{\text{cell}} = 1.23 \text{ V} - 0.08 \text{ V} > 0$ so reaction is spontaneous in standard conditions.</p>			
(b)(i)	<p>The strength of an acid is measured by its ability to donate a proton. This will depend on the strength of the O–H bond. For the three acids with the formula HOX, the acid strength increases ($\text{p}K_{\text{a}}$ decreases) as element X becomes more electronegative. The higher the electronegativity, the greater the attraction for the electron pair in the X–O bond by the X atom. This causes the O–H bond to be more polar and hence more easily ionised so leading to a stronger acid.</p> <p>For the series HClO, HClO₂, and HClO₃, there is a progressive increase in the number of double bonded O atoms (=O) on the central atom. This appears to lead to a weakening in the H–O bond hence an increase in acid strength. As more bonds are formed to electronegative oxygen atoms there is more electron density withdrawn from the O–H bond and hence it is more easily ionised.</p>			
(ii)	<div style="text-align: center;">  </div> <p>$\text{HSO}_3\text{F} > \text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3$</p> <p>$\text{H}_2\text{SO}_4$ is stronger than H_2SO_3. In H_2SO_4 the S atom has two ‘double bonded’ O atoms (=O) compared to one in H_2SO_3. The additional O atom causes more electron density to be removed from the S atoms which, in turn removes electron density from the S–OH bond thus weakening the O–H bond and the acid is stronger (ionisation occurs more easily)</p> <p>HSO_3F is stronger than H_2SO_4. Since F is more electronegative than O, the F atom will remove more electron density from the S atom, which will, in turn, remove electron density from the S–OH bond. The –OH bond is weaker, so the acid is stronger.</p>			

Q	Evidence	1-4 marks	5-6 marks	7-8 marks
FOUR (a)(i)	$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{Cit}^-]}{[\text{H}_3\text{Cit}]} = 10^{-3.13} = \frac{(10^{-2.47})^2}{[\text{H}_3\text{Cit}]}$ $[\text{H}_3\text{Cit}] = \frac{(10^{-2.47})^2}{10^{-3.13}}$ $[\text{H}_3\text{Cit}] = 0.01549 \text{ mol L}^{-1}$ $[\text{H}_2\text{Cit}^-] = [\text{H}_3\text{O}^+] = 10^{-2.47} = 0.003389 \text{ mol L}^{-1}$ $\text{Initial } [\text{H}_3\text{Cit}] = 0.01549 + 0.003389 = 0.01888 \text{ mol L}^{-1}$ $n(\text{H}_3\text{Cit})_{150 \text{ mL}} = 0.01888 \text{ mol L}^{-1} \times 0.150 \text{ L}$ $m(\text{H}_3\text{Cit})_{150 \text{ mL}} = 0.01888 \text{ mol L}^{-1} \times 0.150 \text{ L} \times 192.1 \text{ g mol}^{-1}$ $= 0.5440 \text{ g}$ $m\%(\text{H}_3\text{Cit})_{150 \text{ mL}} = \frac{0.5440 \text{ g}}{9.00 \text{ g}} \times 100\% = 6.044\%$	<p>Any of the following:</p> <ul style="list-style-type: none"> Calculates the concentration of citric acid in the solution. Correct procedure for calculating the mass percent of citric acid. Identifies the buffer nature of the solution in (a) (ii) and attempts to use this in the calculation. Identifies some of the intermolecular forces that affect the melting points of the solids. 	<p>Both calculations use the correct procedure, but there are errors in identifying the concentration of all the species present in the solutions.</p> <p>AND</p> <p>Factors that affect the differences in the melting points are identified but there are some omissions.</p>	<p>Calculation for percentage of citric acid and for mass of sodium hydroxide is correct.</p> <p>AND</p> <p>Comprehensive discussion of factors contributing to the difference in the melting points of the solids.</p>

(ii)	<p>pH change is 2.47 to 3.45 $pK_a(\text{H}_3\text{Cit}) = 10^{-3.13}$</p> <p>For the solution before the addition of NaOH: $[\text{H}_3\text{Cit}] = 0.01549 \text{ mol L}^{-1}$ $[\text{H}_2\text{Cit}^-] = 10^{-2.47} = 0.003389 \text{ mol L}^{-1}$</p> <p>Changes to the equilibrium concentrations are x</p> <table style="margin-left: 40px;"> <tr> <td></td> <td>H_3Cit</td> <td>\rightleftharpoons</td> <td>H_2Cit^-</td> <td>+</td> <td>H_3O^+</td> </tr> <tr> <td>I</td> <td>0.01549</td> <td></td> <td>$10^{-2.47}$</td> <td></td> <td></td> </tr> <tr> <td>C</td> <td>$-x$</td> <td></td> <td>$+x$</td> <td></td> <td></td> </tr> <tr> <td>E</td> <td>$0.01549 - x$</td> <td></td> <td>$10^{-2.47} + x$</td> <td></td> <td></td> </tr> </table> <p>Using pK_a to find x:</p> $\text{pH} = pK_a + \log \left(\frac{[\text{H}_2\text{Cit}^-]}{[\text{H}_3\text{Cit}]} \right)$ $3.45 - 3.13 = \log \left(\frac{[\text{H}_2\text{Cit}^-]}{[\text{H}_3\text{Cit}]} \right)$ $10^{0.32} = 2.09 = \frac{[\text{H}_2\text{Cit}^-]}{[\text{H}_3\text{Cit}]} = \frac{10^{-2.47} + x}{0.01549 - x}$ $2.09(0.01549 - x) = (10^{-2.47} + x)$ $0.03236 - 2.09x = 0.003389 + x$ $3.09x = 0.03226 - 0.003389$ $x = 0.009377 \text{ mol L}^{-1}$ $\text{mass NaOH} = 0.009377 \text{ mol L}^{-1} \times 0.150 \text{ L} \times 40.0 \text{ g mol}^{-1} = 0.0563 \text{ g}$ <p>OR Alternative method to find x:</p> $K_a = 10^{-3.13} = \frac{(10^{-2.47} + x)(10^{-3.45})}{0.1549 - x}$ $10^{-3.13}(0.01549 - x) = 10^{-3.45}(10^{-2.47} + x)$ $\frac{10^{-3.13}}{10^{-3.45}} = 2.09 = \frac{(0.003389 + x)}{(0.01549 - x)}$ $2.09(0.01549 - x) = (10^{-2.47} + x)$		H_3Cit	\rightleftharpoons	H_2Cit^-	+	H_3O^+	I	0.01549		$10^{-2.47}$			C	$-x$		$+x$			E	$0.01549 - x$		$10^{-2.47} + x$					
	H_3Cit	\rightleftharpoons	H_2Cit^-	+	H_3O^+																							
I	0.01549		$10^{-2.47}$																									
C	$-x$		$+x$																									
E	$0.01549 - x$		$10^{-2.47} + x$																									

	$0.03236 - 2.09x = 0.00338 + x$ $x = 0.009377 \text{ mol L}^{-1}$			
(b)	<p>All the solids have high melting points due to the large molecules having large electron clouds giving strong temporary dipole forces between the molecules. The presence of the carboxylate groups and the -OH groups mean that there is also potential for strong hydrogen bonds to exist between the molecules. (In citric and isocitric acid there are 4 H-bond donors (-OH) and 7 acceptors ($\text{-OH} + \text{C=O}$). In tartaric acid there are 4 donors and 6 acceptors, and in malic acid 3 donors and 5 acceptors). The lower molar mass (smaller electron cloud) and fewer places for hydrogen bonding to occur could account for the lower melting point of malic acid. The melting point of tartaric acid is higher than expected from the size of the temporary dipoles and the number of hydrogen bonding sites. This could be related to the shape of the molecule, which would allow the molecules to pack closer together and hence make it harder to separate them, and hence increase the energy needed to melt the solid.</p> <p>Isocitric acid has the lowest melting point, in spite of it having the same number of electrons and the same potential sites for hydrogen bonding as for citric acid. The difference is likely to be caused by the asymmetric shape of the isocitric acid molecule (compared to citric acid), which makes the packing of the molecules in the solid less efficient. The molecules will not be able to pack as closely, and hence less energy is needed to separate them, and the melting point drops.</p>			

Cut Scores

Scholarship	Outstanding Scholarship
17 – 24	25 – 32