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Draw a cross through the box (X) if you have NOT written in this booklet

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# OUTSTANDING SCHOLARSHIP EXEMPLAR



Mana Tohu Mātauranga o Aotearoa  
New Zealand Qualifications Authority

## Scholarship 2023 Chemistry

Time allowed: Three hours  
Total score: 32

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

You should answer ALL the questions in this booklet.

Pull out Resource Booklet 93102R from the centre of this booklet.

Show ALL working.

If you need more room for any answer, use the extra space provided at the back of this booklet.

Check that this booklet has pages 2–24 in the correct order and that none of these pages is blank.

Do not write in any cross-hatched area (AREA NOT TO WRITE). This area may be cut off when the booklet is marked.

**YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE  
END OF THE EXAMINATION.**

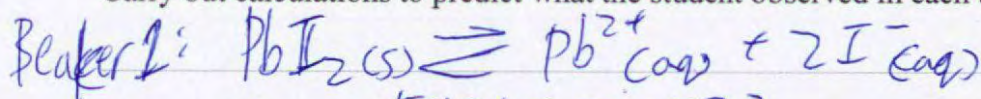
## QUESTION ONE

- (a) The solubility constants for three compounds are given below. Lead(II) hydroxide is a white solid, whilst the two iodide compounds are both yellow in appearance.

$$K_s(\text{PbI}_2) = 8.00 \times 10^{-9} \quad K_s(\text{AgI}) = 8.30 \times 10^{-17} \quad K_s(\text{Pb(OH)}_2) = 8.00 \times 10^{-17}$$

- (i) A student pipetted 25.0 mL of 0.00167 mol L<sup>-1</sup> potassium iodide solution, KI(aq), into each of two beakers. They then added 35.0 mL of 0.0225 mol L<sup>-1</sup> lead(II) nitrate solution, Pb(NO<sub>3</sub>)<sub>2</sub>(aq), to one beaker and added 35.0 mL of 0.0143 mol L<sup>-1</sup> silver nitrate solution, AgNO<sub>3</sub>(aq), to the other.

Carry out calculations to predict what the student observed in each beaker.

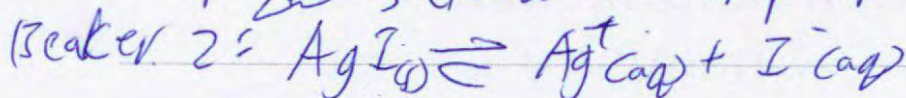


$$I_p = [\text{Pb}^{2+}][\text{I}^{-}]^2$$

$$= (0.0225 \times \frac{35}{60}) \times (0.00167 \times \frac{25}{60})^2$$

$$= 6.35 \times 10^{-9} \quad (\text{yellow})$$

$I_p < K_s(\text{PbI}_2)$  so no precipitate will form.



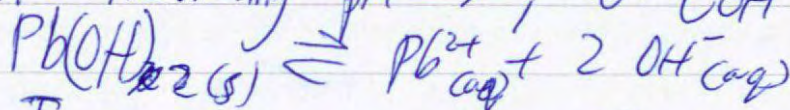
$$I_p = [\text{Ag}^{+}][\text{I}^{-}]$$

$$= (0.0143 \times \frac{35}{60}) \times (0.00167 \times \frac{25}{60})$$

$$= 5.80 \times 10^{-6}$$

$I_p > K_s(\text{AgI})$  so a yellow AgI precipitate will form.

For beaker 2: For Pb(NO<sub>3</sub>)<sub>2</sub> before added to beaker 1: form.



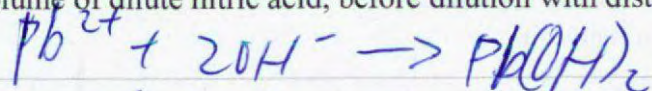
$$I_p = [\text{Pb}^{2+}][\text{OH}^{-}]^2 = (0.0225) \times (10^{-7})^2$$

$$= (0.00167 \times \frac{25}{60}) \times (10^{-7})^2$$

$$= 6.44 \times 10^{-18} = 2.25 \times 10^{-16}$$

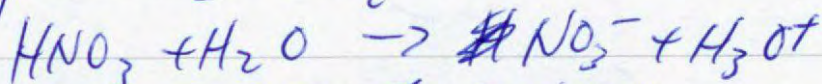
$I_p > K_s(\text{Pb(OH)}_2)$ , so a white Pb(OH)<sub>2</sub> precipitate will form.

- (ii) Explain why, when preparing the lead(II) nitrate solution for the experiment described in (i), it is necessary that the measured mass of  $\text{Pb}(\text{NO}_3)_2(\text{s})$  is first dissolved in a small volume of dilute nitric acid, before dilution with distilled water.



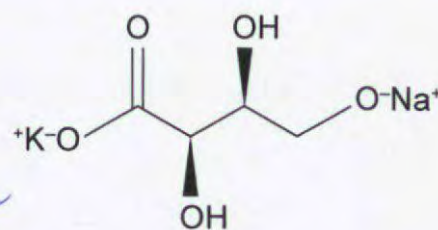
~~From test calculation~~  $\text{Pb}^{2+}$  ions from  $\text{Pb}(\text{NO}_3)_2$

~~But~~ will react with  $\text{OH}^-$  ions ~~to~~ from the dissociation of water to ~~to~~ form a  $\text{Pb}(\text{OH})_2$  precipitate, decreasing  $[\text{Pb}^{2+}]$ . Thus the equilibrium:  $\text{PbI}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^-$  will favor forwards reaction, ~~thereby~~ increasing the solubility of  $\text{PbI}_2$  and preventing  $\text{PbI}_2$  solid from ~~to~~ forming.



~~Dilute~~ nitric acid is necessary ~~as it~~ ~~to~~ dissociates into ~~ions~~  $\text{H}_3\text{O}^+$  ions, which ~~will~~ neutralise the  $\text{OH}^-$  ions, thus decreasing  $[\text{OH}^-]$ .  
 $\therefore$  There will ~~be~~ not be enough  $\text{OH}^-$  ions to form the  $\text{Pb}(\text{OH})_2$  precipitate, thus allowing the  $\text{PbI}_2$  precipitate to form.

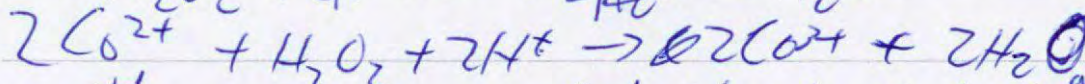
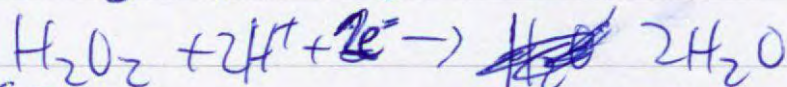
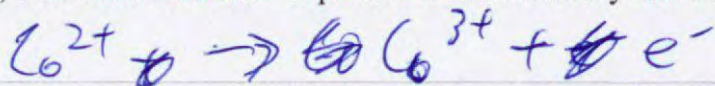
- (b) A reaction between hydrogen peroxide solution,  $\text{H}_2\text{O}_2(\text{aq})$ , and potassium sodium tartrate solution,  $\text{KNaTar}(\text{aq})$ , is commonly used in schools to demonstrate the effect of reaction conditions on the rate of a reaction.



The two colourless solutions are mixed and heated to  $70^\circ\text{C}$ . No obvious reaction is observed at this point. A small amount of a pale pink cobalt(II) chloride solution,  $\text{CoCl}_2(\text{aq})$ , is then added, and changes begin to be observed.

First the solution turns green as the pale pink  $\text{Co}^{2+}$  ions are oxidised into green  $\text{Co}^{3+}$  ions by the hydrogen peroxide. Once the solution has changed colour, large volumes of  $\text{CO}_2$  gas are quickly produced as the tartrate ions react with the hydrogen peroxide. The colour of the solution remains green during the reaction. Once the hydrogen peroxide is consumed, no further gas is produced.

Elaborate on the various reaction conditions required for this demonstration to work according to plan, with clear reference to particle collision theory and the role of  $\text{Co}^{3+}$  ions. *catalyst*



*H<sub>2</sub>O<sub>2</sub>*  
The solutions must be heated to high enough temperature ( $70^\circ\text{C}$ ) so the <sup>reactant</sup> particles have high enough average kinetic energy <sup>for a higher chance to overcome the</sup> activation energy required <sup>during</sup> successful collisions ~~to occur~~ between each other ( $\text{H}_2\text{O}_2$  and  $\text{KNaTar}$  particles). However, no reaction occurs yet because activation is still too high. Thus,  $\text{Co}^{3+}$  acts as a catalyst, which <sup>provides an alternative reaction pathway by lowering</sup> the required activation energy, so  $\text{H}_2\text{O}_2$  and  $\text{KNaTar}$  have a higher chance for successful collisions ~~to occur~~ to occur because ~~they have a higher chance of~~ there is a higher chance of the collisions ~~being~~ being higher than the activation energy. Thus, the rate of reaction increases, and ~~the~~ the reaction proceeds so  $\text{CO}_2$  gas is produced, ~~that the~~ the

$\text{CO}^{3+}$  likely allows for  $\text{H}_2\text{O}_2$  or  $\text{KNO}_3$  ~~to~~ <sup>to</sup> react with it, then ~~react~~ <sup>react</sup> again ~~to~~ <sup>to</sup> form the desired products, with lower total activation energy.

Also, the higher temperature increases rate of ~~movement~~ <sup>movement</sup> of  $\text{H}_2\text{O}_2$  and  $\text{KNO}_3$  particles, ~~allowing~~ <sup>thus</sup> there are higher ~~chances~~ <sup>chance/rates</sup> of collisions between these particles, so a higher chance for successful collisions to occur, therefore, the rate of reaction is increased.

(c) Zirconium forms fluorine-containing compounds and polyatomic ions.

(i) Draw Lewis structures for the following fluorides of zirconium.

Use your existing knowledge to predict logical shapes for each ion, and give estimated bond angles.

| Ion             | $\text{ZrF}_5^-$ <del>40e</del> <sup>40e</sup> | $\text{ZrF}_6^{2-}$ <del>48e</del> <sup>48e</sup> | $\text{ZrF}_7^{3-}$ <del>56e</del> <sup>56e</sup> |
|-----------------|------------------------------------------------|---------------------------------------------------|---------------------------------------------------|
| Lewis structure |                                                |                                                   |                                                   |
| Shape           | Trigonal bipyramidal                           | Octahedral                                        | Pentagonal bipyramidal                            |
| Bond angles     | $120^\circ$ and $90^\circ$                     | $90^\circ$                                        | $108^\circ$ and $90^\circ$                        |

(ii) Explain the bond angles for one of the ions.

~~ZrF5~~ <sup>density around the central Zr atom</sup> ~~ZrF5~~ has 5 regions of electron <sup>density</sup> which will repel ~~to~~ <sup>to</sup> for maximum separation to form trigonal bipyramidal arrangement with bond angles  $120^\circ$  and  $90^\circ$ . The  $120^\circ$  is between the ~~central~~ <sup>central</sup> Zr-F bonds in equatorial positions (3 ~~F~~ bonds), whereas  $90^\circ$  is for the axial positions (2 ~~F~~ bonds). The top and bottom Z-F bond forms  $90^\circ$  angle with ~~central~~ <sup>central</sup> 3 Z-F bonds. All 5 are bonding regions, so final shape is trigonal bipyramidal.

## QUESTION TWO

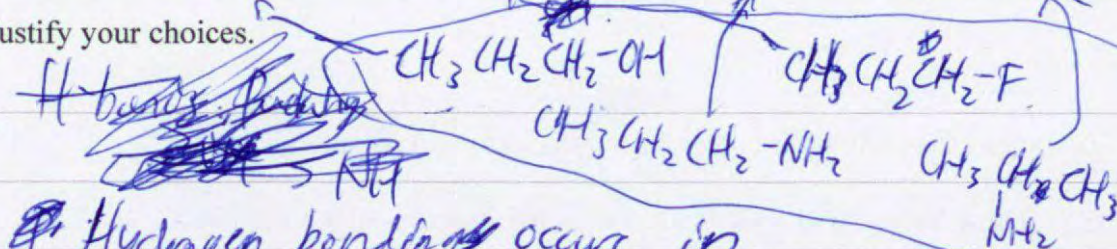
(a) The following is a selection of boiling points for different molecular compounds.

-2.50 °C    31.7 °C    48.5 °C    97.2 °C

(i) Match the following compounds to the boiling points provided.

| propan-1-ol | 1-fluoropropane | 1-aminopropane | 2-aminopropane |
|-------------|-----------------|----------------|----------------|
| 97.2 °C     | -2.50 °C        | 48.5 °C        | 31.7 °C        |

Justify your choices.



Hydrogen bonding occurs in propan-1-ol, 2-aminopropane and 1-aminopropane. It is due to the large difference in electronegativity between ~~H and O~~ the ~~prop H~~ and O ~~in the~~ the O-H bond in propan-1-ol, and ~~the~~ between H and N in the N-H bond in 1-aminopropane and 2-aminopropane.

It is the strongest intermolecular force (IMF) and since all ~~the~~ 3 molecules are small, it is the predominant IMF. In contrast 1-fluoropropane does not have an H-O, H-N or H-F bond, so lacks hydrogen bonding. Its main IMF is permanent dipole-dipole <sup>dipole-dipole</sup> due to it being polar ( $\delta^- \text{F}$ ,  $\delta^+ \text{C}$ ), which is considerably less than hydrogen bonding. So 1-fluoropropane has the weakest IMF and thus lowest BPT.

The electronegativity difference in O-H bonds is greater than N-H bonds, as O is more electronegative than N; therefore, propan-1-ol has stronger hydrogen bonding than the amines.

Since it has an O-H bond, whereas the amine N also only has 1 lone pair available for H-bonding whereas O has 2.

have  $\text{NH}$  bonds.  $\therefore$  Propan-1-ol has the strongest IMFs, so the highest BPT.

~~So~~ 1-aminopropane ~~has the strongest~~ has no branching, whereas 2-aminopropane does (on ~~the~~ - $\text{NH}_2$ ), ~~so~~ so 1-aminopropane can pack more closely than 2-aminopropane (1-aminopropane is more linear). Therefore, 1-aminopropane has stronger IMF, since ~~the~~ electrostatic IMFs are inversely proportional to the distance between molecules,  $\therefore$  2-aminopropane has slightly stronger IMFs than 2-aminopropane, thus having a slightly higher BPT than 2-aminopropane. GO TO BACK

- (ii) Heptane has a boiling point of  $98.4^\circ\text{C}$ .

Explain why the boiling point of heptane is higher than any of the boiling points of the compounds in (i).

Heptane does not have hydrogen bonds and is non-polar so does not have ~~per~~ permanent dipole-dipole attractions. However, it has a significantly larger electron cloud size compared to all ~~the~~ compounds in (i) (7-carbon-chain compared to 3-carbon-chain), ~~so~~ so the large strength of temporary / instantaneous dipole-dipole attractions between heptane ~~the~~ molecules outweighs the ~~the~~ attraction due to hydrogen bonding and permanent dipoles in the compounds in (i). This is because the larger size means a much higher chance for temporary <sup>dipole-dipole</sup> attractions to occur. Therefore, heptane has the strongest IMFs, so the strongest BPT.

Use the mass analysis data provided below, and the IR and  $^{13}\text{C}$  NMR spectra provided in the resource booklet, to determine the structures and names of Compounds A, B, and C.

| Compound A                                                                                                                                                                                          | Compound B                                                                                                                                                   | Compound C                                                                                                                                                                 |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>Name: <del>CH<sub>3</sub>CHCH<sub>3</sub></del><br/>2-amino propanoic acid</p> <p>Structure: <del>CH<sub>3</sub>CHCH<sub>3</sub></del><br/>NH<sub>2</sub><br/>CH<sub>3</sub>CHCH<sub>3</sub></p> | <p>Name: Cyclobutanol</p> <p>Structure: <del>CH<sub>3</sub>CHCH<sub>3</sub></del><br/>OH<br/>H<sub>2</sub>C-CH<br/>   <br/>H<sub>2</sub>C-CH<sub>2</sub></p> | <p>Name: 2-methylpropanoic acid</p> <p>Structure: <del>CH<sub>3</sub>CHCH<sub>3</sub></del><br/>O<br/>  <br/>CH<sub>3</sub>CH<sub>2</sub>C-OH<br/> <br/>CH<sub>3</sub></p> |

(ii) Compounds A, B, and C were isolated after the following chemical treatments: *base hydrolysis*

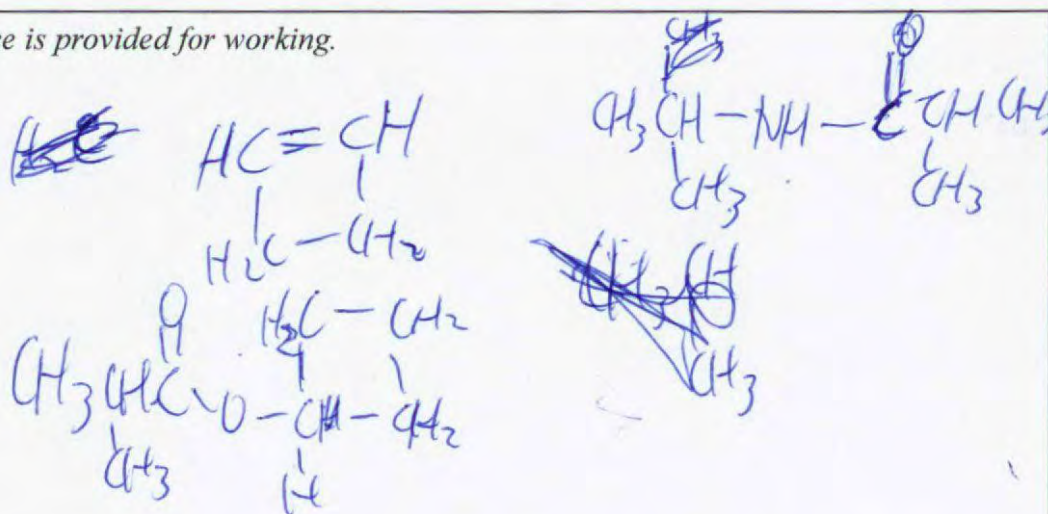
11) A sample of the mixture of X and Y was heated with dilute NaOH solution, forming three products. TWO of these could be distilled from the reaction mixture and separated, and they were labelled Compounds A and B.

2) A second sample of the mixture of **X** and **Y** was heated with dilute HCl solution, and three products were formed. TWO of these could be distilled from the reaction mixture and separated. One was identified as Compound **B**, but the other product was new, and was subsequently labelled Compound **C**.

Use the mass analysis data provided below, and your knowledge of Compounds **A**, **B**, and **C**, to determine the structures of Compounds **X** and **Y**.

$$M(\text{X}) = 142 \text{ g mol}^{-1} \quad M(\text{Y}) = 129 \text{ g mol}^{-1}$$

*This space is provided for working.*



| Compound X                                                                                                                                                             | Compound Y                                                                                                                                          |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|
| Structure:<br>$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}(\text{CH}_3)\text{C}-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2\text{CH}_3 \end{array}$ | Structure:<br>$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}(\text{CH}_3)-\text{NH}-\text{C}-\text{CH}(\text{CH}_3)_2 \end{array}$ |

- (iii) Why could only two of the three products from each treatment process be distilled from the reaction mixtures?

Other product from ① =  $\text{Na}^+\text{O}-\text{C}(\text{CH}_3)(\text{CH}_3)\text{CH}_3$  ✓ ①

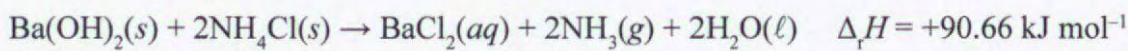
Other product from ② =  $\text{CH}_3\text{CH}(\text{CH}_3)-\text{NH}_3^+\text{Cl}^-$  ✓ ②

The ~~other~~ -ve charged O in ① and +ve charged  $\text{NH}_3^+$  in ② mean that ~~strong~~ ~~ion-dipole~~ ion-dipole / dipole-dipole attractions will occur between the charged end of ~~the~~ the products and the polar end of water ( $\text{O}^-$  attracted to  $\delta^+\text{H}$  from water,  $\text{NH}_3^+$  to  $\delta^-\text{O}$  from water,  $\text{Na}^+$  to  $\delta^-\text{O}$ ,  $\text{Cl}^-$  to  $\delta^+\text{H}$ ). ~~The~~ These intermolecular forces (IMFs) <sup>between product-water (solute-solvent)</sup> are greater than the original hydrogen bonds between water-water (solvent-solvent) and the IMFs between product-product (solute-solute), so ~~the~~ the products will be <sup>very</sup> soluble / insoluble in water, thus making them hard to be distilled.

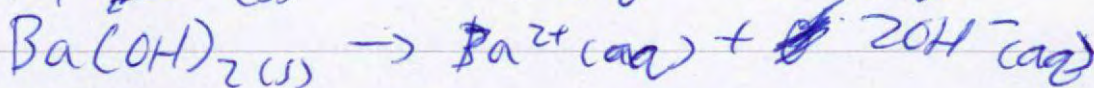
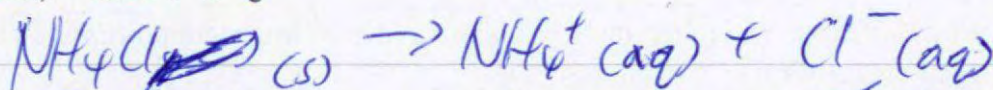
- (c) A mixture of barium hydroxide,  $\text{Ba}(\text{OH})_2(\text{s})$ , and ammonium chloride,  $\text{NH}_4\text{Cl}(\text{s})$ , was made in a glass beaker weighing 90.72 g. A spontaneous reaction occurred between the two solids, producing ammonia gas,  $\text{NH}_3(\text{g})$ .

The ammonia gas was extracted and reacted with 100.0 mL of hydrochloric acid solution;  $\text{HCl}(\text{aq})$ . The pH of the  $\text{HCl}$  solution was initially 0.50. After the addition of  $\text{NH}_3(\text{g})$ , the pH of the mixture had increased to 1.21.

- (i) Predict, by calculation, the temperature change of the  $\text{NH}_4\text{Cl}/\text{Ba}(\text{OH})_2$  beaker once the reaction is complete.

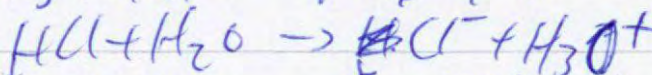
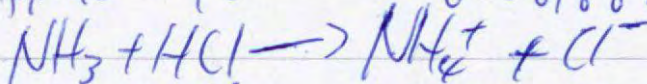


$$c(\text{glass}) = 0.753 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$$



$$\text{H}_3\text{O}^+_{\text{initial}} = 10^{-0.50} = 0.3162 \text{ mol L}^{-1}$$

$$\text{H}_3\text{O}^+_{\text{final}} = 10^{-1.21} = 0.06166 \text{ mol L}^{-1}$$



$$n(\text{NH}_3) = \Delta n(\text{H}_3\text{O}^+) = (0.3162 - 0.06166) \times 0.1 = 0.02545 \text{ mol}$$

$$n(\text{Ba}(\text{OH})_2) = \frac{0.02545}{2} = 0.01273 \text{ mol}$$

$$n(\text{NH}_4\text{Cl}) = 0.02545 \text{ mol}$$

$$q = -\Delta_r H \times n = -90.66 \times 0.01273 = -0.5769 \text{ kJ}$$

$$q = mc\Delta T$$

$$\Delta T = \frac{q}{mc} = \frac{-0.5769 \times 1000}{90.72 \times 0.753}$$

$$= -8.4453$$

$$= -8.45^\circ\text{C}$$

The temperature decreased by  $8.45^\circ\text{C}$

- (ii) Briefly outline thermodynamic factors that contribute to the overall spontaneity of the reaction occurring in the beaker.

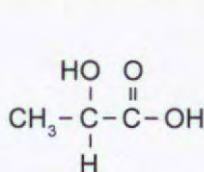
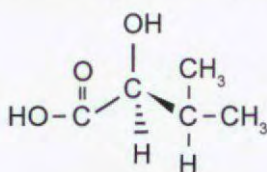
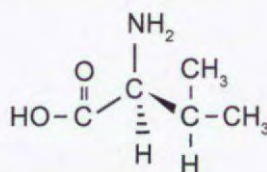
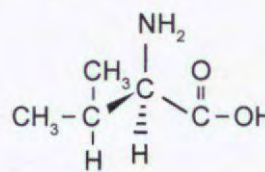
$\Delta H$  is ~~not~~ positive so the reaction is ~~exothermic~~ <sup>endothermic</sup>,  
 ∴ it ~~also~~ absorbs (heat) energy from surroundings,  
 so ~~change in~~  $\Delta S_{\text{surroundings}}$  ( $\Delta S$  is change in  
 entropy) is -ve since surrounding particles have  
 less kinetic energy so less disorder.

The reactants are all solid and change into ~~an~~  
~~an~~ aqueous and gaseous products, ~~so~~ contributing  
 to a ~~+~~ve  $\Delta S_{\text{system}}$  since gas/liquid have  
 higher rate of <sup>freedom</sup> movement than solids, so a greater  
 degree of disorder. ~~Also there~~  
 there is an increase from 3 reactant moles to  
 5 product moles, so ~~there is a higher~~ <sup>the</sup> rate,  
 of collisions ~~are there~~ / amount of <sup>different</sup> arrangements  
 of ~~the~~ particles are increased, thus a  
 positive  $\Delta S_{\text{system}}$

(0 to 2 gaseous moles) Since the reaction is spontaneous,  
 the increase in  $\Delta S_{\text{system}}$  ~~is~~ outweighs  
 is greater than the decrease in  $\Delta S_{\text{surroundings}}$ ,  
 so the overall change in entropy ( $\Delta S_{\text{total}}$   
 $= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ ) is +ve.

## QUESTION THREE

- (a) Valinomycin is an antibiotic which can be obtained from several different bacteria of the *Streptomyces* genus. Four molecules are the building blocks for the structure of valinomycin, and they are given the labels Compounds **W**, **X**, **Y**, and **Z**. Their structures are as follows:

**W****X****Y****Z**

These four molecules can all be synthesised from two other organic molecules, Compounds **F** and **G**.

- Compound **F** has the molecular formula  $\text{C}_3\text{H}_5\text{OCl}$ . It does not produce steamy fumes when added to water, it does not form a silver mirror when added to Tollens' reagent, and it does not decolourise  $\text{Br}_2(\text{aq})$ .
- Compound **G** has the molecular formula  $\text{C}_5\text{H}_{10}\text{O}$ . It has a branched chain structure, and it exists as a pair of geometric isomers.

Use the information provided above to determine the structures of Compounds **F** and **G** and use these to produce logical reaction schemes for the synthesis of Compounds **W**, **X**, **Y**, and **Z**.

You may only select from the reagents provided below.

You can assume you would be able to separate and isolate specific compounds or isomers as required for successive steps.

Reagents available:

$\text{NH}_3(\text{conc})$   
 $\text{HCl}(\text{conc})$

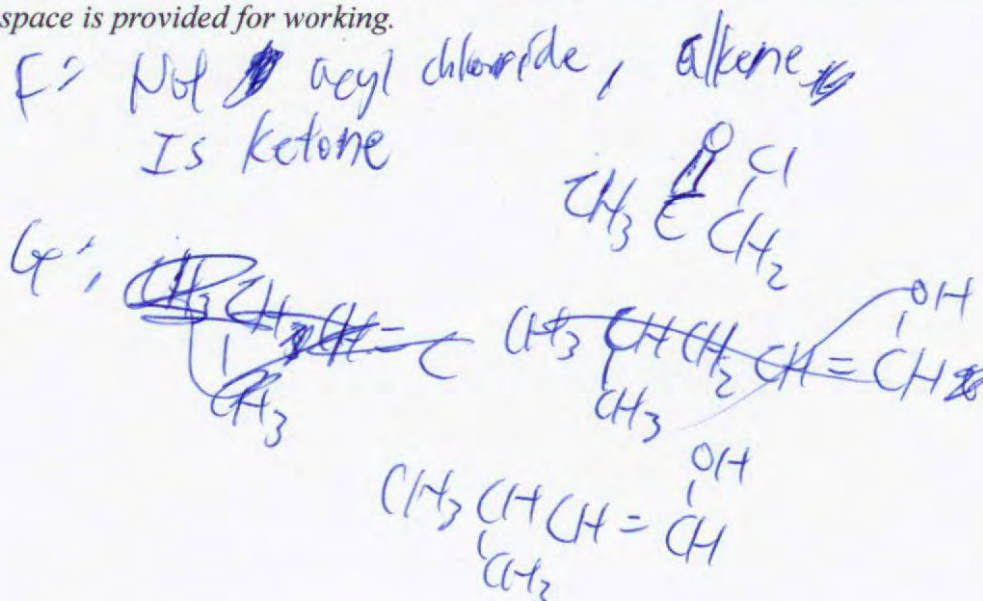
$\text{NaOH}(\text{aq})$   
 $\text{H}_2\text{SO}_4(\text{aq})$

$\text{H}^+/\text{MnO}_4^-(\text{aq})$   
 $\text{NaOH}(\text{alc})$

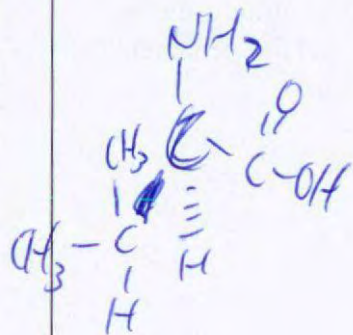
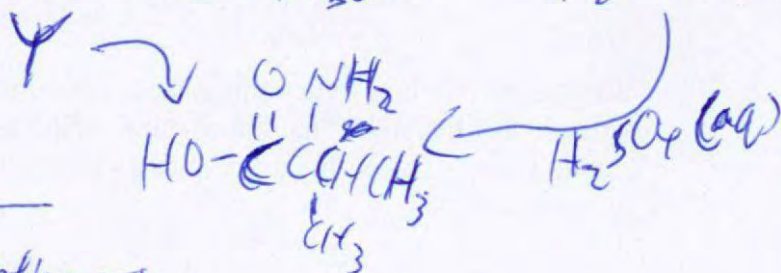
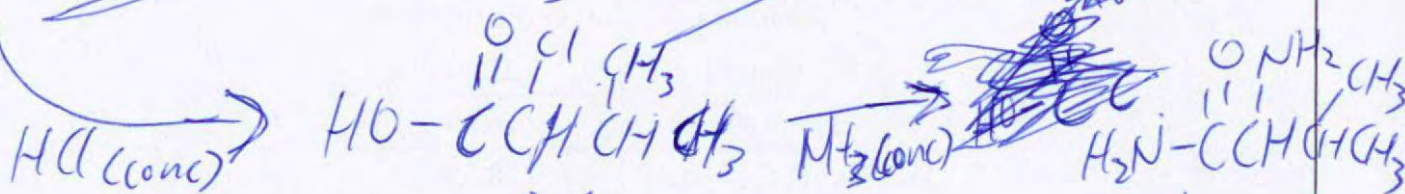
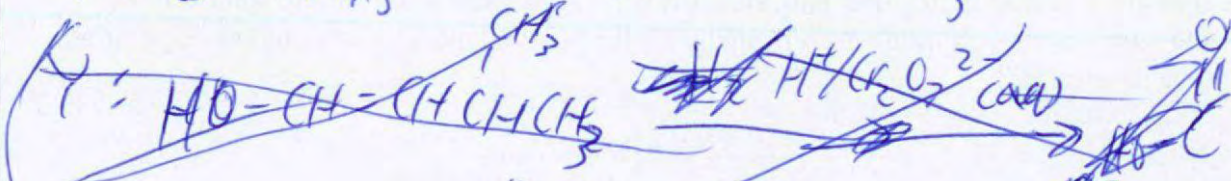
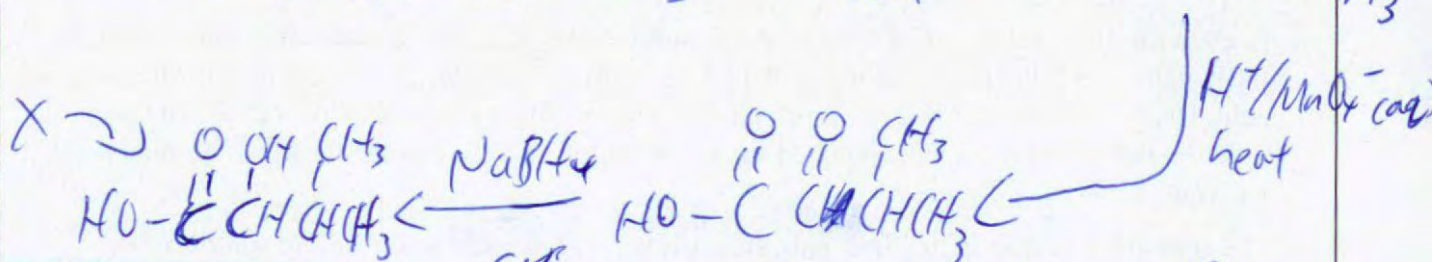
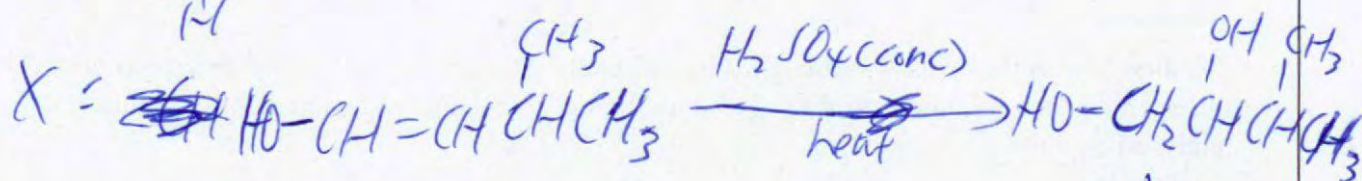
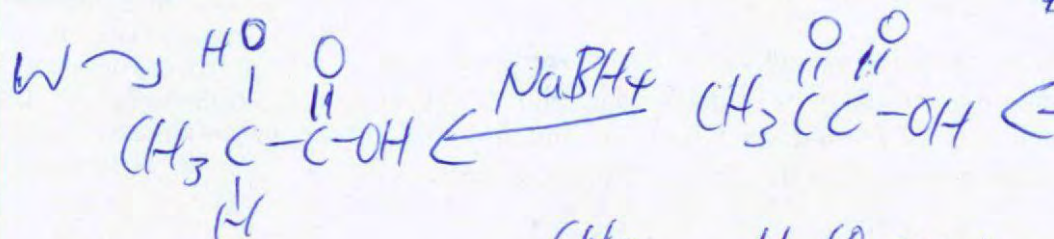
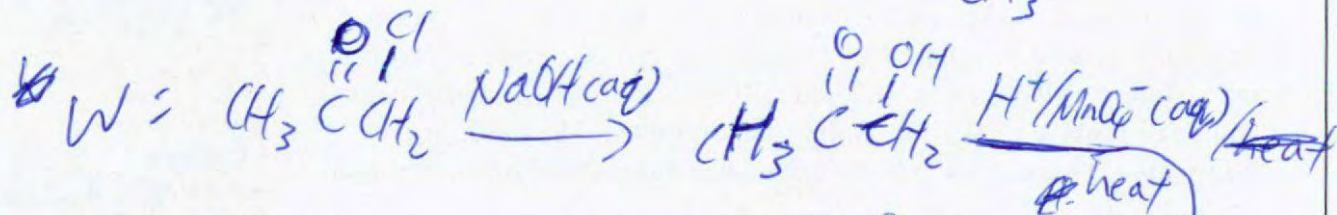
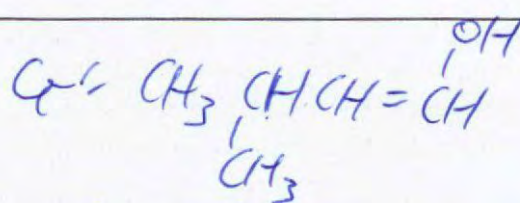
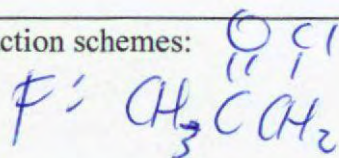
$\text{H}^+/\text{Cr}_2\text{O}_7^{2-}(\text{aq})$   
 $\text{H}_2\text{SO}_4(\text{conc})$

$\text{NaBH}_4$   
 $\text{PCl}_5$

This space is provided for working.



Reaction schemes:



Isolate enantiomers  
using polarized  
light tube  
to get Z (Z and Y  
are enantiomers)

- (b) Vitamin C ( $C_6H_8O_6$ ) is known to degrade over time in aqueous solutions due to reaction with oxygen that is also dissolved in the water. Dry powders are less prone to degradation and can be used to prepare drinks with more reliable and consistent levels of the vitamin.

To investigate the extent of degradation of Vitamin C due to oxygen exposure, an 80.0 g sachet of an orange drink powder was emptied into a 1.00 L volumetric flask, filled to the mark using distilled water, and briefly mixed until all the solids had dissolved. The nutritional information on the drink powder packaging stated that the sachet should contain 130 mg of Vitamin C.

Two halves of the solution, and a blank control, were analysed using an iodometric titration procedure. The primary standard used in the titration was a potassium iodate solution,  $KIO_3(aq)$ . This solution was prepared by dissolving 0.132 g into 1.00 L of distilled water in a volumetric flask.

The first half of the drink was analysed immediately. The second half of the drink was stirred in the open air then left uncovered for 24 hours, before being analysed. The control solution also analysed contained only water.

In each titration, a 20.0 mL aliquot of the solution being analysed was pipetted into a conical flask. This was followed by addition of 150 mL of distilled water, 5 mL of 1 mol L<sup>-1</sup> hydrochloric acid,  $HCl(aq)$ , 5 mL of 1% potassium iodide solution,  $KI(aq)$ , and 20.0 mL of the potassium iodate standard solution. This resulted in the formation of iodine in the flask, which then reacted with any Vitamin C present.

The remaining iodine in the flask was then titrated with a sodium thiosulfate solution,  $Na_2S_2O_3(aq)$ , and the titration was repeated with further 20.0 mL aliquots until average titres could be determined.

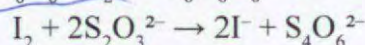
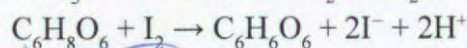
www.woolworths.  
com.au/shop/  
productdetails/264554/  
raro-sweet-navel-orange-  
flavoured-beverage-mix

*S<sub>2</sub>O<sub>3</sub><sup>2-</sup> titration*

| Solution         | Average titre / mL |
|------------------|--------------------|
| Control          | 27.20              |
| Drink (fresh)    | 16.10              |
| Drink (24 hours) | 18.35              |

- (i) Carry out calculations to determine the concentration of the sodium thiosulfate solution used, whether the nutritional information on the sachet was accurate, and the percentage of Vitamin C remaining in the drink after 24 hours of atmospheric exposure.

$$M(\text{Vitamin C}) = 176.1 \text{ g mol}^{-1} \quad M(KIO_3) = 214 \text{ g mol}^{-1}$$



$$[KIO_3] = \frac{0.132}{1.00 \times 214} = 6.168 \times 10^{-4} \text{ mol L}^{-1}$$

$$n(KIO_3) = 6.168 \times 10^{-4} \times 0.02 = 1.234 \times 10^{-5} \text{ mol}$$

$$n(I_2)_{\text{total}} = 3 \times n(KIO_3) = 3.701 \times 10^{-5} \text{ mol}$$

$$[I_2] = \frac{n}{V} = 3.701 \times 10^{-5}$$

$$[I_2] = \frac{n}{V} = 3.701 \times 10^{-5}$$

Control: No Uplaminiso  $I_2$  (remaining) =  $I_2$  (total)

$$n(S_2O_3^{2-} \text{ control}) = 2 \times n(I_2) = 2 \times 3.701 \times 10^{-5} = 7.402 \times 10^{-5} \text{ mol}$$

$$[S_2O_3^{2-}] = \frac{7.402 \times 10^{-5}}{0.02720} = 2.721 \times 10^{-3} \text{ mol/L}$$

Fresh:

$$n(S_2O_3^{2-} \text{ fresh}) = CV = 2.721 \times 10^{-3} \times 0.01610 = 4.381 \times 10^{-5} \text{ mol}$$

$$n(I_2 \text{ remaining}) = \frac{n(S_2O_3^{2-} \text{ fresh})}{2} = 2.191 \times 10^{-5} \text{ mol}$$

$$n(C_6H_8O_6) = n(I_2 \text{ reacted}) = 3.701 \times 10^{-5} - 2.191 \times 10^{-5} = 1.510 \times 10^{-5} \text{ mol}$$

$$m(C_6H_8O_6) = 1.510 \times 10^{-5} \times 176.1 = 2.660 \times 10^{-3} \text{ g}$$

$$n(C_6H_8O_6 \text{ undiluted}) = 1.510 \times 10^{-5} \times \frac{2.660}{2.660} = 1.510 \times 10^{-5} \text{ mol}$$

$$m(C_6H_8O_6 \text{ undiluted}) = 1.510 \times 10^{-5} \times 176.1 = 2.660 \times 10^{-3} \text{ g}$$

So the satellite information is reasonably accurate (2.31% difference to 130 mg).

$$24 \text{ hours: } n(S_2O_3^{2-} \text{ 24 hours}) = 2.721 \times 10^{-3} \times 0.0183 = 4.993 \times 10^{-5} \text{ mol}$$

$$n(I_2 \text{ remaining}) = \frac{4.993 \times 10^{-5}}{2} = 2.497 \times 10^{-5} \text{ mol}$$

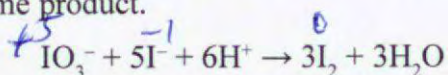
$$n(C_6H_8O_6) = 1.204 \times 10^{-5} \text{ mol}$$

$$m(C_6H_8O_6 \text{ undiluted}) = 1.204 \times 10^{-5} \times \frac{1000}{20} \times 176.1 = 0.1061 \text{ g} = 106.1 \text{ mg}$$

$$\% \text{ degradation} = \frac{133.0 - 106.1}{133.0} \times 100 = 92.0\%$$

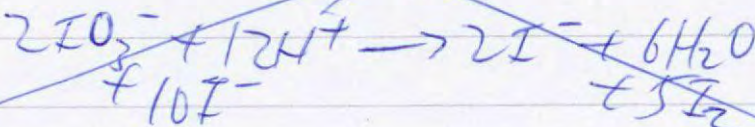
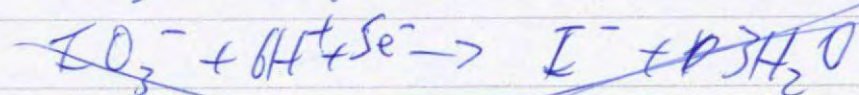
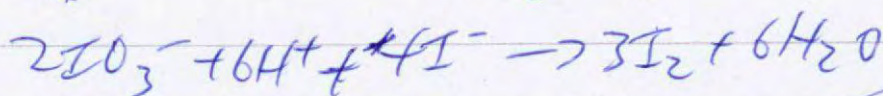
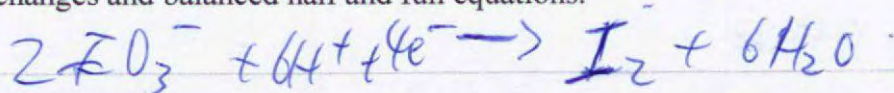
mass remaining

- (ii) In the reaction below, the iodine-containing reactants react by electron-transfer to give the same product.



A similar reaction occurs when potassium permanganate solution,  $\text{KMnO}_4(\text{aq})$ , reacts with manganese(II) sulfate solution,  $\text{MnSO}_4(\text{aq})$ , in neutral conditions to produce manganese(IV) oxide,  $\text{MnO}_2(\text{s})$ .

Identify the oxidants and reductants in both reactions, with support of oxidation number changes and balanced half and full equations.



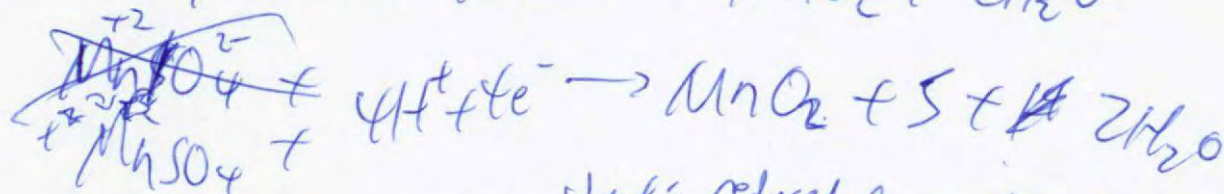
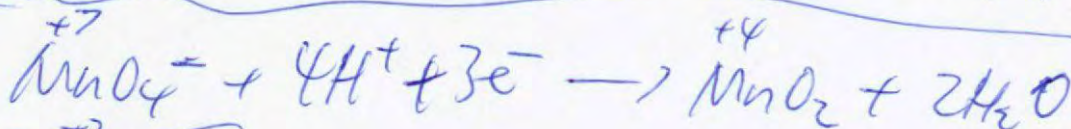
~~$\text{IO}_3^-$  is oxidant and is reduced~~  
~~and oxidises  $\text{I}^-$~~   
~~and oxidises  $\text{I}^-$~~

~~$\text{I}^-$  is both oxidant and reductant~~

~~$\text{IO}_3^-$  is oxidant, reduced from +5~~  
 ~~$\text{I}$  in  $\text{IO}_3^-$  to 0  $\text{I}$  in  $\text{I}_2$ ,~~

~~$\text{I}^-$  is reductant, oxidised from -1~~  
 ~~$\text{I}$  in  $\text{I}^-$  to 0  $\text{I}$  in  $\text{I}_2$ ,~~

~~Electron transfer occurs with  $\text{I}^-$  for both~~



~~$\text{MnO}_4^-$~~  oxidant: reduced from +7 to +4 ( $\text{MnO}_2$ )  
 ~~$\text{Mn}^{2+}$~~  reductant: oxidised from +2 to +4 ( $\text{MnO}_2$ )  
 ~~$\text{MnSO}_4$~~

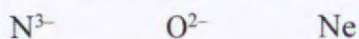
## QUESTION FOUR

- (a) There are various periodic trends observed between elements in the periodic table. These trends are fundamentally due to the protons and electrons within the different atoms.
- (i) Justify the differences in **first ionisation enthalpy** for nitrogen and oxygen.

Give a clear definition for the term, and include references to electron arrangements where appropriate.

First ionisation energy (IE) is the energy required to ~~remove~~ remove 1 ~~e<sup>-</sup> from~~ electron from each atom in 1 mole of substance in gaseous state. N and O are both in period 2, so both ~~have~~ have 2 energy levels so have ~~the~~ <sup>same</sup> amount of ~~the~~ e<sup>-</sup> shielding from inner e<sup>-</sup> ~~atoms~~ ~~O has~~ (N is  $1s^2 2s^2 2p^3$ , O is  $1s^2 2s^2 2p^4$ ). However O has 1 more proton (8) than N (7) therefore O has ~~a~~ ~~stronger~~ <sup>electrostatic</sup> ~~attraction~~ <sup>attraction to</sup> between nucleus and valence e<sup>-</sup> ~~than~~ than N. Therefore, ~~it~~ it requires more energy to remove an e<sup>-</sup> from O than N, ~~so~~ so O has higher IE than N.

(ii) Explain any similarities or differences in the radii of the following three particles.



$N^{3-}$  and  $O^{2-}$  are both anions, so both have larger radii than their atoms <sup>(due to more e<sup>-</sup> repulsion)</sup>, whereas Ne ~~is~~ atom. All 3 have same number of 10 e<sup>-</sup> and a full valence shell with 2 energy levels ( $1s^2 2s^2 2p^6$ ), so experience ~~similar~~ same inner e<sup>-</sup> shielding. However, Ne has 10 protons,  $O^{2-}$  has 8, and  $N^{3-}$  has 7, so the order of <sup>strength of</sup> electrostatic attraction between nucleus and valence e<sup>-</sup> ~~is~~ (decreasing order) is:  $Ne > O^{2-} > N^{3-}$ .  
 Thus, the distance from nucleus to valence e<sup>-</sup> order is:  $Ne < O^{2-} < N^{3-}$ , so  $N^{3-}$  has largest radii,  $O^{2-}$  has (2nd largest), and Ne has smallest radii (because valence e<sup>-</sup> are pulled closer to nucleus with stronger attraction ~~is~~ stronger).

(b) Vanadium is a transition metal that exists in different oxidation states, and can form ions and compounds with different colours. These include the ions shown below.

$VO_2^+$   
Yellow

$VO^{2+}$   
Blue

$V^{3+}$   
Green

$V^{2+}$   
Violet

For an experiment, a student added powdered silver, Ag(s), to a solution containing  $VO_2^+$  ions, and stirred until no further changes were observed. They then repeated the experiment twice more, but using powdered tin, Sn(s), for the second, and powdered zinc, Zn(s), for the third.

Use cell potential calculations to identify the final colour and oxidation number for vanadium in each experiment, following addition of the powdered metal.

You may assume that  $Zn^{2+}$ ,  $Sn^{2+}$ , and  $Ag^+$  are all colourless and do not form any insoluble precipitates.

$$E^\circ(VO_2^+/VO^{2+}) = +1.00 \text{ V}$$

$$E^\circ(Zn^{2+}/Zn) = -0.76 \text{ V}$$

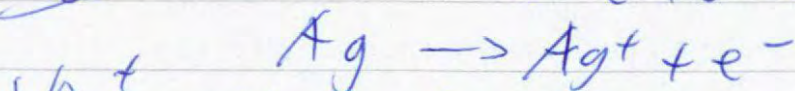
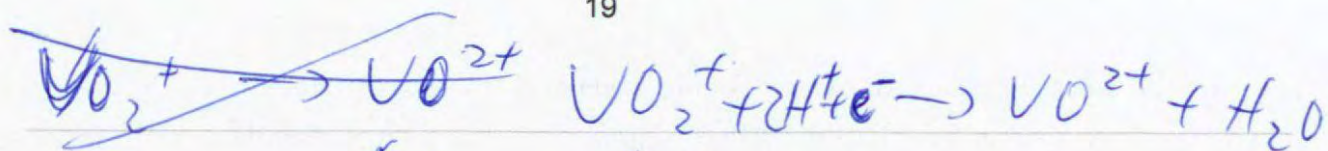
$$E^\circ(VO^{2+}/V^{3+}) = +0.34 \text{ V}$$

$$E^\circ(Sn^{2+}/Sn) = -0.14 \text{ V}$$

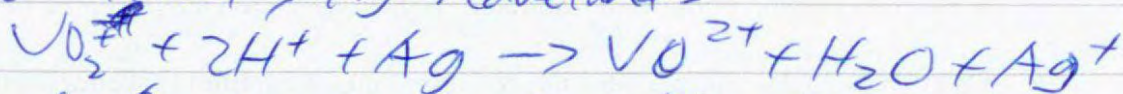
$$E^\circ(V^{3+}/V^{2+}) = -0.26 \text{ V}$$

$$E^\circ(Ag^+/Ag) = +0.80 \text{ V}$$

~~For Ag:~~ ~~the~~  $E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxi}$   
 $= 1.00 - 0.80 = +0.20 \text{ V}$   
 Spontaneous  $\uparrow$   
 ( $> 0$ )

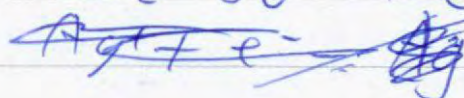
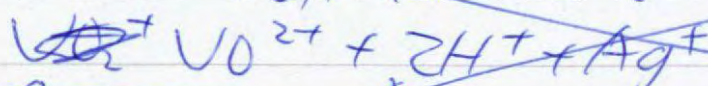


$VO_2^+$  oxidant, Ag reductant.



Then, Ag reductant and  $VO^{2+}$  oxidant.

$$E^\circ_{cell} = \overset{0.34}{\cancel{0.80}} - \overset{0.80}{\cancel{0.34}} = \cancel{0.46} V$$



Non-spontaneous, so that does not occur.

Final colour is blue ( $VO^{2+}$ ), oxidation no. = +4.  
 Sn: Pb<sup>2+</sup>,  ~~$VO_2^+$~~   $VO_2^+$  oxidant, Sn reductant

$$E^\circ_{cell} = 1.00 - (-0.14) = +1.14 V. \text{ Spontaneous}$$

Then,  $VO^{2+}$  oxidant, Sn reductant.

$$E^\circ_{cell} = 0.34 - (-0.14) = +0.48 V \text{ Spontaneous}$$

Then,  $V^{3+}$  oxidant, Sn reductant.

$$E^\circ_{cell} = -0.26 - (-0.14) = -0.12 V$$

Non-spontaneous, so final colour is green ( $V^{3+}$ , oxidation number = +3).

$$Zn: Pb^{2+}, E^\circ_{cell} = 1.00 - (-0.76) = +1.76 V$$

$$\text{Then, } E^\circ_{cell} = 0.34 - (-0.76) = +1.10 V$$

$$\text{Then, } E^\circ_{cell} = -0.26 - (-0.76) = +0.50 V$$

All > 0 so all spontaneous, so final colour is violet ( $V^{2+}$ , oxidation number +2).

Assume excess ~~at~~ Ag, Sn, Zn.

(c) Two acid-base titrations were carried out in a school chemistry laboratory.

- In the first titration,  $0.0886 \text{ mol L}^{-1}$  sodium hydroxide solution,  $\text{NaOH}(aq)$ , was added to  $30.0 \text{ mL}$  of hydrochloric acid,  $\text{HCl}(aq)$ , which had an initial pH of 1.04.
- In the second titration,  $0.0886 \text{ mol L}^{-1}$  sodium hydroxide solution,  $\text{NaOH}(aq)$  was added to a  $30.0 \text{ mL}$  solution of hypochlorous acid,  $\text{HOCl}(aq)$ , which had an initial pH of 4.16.

(i) Carry out calculations to determine key points on the titration curve for each experiment.

Use these points to draw the two predicted curves on the graph space provided.

Key values may include: the initial concentrations of the two acids, the volume and pH at the equivalence point, the pH at halfway to the equivalence point, and the pH after  $10 \text{ mL}$  of excess base has been added.

$$\text{p}K_a(\text{HOCl}) = 7.53$$

~~$$n(\text{NaOH}) = 0.0886 \times$$~~

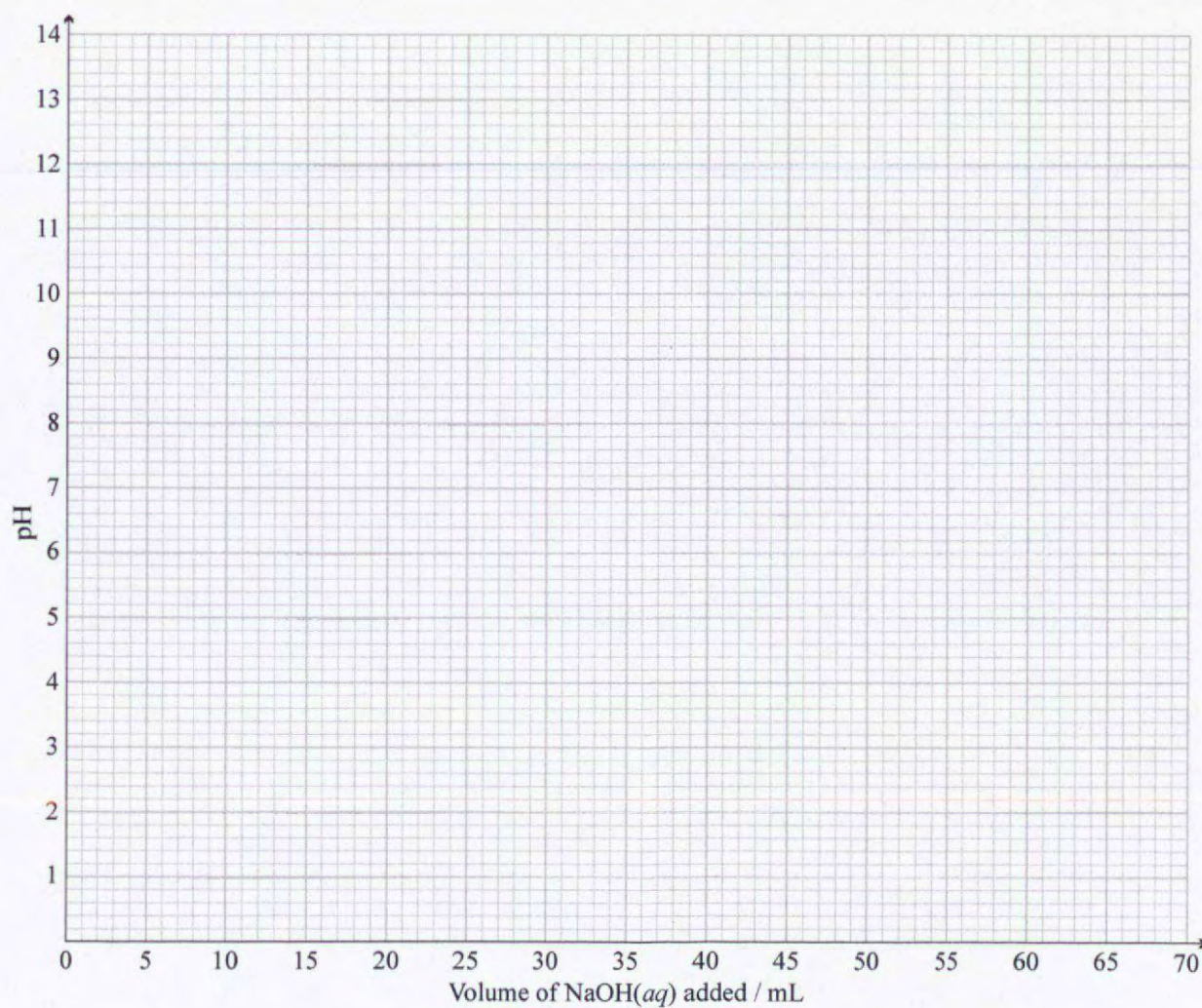
~~$$n(\text{H}_3\text{O}^+) = 10^{-1.04} = 0.0912 \text{ mol L}^{-1}$$~~

$$n(\text{H}_3\text{O}^+) = CV = 2.736 \times 10^{-3} \text{ mol}$$

$$= n(\text{NaOH})$$

$$V(\text{NaOH}) = \frac{n}{C} = 0.03088 \text{ L} = 30.9 \text{ mL}$$

equivalence



Question Four continues  
on the following page.



Extra space if required.

Write the question number(s) if applicable.

QUESTION  
NUMBER

2a) All 4 molecules ~~are~~ have similar electron cloud size (small, 3-carbon chain), so they have similar temporary dipole-dipole attractions (weak), so this factor can be ignored

Extra space if required.  
Write the question number(s) if applicable.

QUESTION  
NUMBER

93102

## Outstanding Scholarship

**Subject:** Chemistry

**Standard:** 93102

**Total score:** 27

| Q | Score | Marker commentary                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
|---|-------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 | 08    | <p>a) Calculated three values of Q and compared them with the appropriate Ks to describe the appropriate observation. Explained that nitric acid neutralised OH<sup>-</sup> ions to prevent the formation of Pb(OH)<sub>2</sub>.</p> <p>b) Recognised the effect of temperature on the kinetic energy of particles in solution and explained that the Co<sup>3+</sup> acted as a catalyst providing an alternative pathway with a lower activation energy.</p> <p>c) Three Lewis diagrams were drawn together with appropriate shape and the majority of bond angles. Explained the effect of repulsion on the shape of a molecule.</p>                                                                                                                                                                                                                                                                                                                                                                                                     |
| 2 | 08    | <p>a) Correctly identified the boiling points of the molecules and explained: the effect of the electron cloud size on temporary dipole forces of attraction; the effect of electronegativity on the polarity of a bond and its contribution to permanent dipole forces of attraction; the contribution of O-H and N-H to hydrogen bonding between molecules; and the influence of molecular shape on packing and thus the strength intermolecular forces.</p> <p>b) Drew all five organic structures.<br/>Identified the products of the hydrolysis reaction and explained that due to their ionic nature and their interaction with water that some of them could not be distilled.</p> <p>c) Calculated the number of moles of NH<sub>3</sub> but made an error in the calculation of the temperature change (Value calculates is half the correct answer).<br/>Explained the effect of the enthalpy change on the entropy of the surroundings and the changes to the entropy of the system that resulted in a spontaneous reaction.</p> |
| 3 | 05    | <p>a) Correctly identified molecules F and G and drew one correct scheme from F to W.</p> <p>b) (i) Calculated that 133mg of Vitamin C were present in the original solution.</p> <p>b) (ii) Correctly identified the oxidant and reductant for the reaction between potassium permanganate and manages sulfate.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| 4 | 06    | <p>a) Recognised the effect of increasing the number of protons on increasing the ionisation energy (Did not recognise the effect of electrons in the 2p3 and 2p4 electron</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |

|  |  |                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
|--|--|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  |  | <p>configuration). Recognised the effect of additional numbers of protons on the radii of a particle.</p> <p>b) Calculated all the <math>E_{\text{cell}}</math> values (both positive and negative) to determine the end point of a series of redox reaction. Included the colour and oxidation number of the final vanadium ion for each reaction.</p> <p>c) Calculated the volume at the equivalence point for the titration between HCl and NaOH.</p> |
|--|--|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|