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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 (). 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.**

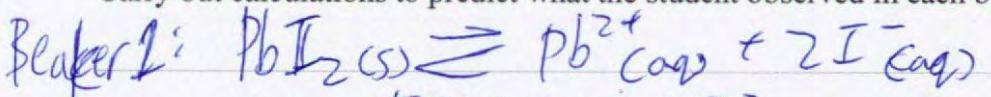
QUESTION ONE

- (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 $0.00167 \text{ mol L}^{-1}$ potassium iodide solution, $\text{KI}(aq)$, into each of two beakers. They then added 35.0 mL of $0.0225 \text{ mol L}^{-1}$ lead(II) nitrate solution, $\text{Pb(NO}_3)_2(aq)$, to one beaker and added 35.0 mL of $0.0143 \text{ mol L}^{-1}$ silver nitrate solution, $\text{AgNO}_3(aq)$, to the other.

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

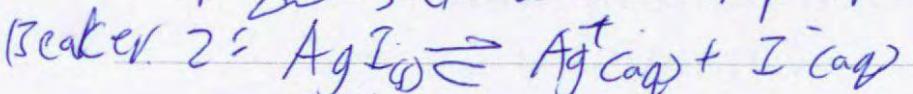


$$I_p = [\text{Pb}^{2+}][\text{I}^-]^2$$

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

$$= 6.35 \times 10^{-9}$$

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



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

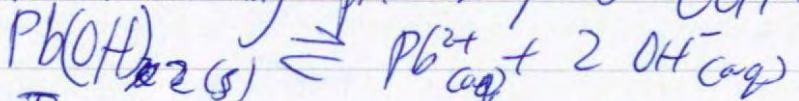
$$= (0.0143 \times \frac{35}{60}) \times (0.00167 \times \frac{25}{60})$$

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

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

~~For beaker 2, for $\text{Pb}(\text{NO}_3)_2$ before added to beaker 1:~~

~~Assuming $\text{pH} = 7$, $[\text{OH}^-] = 1.00 \times 10^{-7}$~~



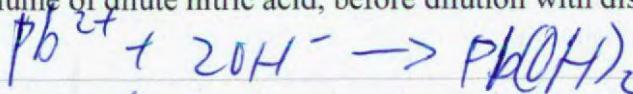
$$I_p = [\text{Pb}^{2+}][\text{OH}^-]^2 = (0.0225) \times (10^{-7})^2$$

$$= (0.00167 \times \frac{35}{60}) \times (10^{-7})^2$$

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

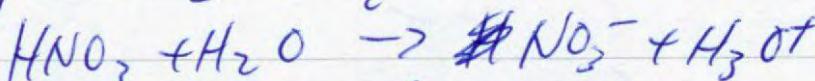
$I_p > K_s(\text{Pb(OH)}_2)$, so a white Pb(OH)_2 precipitate will form.

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



~~From last calculation Pb²⁺ ions from Pb(NO₃)₂~~

Pb²⁺ will react with 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, ~~thus~~ increasing the solubility of PbI_2 and preventing PbI_2 solid from ~~to~~ forming.

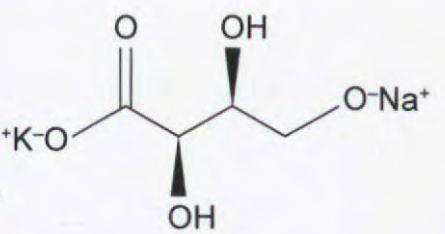


~~Dilute nitric acid is necessary as Pb~~ ~~dissociates into~~ ~~H₃O⁺~~ ions, which ~~neutralise~~ neutralize the OH⁻ ions, thus decreasing OH⁻.

~~∴ There will~~ ~~not be enough~~ OH⁻ ions to form the $\text{Pb}(\text{OH})_2$ precipitate, thus allowing the ~~PbI₂~~ PbI_2 precipitate to form.

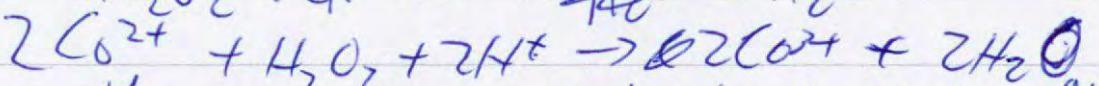
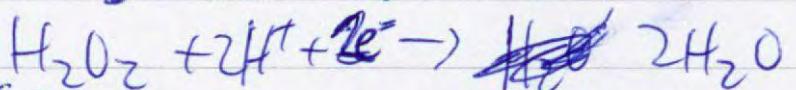
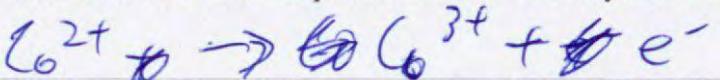
- (b) A reaction between hydrogen peroxide solution, $\text{H}_2\text{O}_2(aq)$, and potassium sodium tartrate solution, $\text{KNaTar}(aq)$, is commonly used in schools to demonstrate the effect of reaction conditions on the rate of a reaction.

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



First the solution turns green as the pale pink Co^{2+} ions are oxidised into green Co^{3+} ions by the hydrogen peroxide. Once the solution has changed colour, large volumes of 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 Co^{3+} ions as catalyst.



The solutions must be heated to high enough temperature (70°C) so the particles have high enough average kinetic energy to overcome the activation energy required for successful collisions to occur. The reaction between each other (H_2O_2 and KNaTar particles). However, no reaction occurs yet because activation is still too high. Thus, Co^{3+} acts as a catalyst, which provides an alternative reaction pathway by lowering the required activation energy, so H_2O_2 and KNaTar have a higher chance for successful collisions to occur because they have a higher chance of occurring. There is a higher chance of the collisions being higher than the activation energy. Thus, the rate of reaction increases, and the reaction proceeds so CO_2 gas is produced, and the

CO_3^{2-} likely allows for H_2O_2 or KNO_3 to react with H, then ~~react again~~ to form the desired product, with lower total activation energy. Also, the higher temperature increases rate of movement of H_2O_2 and KNO_3 particles, ~~therefore~~ thus there are higher ^{chance/rate} 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	$\text{ZrF}_5^{-} \quad 88 \text{e}^{-}$	$\text{ZrF}_6^{2-} \quad 88 \text{e}^{-}$	$\text{ZrF}_7^{3-} \quad 86 \text{e}^{-}$
Lewis structure	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{Zr}-\text{F} \\ \\ \text{F} \end{array}$	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{Zr}-\text{F} \\ \\ \text{F} \\ \\ \text{F} \end{array}$	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{Zr}-\text{F} \\ \\ \text{F} \\ \\ \text{F} \\ \\ \text{F} \end{array}$
Shape	Trigonal bipyramidal	Octahedral	Pentagonal bipyramidal
Bond angles	120° and 90°	90°	108° and 90°

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

ZrF_5^{-} has 5 regions of electron density around the central Zr atom which will repel to form maximum separation to form trigonal bipyramidal arrangement with bond angles 120° and 90° . The 120° is between the ~~2~~ $\text{Zr}-\text{F}$ bonds in equatorial positions (3 $\text{Zr}-\text{F}$ bonds), whereas 90° for the axial positions ($2 \text{Zr}-\text{F}$ bonds). The top and bottom $\text{Zr}-\text{F}$ bond forms 90° angle with the central 3 $\text{Zr}-\text{F}$ bonds. All 5 are bonding regions, so that shape is trigonal bipyramidal.

QUESTION TWO

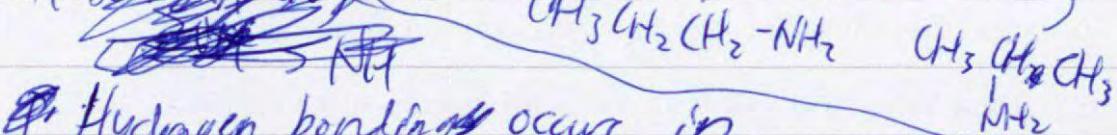
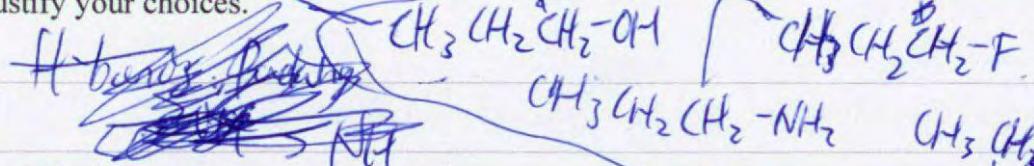
- (a) The following is a selection of boiling points for different molecular compounds.

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

In 1-aminopropane and 2-aminopropane - ~~It is the strongest intermolecular force, and since all 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 attractions due to it being polar (S-F, S+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.

whereas only ~~has~~ has 1 lone pair available for H-bonding, whereas the other O has 2.

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

~~So~~ 1-ortho-propane ~~has~~ ~~no~~ branching whereas 2-ortho-propane does (on ~~the~~-NH₂), \therefore so 1-ortho-propane can pack more closely than 2-ortho-propane (\therefore 1-ortho-propane is more linear). Therefore, 1-ortho-propane has stronger IMF, since ~~the~~ electrostatic IMFs are inversely proportional to the distance between molecules. \therefore 1-ortho-propane has slightly stronger IMFs than 2-ortho-propane, thus having a slightly higher BPT than 2-ortho-propane. GO TO PAGE

- (ii) Heptane has a boiling point of 98.4 °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 ~~permanent~~ 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 outweigh the ~~of~~ attraction due to hydrogen bonding and permanent dipole in the compound in (i). This is because the larger size means a much higher chance for temporary ^{dipole-dipole} attractions to occur. Therefore, heptane has the strongest IMFs, so the strongest BPT.

- (b) (i) A complex organic reaction in a university laboratory yielded a mixture that contained two different organic compounds. Mass analysis determined that they had different molar masses. They were given the provisional labels Compound **X** and Compound **Y**.

Compounds **A**, **B**, and **C** were made from chemical treatments of the mixture of **X** and **Y** and were each subsequently isolated and analysed using spectroscopic techniques.

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

$$M(\mathbf{A}) = 59 \text{ g mol}^{-1} \quad M(\mathbf{B}) = 72 \text{ g mol}^{-1} \quad M(\mathbf{C}) = 88 \text{ g mol}^{-1}$$

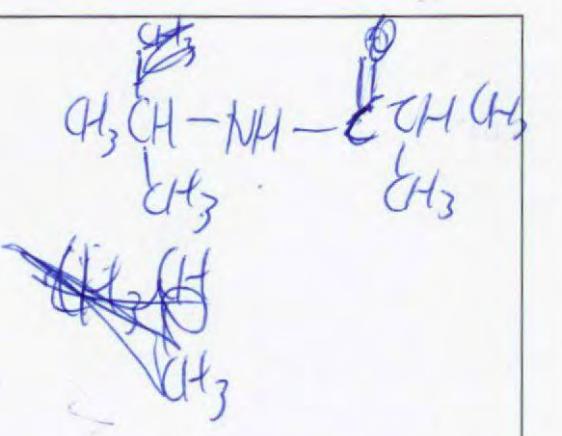
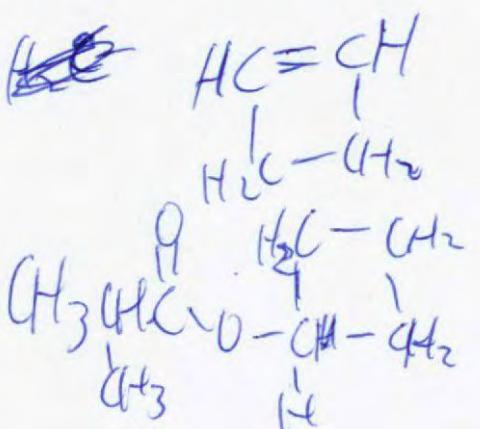
Compound A	Compound B	Compound C
Name: <i>$\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$</i> Structure: <i>$\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$</i>	Name: <i>Cyclobutanol</i> Structure: <i>$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{OH}$</i>	Name: <i>2-methylpropanoic acid</i> Structure: <i>$\text{CH}_3\text{CH}(\text{CH}_3)-\text{CO}-\text{OH}$</i>

- (ii) Compounds **A**, **B**, and **C** were isolated after the following chemical treatments:
- ① 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**.

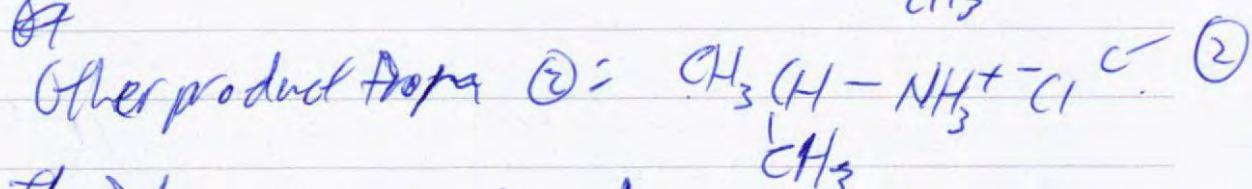
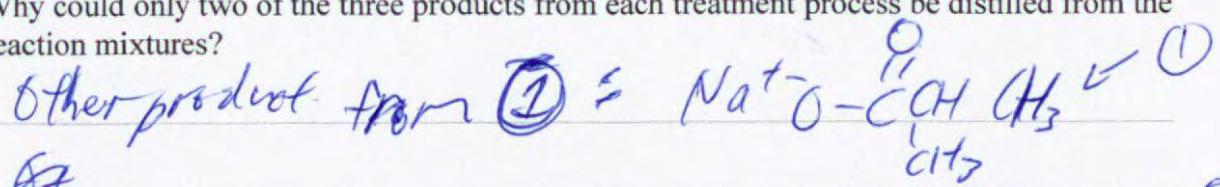
$$M(\mathbf{X}) = 142 \text{ g mol}^{-1} \quad M(\mathbf{Y}) = 129 \text{ g mol}^{-1}$$

This space is provided for working.



Compound X	Compound Y
Structure: $\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CHC}_2\text{O}-\text{CH}-\text{CH}_2 \\ \quad \\ \text{CH}_3 \quad \text{H}_2\text{C}-\text{CH}_2 \end{array}$	Structure: $\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}-\text{NH}-\text{CCH}(\text{CH}_3) \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$

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

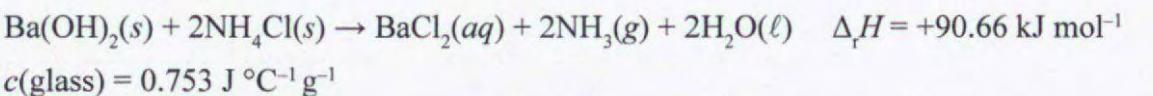


The ~~the~~ -ve charged O in ① and $\text{the charged O, NH}_3^+$ in ② mean that O strong ~~for~~ ~~attraction~~ \rightarrow ~~attraction~~ ion-dipole / dipole-dipole attractions will occur between ~~the~~ the charged end of ~~the~~ the products and the polar end of water (O^- attracted to $\delta^+ \text{H}$ from water, NH_3^+ to $\delta^- \text{O}$ from water, Na^+ to ~~$\delta^- \text{H}$~~ $\delta^- \text{O}$, Cl^- to $\delta^+ \text{H}$). ~~the~~ The Intermolecular Forces (IMFs) ^{between product-water (solute-solvent)} are greater than the original hydrogen bonds between water-water and the IMFs between product-product (solute-solute), so ~~the~~ the product will be ^{very} insoluble in water, thus making them hard to be distilled.

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

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



$$\begin{aligned} \text{NH}_4\text{Cl}(s) &\rightarrow \text{NH}_4^+(aq) + \text{Cl}^-(aq) \\ \text{Ba}(\text{OH})_2(s) &\rightarrow \text{Ba}^{2+}(aq) + 2\text{OH}^-(aq) \\ \cancel{\text{Molar mass}} \quad [\text{H}_3\text{O}^{\text{initial}}] &= 10^{-0.50} = 0.3162 \text{ mol L}^{-1} \\ [\text{H}_3\text{O}^{\text{final}}] &= 10^{-1.21} = 0.06166 \text{ mol L}^{-1} \\ \text{NH}_3 + \text{HCl} &\rightarrow \text{NH}_4^+ + \text{Cl}^- \\ \text{HCl} + \text{H}_2\text{O} &\rightarrow \text{Cl}^- + \text{H}_3\text{O}^+ \\ \cancel{\Delta n} \quad \Delta n(\text{NH}_3) &= \Delta n(\text{H}_3\text{O}^+) = (0.3162 - 0.06166) \\ &\times 0.1 = 0.02545 \text{ mol} \\ n(\text{Ba}(\text{OH})_2) &= \frac{0.02545}{2} = 0.01273 \text{ mol} \\ n(\text{NH}_4\text{Cl}) &= 0.02545 \text{ mol} \\ \cancel{q = \Delta H \times n} \quad q &= -\Delta H \times n \\ &= -90.66 \times 0.01273 = -0.5769 \text{ kJ} \\ q &= mc\Delta T \\ \Delta T &= \frac{q}{mc} = \frac{-0.5769 \times 1000}{90.72 \times 0.753} \\ &= \cancel{-6.38} - 8.4453 \\ &= -8.45^\circ\text{C} \end{aligned}$$

The temperature decreased by 8.45°C

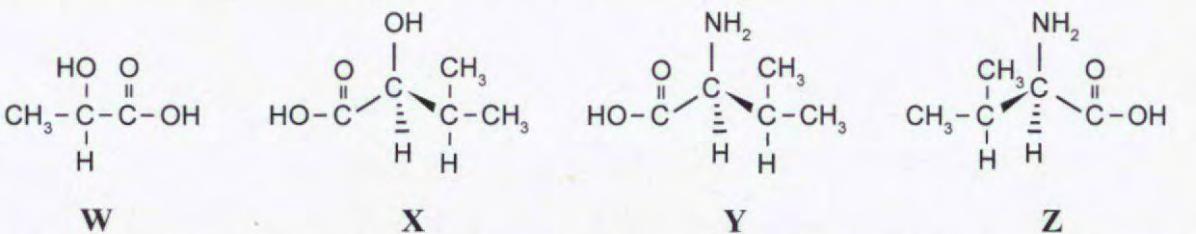
- (ii) Briefly outline thermodynamic factors that contribute to the overall spontaneity of the reaction occurring in the beaker.

ΔH is ~~not~~ positive so the reaction is ~~exothermic~~,
 & it ~~also~~ absorbs (heat) energy from surroundings.
 So ~~that's to~~ $\Delta S_{\text{surroundings}}$ (ΔS is change in entropy) is -ve since surrounding particles have less kinetic energy so less disorder.
 The reactions are all solid and change into ~~the~~ aqueous and gaseous products, contributing to a ~~five~~ ΔS system since gas/liquid have higher rate of movement than solids, so a greater degree of disorder. ~~It also shows that~~
 There is an increase from 3 reactant moles to 5 products mole, so ~~the~~ ^{the} rate of collisions ~~are more~~ / amount of arrangements of ~~the~~ particles are increased, thus a positive ΔS_{system}

(0 to 2 gaseous moles) Since the reaction is spontaneous, the increase in ΔS_{system} ~~outweighs~~ is greater than the decrease in $\Delta S_{\text{surroundings}}$. In 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:



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

- Compound **F** has the molecular formula C_3H_5OCl . 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 $Br_2(aq)$.
- Compound **G** has the molecular formula $C_5H_{10}O$. 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**.

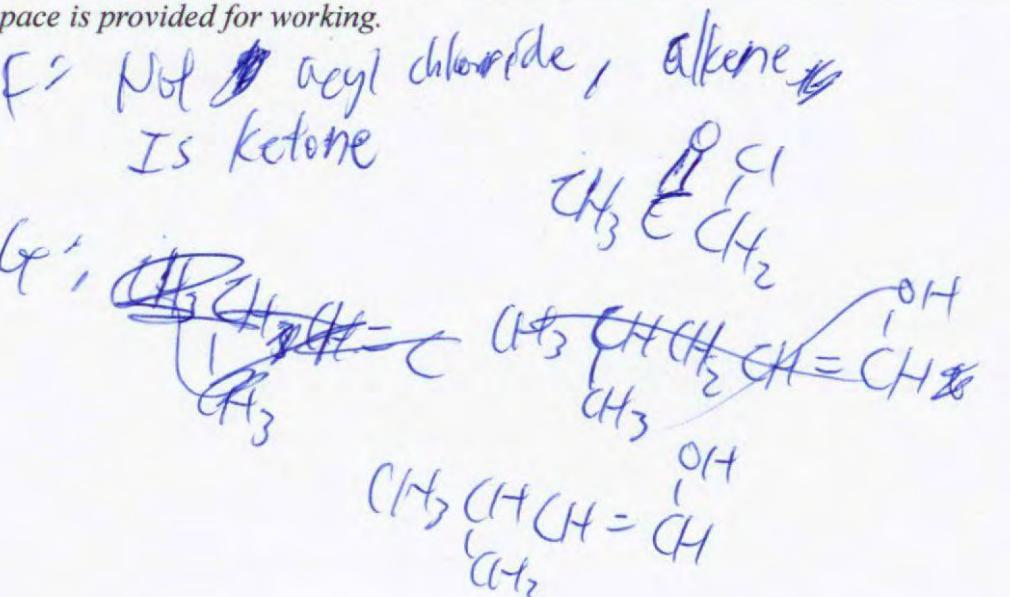
You may only select from the reagents provided below.

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

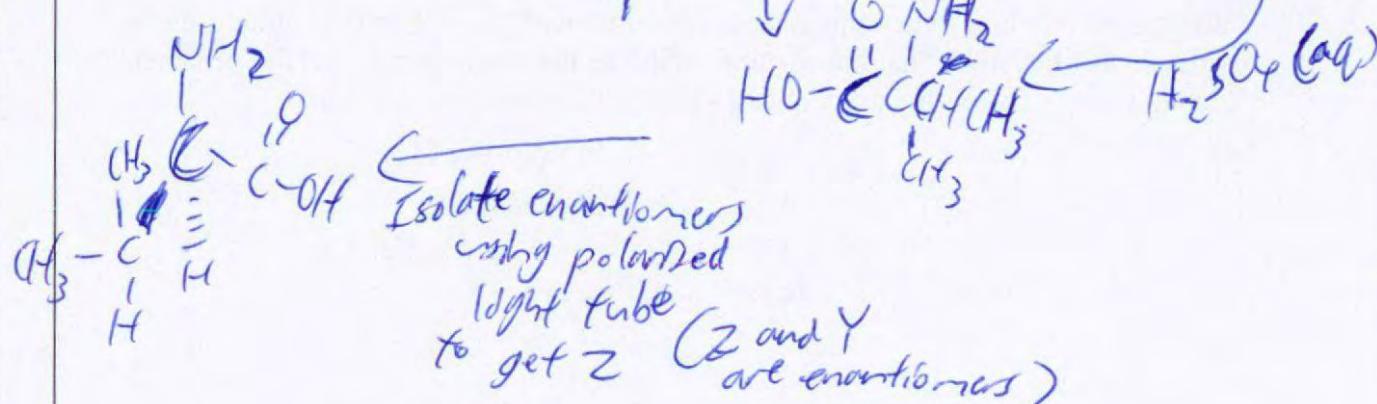
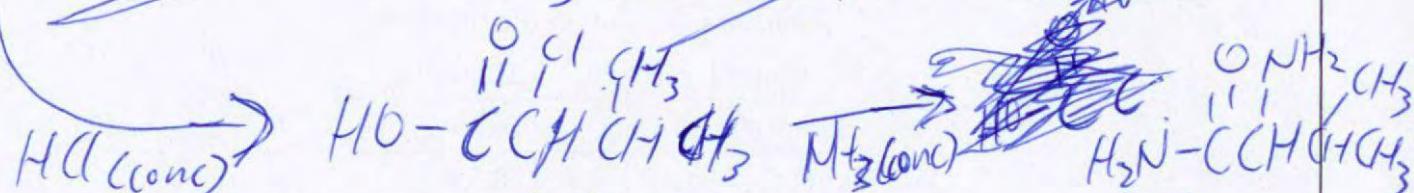
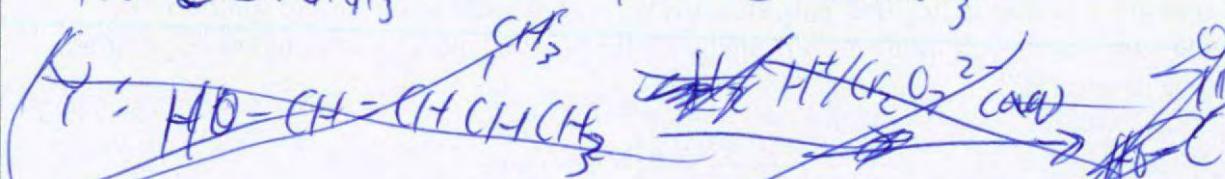
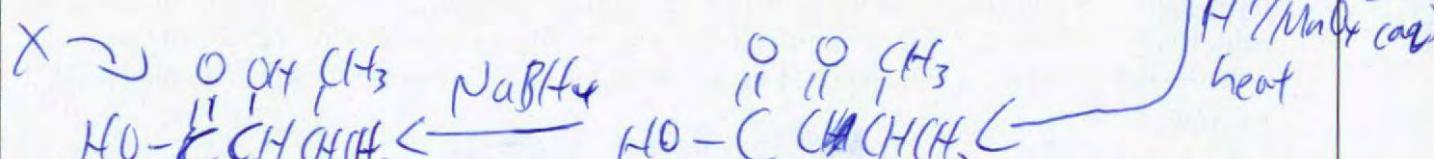
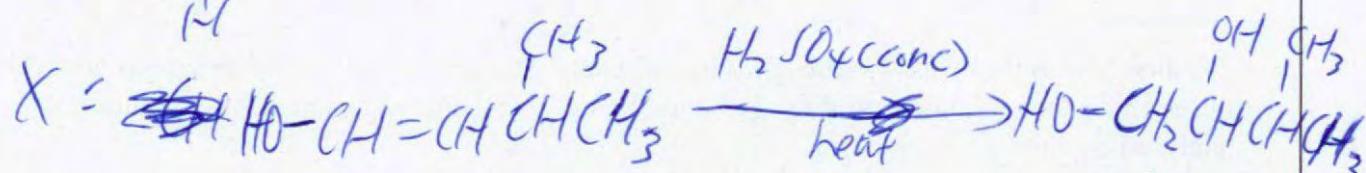
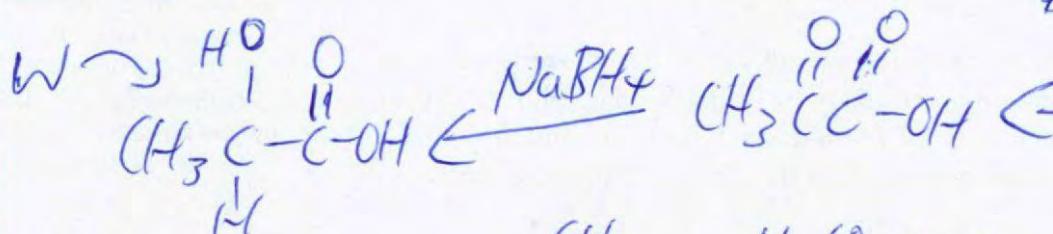
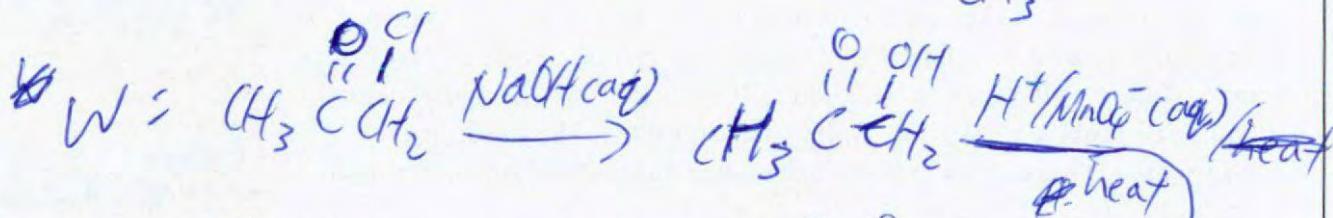
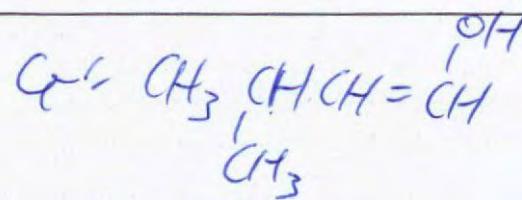
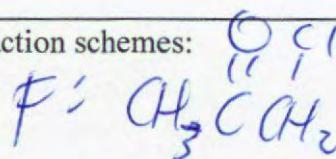
Reagents available:

NH_3 (conc)	$NaOH(aq)$	H^+/MnO_4^- (aq)	$H^+/Cr_2O_7^{2-}$ (aq)	$NaBH_4$
HCl (conc)	H_2SO_4 (aq)	$NaOH(alc)$	H_2SO_4 (conc)	PCl_5

This space is provided for working.



Reaction schemes:



- (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^{-1} 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.

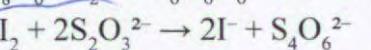
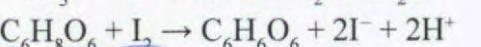
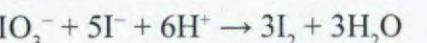
The remaining iodine in the flask was then titrated with a sodium thiosulfate solution, $Na_2S_2O_3(aq)$, and the titration was repeated with further 20.0 mL aliquots until average titres could be determined.

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

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.

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



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

$$n(KIO_3) = 6.168 \times 10^{-4} \times 0.02 = 1.237 \times 10^{-5} \text{ mol}$$

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

~~$$T_{I_2} = \frac{n}{V} = 3.701 \times 10^{-5}$$~~

~~$$T_{I_2} = \frac{n}{V} = 3.701 \times 10^{-5}$$~~

Control: No Uptake $I_2(\text{remaining}) = I_2(\text{total})$

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

$$[S_2O_3^{2-}] = \frac{7.402 \times 10^{-5}}{0.02720} = (2.721 \times 10^{-3}) \text{ mol/L}^{-1}$$

Fresh:

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

$$n(I_2\text{ remaining}) = \cancel{n(S_2O_3^{2-}\text{fresh})} \text{ mol}$$

$$n(C_6H_8O_6) = n(I_2\text{ reacted}) = \frac{2}{2} = 2.191 \times 10^{-5} \text{ mol}$$

~~$$m(C_6H_8O_6) = 1.510 \times 10^{-5} = 1.810 \times 10^{-5} \times 176.1 = 2.191 \times 10^{-5} \text{ mol}$$~~

~~$$n(C_6H_8O_6 \text{ undiluted}) = 1.510 \times 10^{-5} \times 2.660 \times 10^{-3}$$~~

~~$$m(C_6H_8O_6) = 2.326 \times 10^{-4} \times 200 = 2.552 \times 10^{-4} \text{ mol}$$~~

~~$$So \cancel{\text{if the saltet's information is accurate}} \text{ difference to } 130 \text{ mg} = 0.133 \text{ g}$$~~

Accurate (2.31% difference to 130 mg)

24 hours: $n(S_2O_3^{2-}\text{24 hours}) = 2.721 \times 10^{-3} \times 0.01835$

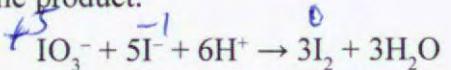
~~$$n(I_2\text{ remaining}) = 2.493 \times 10^{-5} \text{ mol}$$~~

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

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

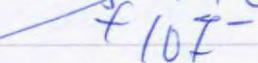
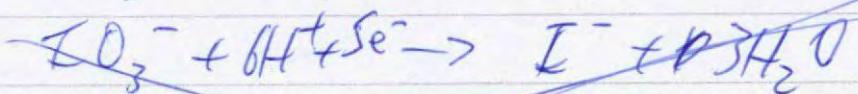
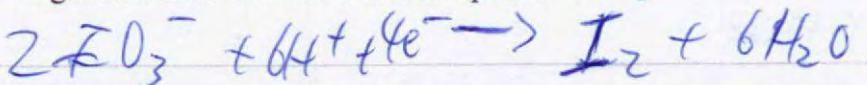
$$\alpha \text{ % degradation} = \frac{133.0 - 106.1}{133.0} \times 100 = 92.0 \%$$

- (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, $\text{KMnO}_4(aq)$, reacts with manganese(II) sulfate solution, $\text{MnSO}_4(aq)$, in neutral conditions to produce manganese(IV) oxide, $\text{MnO}_2(s)$.

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



~~IO_3^-~~ . ~~IO_3^-~~ is oxidant and is reductant

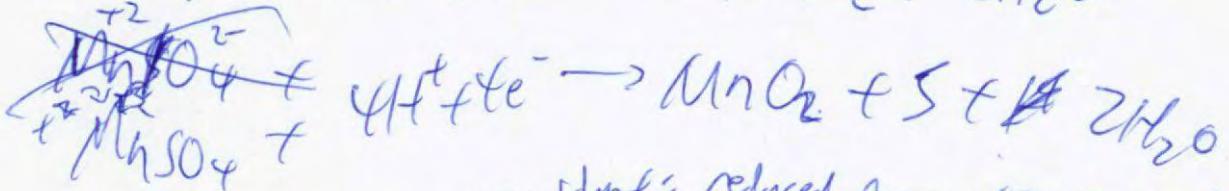
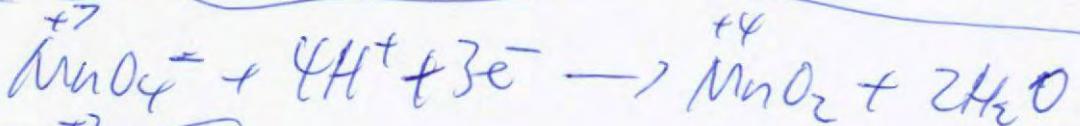
~~I^-~~ and ~~I_2~~ is oxidant

~~I^-~~ is both oxidant and reductant

~~IO_3^-~~ is oxidant, reduced from ~~I^-~~ to ~~I_2~~ in IO_3^- to 0 I in I_2 .

~~I^-~~ is reductant, oxidized from ~~I^-~~ to ~~I_2~~ in I^- to 0 I in I_2 .

~~I^-~~ electron transfer occurs with I^- for both



Mn ~~is~~ oxidant: reduced from $+7$ to $+4$ (MnO_4^-)
 Mn ~~is~~ reductant: oxidized from $+2$ to $+4$ (Mn^{2+})

QUESTION FOUR

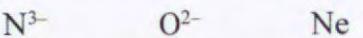
- (a) There are various periodic trends observed between elements in the periodic table. These trends are fundamentally due to the protons and electrons within the different atoms.

- (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 1 ~~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 ~~some~~ amount of ~~the~~ e- shielding from other e-. ~~However 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 ~~electrostatic~~ ~~attraction~~ ~~between nucleus and valence e-~~ than N. Therefore, ~~it requires~~ more energy to remove an e- from O than N, ~~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, whereas Ne is an atom. All 3 have same number of $10 e^-$ and a full valence shell with 2 energy levels ($1s^2 2s^2 2p^6$), so experience ~~the~~ same inner e^- shielding. However, Ne has 10 protons, O^{2-} has 8 and N^{3-} has 7, so the order of electrostatic attraction between nucleus and valence e^- (decreasing order) is $\text{Ne} > \text{O}^{2-} > \text{N}^{3-}$. Thus, the distance from nucleus to valence e^- order is $\text{Ne} < \text{O}^{2-} < \text{N}^{3-}$, so N^{3-} has largest radius, O^{2-} has (and largest, and Ne has smallest radius (because e^- are pulled closer to nucleus \therefore 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^+	VO^{2+}	V^{3+}	V^{2+}
Yellow	Blue	Green	Violet

For an experiment, a student added powdered silver, $\text{Ag}(s)$, 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, $\text{Sn}(s)$, for the second, and powdered zinc, $\text{Zn}(s)$, 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.

$$E^\circ(\text{VO}_2^+/\text{VO}^{2+}) = +1.00 \text{ V}$$

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

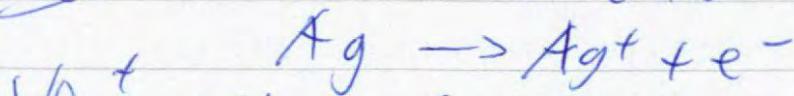
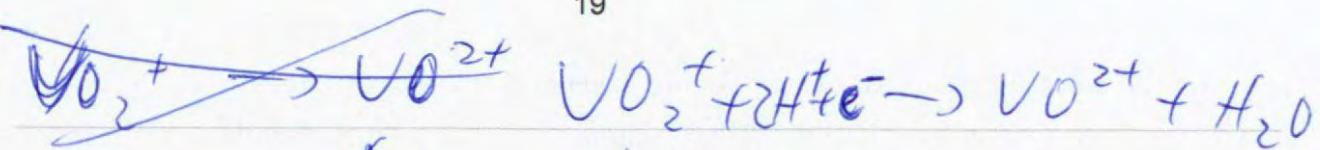
$$E^\circ(\text{VO}^{2+}/\text{V}^{3+}) = +0.34 \text{ V}$$

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

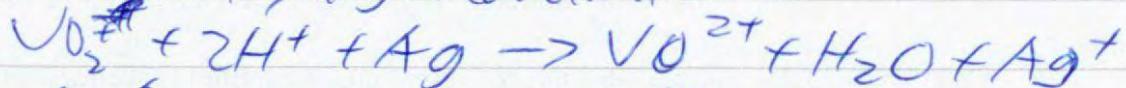
$$E^\circ(\text{V}^{3+}/\text{V}^{2+}) = -0.26 \text{ V}$$

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

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

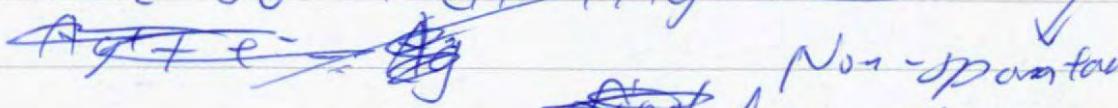
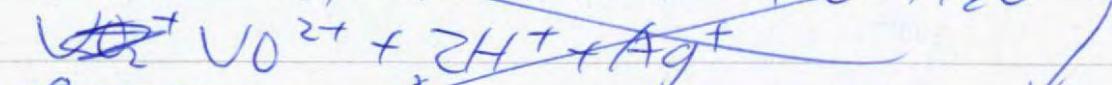
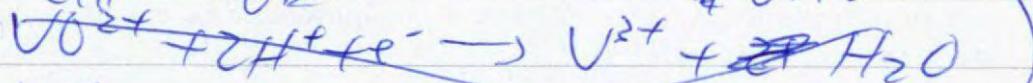


VO_2^+ oxidant, Ag reductant.



Then, Ag⁺ reductant and VO²⁺ oxidant.

$E^\circ_{\text{Cell}} = 0.580 - 0.154 = +0.46 \text{ V}$



Non-spontaneous, so ~~that~~ does not occur.

Final colour is blue (VO^{2+}), oxidation no. = +4.

Sn = Redox, ~~C~~ VO_2^+ oxidant, Sn reductant

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

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

$E^\circ_{\text{Cell}} = 0.74 - (-0.14) = +0.88 \text{ V. Spontaneous}$

Then, ~~C~~ V^{2+} ~~red~~ oxidant, Sn reductant

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

Non-spontaneous, so final colour is ~~green~~ (green, oxidation number = +3)

Zn = Redox, ~~C~~ $E^\circ_{\text{Cell}} = 1.00 - (-0.76) = +1.76 \text{ V}$

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

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

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

Assume excess ~~metal~~ Ag, In, 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 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 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 mL of excess base has been added.

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

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

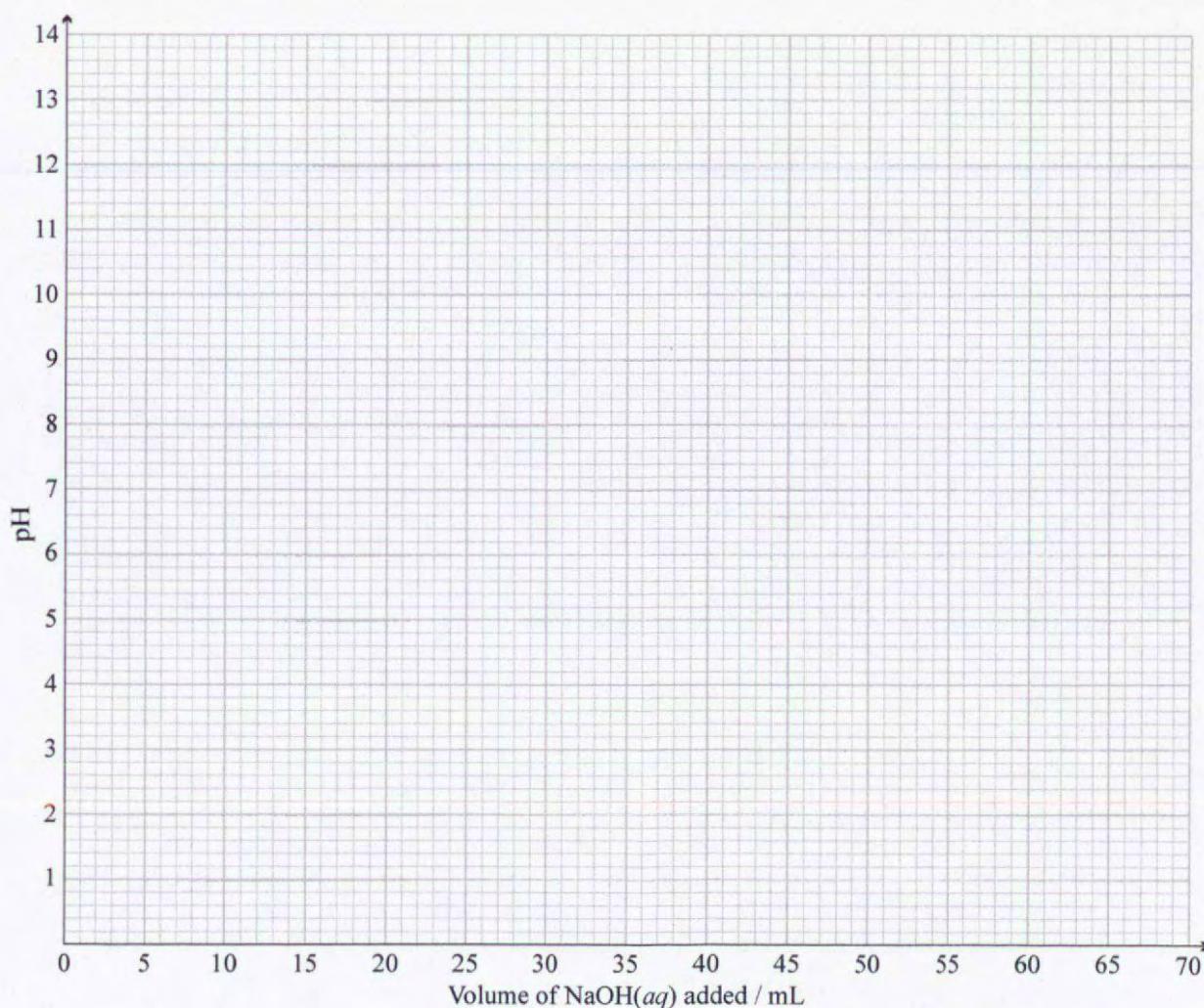
~~$n(\text{HCl}) \cdot 10^{-10.4} = 0.0886 \times 0.030 \text{ mol} \rightarrow$~~

~~$n(\text{H}_3\text{O}^+) = CV = 2.736 \times 10^{-2} \text{ mol}$~~

~~$= 4 \text{ mol NaOH}$~~

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

equivalence



Question Four continues
on the following page.

- (ii) Calculate the pH at the point where the two curves intersect.

QUESTION
NUMBER

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

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

QUESTION
NUMBER

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

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- ions to prevent the formation of Pb(OH)₂.</p> <p>b) Recognised the effect of temperature on the kinetic energy of particles in solution and explained that the Co³⁺ 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. 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 NH₃ but made an error in the calculation of the temperature change (Value calculates is half the correct answer). 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 E_{cell} 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>
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