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SCHOLARSHIP



Mana Tohu Mātauranga o Aotearoa
New Zealand Qualifications Authority

Scholarship 2025 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 2–28 in the correct order and that none of these pages is blank.

Do not write in the margin (✂). 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) Sodium hydrogen carbonate, $\text{NaHCO}_3(s)$, and citric acid, $\text{H}_3\text{Cit}(s)$, are used in fizzy vitamin tablets. Once a tablet is dropped into a glass of water, a spontaneous reaction is observed, resulting in the formation of bubbles of gas which mix the contents of the tablet throughout the solution, and there is a decrease in the temperature of the solution.

- (i) Discuss the entropy changes occurring during this reaction.

Include a balanced chemical equation in your answer.

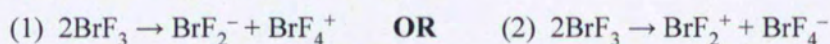
When the tablet is dropped into the water, both $\text{NaHCO}_3(s)$ and $\text{H}_3\text{Cit}(s)$ dissociate completely to form aqueous ions:
 $\text{NaHCO}_3(s) \rightarrow \text{Na}^+_{(aq)} + \text{HCO}_3^-_{(aq)}$ and $\text{H}_3\text{Cit}(s) \xrightarrow{+\text{H}_2\text{O}_{(l)}} \text{H}_3\text{O}^+_{(aq)} + \text{H}_2\text{Cit}^-_{(aq)}$.
 This means the entropy (S) of the system increases as the ^{ordered} solid particles become more disordered aqueous ions. Then, the ions react: $\text{Na}^+_{(aq)} + \text{HCO}_3^-_{(aq)} + \text{H}_3\text{O}^+_{(aq)} + \text{H}_2\text{Cit}^-_{(aq)} \rightarrow \text{NaH}_2\text{Cit}_{(aq)} + 2\text{H}_2\text{O}_{(l)} + \text{CO}_2(g)$, where the $\text{CO}_2(g)$ is observed as the formation of gas bubbles. The solution decreases in temperature which means the reaction is endothermic, removing energy from the surroundings and therefore surrounding particles become less disordered; $S_{\text{surr.}}$ decreases. The dissolving of the tablet is a spontaneous reaction which means the overall entropy must increase. This means that the increase in $S_{\text{sys.}}$ must outweigh the decrease in $S_{\text{surr.}}$ giving $S_{\text{sys.}} + S_{\text{surr.}} = S_{\text{total}}$ which increases. $S_{\text{sys.}}$ outweighs $S_{\text{surr.}}$ as the contents of the tablet are mixed throughout the solution, meaning there is a greater dispersal of energy and matter.

- (ii) Explain why a reaction is only observed once the tablet is dissolved in water.

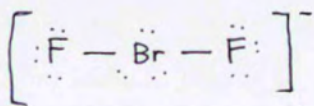
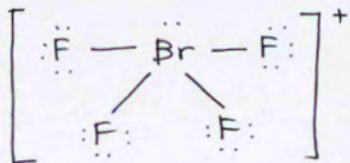
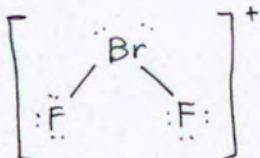
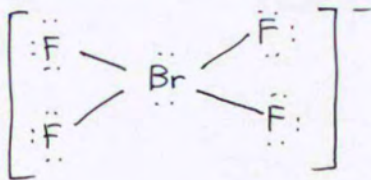
When $\text{NaHCO}_3(\text{s})$ and $\text{H}_2\text{Cit}(\text{s})$ are in solid form, there are strong ionic bonds between the atoms. Only when they are dissolved in water can the water pull away each separate ion as the solute-solvent attractions overcome the solvent-solvent and solute-solute attractions. Once the ions are in solution, they can then react with one another by colliding in the right orientation with sufficient energy to overcome the activation energy requirement of the reaction.

- (b) Pure bromine trifluoride, BrF_3 , can conduct electricity in the liquid form, owing to its ability to undergo autoionisation. This involves the reaction of two BrF_3 molecules to form ions.

Two proposed reactions for the autoionisation are:



- (i) Predict, with support of Lewis diagrams, the shapes and F-Br-F bond angles for the four different ions which could be produced during autoionisation.

BrF_2^- Lewis diagram: 	BrF_4^+ Lewis diagram: 
Shape/bond angle: Linear, 180°	Shape/bond angle: See-saw, $90^\circ/120^\circ$
BrF_2^+ Lewis diagram: 	BrF_4^- Lewis diagram: 
Shape/bond angle: bent, 109.5° → a little less than this	Shape/bond angle: square planar, 90°

- (ii) Each reaction involves the transfer of a fluorine ion.

Justify which reaction, (1) or (2), is more likely to give the ions responsible for the conductivity.

- (iii) The two possible shapes for BrF_3 molecules are T-shaped or trigonal planar.

Explain which of the two shapes is correct, and justify whether the BrF_3 molecules will be polar or non-polar.

BrF_3 has 5 regions of e^- density around the central Br atom, 3 of which are $\overset{\delta+}{\text{Br}}-\overset{\delta-}{\text{F}}$ polar covalent bonds due to the electronegativity difference between them (F is more electronegative) and 2 which are lone pairs.

~~One~~ This gives the two possible shapes: T-shaped or trigonal planar, from the trigonal bipyramid parent geometry. However, lone pairs occupy more space, which means that they tend to exist in the equatorial plane rather than the axial plane^{as they are 120° rather than 90° apart.}. In a trigonal planar shape, the lone pairs occupy axial positions which is unlikely. Therefore, BrF_3 exists ~~is~~ as a T-shaped molecule where the 2 lone pairs occupy equatorial positions. This means that the $\overset{\delta+}{\text{Br}}-\overset{\delta-}{\text{F}}$ dipoles are arranged asymmetrically and thus do not cancel, meaning BrF_3 is overall polar.

- (c) A titration was carried out using 25.00 mL of ethylamine solution, $\text{CH}_3\text{CH}_2\text{NH}_2(\text{aq})$, to which 0.1300 mol L^{-1} nitric acid, $\text{HNO}_3(\text{aq})$, was added. The volume of $\text{HNO}_3(\text{aq})$ at the equivalence point was 34.98 mL.

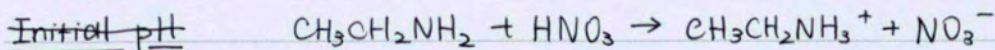
$$\rightarrow 34.98 \div 2 = 17.49$$

- (i) Carry out sufficient calculations to draw the predicted curve for this titration on the grid on the opposite page.

Key values may include: The initial concentration and pH of the base, the pH at the equivalence point, the pH at halfway to the equivalence point, and the pH after 20.00 mL of excess acid has been added.

$$\rightarrow \text{p}K_a = 10.64$$

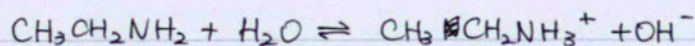
$$\text{p}K_a(\text{CH}_3\text{CH}_2\text{NH}_3^+) = 10.64$$



$$n(\text{HNO}_3) = 0.1300 \text{ mol L}^{-1} \times 0.03498 \text{ L} = 4.5474 \times 10^{-3} \text{ mol}$$

$$n(\text{HNO}_3) = n(\text{CH}_3\text{CH}_2\text{NH}_2)_{\text{initial}}$$

$$c(\text{CH}_3\text{CH}_2\text{NH}_2)_{\text{initial}} = \frac{n}{V} = \frac{4.5474 \times 10^{-3} \text{ mol}}{0.025 \text{ L}} = 0.181896 \text{ mol L}^{-1}$$

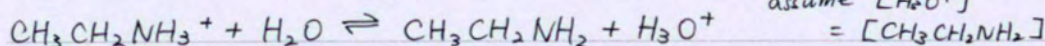


$$\frac{[\text{CH}_3\text{CH}_2\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}_2\text{NH}_3^+]} = 10^{-10.64} \quad \text{assume } [\text{CH}_3\text{CH}_2\text{NH}_3^+] = [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+] = \sqrt{\frac{10^{-10.64} \times 1 \times 10^{-14}}{0.181896}} = 1.1222469 \times 10^{-12} \text{ mol L}^{-1}$$

$$\text{pH}_{\text{initial}} = -\log [\text{H}_3\text{O}^+] = -\log (1.12 \times 10^{-12}) = \boxed{11.95 \text{ (4s.f.)}}$$

$$c(\text{CH}_3\text{CH}_2\text{NH}_3^+) = 0.1300 \text{ mol L}^{-1} \times \frac{34.98}{34.98 + 25} = 0.075815 \text{ mol L}^{-1}$$

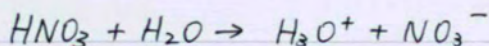


$$[\text{H}_3\text{O}^+]^2 = \frac{K_a}{1} \times [\text{CH}_3\text{CH}_2\text{NH}_3^+]$$

$$[\text{H}_3\text{O}^+] = \sqrt{10^{-10.64} \times 0.075815} = 1.31788 \times 10^{-6} \text{ mol L}^{-1}$$

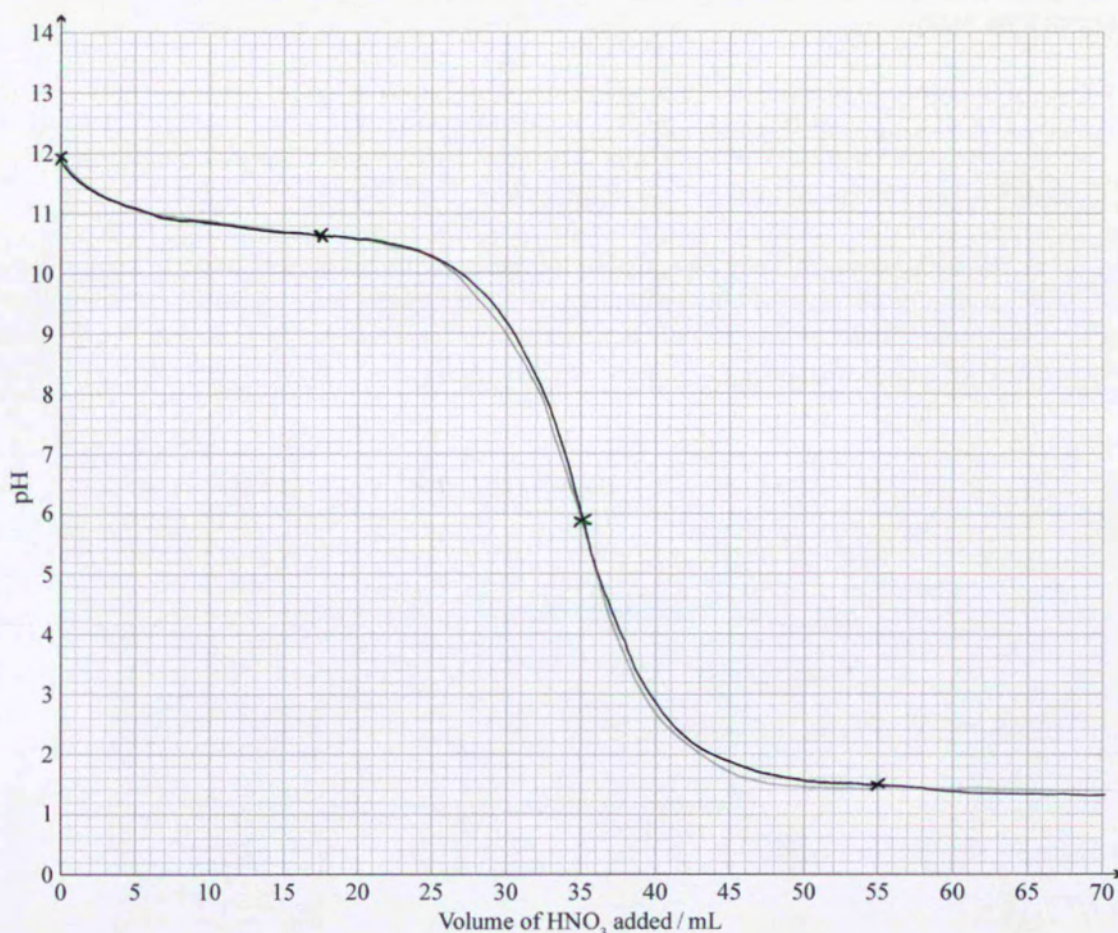
$$\text{pH}_{\text{equi.}} = -\log [\text{H}_3\text{O}^+] = -\log (1.31788 \times 10^{-6}) = \boxed{5.880 \text{ (4sf.)}}$$

$$\begin{aligned} 20 \text{ mL excess acid: } [\text{HNO}_3] &= 0.13 \times \frac{20}{34.98 + 25 + 20} \\ &= 0.032508 \text{ mol L}^{-1} \end{aligned}$$



$$[\text{HNO}_3] = [\text{H}_3\text{O}^+]$$

$$\text{pH}_{\text{excess}} = -\log (0.0325 \dots) = \boxed{1.488 \text{ (4sf.)}}$$



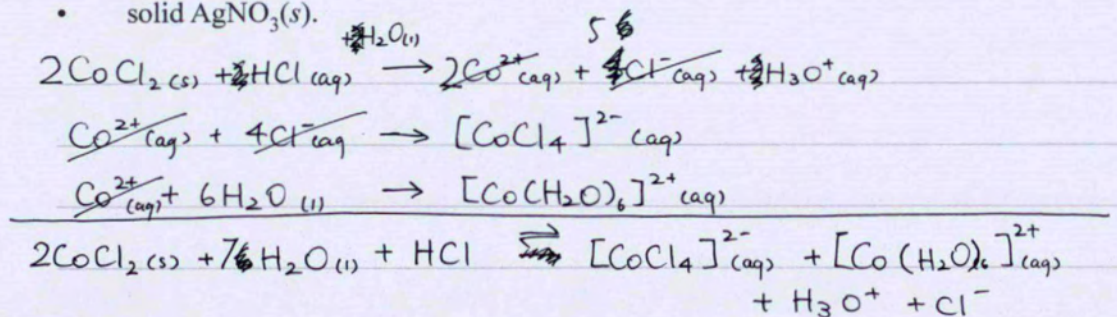
- (ii) For the solutions formed after 18 mL and 28 mL of HNO_3 have been added, evaluate their buffering capacity against strong acid and strong base.

Calculations are not required.

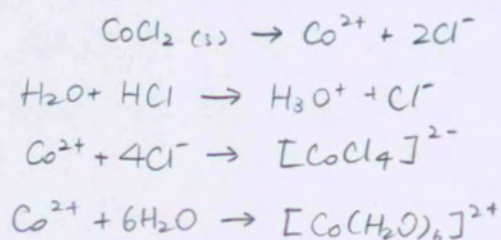
Halfway to the equivalence point, $\frac{34.98}{2} = 17.49 \text{ mL}$ of $\text{HNO}_3(\text{aq})$ has been added so $[\text{CH}_3\text{CH}_2\text{NH}_2] \approx [\text{CH}_3\text{CH}_2\text{NH}_3^+]$ and the solution is equally effective for ^{small} added ^{volumes} of strong acid/base. At 18 mL of HNO_3 , there is only a slightly greater $[\text{CH}_3\text{CH}_2\text{NH}_3^+]$ than $[\text{CH}_3\text{CH}_2\text{NH}_2]$ so it is only slightly more effective at neutralising added strong base: $\text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{O}$, buffering pH changes. At 28 mL of HNO_3 , there is a significantly greater $[\text{CH}_3\text{CH}_2\text{NH}_3^+]$ than $[\text{CH}_3\text{CH}_2\text{NH}_2]$ so the solution is ^{significantly} more effective at buffering against added strong base (same equation) than added strong acid.

QUESTION TWO

- (a) A common equilibrium demonstration in classrooms utilises a solution made when cobalt(II) chloride, $\text{CoCl}_2(s)$, has been dissolved in hydrochloric acid, $\text{HCl}(aq)$. This solution is purple in colour when it contains an equimolar mixture of two coloured complex ions, $[\text{CoCl}_4]^{2-}(aq)$ which is blue, and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(aq)$ which is pink.
- (i) Write a balanced chemical equation for this equilibrium system, and use it to explain what would be observed if either of the following chemicals were added to a sample of the purple solution:
- concentrated $\text{HCl}(conc)$
 - solid $\text{AgNO}_3(s)$.

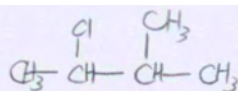


Added conc. HCl increases the $[\text{Cl}^-]$, a common ion to



- (ii) Cobalt chloride paper is prepared by soaking pieces of filter paper in a pink-coloured cobalt(II) chloride solution, and then drying the paper. The paper becomes dark blue in appearance once it is dry, and it can be used as a chemical indicator.

Predict which chemical the paper can be used to test for, and justify your prediction.

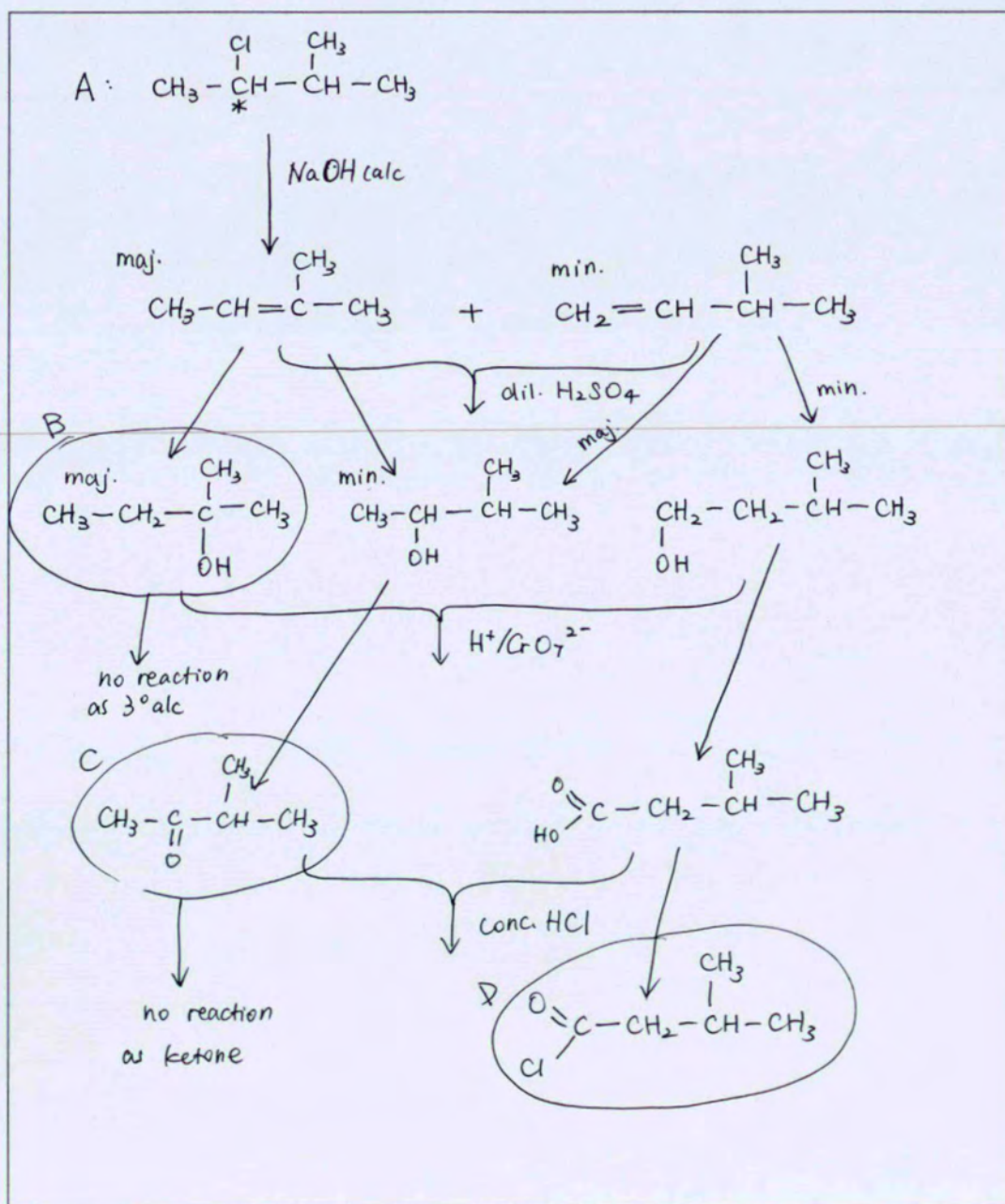


(b) Compound A, $\text{C}_5\text{H}_{11}\text{Cl}$, rotates plane-polarised light, and produces a ^{13}C NMR spectrum with four peaks.

- (i) Four reactions were carried out in sequence in a round-bottomed flask, starting with a sample of Compound A. After each reaction was complete, all inorganic substances were removed, and any organic compounds remaining were left unseparated in the flask to be used as reactants in the next reaction.

The reagent used in the first reaction was $\text{NaOH}(\text{alc})$. The reagent in the second reaction was dilute H_2SO_4 . The reagent in the third reaction was acidified potassium dichromate solution, $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$, and the reagent in the fourth reaction was $\text{HCl}(\text{conc})$.

Determine the structure of Compound A, and construct a reaction scheme which shows all possible organic products formed during these reactions. Label any major and minor products formed.



- (ii) Explain how ^{13}C NMR and IR spectroscopy could be used to distinguish the final reaction products from each other.

You may apply labels to these compounds in your scheme and refer to these in your answer below.

The ^{final} products in the flask are B: 2-methylbutan-2-ol,

C: 3-methylbutan-2-one D: 3-methylbutanoyl chloride.

For B, it would have an $M^+ = 88\text{m/z}$ and 4 carbon environments for ^{13}C NMR with the RCH_3 environment being

double the height of the R_3COH , RCH_2R and other RCH_2

environments. ^{There will be a CH_3COH shift at 50-70 ppm} B has ~~an~~ alkyl groups and an alcohol $-\text{OH}$ group

so an $\text{O}-\text{H}$ stretch would be observed at $3300-3600\text{cm}^{-1}$

and the $\text{C}-\text{H}$ stretches at $2800-2950\text{cm}^{-1}$.

C also has 4 carbon environments with the RCH_3 environment being double the height of the R_3COH , $\text{R}_2\text{C}=\text{O}$ and other RCH_2 environments.

Due to the ketone $\text{C}=\text{O}$ group, a downfield shift would be observed

between $200-230\text{ppm}$. C has alkyl groups and a ketone group so

the $\text{C}-\text{H}$ stretches at $2800-2950\text{cm}^{-1}$ and a strong ketone fingerlike

stretch at 1715cm^{-1} would be observed.

D has 4 carbon environments too, with the RCH_3 being double the

height of R_3COH , R_2CH_2 and RCOCl environments. It has alkyl groups

and an acid chloride group which will be observed as $\text{C}-\text{H}$ stretches

at $2800-2950\text{cm}^{-1}$ and $\text{C}=\text{O}$ and $\text{C}-\text{Cl}$ stretches at $1775-1810\text{cm}^{-1}$

and $550-730\text{cm}^{-1}$ respectively.

To distinguish the three, B's $\text{O}-\text{H}$ stretch for IR is absent in ~~the~~ C and D,

then C can be distinguished by its downfield ~~at~~ $\text{RC}=\text{OR}$ shift for ^{13}C NMR,

~~which~~ confirmed by a peak at 1715cm^{-1} on the IR, leaving D to be

confirmed by a $\text{C}=\text{O}$ peak at $1775-1810\text{cm}^{-1}$ and the $\text{C}-\text{Cl}$ stretch from $550-730\text{cm}^{-1}$.

(c) The table below lists five descriptions that each identify a particular element.

- (i) Place the symbol for the correct element in each box in the table below. The first one has been done as an example for you.

Description	Element symbol
The lightest element with one electron in the 1s orbital.	H
Found in Period 2, this element has no paired p electrons and does not follow the general trend in ionisation energy across a period.	B
This element has the highest ionisation energy of any element.	F
Ions of this Period 3 element have the smallest ionic radius of all ions in this period.	Al ³⁺
This element exists as a gaseous diatomic molecule, with the highest bond enthalpy of any of the diatomic molecules.	N

- (ii) For THREE of the elements you have identified, discuss your choices, with clear references to the details provided in the descriptions.

(1) Element: F Fluorine

Discussion: F has the highest ionisation energy of any element due to the strong electrostatic forces between its valence e⁻s and nucleus. This is because its valence e⁻s are in the 2nd energy level, experiencing shielding only from one inner level, and are therefore also close to the nucleus. This is coupled with F ~~has~~ having the highest no. of protons in its period with an atomic number of 9 and therefore a high nuclear charge. Therefore, its valence e⁻s are the most tightly held of any element and require the most energy to remove the outmost e⁻.

(2) Element: Al Aluminium

Discussion: In period 3, elements which have small ionic radii will be in groups 1, 2 or 13 as these lose their 3rd level valence e⁻s forming an ion with smaller radius as its valence e⁻s are now in the

2nd energy level. Out of Na, Mg and Al, they ionise to Na^+ , Mg^{2+} and Al^{3+} , all having 8 valence e^- s in the 2nd energy level which experience the same shielding from ^{#e}inner level 1. However, Al has the greatest no. of protons and thus, nuclear charge; so Al^{3+} 's valence e^- s experience the strongest electrostatic force, pulling them closer to the nucleus. Therefore, the Al^{3+} ion has the smallest ionic radius in the 3rd period.

(3) Element: N Nitrogen.

Discussion: N is in the 2nd period and group 15, forming the diatomic N_2 gaseous molecule: $:\text{N}\equiv\text{N}:$. Due to its 5 valence e^- s, it forms a triple bond with itself, which has a higher bond enthalpy than single or double bonds. Furthermore, N is the smallest element which forms triple bonds, meaning its bonding ^{valence} e^- s are only in the 2nd energy level, and experience the least shielding from inner levels and are closest to the nucleus. This makes N's valence e^- s experience the greatest electrostatic force between them and the nucleus. Therefore, N_2 has the highest bond enthalpy of any diatomic molecule.

QUESTION THREE

- (a) In the standardisation of a solution of hydrochloric acid, HCl(aq) , students were advised to measure 2.691 g of anhydrous sodium carbonate, $\text{Na}_2\text{CO}_3(\text{s})$, and carefully transfer it into a 250.0 mL volumetric flask. This flask was then to be filled to the line using distilled water and labelled.

10.00 mL aliquots of the sodium carbonate solution were then to be titrated against a provided hydrochloric acid solution, HCl(aq) .

Two students independently gathered results by following the method, and their measurements are shown in the tables below:

Student A results (mL)		
Initial	Final	Titre
0.00	16.55	16.55
16.55	32.35	15.80
32.35	48.05	15.70
0.05	15.75	15.70
15.75	31.40	15.65

} concordant

Student B results (mL)		
Initial	Final	Titre
0.00	22.25	22.25
22.25	42.45	20.20
0.15	20.70	20.55
20.70	40.60	19.90
0.25	19.75	19.50

The teacher then determined the hydrochloric acid concentration to be $0.1040 \text{ mol L}^{-1}$ using the same method.

Use the data collected by each student to calculate their final HCl(aq) concentrations.

For each student, comment on the **validity** of their method and the **accuracy** of their results, and suggest any possible sources of error in each of their procedures.

$$M(\text{Na}_2\text{CO}_3) = 106.0 \text{ g mol}^{-1}$$

Student B does not have concordant titre values and therefore should repeat the titration to obtain ^{at least 3 that are maximum} titres ^{of} 0.1 mL apart from one another. The source of error for student B may be a faulty burette, or poor practice at titration; ^{results are invalid.} Both students may experience sources of error when ~~fitting~~ weighing the $\text{Na}_2\text{CO}_3(\text{s})$, depending on ~~how many~~ the resolution of the scales and also if it is faulty or not tared properly, when filling the flask with distilled water, the amount may be inaccurate if the line is not seen at eye level and it is not read from the bottom of the meniscus. The aliquots could also be a source of error, if slightly more or less than 10 mL of solution is ~~not~~ titrated with. The initial and final readings of the burette must also be at eye level and read from the bottom of the meniscus to reduce error.

Calculations for student A only: titre average = $\frac{15.80 + 15.70 + 15.70}{3}$
 $= 15.73 \text{ (4sf.) mL}$



$$n(\text{Na}_2\text{CO}_3)_{\text{initial}} = \frac{2.691\text{g}}{106.0\text{g mol}^{-1}} = 0.0253867... \text{ mol}$$

$$n(\text{Na}_2\text{CO}_3)_{\text{titrated}} = 0.02538... \text{ mol} \times \frac{10\text{ mL}}{250\text{ mL}} = 1.01547... \times 10^{-3} \text{ mol}$$

$$n(\text{HCl}) = 2n(\text{Na}_2\text{CO}_3)_{\text{titrated}} = 2 \times 1.015... \times 10^{-3} = 2.0309... \times 10^{-3} \text{ mol}$$

$$c(\text{HCl}) = \frac{n}{V} = \frac{2.0309 \times 10^{-3} \text{ mol}}{0.01573 \text{ L}} = \boxed{0.1291 \text{ mol L}^{-1} \text{ (4sf.)}}$$

$$\frac{1291}{1040} = 1.24 \rightarrow 24\% \text{ error}$$

Student A's result was 24% higher than the concentration the teacher obtained, suggesting their result was inaccurate. Their method is valid however, including weighing, diluting and titrating multiple times to reduce random error. This means that the inaccuracy of their result is likely due to a combination of the aforementioned error sources.

- (b) The enthalpy change for a reaction can be calculated using a number of different methods. Relevant chemical data book values at 25 °C, which can be utilised in thermochemical calculations are:

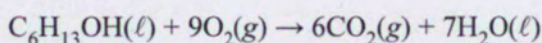
Bond enthalpies / kJ mol ⁻¹			
C-O	358	O-H	463
C=O	745	O=O	498

Enthalpies of formation / kJ mol ⁻¹	
CO ₂ (g)	-393
H ₂ O(l)	-286
C ₆ H ₁₃ OH(l)	-320

Enthalpies of reaction / kJ mol ⁻¹	
C(g) + 4H(g) → CH ₄ (g)	Δ _r H° -1652
2C(g) + 6H(g) → C ₂ H ₆ (g)	Δ _r H° -2826

The specific heat capacity of water is 4.18 J g⁻¹ °C⁻¹. $M(\text{C}_6\text{H}_{13}\text{OH}(\ell)) = 102.2 \text{ g mol}^{-1}$

- (i) Calculate the enthalpy of combustion, Δ_cH°, for hexan-1-ol, C₆H₁₃OH(l), using the three methods below.



Method 1: Using experimental data

1.35 g of hexan-1-ol was completely combusted by a student, and the heat produced raised the temperature of 300 mL of water from 22.3 °C to 51.5 °C.

$$\Delta T = 22.3 - 51.5 = -29.2^\circ\text{C} \quad m = 300\text{g} \quad c = 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$$

$$q = mc\Delta T = (-29.2)(300)(4.18) = -36616.8 \text{ J (energy released)}$$

$$n = \frac{m}{M} \rightarrow n(\text{hexan-1-ol}) = \frac{1.35 \text{ mol}}{102.2 \text{ g mol}^{-1}} = 0.013209... \text{ mol}$$

$$\Delta_c H^\circ = \frac{q}{n} = \frac{-36616.8 \text{ J}}{0.013209... \text{ mol}} = -2772027.377... \text{ J mol}^{-1} \approx \boxed{-2772 \text{ kJ mol}^{-1} \text{ (4sf)}}$$

Method 2: Using enthalpies of formation

6CO₂(g) formed: 6 × -393, 7H₂O(l) formed: 7 × -286, C₆H₁₃OH(l) combusted: +320

$$\Delta_c H^\circ = 6 \times -393 + 7 \times -286 + 320 = \boxed{-4040 \text{ kJ mol}^{-1}}$$

Method 3: Using bond enthalpies and enthalpies of reaction

forming 4 C-H bonds: $-1652 \text{ kJ mol}^{-1} \xrightarrow{\text{released}} 1 \text{ C-H} = \frac{1652}{4} = 413 \text{ kJ mol}^{-1}$

forming 1 C-C and 6 C-H bonds: $-2826 \rightarrow 1 \text{ C-C} = 2826 - 6 \times 413 = 348 \text{ kJ mol}^{-1}$

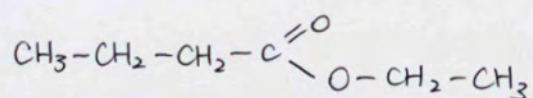
$$\Delta_c H^\circ = \sum \text{bonds formed} - \sum \text{bonds broken} = (12\text{C-O} + 14\text{H-O}) - (13\text{C-H} + 5\text{C-C})$$

$$= 7930 - 10778 = \boxed{-2848 \text{ kJ mol}^{-1}}$$

- (ii) Compare the answers obtained for each of the three methods, suggesting reasons for any differences observed.

The value obtained using the enthalpies of formation are most likely to be accurate as this is using Hess's law and takes into account the state of each substance. The bond enthalpy calculation obtained a less negative $\Delta_c H^\circ$ since all bond enthalpies are based on the substances in their gaseous state. Since both $C_6H_{12}OH$ and H_2O are in their liquid state, ~~the reaction~~ the missing energy ^{is} due to ^{them partially} forming intermolecular attractions between molecules in order to be in their liquid state and hence the ^{actual} reaction releases more energy than calculated as forming ^{intermolecular} bonds releases energy. Method 1 also obtains a less $\Delta_c H^\circ$ since it is experimental and not ideal. The experiment may not have been conducted ~~in~~ under standard conditions and heat energy would be lost to the surroundings and equipment and therefore not all transferred to heating the water. This means that the ΔT value is less negative than it should have been and therefore the energy released (q) the student calculated was lower than theoretical / ideal situations, resulting in a lower final $\Delta_c H^\circ$.

- (c) (i) Identify, by name and structural formula, the ester formed between butanoic acid and ethanol.

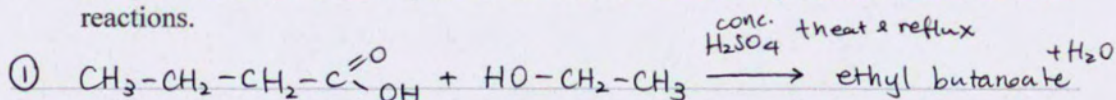


ethyl butanoate.

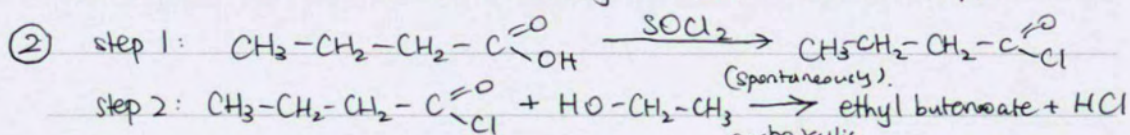
- (ii) Outline two different reactions that could be used to prepare this ester in a chemistry laboratory.

In your answer:

- give structural equations and include clear references to any other reagents or steps which might be required
- compare and contrast the experimental conditions and safety considerations for these reactions.

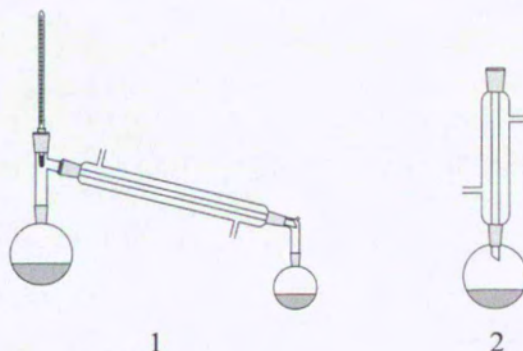


This lab reaction prepares the ester in a condensation reaction which joins the two smaller butanoic acid and ethanol molecules into the ester, releasing an H_2O in the process as $-\text{OH}$ is removed from butanoic acid and $-\text{H}$ from ethanol (or vice versa). The reaction requires heat and reflux to speed up the rate of reaction since it is relatively slow, but this also makes it easy to control and safe.



This lab reaction firstly converts the acid to an acid chloride, butanoyl chloride, which can then spontaneously react with ethanol. However, the reaction is dangerous as butanoyl chloride is highly reactive and reacts violently to water and other compounds, making it dangerous for the safety of lab technicians.

- (iii) Acid hydrolysis of the ester, to give butanoic acid and ethanol, will require use of both apparatuses shown below.



Discuss how each apparatus would be used in the preparation and separation of ethanol and butanoic acid from the ester.

To hydrolyse the ~~ester~~ ester under acidic conditions, a dilute strong acid e.g. dil. H_2SO_4 is used with reflux equipment. This speeds up the rate of reaction and returns volatile species to the reaction flask, ensuring the reaction goes to completion and all the ester becomes butanoic acid and ethanol.

The fully reacted mixture is then distilled by heating to the boiling point of ethanol (lower BP than butanoic acid due to $-\text{OH}$ group vs $\text{C}(=\text{O})\text{OH}$ group) so that the ethanol becomes volatile and is separated from the butanoic acid by ^{condensing &} dripping ~~back~~ down into a separate collection flask. The butanoic acid does not evaporate & this remains in the round bottom flask, separating the two species.

QUESTION FOUR

- (a) A beaker was filled with 125 mL of a solution containing a mixture of $1.68 \times 10^{-4} \text{ mol L}^{-1}$ potassium chloride, $\text{KCl}(aq)$, and $1.39 \times 10^{-4} \text{ mol L}^{-1}$ potassium chromate, $\text{K}_2\text{CrO}_4(aq)$. Small crystals of silver nitrate, $\text{AgNO}_3(s)$, were slowly added to the beaker, with stirring until the formation of two solids had been observed, each with different appearances. No change in volume was observed.

$$K_s(\text{AgCl}) = 1.80 \times 10^{-10}$$

$$K_s(\text{Ag}_2\text{CrO}_4) = 2.60 \times 10^{-12}$$

- (i) Determine the identity of the first solid to precipitate from the solution.

~~Ag_2CrO_4 will precipitate first as it has a lower solubility than AgCl , indicated by AgCl will precipitate first.~~
Although it is more soluble than Ag_2CrO_4 as indicated by its higher K_s value, Ag_2CrO_4 requires 2Ag^+ ions per CrO_4^{2-} rather than 1Ag^+ ion per Cl^- or CrO_4^{2-} respectively.

$$[\text{CrO}_4^{2-}] = 1.39 \times 10^{-4} \text{ mol L}^{-1} \quad [\text{Cl}^-] = 1.68 \times 10^{-4} \text{ mol L}^{-1}$$

$$[\text{Ag}^+] = \sqrt{\frac{K_s(\text{Ag}_2\text{CrO}_4)}{[\text{CrO}_4^{2-}]}}$$

$$[\text{Ag}^+] = \frac{K_s(\text{AgCl})}{[\text{Cl}^-]}$$

$$= 1.3676 \times 10^{-4} \text{ mol L}^{-1}$$

$$= 1.0714 \times 10^{-6} \text{ mol L}^{-1}$$

As shown, AgCl requires a much smaller $[\text{Ag}^+]$ before the solution becomes saturated and hence AgCl will precipitate first once $[\text{Ag}^+]$ exceeds $1.071 \times 10^{-6} \text{ mol L}^{-1}$ (4 sf).

- (ii) Determine the concentration of the anion from the first solid that still remains in the solution when the second solid begins to precipitate. Use this to decide whether this procedure could be used to separate the Cl^- ions from CrO_4^{2-} ions in this solution. For this to be the case, more than 99.9% of the first ion must have precipitated before the second solid begins to precipitate.

$[\text{Cl}^-]$ starts $\downarrow$ when $[\text{Ag}^+]$ exceeds $1.0714 \times 10^{-6} \text{ mol L}^{-1}$

At $1.3676 \times 10^{-4} \text{ mol L}^{-1} [\text{Ag}^+]$, $[\text{Cl}^-] = ?$

$$n(\text{Cl}^-) = 1.39 \times 10^{-4} \text{ mol L}^{-1} \times 0.125 \text{ L} = 1.7375 \times 10^{-5} \text{ mol}$$

$$n(\text{Ag}^+) = 1.3676 \times 10^{-4} \text{ mol L}^{-1} \times 0.125 \text{ L} = 1.70957 \times 10^{-5} \text{ mol}$$

$$1.7375 \times 10^{-5} - 1.70957 \times 10^{-5} = 2.79205 \times 10^{-7} \text{ mol}$$

$$[\text{Cl}^-] \text{ when ppt } \text{Ag}_2\text{CrO}_4 = \frac{n}{V} = \frac{2.792 \times 10^{-7}}{0.125} = \boxed{2.2336 \times 10^{-6} \text{ mol L}^{-1}}$$

$$n(\text{Cl}^-)_{\text{initial}} - n(\text{Cl}^-)_{\text{final}} = 1.7375 \times 10^{-5} - 2.79205 \times 10^{-7} \\ = 1.70957 \times 10^{-5}$$

$$\frac{1.70957 \times 10^{-5}}{1.7375 \times 10^{-5}} = 98.39\% \text{ (4sf.)} < 99.90\%$$

The procedure cannot be used to separate the Cl^- from CrO_4^{2-} ions in solution since only 98.39% of the Cl^- ion was precipitated when Ag_2CrO_4 begins to precipitate.

- (iii) A second experiment was carried out. In this case, a dilute solution of $\text{AgNO}_3(\text{aq})$ was instead slowly titrated into a beaker containing 125 mL of the solution described at the beginning of part (a).

The first precipitate was observed after a small volume of the AgNO_3 solution had been added, and the second precipitate was observed once a total of 16.8 mL AgNO_3 solution had been added.

Calculate the concentration of the $\text{AgNO}_3(\text{aq})$ solution used in the titration.

You should consider the amount of Ag^+ precipitated, as well as the amount remaining in solution.

$$125 \text{ mL} + 16.8 \text{ mL} = 141.8 \text{ mL} \quad [\text{AgNO}_3] = ?$$

$$[\text{AgNO}_3] = 1.3676 \times 10^{-4} \text{ mol L}^{-1} \text{ when } 16.8 \text{ mL added}$$

$$n(\text{AgNO}_3) = 1.3676 \times 10^{-4} \times 0.0168 = 2.29767 \times 10^{-6} \text{ mol}$$

$$n(\text{AgNO}_3)_{\text{total}} = 2.29767 \times 10^{-6} + 1.70957 \times 10^{-5}$$

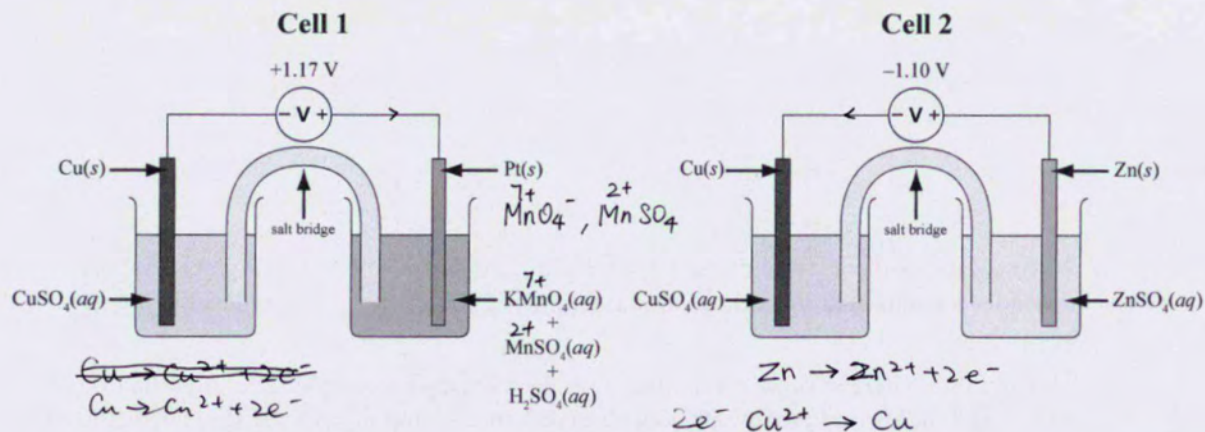
$$= 1.9393 \times 10^{-5} \text{ mol}$$

$$[\text{AgNO}_3]_{\text{initial}} = \frac{1.9393 \times 10^{-5}}{0.125} = \boxed{1.55 \times 10^{-4} \text{ mol L}^{-1} \text{ (3sf.)}}$$

- (b) A student set up two electrochemical cells under standard conditions at 25 °C.

The internal circuit of both cells consisted of a salt bridge containing potassium sulfate solution, $K_2SO_4(aq)$, and the external circuit consisted of a voltmeter with wires connected to solid electrodes. The metals used for the electrodes, and solutions prepared, are indicated in the diagrams below.

The student recorded the voltages shown on each voltmeter.



The voltmeters were then removed and replaced with a conductive wire. After some time, the student recorded any observed changes that had occurred.

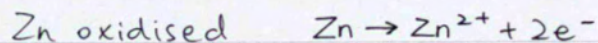
- (i) Describe the changes that occurred in each of the electrochemical cells, and justify them in terms of oxidation-reduction processes, flow of charge, and movement of particles.

In cell 1, $KMnO_4$ is a strong oxidant which oxidises $MnSO_4$ under acidic conditions. This means reduction takes place in the $KMnO_4$ beaker while copper is oxidised in the other beaker and we observe that the copper ^{anode} ~~electrode~~ shrinks in size as $Cu \rightarrow Cu^{2+} + 2e^-$. The electrons then flow to the inert $Pt(s)$ cathode, reducing MnO_4^{2-} with Mn 's ON at +7 to $MnSO_4$ with $ON = +2$.

In cell 2, the voltage is negative meaning current is flowing in the opposite direction so Cu^{2+} is reduced and Zn is oxidised. The Zn anode will decrease in size as $Zn \rightarrow Zn^{2+} + 2e^-$ and the electrons will flow to the Cu cathode which increases in size as $Cu^{2+} + 2e^- \rightarrow Cu(s)$.

- (ii) Determine the standard reduction potentials, $E^\circ(\text{Cu}^{2+}/\text{Cu})$ and $E^\circ(\text{MnO}_4^-/\text{Mn}^{2+})$, and use appropriate calculations to justify what would be observed if a piece of zinc metal, $\text{Zn}(s)$, was added to a beaker containing a solution of acidified potassium permanganate, $\text{H}^+/\text{MnO}_4^-(aq)$.

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



Question Four continues
on the next page.

- (c) The energy required to break apart an ionic crystal, to form gaseous ions, is different for magnesium chloride, $\text{MgCl}_2(\text{s})$, and sodium chloride, $\text{NaCl}(\text{s})$.

Justify which compound will require the greater amount of energy for this change to occur.

MgCl_2
~~NaCl~~ will require more energy to $\text{MgCl}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{g}) + 2\text{Cl}^{-}(\text{g})$
 ~~$\text{NaCl}(\text{s}) \rightarrow \text{Na}^{+}(\text{g}) + \text{Cl}^{-}(\text{g})$~~

This is because NaCl only has one bond and Na is also less electronegative than Mg. Mg^{2+} is more electronegative since its valence e⁻s are also at the 2nd energy level as ~~Na~~ Na^{+} ^{the EN and therefore diff. is lesser} and thus experience the more shielding from inner e⁻s. Mg^{2+} has a greater charge and therefore a greater electrostatic attraction between its valence e⁻s and nucleus. This means that the shared valence e⁻s between Mg and Cl are more tightly bound to Mg^{2+} . This contrasts with NaCl where ~~the~~ the EN difference ^{between Na & Cl is greater so} Cl attracts most of the e⁻s in the ionic bond, making ~~the bond~~ ~~Na easier to remove~~. the bond stronger. MgCl_2 retains more of its valence e⁻s due to the smaller EN difference and therefore the ionic bonds are weaker and easier to break. However, MgCl_2 has two bonds whilst NaCl has only 1 per equimolar amount and therefore MgCl_2 requires more energy to break both bonds to form 3 gaseous ions instead of 2. $\therefore$ energy required to break $\text{MgCl}_2(\text{s})$ into gaseous $\text{Mg}^{2+} + 2\text{Cl}^{-}$ ions is greater.

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QUESTION
NUMBER

93102

Scholarship

Subject: Chemistry

Standard: 93102

Total score: 22

Q	Score	Marker commentary
1	8	(a) Wrote a chemical equation recognising CO₂ production, discussed the entropy changes in the surroundings, and reasoned for the reaction in water. (b) Completed all Lewis diagrams, shapes, and bond angles correctly, and discussed the correct shape and polarity of BrF₃ molecules. (c) Completed all calculations in the titration curve neatly and succinctly, drew a clear curve, and discussed the buffering capacity of the different solutions.
2	5	(a) Incomplete answer. (b) Completed a scheme to produce one correct product and provided a good discussion of the use of IR and ¹³C NMR to differentiate compounds. (c) Explained Al and N with good use of chemistry vocabulary.
3	5	(a) Attempted calculations with one correct value and attempted comments addressing validity and accuracy. (b) Completed two of the three enthalpy calculations correctly and provided reasons for variation in the values. (c) Drew / named correct ester, addressed aspects of the two different synthesis routes, addressed limited safety risks, and explained both distillation and reflux.
4	4	(a) Calculated the Ag⁺ concentrations for the two solutions in (i), with correct conclusion, and attempted partial calculations in both (ii) and (iii). (b) Limited aspects of both electrochemical cells attempted, particularly the oxidation-reduction reactions and the flow of charge. (c) Discussion of ionic bonding attempted but limited correct chemical understanding demonstrated.