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SCHOLARSHIP EXEMPLAR



Mana Tohu Mātauranga o Aotearoa
New Zealand Qualifications Authority

Scholarship 2024 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 will 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) Hydrated salts contain a discrete number of molecules of water as part of their crystal structure (as opposed to anhydrous salts, which have no water as part of their crystal structure).

Epsom salts, a common health supplement, are hydrated magnesium sulfate crystals, $\text{MgSO}_4 \cdot n\text{H}_2\text{O}(s)$.

To determine the value for n in the crystal structure, a student carried out the following:

- An accurately weighed sample of the hydrated salt was heated strongly for 5 minutes in a crucible with the lid partially off.
- After heating, the lid was replaced, and the crucible with its lid was cooled and weighed.
- The heating, cooling, and weighing process was then repeated until the mass remained constant.

The results are summarised below:

Item	Mass (g)
Crucible + lid	23.920
Crucible + lid + hydrated salt	27.712
Crucible + lid + contents after first heating	26.306
Crucible + lid + contents after second heating	25.902
Crucible + lid + contents after third heating	25.775
Crucible + lid + contents after fourth heating	25.775

- (i) Use the results given to determine the whole number value for n in hydrated magnesium sulfate, $\text{MgSO}_4 \cdot n\text{H}_2\text{O}(s)$, and then calculate the mass of Epsom salts required to make a standard solution of a $0.255 \text{ mol L}^{-1} \text{ Mg}^{2+}$ ions in a 250.0 mL volumetric flask.

$$27.712 - 23.920 = 3.792 \text{ g} = \text{initial mass}$$

$$27.712 - 25.775 = 1.937 \text{ g} = \text{final mass}$$

$$3.792 \text{ g} - 1.937 \text{ g} = 1.855 \text{ g H}_2\text{O lost}$$

$$M(\text{H}_2\text{O}) = 16 + 2 = 18$$

$$n = \frac{m}{M} \frac{1.855}{18} = 0.10305 \dots \text{ mol}$$

$$M(\text{MgSO}_4) = 24.3 + 32.1 + 16 \times 4 = 120.4 \quad \frac{1.937}{120.4} = 0.016088 \dots \text{ mol}$$

$$\frac{0.10305}{0.016088} = 6.405 \dots \approx n = 6$$

$$120.4 + 18 \times 6 = 228.4 \text{ g mol}^{-1}$$

$$0.255 \text{ mol L}^{-1} \times 250 \times 10^{-3} \text{ L} = 0.06375 \text{ mol}$$

$$0.06375 \text{ mol} \times 228.4 \text{ g mol}^{-1} = 14.5605 \text{ g} \approx 14.6 \text{ g}$$

- (ii) After the fourth heating cycle, the contents of the crucible were left with the lid off for an hour. When the contents in the crucible were reweighed after this time, the mass had increased.

Discuss the thermodynamics of the process that has occurred over this period of time, including a balanced equation to support your answer.

- (b) An unknown organic compound, Compound A, was produced during a multi-step reaction process. It was determined by elemental analysis to have the molecular formula $C_8H_{16}O_3$.
- (i) IR spectroscopic analysis was carried out on a sample of Compound A. The IR spectra is provided in the resource booklet.

Identify, with reasons, the possible combinations of functional groups which could be present in Compound A.

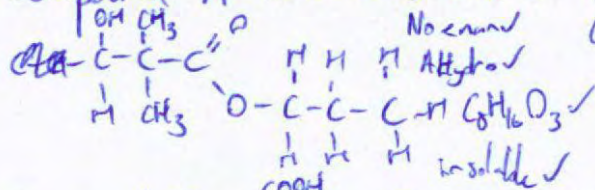
There is a ^{strong} O-H stretch peak between $3600-3300\text{ cm}^{-1}$. This indicates that there is a OH functional group in $C_8H_{16}O_3$. There are also ^{strong} C-H stretch peaks between $2950-2800\text{ cm}^{-1}$, so there are C-H bonds in $C_8H_{16}O_3$. There is a strong peak between $1700-1800\text{ cm}^{-1}$, which could indicate that there is a ^{strong} C=O stretch peak for aldehyde and ketone as they tend to have peaks around 1725 or 1715 . It would not be a COOH functional group as the O-H peak is symmetrical. It would also not be acyl chloride because there is no Cl, and not Amide because there is no N. There may be an ester functional group as there are strong peaks at $1750-1735\text{ cm}^{-1}$ and $1260-1160\text{ cm}^{-1}$.

- (ii) Compound A was reacted to form a range of other compounds, which were given the labels Compounds B-F. None of A-F rotated plane-polarised light. No enantiomers
- Compound A was not water-soluble, and did not change the colour of damp red or blue litmus paper. No acid or Amine/Amide
 - Compound A reacted with dilute H_2SO_4 under reflux to produce Compounds B and C, which were separated by distillation. Acidic Hydrolysis
 - Compounds B and C were both water-soluble. Compound B had a molar mass of 118 g mol^{-1} , and Compound C had a molar mass of 60 g mol^{-1} .
 - Compound B did not react on heating with concentrated H_2SO_4 . No elimination or double bond
 - When Compound B was reacted with $H^+/Cr_2O_7^{2-}$, it gave Compound D, with the molecular formula $C_5H_8O_4$. Oxidation
 - Both Compounds C and D were treated separately with $SOCl_2$ to give Compounds E and F respectively. Compound F reacted violently with water, while Compound E did not. Formed Halide H_2O Soluble Chloride

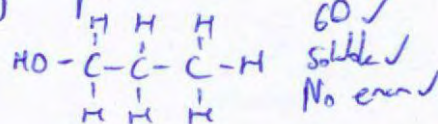
Use the information provided to identify the structures of Compounds A-F.

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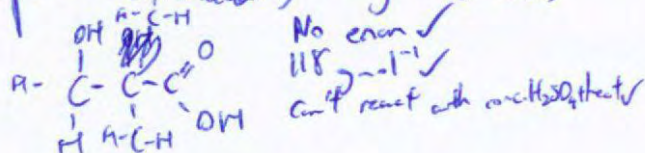
Compound A (insoluble) $C_8H_{16}O_3$



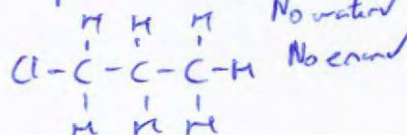
Compound C (Alcohol) $C_6H_{12}O$



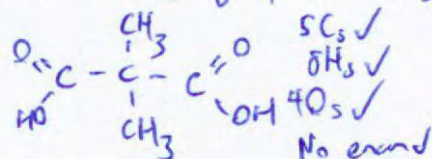
Compound B (Alcohol) $C_5H_{10}O_3$



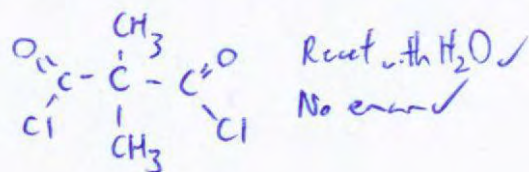
Compound F (Chloroalkane) C_4H_9Cl



Compound D - $C_5H_8O_4$ (COOH)



Compound F - Violet Water (Acyl Chloride)



All no enantiomers

Compound A $ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{HO} - \text{C} - \text{C} - \text{C} = \text{O} \\ \quad \quad \\ \text{H} \quad \text{H} - \text{C} - \text{H} \quad \text{O} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $	Compound B $ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{HO} - \text{C} - \text{C} - \text{C} = \text{O} \\ \quad \quad \\ \text{H} \quad \text{H} - \text{C} - \text{H} \quad \text{OH} \end{array} $
Compound C $ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{HO} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $	Compound D $ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{O} = \text{C} - \text{C} - \text{C} = \text{O} \\ \quad \quad \\ \text{HO} \quad \text{H} - \text{C} - \text{H} \quad \text{OH} \\ \\ \text{H} \end{array} $
Compound E $ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{Cl} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} $	Compound F $ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{O} = \text{C} - \text{C} - \text{C} = \text{O} \\ \quad \quad \\ \text{Cl} \quad \text{H} - \text{C} - \text{H} \quad \text{Cl} \\ \\ \text{H} \end{array} $

(iii) ^{13}C NMR spectra for THREE of Compounds A-F are provided in the resource booklet.

Identify, with brief reasons, which of Compounds A-F could have produced the three spectra provided.

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Spectrum 1:

Compound B would've produced spectrum 1. Compound B is the only compound out of the 6 to have 4 unique Carbon Environments. To confirm it's Compound B, there is a peak between 185-180 ppm, which falls under the range of most acids, with peaks found around 170-170 ppm, so it confirms there must be a COOH functional group. There is also a peak at 70 ppm, which falls in range of 50-80 ppm for an alcohol functional group, so there must be an alcohol functional group. There are two peaks, one in 45 ppm and between 20-25 ppm. These belong to the CH_3 side chain (20-25 ppm) and 45 ppm is the one

Spectrum 2:

Compound D would've produced spectrum 2. Compound D has 3 unique carbon environments which matches the three peaks of spectrum 2. Since there is a peak around 174 ppm it must have an acid (COOH) functional group as it falls in range of 170-170 ppm for acids. Compound D is the only compound with 3 unique carbon environment that has a COOH functional group so spectrum 2 must belong to compound D. The two other peaks belong to the C bonded adjacent to 2 carbons with COOH (around 49 ppm) and

Spectrum 3:

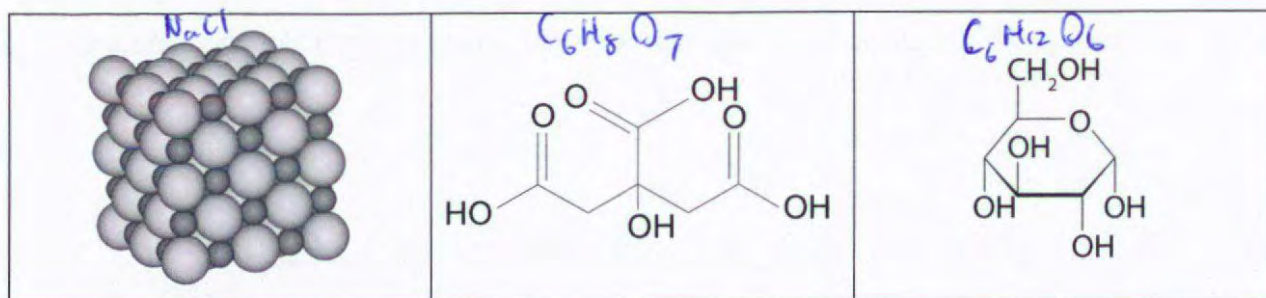
Compound C would've produced spectrum 3. Compound C has 3 unique carbon environments which matches the 3 peaks of spectrum 3. Since there is a peak around 60-65 ppm, it must have an alcohol functional group as it falls in range of the 50-80 ppm for an alcohol functional group. Compound C is the only compound with 3 unique carbon environment that has a C-OH functional group, so spectrum 3 must belong to compound C. The two other

QUESTION TWO

- (a) Rehydration powders are commonly sold as medical treatments for people who are mildly dehydrated, or for use in sports drinks to help replenish water and electrolytes (salts) that have been lost through sweat.

The solution resulting from dissolving the powders in water contains a mixture of substances.

Three compounds that are present in many rehydration powders are sodium chloride, $\text{NaCl}(s)$, citric acid, $\text{C}_6\text{H}_8\text{O}_7(s)$, and glucose, $\text{C}_6\text{H}_{12}\text{O}_6(s)$.



Discuss the particle interactions which occur when these compounds are dissolved in water.

Include clear references to particles and attractive forces.

When NaCl is dissolved in water, the attraction between the Na^+ ion and the partial negative O end of water and the attraction between the Cl^- ion and the partial positive H end of water is greater than the attractive forces between the ionic solid NaCl and the intermolecular attraction between water molecules. Because this attraction force overcomes the self attractions, NaCl is able to dissolve in H_2O .

When citric acid is added to water, the O is able to form hydrogen bonding with the H of the water and the H is also able to form Hydrogen bonding with the O of the water. Since there are 11 sites of possible Hydrogen Bonding formation, these attractions overcome the ~~intermolecular~~ attractions within H_2O itself and citric acid itself, allowing citric acid to be dissolved in water.

(b) Consider the four aqueous solutions below.

Solution A: $0.350 \text{ mol L}^{-1} \text{ CH}_3\text{CH}_2\text{OH}$

Solution B: $0.350 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$

Solution C: $0.350 \text{ mol L}^{-1} \text{ CH}_3\text{COONa}$

Solution D: 0.350 mol L^{-1} of both CH_3COOH and CH_3COONa

$$\text{p}K_a(\text{CH}_3\text{COOH}) = 4.76$$

(i) Using relevant chemical equations, compare the pH of each solution to that of pure water.

Include in your answer, an outline of the relative concentrations of chemical species present in each solution.

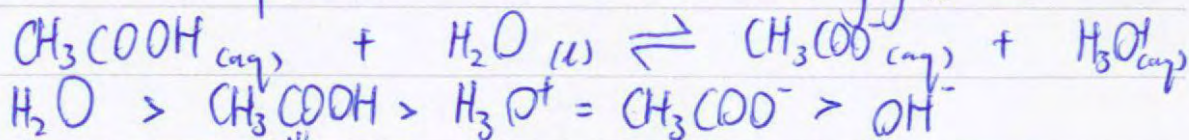
No calculations are necessary.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad K_a = [\text{H}_3\text{O}^+] \quad \text{pH} = 4.76$$

Solution A should have a similar pH when compared to that of pure water. This is because Ethanol is soluble in water, but does not dissociate with water to form any H_3O^+ or OH^- , so the pH remains close to 7.

$\text{H}_2\text{O} > \text{CH}_3\text{CH}_2\text{OH} > \text{solution A} \quad \text{OH}^- = \text{H}_3\text{O}^+ \text{ in solution A}$

Solution B should have a pH close to 2.61, because the solution is filled mostly with Ethanoic Acid which is a weak acid that partially dissociates with water to form H_3O^+ ions, which makes the pH of the solution be much lower than 7, as H_3O^+ concentration is increased. As H_3O^+ is produced, some CH_3COO^- are also produced as it is the conjugate base.

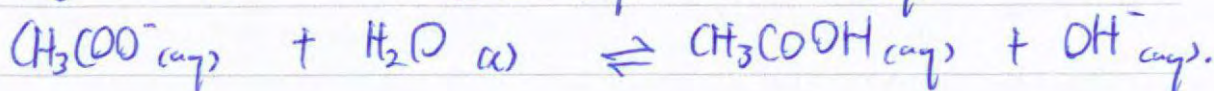
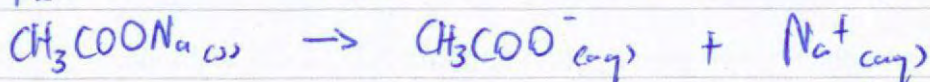
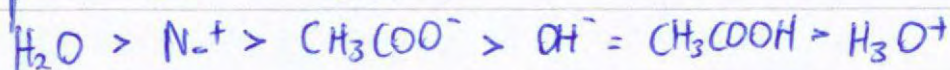


$\text{H}_2\text{O} > \text{CH}_3\text{COOH} > \text{H}_3\text{O}^+ = \text{CH}_3\text{COO}^- > \text{OH}^-$

There is ~~some~~ ^{very little} OH^- due to the K_w dissociation.

Solution C should have a pH greater than 7, because the solution is filled with Sodium Ethanoate, which is a basic salt, causing the pH to be around 9.15. The basic salt fully dissociates in water.

to produce its ions, CH_3COO^- and Na^+ . The CH_3COO^- would further ^{partially} dissociate with water to produce OH^- and CH_3COOH as it is a weak base. There will still be some H_3O^+ present due to dissociation of water.



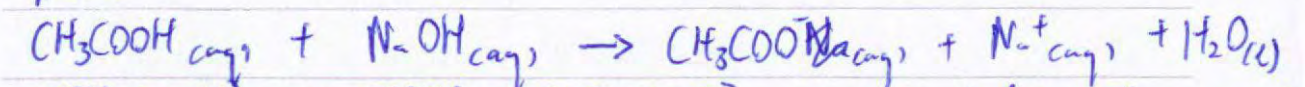
Solution D should have a pH greater than Solution B but less than water as it is a buffer solution of CH_3COOH , which pH of 4.76. The buffer solution contains both

- (ii) 10.0 mL of 0.460 mol L⁻¹ sodium hydroxide solution, $\text{NaOH}_{(aq)}$, was mixed with 45.0 mL of Solution D (0.350 mol L⁻¹ of both CH_3COOH and CH_3COONa).

Calculate the pH of the resulting solution after mixing.

	CH_3COOH	NaOH	CH_3COO^-
n	0.01575 mol	4.6×10^{-3} mol	0.01575 mol
c	0.35 mol L ⁻¹	0.46 mol L ⁻¹	0.35
V	45×10^{-3} L	10×10^{-3} L	55×10^{-3} L

$$n = cV$$



$$n(\text{CH}_3\text{COOH}) = 0.01575 - 4.6 \times 10^{-3} = 0.01115 \text{ mol} / 55 \times 10^{-3} \text{ L} = 0.2027 \text{ mol L}^{-1}$$

$$n(\text{CH}_3\text{COO}^-) = 0.01575 + 4.6 \times 10^{-3} = 0.02035 \text{ mol} / 55 \times 10^{-3} \text{ L} = 0.37 \text{ mol L}^{-1}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad 10^{-4.76} = \frac{[\text{H}_3\text{O}^+] \cdot (0.37 \text{ mol L}^{-1})}{(0.2027 \text{ mol L}^{-1})}$$

$$10^{-4.76} \times \frac{(0.2027)}{(0.37)} = [\text{H}_3\text{O}^+] \quad [\text{H}_3\text{O}^+] = 2.4637 \times 10^{-5} \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = 2.4637 \times 10^{-5} \text{ mol L}^{-1} \quad -\log([\text{H}_3\text{O}^+]) = \text{pH} = 5.021 \dots$$

$$\text{pH} \approx 5.02 \quad (3 \text{ s.f.})$$

- ### Solution A

- ### Solution B

- The student concluded Solution A contained CO_3^{2-} ions, and Solution B contained Cl^- ions.

Use equilibrium principles and balanced chemical equations to justify the observations made during the qualitative analysis.

- (ii) To determine the cations, the student added sodium hydroxide solution, NaOH(aq) , to samples of **A** and **B**, but neither produced a precipitate. The student concluded that the cation in each solution must be sodium ions, Na^+ .

Their teacher noted this was the incorrect result for Solution **B**, and they told the student that it contains either Mg^{2+} or Ba^{2+} ions, and should have formed a hydroxide precipitate.

The student had placed 2 mL of Solution **B** in a test tube and slowly added up to 5 mL of $0.0875 \text{ mol L}^{-1} \text{ NaOH(aq)}$ without getting any precipitate. The teacher repeated the procedure, and the result was the same.

Solution **B** had been prepared by taking 30.0 mL of a 0.100 mol L^{-1} stock solution, diluting it to 150.0 mL using distilled water, before placing it into dropper bottles.

Use calculations to determine the cation and show why no precipitate was formed in Solution **B**.

$$K_s(\text{Ba(OH)}_2) = 3.00 \times 10^{-4} \quad K_s(\text{Mg(OH)}_2) = 7.10 \times 10^{-12}$$

$$\frac{30}{150} \times 0.1 = 0.02 \text{ mol L}^{-1} \text{ of } \text{Ba}^{2+} \text{ or } \text{Mg}^{2+}$$

$$K_s = [\text{Ba}^{2+}][\text{OH}^-]^2 \quad \text{or} \quad K_s = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$Q_s = (0.02) \times (0.0875)^2$$

$$\frac{2}{7} \times 0.02 \text{ mol L}^{-1} = 5.714 \dots \times 10^{-3} \text{ mol L}^{-1}$$

$$Q_s = (5.714 \times 10^{-3}) \times (0.0875 \times \frac{5}{7})^2$$

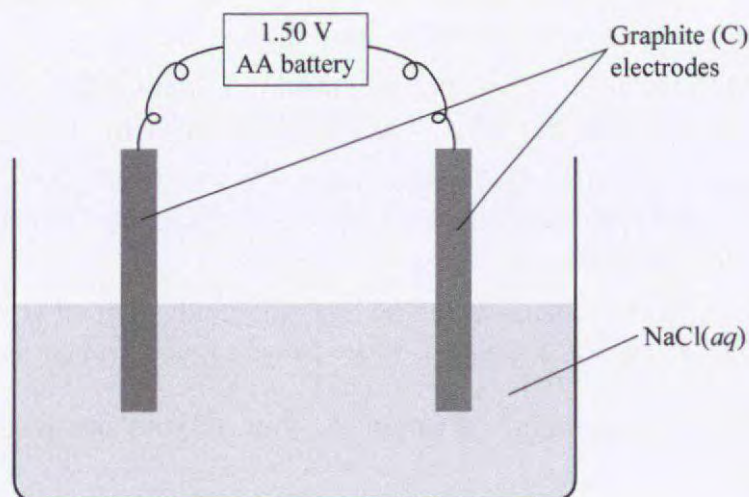
$$Q_s = 2.232 \dots \times 10^{-5}$$

$K_s(\text{Ba(OH)}_2) > Q_s$, so the cation must be Ba^{2+} for no precipitate to be formed, as in this case the solution is yet to be saturated if $K_s(\text{Ba(OH)}_2) > Q_s$.

QUESTION THREE

- (a) Saltwater chlorination, a process involving electrolysis, is an alternative to directly adding chlorine-based chemicals to swimming pool water. In standard electrolysis conditions, the strongest oxidant reacts at one electrode, and the strongest reductant reacts at the other. However in high salt concentrations, electrolysis of salt water, $\text{NaCl}(aq)$, results in the production of aqueous chlorine $\text{Cl}_2(aq)$ instead. This then provides protection to the water.

To replicate this process for a science fair project, a student set up the equipment shown in the diagram below, to demonstrate the chlorination of salt water. Their apparatus included two graphite electrodes, a 1.50 V AA battery, conductive wires, and a concentrated solution of sodium chloride. Once set up, however, no reaction was observed.



Outline modifications the student would need to make to their demonstration to enable the production of chlorine in the solution.

In your answer you should clearly explain all aspects of the electrolytic process, including an outline of the changes occurring at the cathode, the anode, and to the solution, during chlorine production, with support of relevant calculations and equations.

$$E^\circ(\text{Na}^+/\text{Na}) = -2.71 \text{ V}$$

$$E^\circ(\text{H}_2\text{O}/\text{H}_2) = -0.83 \text{ V}$$

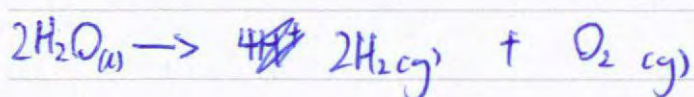
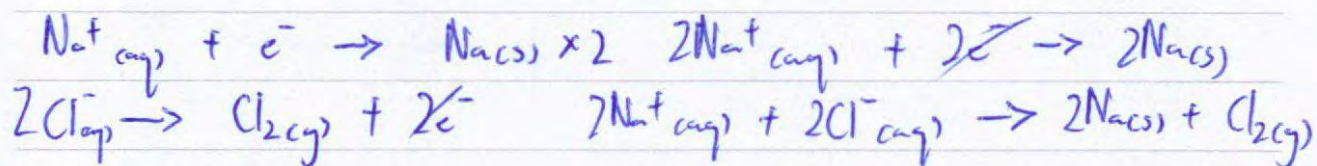
$$E^\circ(\text{Cl}_2/\text{Cl}^-) = +1.36 \text{ V}$$

$$E^\circ(\text{O}_2/\text{H}_2\text{O}) = +0.82 \text{ V}$$

$$E_0 = \text{reduced} - \text{oxidized} \quad E_0 = -2.71 - 1.36 = -4.07 \text{ V}$$

The student would need to increase the voltage of the battery to 4.07 V. This is because for an electrolytic process, a potential difference must be applied to bring about a non-spontaneous reaction. Since E_0 is negative, it means 4.07 V must be applied to allow oxidation of Cl^- and reduction of Na^+ to occur. If the voltage is applied, the positive anode would attract the ^{negative} Cl^- ions.

towards it so that it can be oxidised from Cl^- to Cl_2 gas. The production of Cl_2 gas would cause yellow green gas to be bubbled at the anode. At the negative cathode positive Na^+ ions is being attracted and will be reduced from Na^+ to Na solid. The production of Na solids would cause grey metal to coat the cathode. During electrolysis, ions are being removed from the solution, so when the solution no longer has any more Na^+ or Cl^- ions, H_2O may become reduced to H_2 at the cathode and become oxidised to O_2 gas at the anode, as the voltage is greater than the E° of $-0.83 - 0.82 = -1.65 \text{ V}$, so will oxidise and reduce H_2O as it is the strongest oxidant and reductant left in the solution.



Galvanic - Normal.

Negative Anode

Positive Cathode

Reduction Cathode

Oxidation Anode

Electrolytic - Opposite

Positive Anode

Negative Cathode

- (b) An alternative to saltwater chlorination is to directly add sodium hypochlorite, $\text{NaOCl}(aq)$, to swimming pools.

As part of an investigation into chemical products, a student brought a bottle of pool chlorine into school from home. The pool chlorine was a solution of sodium hypochlorite, $\text{NaOCl}(aq)$; however the label stating the concentration had deteriorated and fallen off the bottle.

The student was tasked with determining the concentration of NaOCl in the bottle.

To analyse the solution, the following method was followed by the student:

Standardisation of $\text{Na}_2\text{S}_2\text{O}_3$

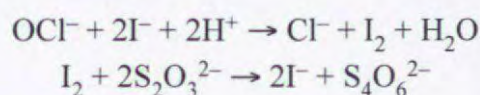
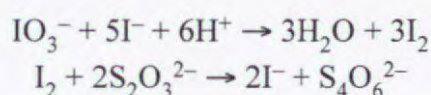
0.533 g of potassium iodate, $\text{KIO}_3(s)$, was dissolved in distilled water in a 100.0 mL volumetric flask. 10.0 mL aliquots of this solution were mixed in conical flasks with excess potassium iodide solution, $\text{KI}(aq)$, and 10 mL of dilute sulfuric acid, $\text{H}_2\text{SO}_4(aq)$. This was then titrated with sodium thiosulfate solution, $\text{Na}_2\text{S}_2\text{O}_3(aq)$, using a starch indicator. The student recorded their data in the first table below.

Pool chlorine analysis

5.00 mL of the pool chlorine solution was pipetted into a 250.0 mL volumetric flask, and filled to the mark. 25.0 mL aliquots of the dilute solution were mixed in conical flasks with excess potassium iodide solution, $\text{KI}(aq)$, and 10 mL of dilute sulfuric acid, $\text{H}_2\text{SO}_4(aq)$. This was then titrated with the same sodium thiosulfate solution, $\text{Na}_2\text{S}_2\text{O}_3(aq)$, using the starch indicator. The student recorded their data in the second table below.

Standardisation of $\text{Na}_2\text{S}_2\text{O}_3$	
Titre	Volume $\text{Na}_2\text{S}_2\text{O}_3(aq)$ (mL)
1	16.50
2	16.45
3	17.10
4	17.45
5	16.40

Pool chlorine analysis	
Titre	Volume $\text{Na}_2\text{S}_2\text{O}_3(aq)$ (mL)
1	18.75
2	18.15
3	18.10
4	17.95
5	18.55



Use the student data provided to determine the concentration of sodium hypochlorite, NaOCl , in the pool chlorine bottle, in g L^{-1} .

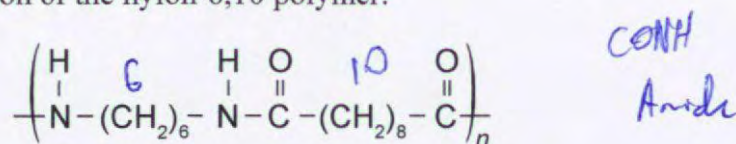
$$M(\text{KIO}_3) = 214 \text{ g mol}^{-1}$$

$$M(\text{NaOCl}) = 74.4 \text{ g mol}^{-1}$$

- (c) Nylons are a family of synthetic polymers. Some types of nylon are combined with other polymers and used in textiles such as clothing and swimwear.

Nylons may be designated nylon-X,Y, where the X and Y are derived from carbon chain lengths in the monomers. An example is nylon-6,10. Nylons designated as nylon-Z, are produced from single monomers with carbon chain length Z.

This diagram shows a section of the nylon-6,10 polymer:



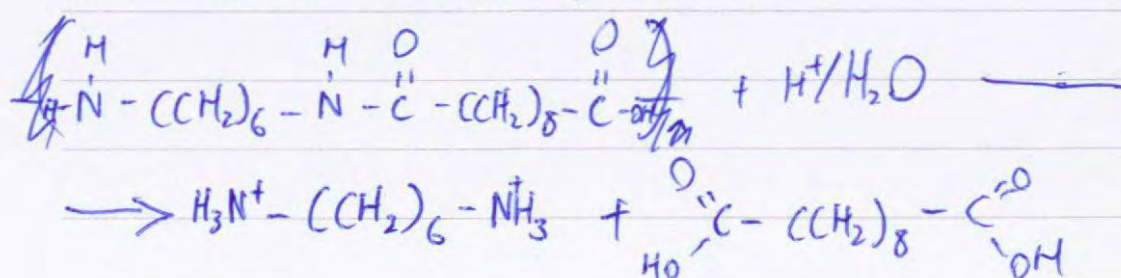
- (i) Nylon-6,10 fabrics may degrade if they are exposed to other chemical substances.

Considering the type of functional groups present in nylon-6,10, discuss which chemical substances may cause damage to such fabrics.

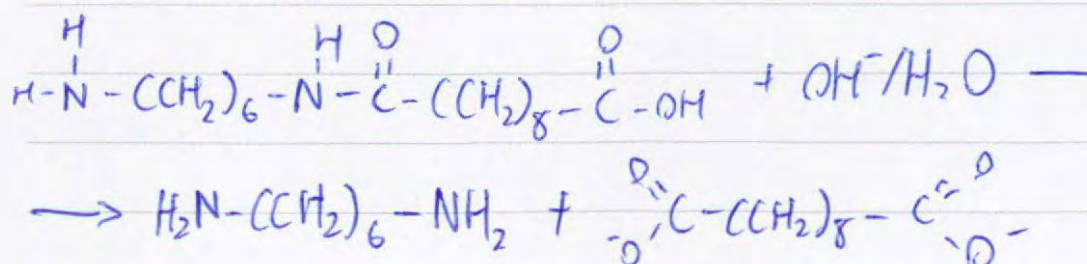
Include structural equations where relevant.

Nylon-6,10 is a polyamide, which is a polymer linked together by many amide linkages. Basic and Acidic Water ($\text{OH}^-/\text{H}_2\text{O}$ or $\text{H}^+/\text{H}_2\text{O}$) will cause damage to such fabrics as it causes the amide linkage to undergo hydrolysis in acidic and basic conditions respectively to form its original monomer as the linkage of the polymer is broken. Protonated monomers are formed in acidic conditions and deprotonated in basic conditions.

Acidic Conditions: (1 unit)



Basic Conditions: (1 unit)



- (ii) Nylon-6,6 and nylon-6 are produced from some of the compounds given in the table.

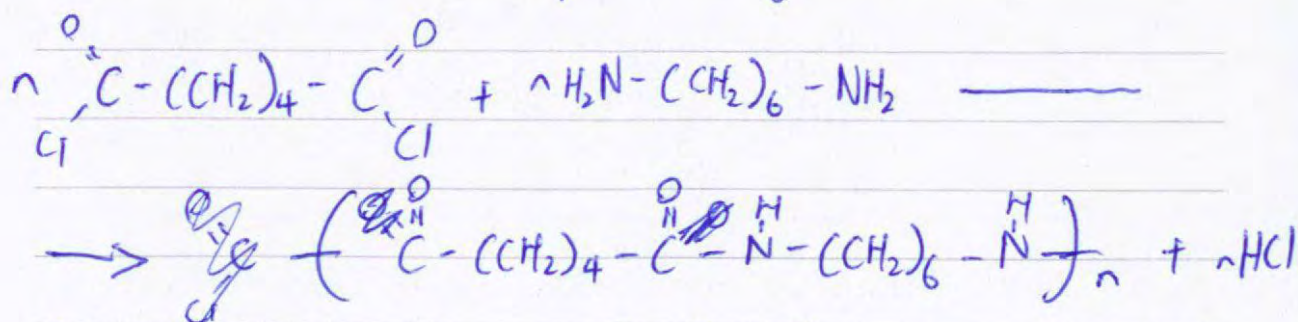
Compound U $\text{HO}(\text{CH}_2)_6\text{OH}$	Compound V $\text{ClOC}(\text{CH}_2)_4\text{COCl}$
Compound W $\text{H}_2\text{N}(\text{CH}_2)_5\text{COCl}$	Compound X $\text{H}_2\text{NOC}(\text{CH}_2)_4\text{CONH}_2$
Compound Y $\text{HOOC}(\text{CH}_2)_4\text{COOH}$	Compound Z $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$

2+V and 2+Y
can both form
Nylon-6,6

Choose monomer(s) which could be used to manufacture these two nylons and justify your decision.

Include a structural equation for the formation of one nylon.

Compound Z and Compound Y or V can be used to produce Nylon-6,6. This is because Nylon-6,6 must mean there are two types of monomers undergoing condensation polymerisation reaction to join up and form a large repeating molecule with a small molecule removed at each amide linkage (HCl if compound V, H_2O if compound X). Because NH_2 can react with COOH or COCl to form an amide linkage, Compound Z can be used with either X or V to produce Nylon-6,6.



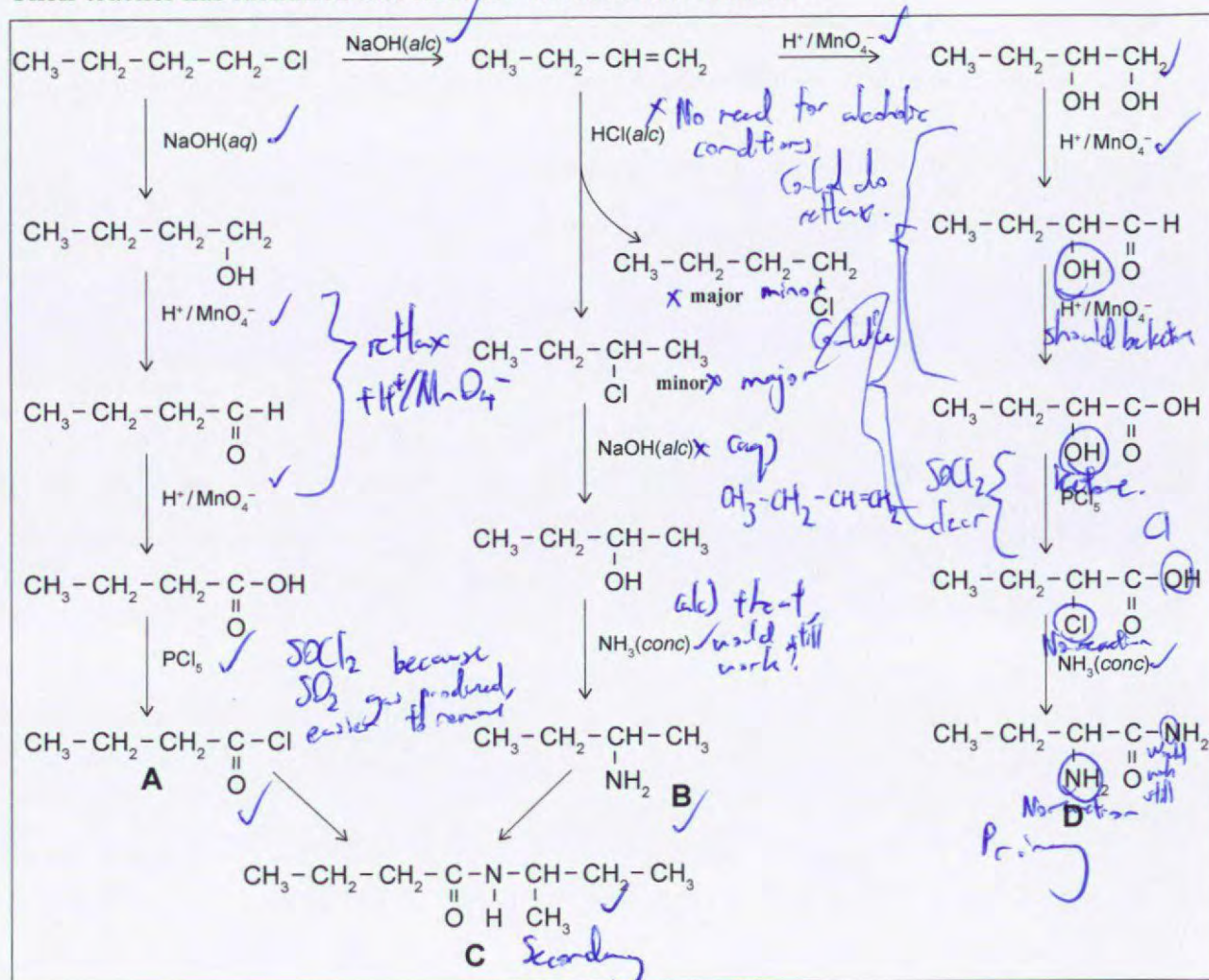
Nylon-6 can be produced with just compound W. Because there is only one monomer, the ends must have two different functional groups (H_2NH_2 and COCl) to allow 1 monomer to react with itself in a condensation polymerisation reaction to produce a long polymer of Nylon-6 (Polyamide) releasing a HCl at each amide linkage formation.

QUESTION FOUR

- (a) Organic chemists apply their knowledge to the development of new reaction pathways for the synthesis of organic compounds.

A student studying organic chemistry has attempted to construct reaction pathways from 1-chlorobutane to a primary and secondary amide, and has described these in the scheme shown below.

Their teacher has identified that there are errors in their scheme.



- (i) Identify and discuss any errors in the reagents or structures in the scheme above. Propose suitable alternative reagents or steps necessary to produce the intended final products.

Four products, A–D, have been labelled to assist in your discussion.

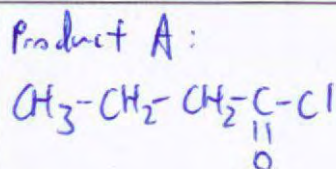
To produce product A, the reagents are correct but 1 step could've been saved by using reflux rather than 2 step oxidation. SOCl_2 would be preferable to PCl_5 as chlorination to acyl chloride with SOCl_2 produces gaseous products which are easier to remove than the products of PCl_5 .

Producing product B would not require (alc) HCl, only HCl(aq) needed for addition. The product used to continue synthesis would be the major and not the minor product. Using NaOH(alc) would cause elimination rather than substitution at Cl so NaOH(aq) should be used instead. If product A and B are produced correctly product C should be fine.

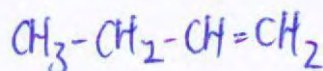
(Read Last Page)

To produce Product D, the 1-chlorobutane should not be eliminated, but should use substitution with NaOH(aq) to produce butan-1-ol. Then, undergo reflux with H^+/KMnO_4 to produce butanoic acid, then chlorinate with SOCl_2 to produce butanoyl chloride, then adding NH_3 (conc) which may require (alc) + heat to produce butanamide. Then, through substitution of Br_2 (aq) in the presence of UV light, get 2-Bromobutanamide to form, and substitute the Br group with NH_2 with the use of conc. NH_3 (alc) + heat. This process wouldn't work although the reagents are correct, because a ketone functional group will be produced when oxidised by H^+/KMnO_4 , resulting in the following chlorination reaction not working and resulting in the

- (ii) Give the structures for the products which would be formed if the synthesis process was carried out using the reagents that the student has proposed in their reaction scheme.

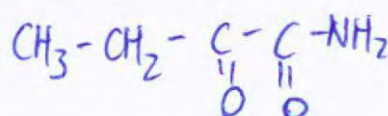


Product B:

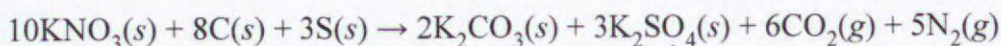


Product C cannot be produced, would still be A and B.

Product D:



- (b) Black powder, a key component in many fireworks, is a mixture of chemicals that react together to release a large amount of heat and gaseous products. Manufacturers of black powder follow recipes that require a careful ratio of reactants to ensure good fireworks displays. A simplified equation representing the reaction of black powder is shown below.



Calculate the energy released when a sample of black powder containing 200.0 g KNO_3 is completely reacted according to the equation given above.

You can assume all other reactants are present in the correct amounts for a complete reaction.

Enthalpy changes (kJ mol^{-1})

$$\Delta_f H^\circ (\text{KNO}_3(s)) = -493.0$$

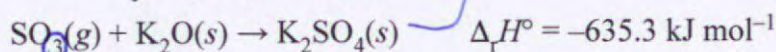
$$\Delta_f H^\circ (\text{K}_2\text{CO}_3(s)) = -1146$$

$$\Delta_f H^\circ (\text{K}_2\text{O}(s)) = -361.0$$

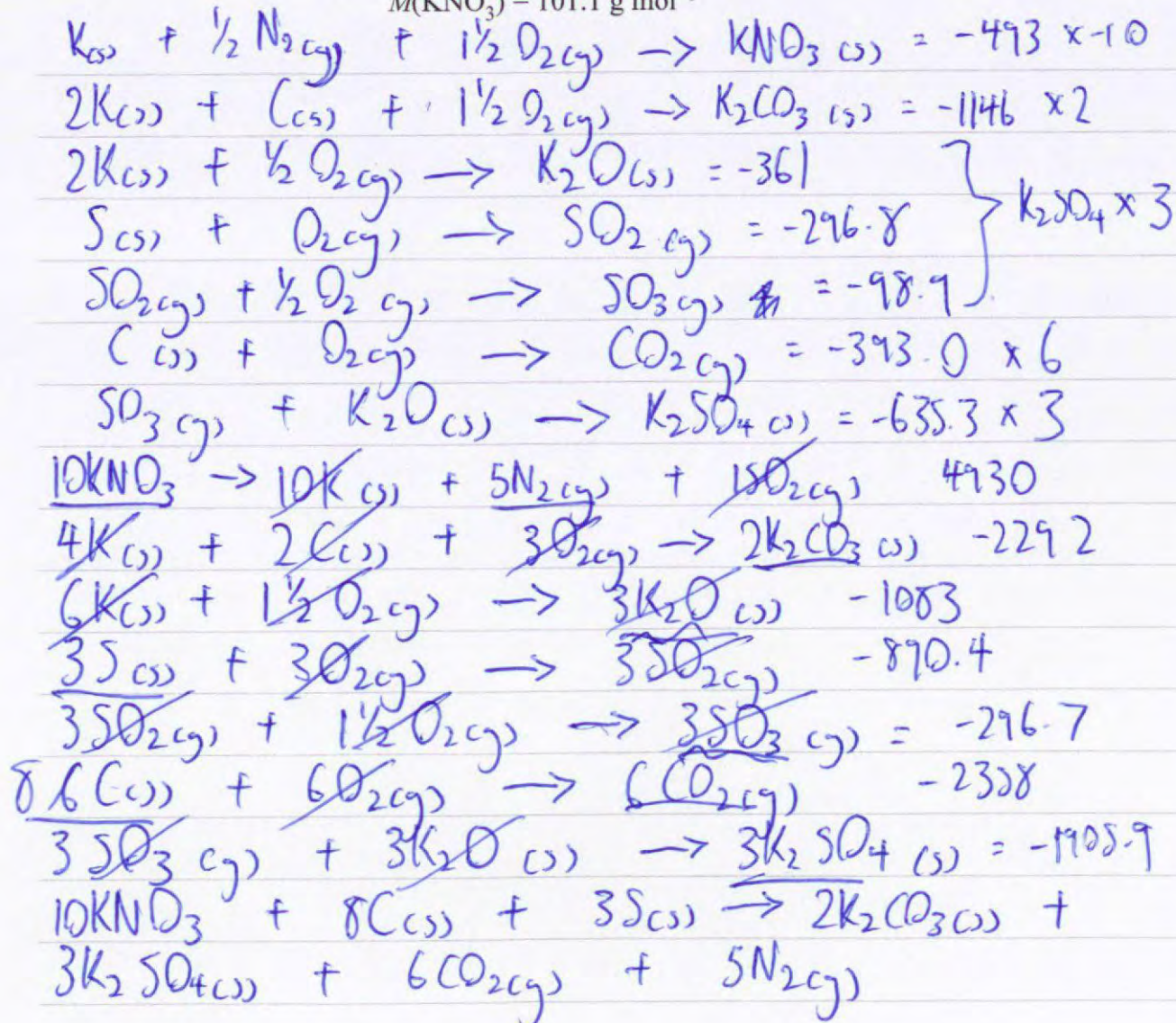
$$\Delta_f H^\circ (\text{SO}_2(g)) = -296.8$$

$$\Delta_c H^\circ (\text{SO}_2(g)) = -98.9$$

$$\Delta_c H^\circ (\text{C}(s)) = -393.0$$



$$M(\text{KNO}_3) = 101.1 \text{ g mol}^{-1}$$



$$\sum \Delta H = \text{reaction}$$

$$\sum \Delta H = 4930 + -2292 + -1083 + -890.4 + -296.7 \\ + -2358 + -1905.9 = -3876 \text{ kJ mol}^{-1}$$

$$\Delta H = \frac{-q}{n}$$

$$n = \frac{m}{M}$$

$$n = \frac{200\text{g}}{101.1\text{g mol}^{-1}}$$

$$n = 1.978 \dots \text{ mol}$$

$$\Delta H \times n = -q$$

$$-3876 \times 1.978 \dots = -7707.2205 \dots$$

$$q = 7707.2205 \dots \approx 7710 \text{ kJ}$$

7710 kJ of energy is released when 200g of KNO_3 is completely reacted.

Question Four continues
on the following page.

- (c) Samples of four chemicals were lined up on a laboratory bench at room temperature. Three of the chemicals were white solids, and one was a colourless liquid.

The chemicals were: silicon dioxide, SiO_2
ethanamide, CH_3CONH_2
methylammonium chloride, $\text{CH}_3\text{NH}_3\text{Cl}$
phosphorus trichloride, PCl_3

Use your understanding of structure and bonding to account for the states of each chemical at room temperature.

Extra space if required.

Write the question number(s) if applicable.

QUESTION
NUMBER

Q1biii) Spectrum 1: bonded to the two carbons bonded to COOH and Alcohol. This peak is shifted further upfield due to being adjacent to the carbons having an Alcohol and COOH functional group, causing the carbon to be more deshielded. The two CH₃s are found in 20-25 ppm as they are less adjacent to the COOH and Alcohol, so peak further downfield.

Spectrum 2: the peak between 20-25 ppm belongs to the CH₃ groups, as they are less deshielded than the carbon bonded to the two carbons with COOH, so their peaks are found further downfield.

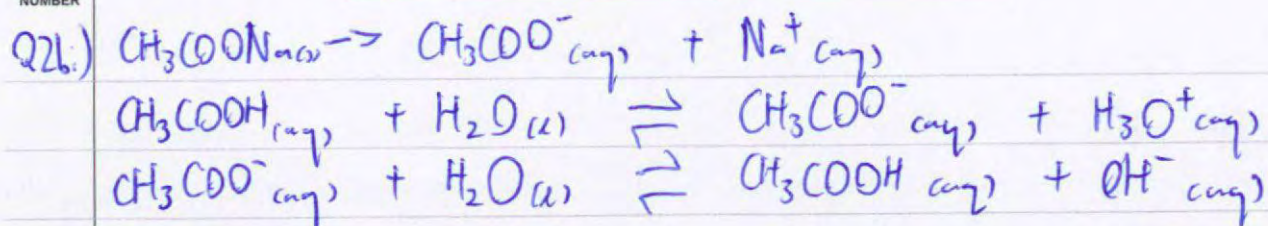
Spectrum 3: peaks belongs to the CH₂ and CH₃. The CH₂ peak is further upfield at around 26 ppm as it is bonded directly to the C bonded to OH, so it is more deshielded than the CH₃ which is further away from the C-OH, so is less deshielded and the peak is found at 10 ppm. These are in range for the saturated alkanes peak found between 40-0 ppm.

Q2b) CH₃COOH and CH₃COONa at equal concentrations so pH = pK_a and the pH is less than water at 7. This is because CH₃COOH is a stronger acid and CH₃COO⁻ is a weaker base, so CH₃COOH dissociates more in water than CH₃COO⁻, producing more H₃O⁺ than OH⁻ ions, resulting in the solution pH being less than 7.

$$\text{H}_2\text{O} > \text{Na}^+ > \text{CH}_3\text{COO}^- > \text{CH}_3\text{COOH} > \text{H}_3\text{O}^+ > \text{OH}^-$$

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

QUESTION
NUMBER



Q2a) When glucose is added to water, like citric acid, the O is able to form Hydrogen Bonding with H of the water and H is also able to form Hydrogen Bonding with O of the water. Hydrogen Bonding is a strong bond type of strongest intermolecular force formed when O is bonded to H. Like Citric Acids there is also 11 possible sites of Hydrogen Bonding to occur. These attractive forces overcome the intermolecular attraction within glucose and water, so allowing glucose to be dissolved in water.

Q4c) After chlorinating the ~~2-chloro~~ butanoic Butanoic Acid with a ketone functional group on carbon 2, the student ~~could~~ ^{should} reduce the ketone group back to an OH group, then chlorinating that with SOCl_2 to form 2-chlorobutanoyl chloride. Then he can add NH_3 conc (alc) + heat to allow NH_2 to be substituted into both Cl to produce 2-amino~~butanoyl~~ butanamide.

93102

Scholarship

Subject: Chemistry

Standard: 93102

Total score: 20

Q	Score	Marker commentary
1	5	a) Formula and mass incorrect. b) Six structures drawn correctly. Peaks in ir spectrum linked to bonds and possible functional groups. Signal in ^{13}C nmr linked to carbon environments.
2	5	a) Describes interactions between NaCl and water. Identifies hydrogen bonding between citric acid and glucose and water. The pH of all four solutions is explained using equations and relative concentrations. The pH of a mixture is calculated. b) Q value calculated correctly and a reason for Ba^{2+} given but Mg^{2+} not eliminated. c)
3	5	a) For the incorrect cell observations, equations, E_{cell} value and energy requirement are given. b) No response. c) Acidic and basic hydrolysis explained with the correctly drawn products. Correct monomers identified and one structural equation drawn. Explained that monomer W has two different functional groups.
4	5	a) Identifies three of the possible errors and correctly draws the products of the given scheme. b) Calculates the energy released a factor of ten error (i.e. 7710kJ compared to 771kJ). c) No response.