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93102



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TOP SCHOLAR



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.

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

Yellow *White*

- (i) A student pipetted 25.0 mL of 0.00167 mol L⁻¹ potassium iodide solution, KI(*aq*), into each of two beakers. They then added 35.0 mL of 0.0225 mol L⁻¹ lead(II) nitrate solution, Pb(NO₃)₂(*aq*), to one beaker and added 35.0 mL of 0.0143 mol L⁻¹ silver nitrate solution, AgNO₃(*aq*), to the other.

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

Beaker One contains KI, Pb(NO₃)₂, Beaker 2 has KI, AgNO₃.

$$\text{Beaker } 1 \quad C = \frac{n}{V}$$

$$[\text{KI}] = \frac{0.025 + 0.00167}{0.06}$$

$$= 6.058 \times 10^{-4} \text{ M}$$

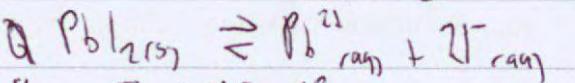
$$= [\text{K}^+]$$

$$= [\text{I}^-]$$

$$[\text{Pb}(\text{NO}_3)_2] = \frac{0.035 + 0.0225}{0.06}$$

$$= 0.013125 \text{ M}$$

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



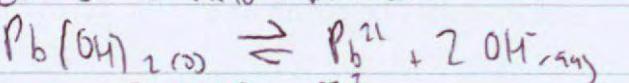
$$K_s = [\text{Pb}^{2+}][\text{I}^-]^2$$

$$\cancel{= 6.35 \times 10^{-4}} \text{. } Q_s = 0.013125 \times (6.058 \times 10^{-4})^2$$

$$Q_s = 6.35 \times 10^{-9} \text{. } K_s > Q_s \text{ so no PbI}_2 \text{ precipitate forms.}$$

But it is assumed pH = 7 in both beakers. $\therefore [\text{OH}^-] = 1 \times 10^{-7} \text{ mol L}^{-1}$

$$[\text{OH}^-] = 1 \times 10^{-7} \text{ mol L}^{-1}$$



$$K_s = [\text{Pb}^{2+}][\text{OH}^-]^2$$

$$Q_s = 0.013125 \times (1 \times 10^{-7})^2$$

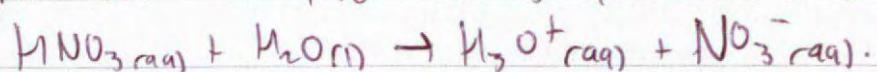
$$= 1.31 \times 10^{-16} \text{ (3s)}$$

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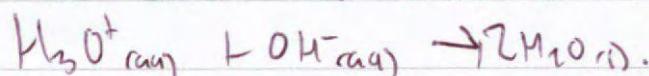
Common ion

- (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.

In dilute nitric acid, the following reaction occurs



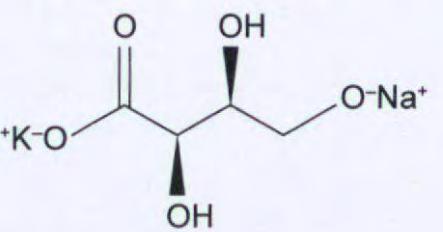
When $\text{Pb}(\text{NO}_3)_2(s)$ is being dissolved into its soln, the following equilibrium occurs: $\text{Pb}(\text{NO}_3)_2(s) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq})$. Although there is a common ion, NO_3^- , the common ion effect that would otherwise decrease solubility (as higher $[\text{NO}_3^-]$, according to Le Chatelier's principle, would cause reverse rxn to be favored to consume NO_3^-) is not considered. Since HNO_3 is a strong acid, there is a low pH (and is a high $[\text{H}_3\text{O}^+]$). This reacts with any $[\text{OH}^-]$ to consume it in the following



Extra space

- (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.

heat ✓ 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.

The first condition for the reaction is it being heated to 70°C . This increases the kinetic energy of H_2O_2 and KNaTar particles, which does 2 things. First it means more particles have enough energy to overcome the activation energy of the reaction, increasing amount of successful collisions per second. Second, since the particles have a higher kinetic energy, they vibrate at a higher rate. Thus increases the chance of collision (given particles have correct orientation and sufficient energy) as they are moving faster. In turn, the frequency of successful collisions in the given volume increases so thus the rate of reaction has increased.

Co^{2+} ions are oxidised by H_2O_2 to Co^{3+} . Co^{3+} ions act as a catalyst, as their oxidation gets H_2O_2 going and reacting with KNaTar . This is because Co^{3+} provides an alternative reaction pathway with lower activation energy for H_2O_2 and KNaTar and as a result combined with the increase in temperature, more particles are at activation energy (due to an increase in kinetic energy), allowing for more successful reactions per second in the given volume, thus increasing rate of reaction. It is important to note the importance of having both these

things. Before addition of the catalyst, although the temperature was 70°C , the reaction was proceeding very slow as the activation energy wasn't too high for the reaction to occur. Upon addition of the catalyst, the activation energy was lowered and thus the particles could overcome it, thus the reaction rate sped up significantly.

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

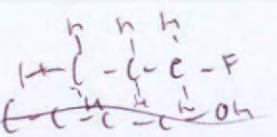
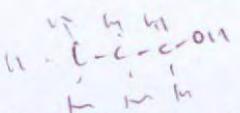
- (i) Draw Lewis structures for the following fluorides of zirconium.

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

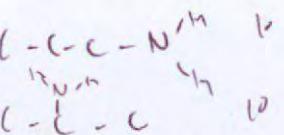
Ion	ZrF_5^-	ZrF_6^{2-}	ZrF_7^{3-}
Lewis structure	 Formal charge on Zr		
Shape	Trigonal bipyramidal	Octahedral	
Bond angles	120° equatorial, 90° axial	90° between all F	

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

For ZrF_6^{2-} , there are 6 regions of electron density about the central atom Zr. For maximum separation, these regions repel into an octahedral arrangement to minimize repulsion. In an octahedral arrangement, the bond angles are 90° between Zr and F for all 6 bonds.



6



Amino

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.

All 4 molecules have temporary dipole-dipole attractions, and permanent dipole-dipole attractions. Of the 4, only 1-fluoropropane does not have H-bonding. Hydrogen bonding is when an H atom is bonded to a highly electronegative atom (O, N, F), and due to the large electronegativity differences a strong positive dipole forms on H. This allows it to form attractions with the lone pairs on and electronegative atom or OTHER molecules.

H-bonding is the strongest type of ~~force~~ intermolecular force. Since there is no F-H bond, 1-fluoropropane doesn't have this so has the weakest sum of intermolecular forces of the 4, and thus less energy is required to overcome these forces so it has the lowest boiling point of -2.50 °C.

The remaining 3 all have similar molar masses so a similar sized electron cloud, thus a similar strength temporary dipole-dipole attraction. Propan-1-ol has H-bonds due to O-H bond, while the amines have H-bonds due to the N-H bond. Since O is more electronegative than N, the O-H bond is more polarized than N-H, so the positive dipole on H in propan-1-ol is stronger than in the amines, giving propan-1-ol stronger H-bonding between molecules. It ∴ has stronger intermolecular forces overall than the 2 amines, thus the most energy is required to overcome these bonds so propan-1-ol has the highest boiling point of 97.2 °C.

The two amines have identical molar masses so the same size electron cloud, thus the same magnitude of induced temporary dipole-dipole attractions. The

Difference in boiling points can be explained by the shape of the molecules (how they pack together). 1-amino propane is more linear than 2-amino propane (which has a protruding NH_2 group on carbon 2), so t-amino propane molecules can pack closer together, meaning there is stronger temporary-dipole-dipole attractions. Thus, 1-amino propane has stronger intermolecular forces than 2-amino propane so more energy is required to overcome the forces, i.e. 1-amino propane has a higher boiling point (68.5°C) than 2-amino propane (31.7°C).

- (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).

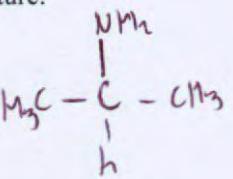
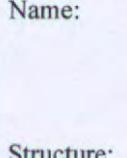
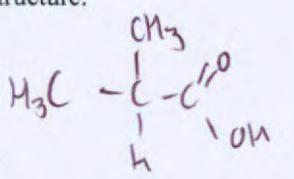
Heptane is a straight chain alkane, so does not have permanent dipole-dipole attractions (as its non-polar) or H -bonding. However all 4 of compounds in (i) have C_2H_5- carbon chains with molar masses of $\sim 60 \text{ g mol}^{-1}$ ($59-62 \text{ g mol}^{-1}$ is the range). Heptane is a much longer, ~~short~~ 7-carbon straight chain molecule with a molar mass of 100 g mol^{-1} (ignoring its large electro-cloud and therefore a stronger temporary dipole-dipole attraction). It also packs better due to a linear shape and balanced polarity so the heptane molecules can be closer together. As a result, its net temporary dipole-dipole attractions are stronger than the ~~sum of the~~ other molecules intermolecular forces, so more energy is required to overcome it so it has a higher boiling point.

- (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: Propan-2-amine 	Name: 	Name: 2-methylpropanoic acid. 

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

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**.

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**.

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

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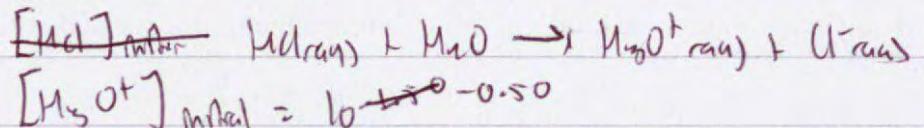
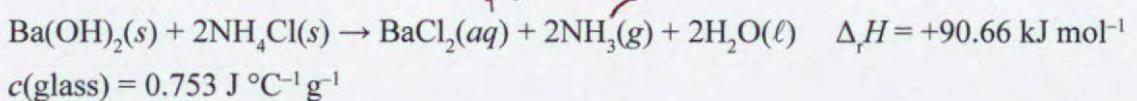
Compound X	Compound Y
Structure:	Structure:

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

- (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.



$$= 0.0316 \text{ mol L}^{-1} \quad 0.316 \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+]_{\text{final}} = 10^{-1.21}$$

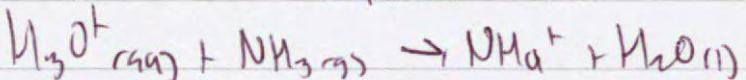
$$= 0.0617 \text{ mol L}^{-1}$$

$$n(\text{H}_3\text{O}^+)_{\text{initial}} = 0.316 + 0.100$$

$$= 0.0316 \text{ mol}$$

$$n(\text{H}_3\text{O}^+)_{\text{final}} = 0.0617 + 0.1$$

$$= 6.17 \times 10^{-3} \text{ mol}$$



$\Delta n(\text{H}_3\text{O}^+) = n(\text{NH}_3)_{\text{reacted}}$. Assume H_3O^+ from NH_4^+ is negligible.

$$\Delta n(\text{H}_3\text{O}^+) = 0.02546 \text{ mol}$$

$$= n(\text{H}_3\text{O}^+ \text{NH}_3)_{\text{reacted}}$$

$$\therefore n(\text{Ba(OH)}_2)_{\text{final}} = \frac{n(\text{NH}_3)}{2} = \frac{0.02546}{2}$$

$$= 0.0127 \text{ mol}$$

$$q = -\Delta H_n$$

$$q = -(90.66) \times 0.0127$$

$$= -1.15 \text{ kJ}$$

$$q = -115 \text{ J}$$

$$q = m \cdot \Delta T$$

$$\Delta T = \frac{q}{mc}$$

$$\Delta T = \frac{-1154}{90.72 \times 0.753}$$

$$\Delta T = -16.9^\circ\text{C} \quad (3sf)$$

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

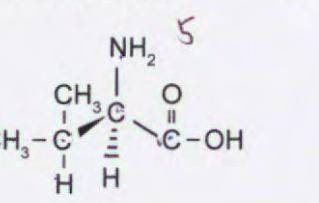
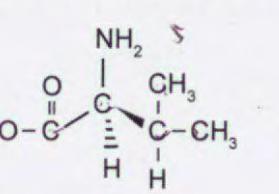
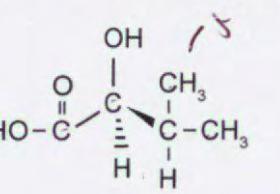
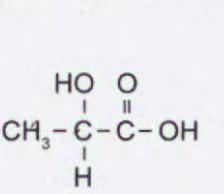
For the reaction to be spontaneous, $\Delta S_{\text{r}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ must be positive. The system goes from 3 moles of highly ordered solid to 2 mol in the reactants ^{to} 2 moles of gas, 1 mole of aqueous solution and 1 mole of liquid. The highly ordered ~~solid~~ lattice has ~~been~~ formed highly disordered and free to move gas, liquid and solution. There is more disorder, so an increase in entropy of the system. ~~This is also~~ ~~an increase in~~

The reaction is endothermic so removes energy from the surroundings, so surrounding particles have a lower kinetic energy and is more slower, decreasing random motion and disorder. The $\Delta S_{\text{surroundings}}$ is less dispersal of energy and disorder so is the entropy of the surroundings increased.

For ΔS_{r} to be positive the increase in ΔS_{system} must offset increase in $\Delta S_{\text{surroundings}}$.

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**.

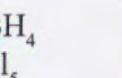
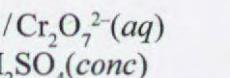
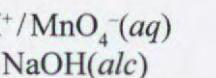
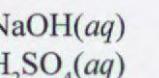
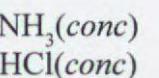
- Compound **F** has the molecular formula $\text{C}_3\text{H}_5\text{OCl}$. It does not produce steamy fumes when added to water, it does not form a silver mirror when added to Tollens' reagent, and it does not decolourise $\text{Br}_2(aq)$. *no aldehyde* *1 DB* *1 DB*
- Compound **G** has the molecular formula $\text{C}_5\text{H}_{10}\text{O}$. It has a branched chain structure, and it exists as a pair of geometric isomers. *alcohol*

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.

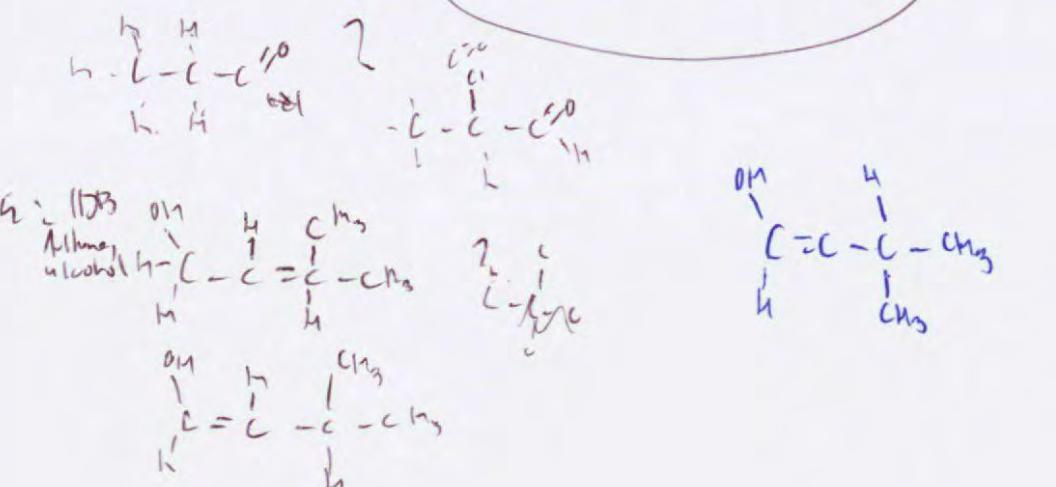
Reagents available:



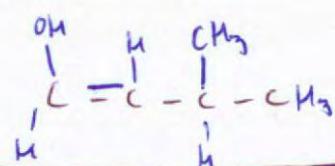
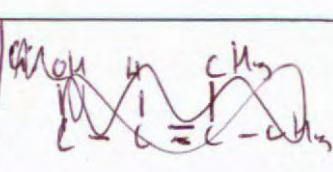
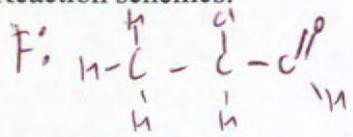
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~~F: 1 DB (acid) Anhydride~~

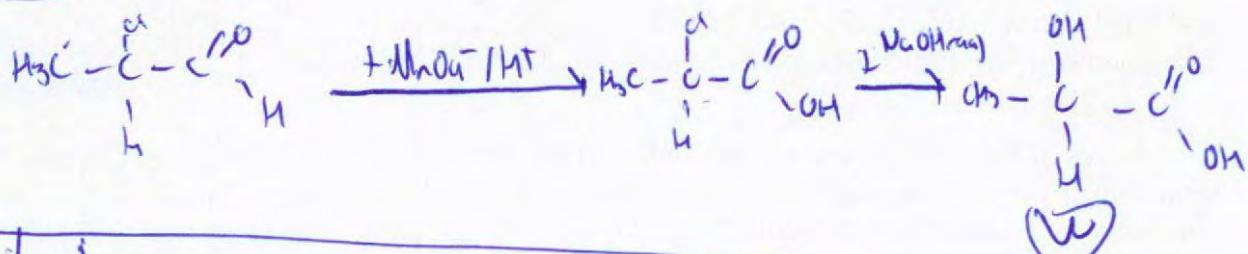
Chloroalkene in benzene or aldehyde



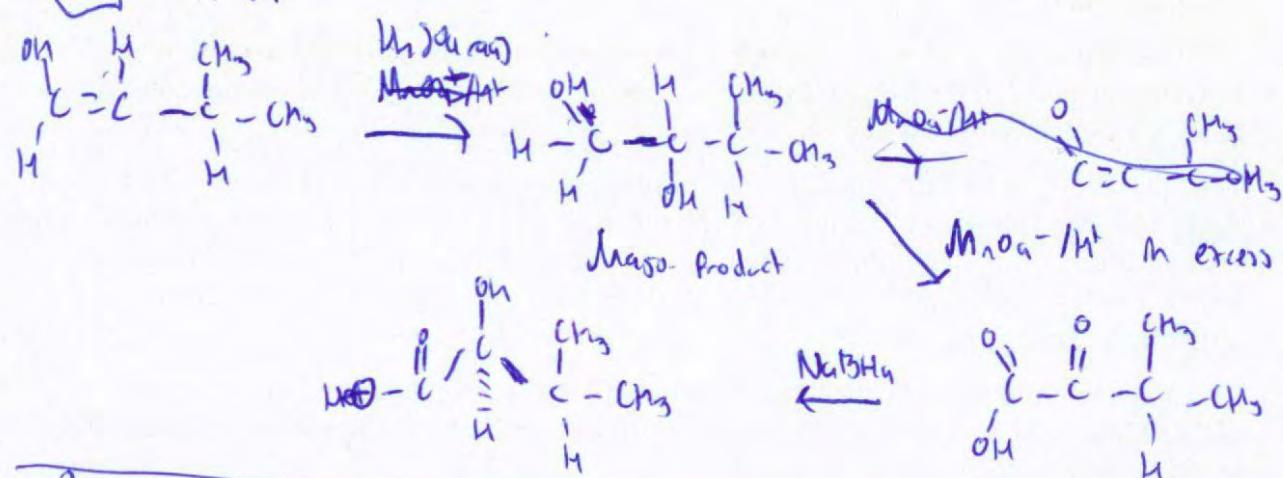
Reaction schemes:



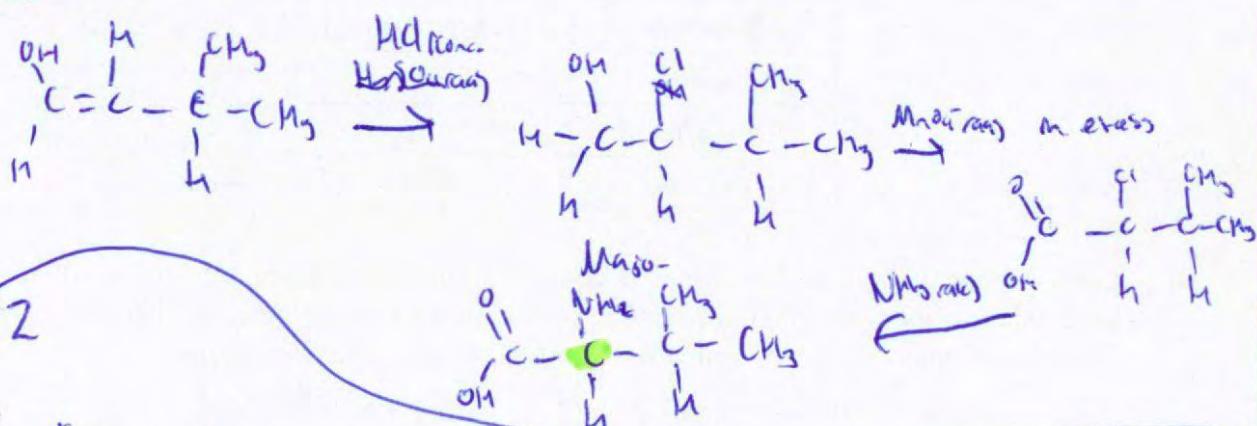
(W) Start w/ F



(X) Start w/ G



(Y) Start w/ H



Z is made same way as Y as they are optical isomers.

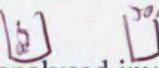
~~but rotate w/ Hg~~

Z is chiral carbon

- (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.

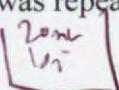
Two halves of the solution, and a blank control, were analysed using an iodometric titration procedure. The primary standard used in the titration was a potassium iodate solution, $KIO_3(aq)$. This solution was prepared by dissolving 0.132 g into 1.00 L of distilled water in a volumetric flask.



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.

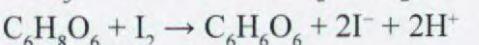
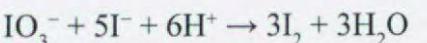
The remaining iodine in the flask was then titrated with a sodium thiosulfate solution, $Na_2S_2O_3(aq)$, and the titration was repeated with further 20.0 mL aliquots until average titres could be determined.



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.

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



$$n(KIO_3) = \frac{m}{M} = \frac{0.132}{214}$$

$$= 6.168 \times 10^{-4} \text{ mol}$$

$$c(KIO_3) = \frac{n}{V} = \frac{6.168 \times 10^{-4}}{1}$$

$$c(KIO_3) = 6.168 \times 10^{-4} \text{ mol L}^{-1}$$

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

Control to find $c(\text{Na}_2\text{S}_2\text{O}_3)$

$$n(\text{I}^-) = 0.02 \times 6.16 \times 10^{-4}$$

$$= 1.232 \times 10^{-5} \text{ mol added}$$

$$n(\text{I}_2)_{\text{produced}} = 3n(\text{I}^-)$$

$$= 3 \times 1.232 \times 10^{-5}$$

$$n(\text{I}_2) = 3.701 \times 10^{-5} \text{ mol. This is the same for each test.}$$

Assuming in the control there is no Vitamin C.

$$n(\text{S}_2\text{O}_3^{2-}) = 2n(\text{I}_2) = 2 \times 3.701 \times 10^{-5}$$

$$= 7.402 \times 10^{-5} \text{ mol}$$

$$c(\text{Na}_2\text{S}_2\text{O}_3) = \frac{7.402 \times 10^{-5}}{0.0272}$$

$$c(\text{Na}_2\text{S}_2\text{O}_3) = 2.721 \times 10^{-3} \text{ mol L}^{-1}$$

Fresh vit C content

$$n(\text{S}_2\text{O}_3^{2-}) = cV = 2.721 \times 10^{-3} \times 0.0161$$

$$= 4.381 \times 10^{-5} \text{ mol}$$

$$n(\text{I}_2)_{\text{remaining}} = \frac{n(\text{S}_2\text{O}_3^{2-})}{2} = \frac{4.381 \times 10^{-5}}{2}$$

$$= 2.191 \times 10^{-5} \text{ mol}$$

$$n(\text{I}_2)_{\text{reacted with C}} = 3.701 \times 10^{-5} - 2.191 \times 10^{-5}$$

$$= 1.5103 \times 10^{-5} \text{ mol}$$

$$n(\text{Vit C})_{\text{new}} = 1.5103 \times 10^{-5} \text{ mol}$$

$$m(\text{Vit C})_{\text{initially in M}} = 1.5103 \times 10^{-5} \times 176.1$$
~~$$= 2.6542.6605 \times 10^{-7} \text{ g}$$~~

$$n(\text{Vit C})_{\text{total}} = 50 \times 1.5103 \times 10^{-5}$$

$$= 7.552 \times 10^{-4} \text{ mol in 1 L solution}$$

$$m(\text{Vit C})_{\text{total}} = nM = 7.552 \times 10^{-4} \times 176.1$$

$$= 0.133 \text{ g}$$

$$= 133 \text{ mg.}$$

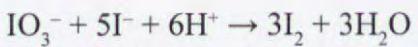
Packet is slightly inaccurate as there is 3mg more.

Degrad % remaining

$$n(\text{S}_2\text{O}_3^{2-}) = 2.721 \times 10^{-3} \times 0.01935$$

(Extra space)

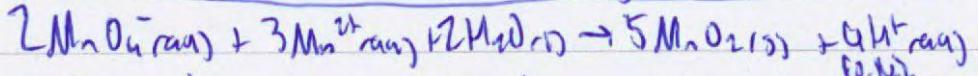
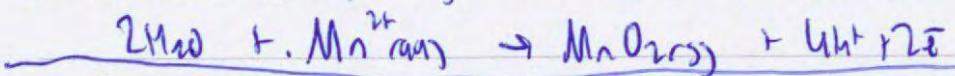
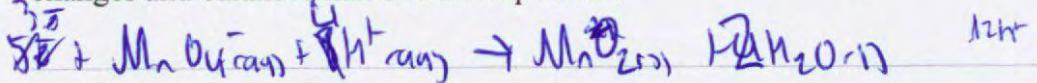
- (ii) In the reaction below, the iodine-containing reactants react by electron-transfer to give the same product.



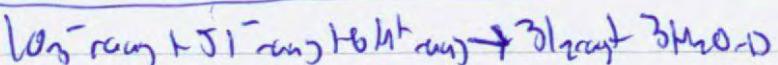
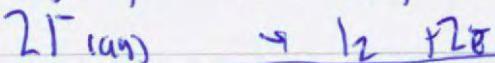
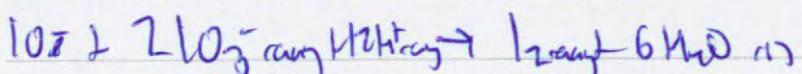
MnO₄

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, $\text{MnO}_2(s)$.

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

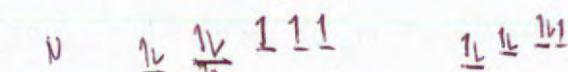


MnO_4^- is the oxidant as the oxidation number of Mn decreases from +7 in MnO_4^- to the Mn in MnO_2 , and a decrease in O.N. corresponds to oxidants. Mn^{2+} is the reductant as the O.N. of Mn increases from +2 in Mn^{2+} to the Mn in MnO_2 and a increase in O.N. is reductant.



IO_3^- is the oxidant as the O.N. of I decreases from +5 in IO_3^- to 0 in I_2 , which corresponds to oxidant. I^- is the reductant as the O.N. of I increases from -1 in I^- to 0 in I_2 , which corresponds to reductant.

More stable 17

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.

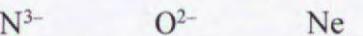
Give a clear definition for the term, and include references to electron arrangements where appropriate. (1.E)

First ionisation enthalpy is the enthalpy change when 1 mole of electrons is removed from one mole of gaseous atom.

Although N and O are both in Period 2, so have the same amount of energy levels (2). O is further to the right so has 1 more proton (so a greater nuclear charge) and 1 more electron (so more repulsive forces). Although this normally would mean the electrostatic force between O's nucleus and valency electron is stronger than in N due to a greater nuclear charge does not give O a higher 1st I.P. than N. The electron arrangement of O is $1s^2 2s^2 2p^4$ so oxygen has 2 half filled 2p orbital and 1 full 2p orbital, while N has an arrangement of $1s^2 2s^2 2p^3$, with 3 half filled 2p orbitals. The 3 half filled 2p orbitals are more stable than the half filled and 1 fully filled 2p orbitals in O, as the fully filled orbital adds significant σ -repulsion compared to 3 half filled orbitals. This means more energy is required to remove an electron from an N $2p$ orbital than a O $2p$ due to stability, thus N has a higher 1st I.P. than O.

* So experience the same amount of shielding from inner shells

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



- (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.

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

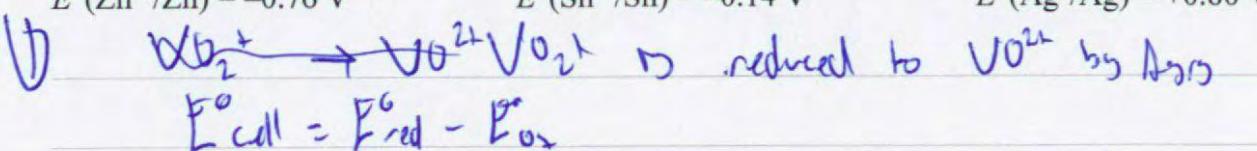
$$E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$$

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

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

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

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



$$E_{\text{cell}}^{\circ} = E^{\circ}(VO_2^+ / VO^{2+}) - E^{\circ}(As^+ / As)$$

$$\approx 1.00 - 0.10$$

$\approx 0.70V$. $E_{\text{cell}}^{\circ} > 0$ so spontaneous. VO^{2+} ions cannot

E° is reduced by $As^{(s)}$ as As is too weak an reductant

$$E_{\text{cell}}^{\circ} = E^{\circ}(VO^{2+} / V^{3+}) - E^{\circ}(As^+ / As)$$

$$\approx 1.03V - 0.10$$

$\approx 0.93V$. Not spontaneous so only VO^{2+} ions remain

Final colour is blue, oxidation number of V is +4.

(2) $E_{\text{cell}}^{\circ} = E^{\circ}(NO_2^+ / NO^{2+}) - E^{\circ}(S_n^{2+} / S_n)$

$$\approx 1.00 - 0.10$$

$\approx 0.90V$. $E_{\text{cell}}^{\circ} > 0$ so VO_2^+ is reduced by S_n to VO^{2+}

$$E_{\text{cell}}^{\circ} = E^{\circ}(VO^{2+} / V^{3+}) - E^{\circ}(S_n^{2+} / S_n)$$

$$\approx 1.03V - 0.10$$

$\approx 0.93V$. $E_{\text{cell}}^{\circ} > 0$, so VO^{2+} is reduced to V^{3+}

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

$$\approx -0.76 - (-0.10)$$

$\approx -0.66V$. $E_{\text{cell}}^{\circ} < 0$, so V^{3+} is not reduced to V^{2+} by S_n .

Final colour is green, oxidation number of V is +3.

(3) $E_{\text{cell}}^{\circ} = E^{\circ}(VO_2^+ / NO^{2+}) - E^{\circ}(Z_n^{2+} / Z_n)$

$$\approx 1.00 - 0.76$$

$\approx 0.24V$. $E_{\text{cell}}^{\circ} > 0$ so VO_2^+ is reduced by Z_n to VO^{2+}

$$E_{\text{cell}}^{\circ} = E^{\circ}(VO^{2+} / V^{3+}) - E^{\circ}(Z_n^{2+} / Z_n)$$

$$\approx 1.03V - (-0.76)$$

$\approx 1.79V$. $E_{\text{cell}}^{\circ} > 0$ so VO^{2+} is reduced to V^{3+} by Z_n

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

$\approx -0.76 - (-0.76)$

$$E_{\text{cell}}^{\circ} = 0.50V$$
. $E_{\text{cell}}^{\circ} > 0$, so V^{3+} is reduced to V^{2+} by S_n .

V^{2+} is the only ND remaining, so final colour is violet. Oxidation

Extra space

(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.

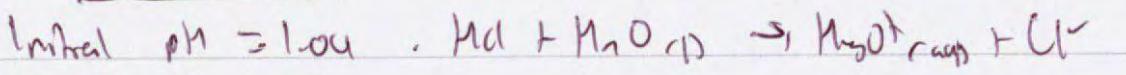
(i) Carry out calculations to determine key points on the titration curve for each experiment.

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.

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

Titration ① - HCl

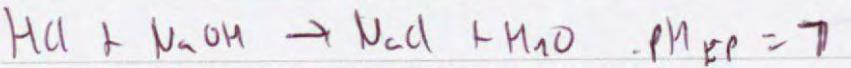


$$[\text{H}^+] = [\text{Na}^+ \text{OH}^-] \\ = 10^{-1.04}$$

$$= 0.0912 \text{ M}$$

$$n(\text{HCl})_{\text{initial}} = 0.0912 \times 0.03$$

$$= 2.736 \times 10^{-3} \text{ mol}$$



$$n(\text{NaOH})_{\text{equivalence}} = 2.736 \times 10^{-3}$$

$$V(\text{NaOH})_{\text{at E.P.}} = \frac{n}{c} = \frac{2.736 \times 10^{-3}}{0.0886} \\ = 0.0309 \text{ L (30.9 mL)}$$

Halfway = 15.4 mL added

$$n(\text{NaOH})_{\text{added}} = 0.0450 \times 0.0986 \\ = 1.368 \times 10^{-3} \text{ mol}$$

$$n(\text{HCl})_{\text{remaining}} = 2.736 \times 10^{-3} - 1.368 \times 10^{-3} = 1.368 \times 10^{-3}$$

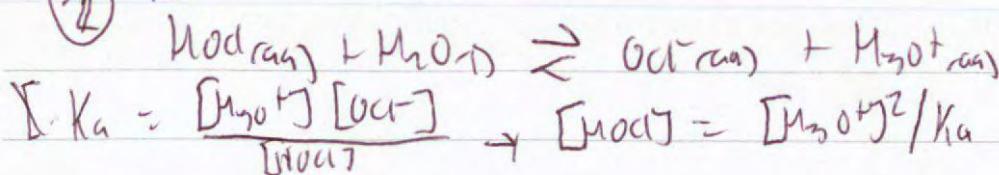
$$[\text{H}^+] = -\log [\text{Na}^+ \text{OH}^-] = \frac{1.368 \times 10^{-3}}{0.0450} \\ = 3.030 \text{ M} \approx 0.0886 \text{ M}$$

$$\text{pH} = -\log(0.0886) = 1.52 + 0.51 = 2.03$$

Excess of 10 mL base

$$[\text{OH}^-] = \frac{0.01 \times 0.0986}{0.0708} \\ = 0.0125 \text{ M}$$

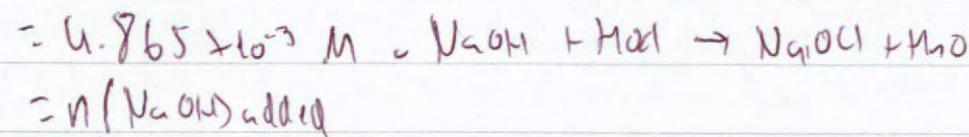
$$\rightarrow \text{pOH} = -\log 0.0125 \quad | \quad \text{pH} = 12.1 \\ -1.9$$

(2) **III**

$$[\text{HOCl}] = (10^{-11.6})^2 / 10^{-7.53}$$

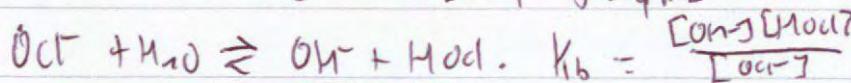
$$= 0.162 \text{ mol/L}$$

$$n(\text{HOCl})_{\text{min.}} = 0.162 \times 0.03$$



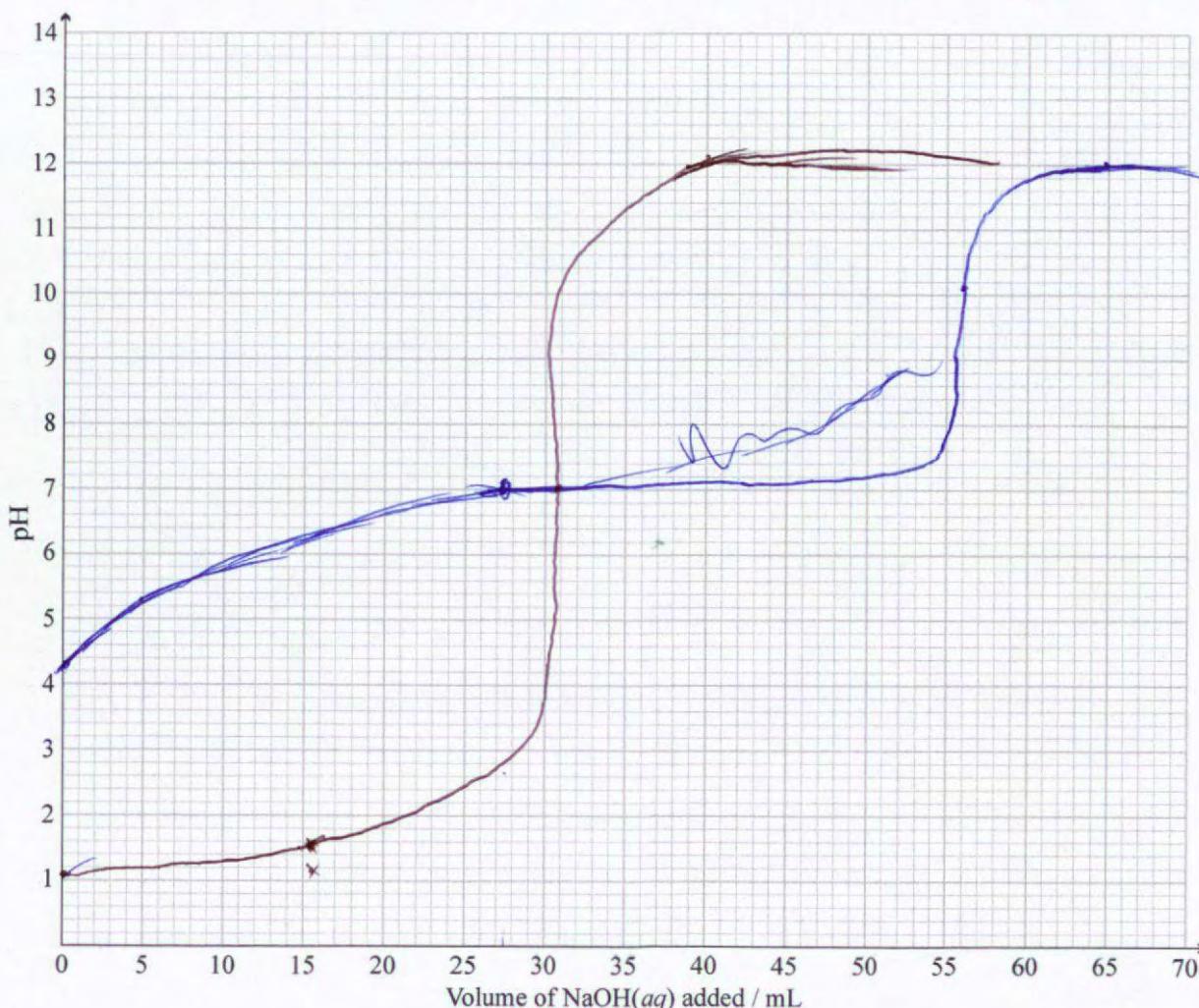
$$V(\text{NaOH})_{\text{c.p.}} = \frac{4.865 \times 10^{-3}}{0.0886}$$

$$= 0.0549 \text{ L} \rightarrow 54.9 \text{ mL}$$



$$[\text{OH}^-] = \sqrt{K_b[\text{OCl}^-]}$$

Extra space



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.

1ai $Q_s > K_s$ so a Pb(OH)_2 precipitate forms - In beaker 1 a white solid can be appeared forming

Beaker 1 ($C = \frac{n}{V}$)

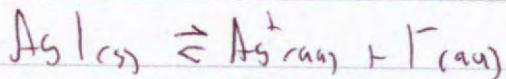
$$[K\text{I}] = \frac{0.025 > 0.00167}{0.06}$$

$$= 6.458 \times 10^{-4} \text{ mol L}^{-1}$$

$$= [\text{I}^-]$$

$$[\text{AgNO}_3] = \frac{V}{V} = \frac{0.035 \times 0.0147}{0.06}$$

$$= 8.342 \times 10^{-3} \text{ mol L}^{-1}$$



$$K_s = [\text{As}^+] [\text{I}^-]$$

$$Q_s = 6.458 \times 10^{-4} \times 8.342 \times 10^{-3}$$

$$= 5.30 \times 10^{-6} (\gg K_s)$$

$Q_s > K_s$, so a AgI precipitate forms. In beaker 2, a yellow precipitate can be observed to form.

1aii This greatly decrease $[\text{OH}^-]$, which prevents a Pb(OH)_2 precipitate from forming as it is a very insoluble salt ($K_s \approx 8.00 \times 10^{-17}$). This ~~removes the amount of Lead ions~~ some would be consumed, therefore less accurate results would be observed.

3b $n(\text{S}_2\text{O}_3^{2-}) = 4.096 \times 10^{-4} \text{ mol}$

 $n(\text{I}_2)_{\text{remained}} = \frac{4.096 \times 10^{-4}}{2}$
 $= 2.047 \times 10^{-5} \text{ mol}$

$$n(\text{I}_2)_{\text{reacted}} = 3.701 \times 10^{-5} - 2.047 \times 10^{-5}$$
 $= 1.654 \times 10^{-5} \text{ mol}$

$$n(\text{VIL})_{20\text{mL}} = 1.654 \times 10^{-5} \text{ mol}$$

$$n(\text{VIL})_{\text{total}} = 1.654 \times 10^{-5} \times 50$$

QUESTION
NUMBER

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

$$3b \quad n(Vit \text{ C}) = 6.021 \times 10^{-4}$$

$$m(Vit \text{ C})_{\text{total}} = 6.021 \times 10^{-4} \times 176.1 \\ \approx 0.106 \text{ g}$$

$$\approx 106 \text{ mg}$$

$$\% \text{ remaining} = \frac{106}{133} \times 100$$

$$= 79.7\% (\text{3sf}) \text{ remaining}$$

$$4c \quad [OH^-] = \sqrt{\frac{1 \times 10^{-14}}{1.001 \times 10^{-3}} \times \frac{1.4 \times 10^{-5} \times 10^{-3}}{0.0849}}$$

$$\approx 1.34 \times 10^{-11} \rightarrow pOH = -\log 1.34 \times 10^{-11}$$

$$pOH = 3.86$$

$$pH_{\text{ep}} = 10.1$$

$$V_{\text{1/2 ep}} = 27.45 \text{ mL}$$

10mL of added base

$$[OH^-] = \frac{0.01 + 0.0786}{0.0449}$$

$$\approx 0.33 \times 10^{-3} \rightarrow pOH = -\log 0.33 \times 10^{-3}$$

$$pOH = 2.63$$

$$pH = 14 - 2.63 = 11.37, 12.0$$

Ub number of V is +2.