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OUTSTANDING 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

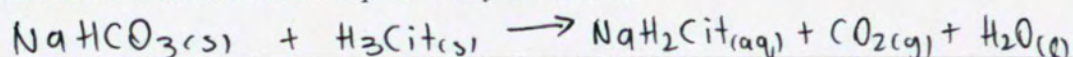
- (a) Sodium hydrogen carbonate, $\text{NaHCO}_3(s)$, and citric acid, $\text{H}_3\text{Cit}(s)$, are used in fizzy vitamin tablets. Once a tablet is dropped into a glass of water, a spontaneous reaction is observed, resulting in the formation of bubbles of gas which mix the contents of the tablet throughout the solution, and there is a decrease in the temperature of the solution.

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

water particle?

$\Delta S_{\text{solvent}}?$

Include a balanced chemical equation in your answer.



Entropy of the system increases. This is because 2 highly-ordered solid moles of reactant form less-ordered aqueous (1 mol), gaseous (1 mol) and liquid (1 mol) products. Thus, the dispersal of matter and energy increases, increasing disorder ($\Delta S_{\text{system}} > 0$).

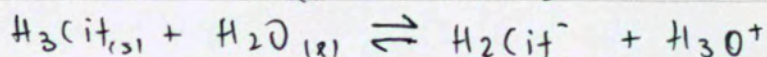
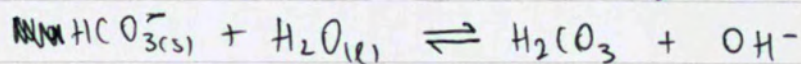
Entropy of the surroundings decreases. Since the solution's temperature decreases, the reaction is ~~exothermic~~ endothermic - that is, ^{heat} energy is absorbed from the surroundings. This decreases the kinetic energy of surrounding particles, reducing their random motion and disorder ($\Delta S_{\text{surroundings}} < 0$).

Overall, $\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$. The increase in entropy of the system must outweigh the decrease in entropy of the surroundings, such that total entropy increases, so the reaction is spontaneous.

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

This acid-base reaction occurs via the following: $\text{H}_3\text{O}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow 2\text{H}_2\text{O}_{(\text{l})}$.

When $\text{NaHCO}_{3(\text{s})}$ and $\text{H}_2\text{Cit}_{(\text{s})}$ are in solid state, no H_3O^+ or OH^- is present, as these are only released when the compounds dissolve in water: $\text{NaHCO}_3 \rightarrow \text{Na}^+ + \text{HCO}_3^-$



- (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: $\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\ \\ \text{:}\ddot{\text{Br}}\text{:} \\ \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$	BrF_4^+ Lewis diagram: $\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\ \\ \text{:}\ddot{\text{F}}\text{:} \cdots \text{Br} \cdots \text{:}\ddot{\text{F}}\text{:} \\ \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$
Shape/bond angle: linear, 180°	Shape/bond angle: see-saw, $90^\circ + 117.5^\circ + 180^\circ$
BrF_2^+ Lewis diagram: $\begin{array}{c} \text{:}\ddot{\text{Br}}\text{:} \\ / \quad \backslash \\ \text{:}\ddot{\text{F}}\text{:} \quad \text{:}\ddot{\text{F}}\text{:} \end{array}$	BrF_4^- Lewis diagram: $\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \cdots \text{Br} \cdots \text{:}\ddot{\text{F}}\text{:} \\ / \quad \backslash \\ \text{:}\ddot{\text{F}}\text{:} \quad \text{:}\ddot{\text{F}}\text{:} \end{array}$
Shape/bond angle: non-linear/bent, 104.5°	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.

Reaction (1).

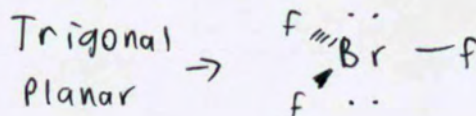
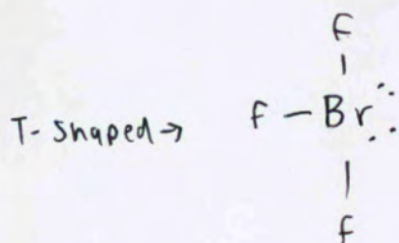
↑ bond angles

Reaction 1 produces ions with a greater bond angles ($180^\circ, 90^\circ, 117.5^\circ$) than reaction 2 ($104.5^\circ, 90^\circ$). Therefore, the products of reaction 1 are more stable as repulsion is minimised, so the reaction is favoured (the F^- ion will more readily be transferred).

- (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.

Molecular shape is determined by the number of electron areas around a central atom, which arrange to minimise repulsion and maximise separation, in accordance with VSEPR theory. In ~~BrF~~ BrF_3 , there are 5 electron densities around the central Br atom, giving a ~~trig~~ trigonal bipyramidal arrangement: 2 axial areas with 90° bond angles, and 3 ~~ax~~ equatorial areas with 120° bond angles. Of the ~~5~~ 5 densities in BrF_3 , 3 are bonding f's, and 2 are lone pairs which have greater repulsion and take up more space due to being closer to the nucleus. Thus, the preferred shape is the one where lone pairs are in the equatorial plane, with the most space (largest bond angle), minimising repulsion. This is the T-shaped molecule where both lone pairs are equatorial, while the 2 lone pairs are axial in a trigonal planar shape:



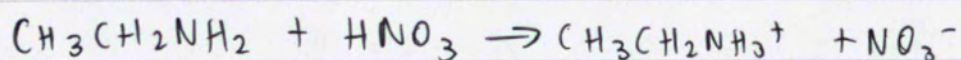
[see back]

- (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 $0.1300 \text{ mol L}^{-1}$ 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.

- (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.

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



$$n(\text{HNO}_3) = (0.1300)(0.03498)$$

$$= 0.0045474 \text{ mol}$$

$$\therefore [\text{CH}_3\text{CH}_2\text{NH}_2]_i = \frac{0.0045474}{0.02500} = 0.1819 \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+]_i = \sqrt{\frac{10^{-10.64} \times 10^{-14}}{0.1819}}$$

$$= 1.122 \times 10^{-12} \text{ mol L}^{-1}$$

$$\text{pH} = -\log(1.122 \times 10^{-12})$$

$$= 11.95, \text{ initial pH}$$

half-equivalence:

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

$$V = \frac{V_{\text{eqn}}}{2} = 17.49 \text{ mL}$$

equivalence:

$$n(\text{CH}_3\text{CH}_2\text{NH}_3^+) = 0.0045474 \text{ mol}$$

$$[\text{CH}_3\text{CH}_2\text{NH}_3^+] = \frac{0.0045474}{0.025 + 0.03498}$$

$$= 0.07582 \text{ mol L}^{-1}$$

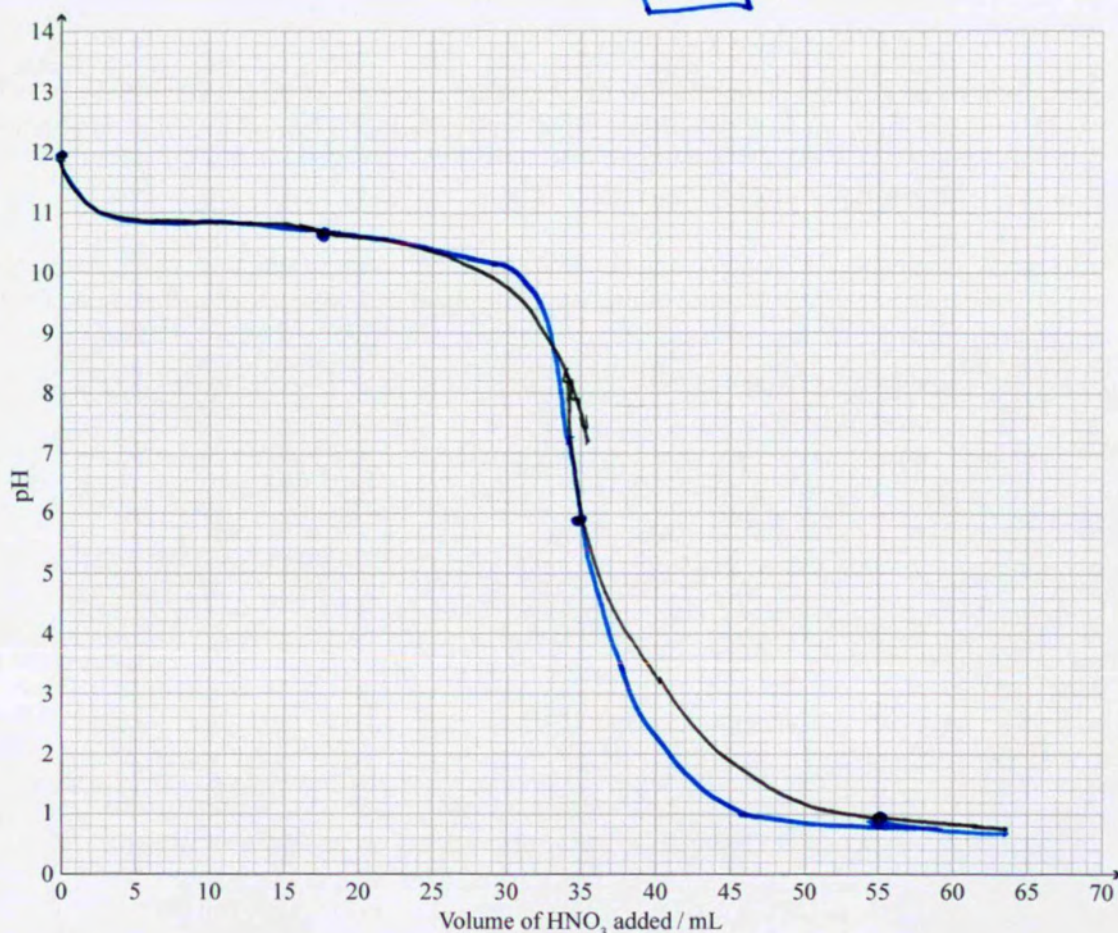
$$[\text{H}_3\text{O}^+] = \sqrt{10^{-10.64} \times 0.07582}$$

$$= 1.318 \times 10^{-6} \text{ mol L}^{-1}$$

$$\text{pH} = -\log(1.318 \times 10^{-6})$$

$$\text{pH} = 5.880 \text{ at eq.}$$

blue



- (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.

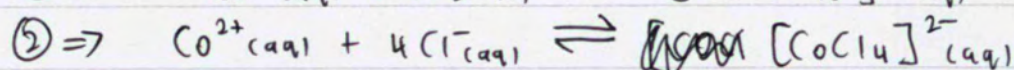
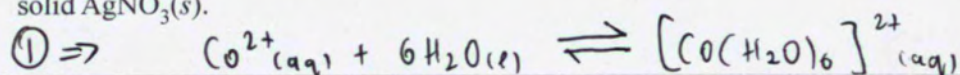
18 mL is almost exactly half-way to equivalence, ^{just over} so half of the initial $\text{CH}_3\text{CH}_2\text{NH}_2$ has been neutralised by HNO_3 , forming $\text{CH}_3\text{CH}_2\text{NH}_3^+$ (conjugate acid). Thus $\text{pH} \approx \text{pK}_a$, and $[\text{CH}_3\text{CH}_2\text{NH}_2] \approx [\text{CH}_3\text{CH}_2\text{NH}_3^+]$, so the buffer is equally as effective at neutralising added strong acid and base to resist pH change: $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_3\text{O}^+ \rightleftharpoons \text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{H}_2\text{O}$
 $\text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{O}.$

At 28 mL most of the ethylamine has been neutralised by HNO_3 to form $\text{CH}_3\text{CH}_2\text{NH}_3^+$. Thus, $\text{pH} < \text{pK}_a$, and $[\text{CH}_3\text{CH}_2\text{NH}_3^+] > [\text{CH}_3\text{CH}_2\text{NH}_2]$, so it is more effective at neutralising added strong base, compared to strong acid.

QUESTION TWO

- (a) A common equilibrium demonstration in classrooms utilises a solution made when cobalt(II) chloride, $\text{CoCl}_2(\text{s})$, has been dissolved in hydrochloric acid, $\text{HCl}(\text{aq})$. This solution is purple in colour when it contains an equimolar mixture of two coloured complex ions, $[\text{CoCl}_4]^{2-}(\text{aq})$ which is blue, and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ 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 $\text{HCl}(\text{conc})$
- solid $\text{AgNO}_3(\text{s})$.



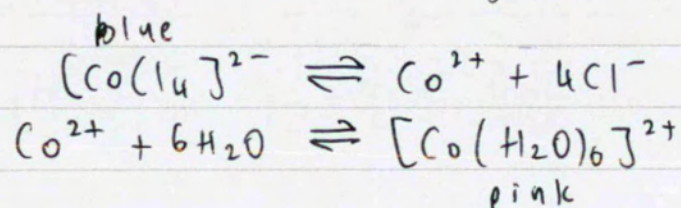
• Adding $\text{HCl}(\text{conc})$ increases $[\text{Cl}^{-}]$ significantly as a common ion solution is now present. This shifts equilibrium position in 2 to the right to use up excess Cl^{-} by favouring forward reaction. Thus, more ~~pink~~ blue ~~Co~~ $[\text{CoCl}_4]^{2-}$ is formed. Also, shifting equilibrium ² right will use up $\text{Co}^{2+}(\text{aq})$, reducing ~~Co~~ $[\text{Co}^{2+}]$, so equilibrium 1 shifts left to replace used up Co^{2+} . This decreases $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. Overall, the solution becomes more blue and less pink (darker purple).

[back page]

- (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.

The dark blue colour may be due to $[\text{CoCl}_4]^{2-}$ which has crystallised upon drying. Thus, it can be used as a test for H_2O , as putting the ^{blue} paper in water would allow $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ to form, turning the paper pink.

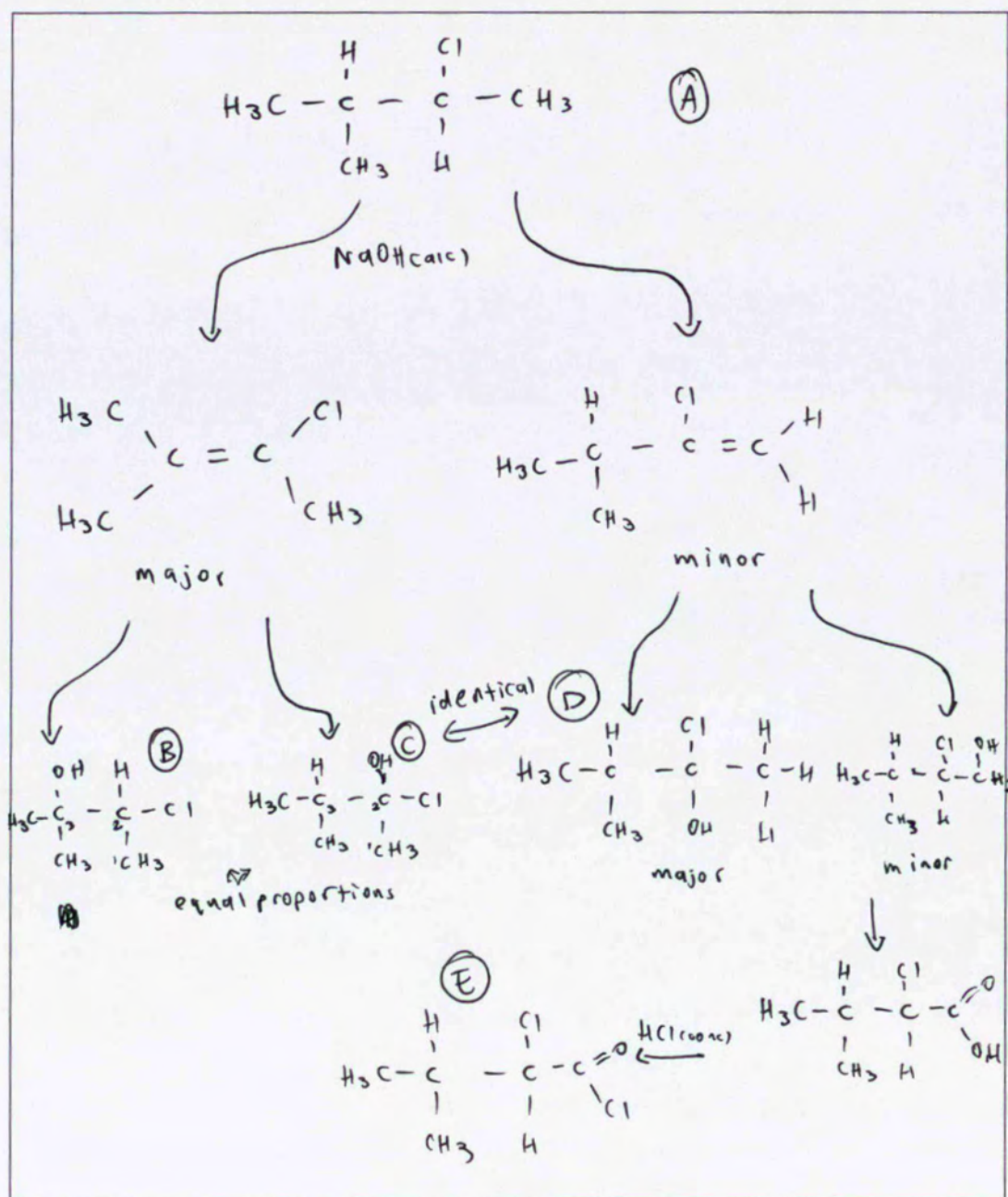


- (b) Compound A, $C_5H_{11}Cl$, rotates plane-polarised light, and produces a ^{13}C NMR spectrum with four peaks. sym.

- (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 $NaOH(alc)$. The reagent in the second reaction was dilute H_2SO_4 . The reagent in the third reaction was acidified potassium dichromate solution, $H^+/Cr_2O_7^{2-}$, and the reagent in the fourth reaction was $HCl(conc)$.

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.

There are ³ final products: B, C, ~~D~~, E.

firstly, E can be distinguished. It was the only product that was oxidised, so has a $\text{C}=\text{O}$ bond. Thus, on IR, it will have a

sharp peak at about 1800cm^{-1} , and a $\sim 180\text{ppm}$ peak on NMR - no other compounds have these features, so E can be determined on this basis.

~~B and C~~ ^{and both} have alcohol groups, so will have a broad, symmetrical O-H stretch on IR around $3600-3300\text{cm}^{-1}$ (that E won't have).

Furthermore, all ~~the~~ molecules have ^{weak} $\text{C}-\text{Cl}$ stretch around $785-540\text{cm}^{-1}$ on IR. Thus, NMR must be used to distinguish ~~B and C~~ B and C.

* In C, the two methyl groups on ~~the~~ C_3 are more shielded than those in B, as they are further from the OH and Cl. Thus, although both molecules have 4 unique C environments, and hence 4 peaks on NMR, the lowest peak for B (around 20ppm) will be further upfield than that in C. ~~one~~ (around 15ppm).

Moreover, ~~the~~ B has the OH and Cl on different atoms, so will represent different peaks (as unique environments) - 1 at $\sim 60\text{ppm}$ for OH and one $\sim 40\text{ppm}$ for $\text{C}-\text{Cl}$. In C, the OH and Cl are part of the same environment, so will be seen as one peak around 60ppm , with 3 peaks 40ppm or lower.

* with 2 peaks below 40ppm .

(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.	N
This element has the highest ionisation energy of any element.	He
Ions of this Period 3 element have the smallest ionic radius of all ions in this period.	Al
This element exists as a gaseous diatomic molecule, with the highest bond enthalpy of any of the diatomic molecules.	Cl

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

(1) Element: Al

Discussion: In period 3, Na-Al form cations by losing electrons, while P-Cl tend to form anions by gaining electrons (Na^+ , Mg^{2+} , Al^{3+} , P^{3-} , S^{2-} , Cl^-). The cations have outer

*(Si + Ar do not tend to ionise).

electrons in a lower energy level (inner shell) than the anions, ~~Na~~ (cations: $1s^2 2s^2 2p^6$, anions: $1s^2 2s^2 2p^6 3s^2 3p^6$). Thus, the cations are

smaller. Of these 3, Al has the greatest nuclear charge as its proton number is greatest. Thus, since all 3 cations are isoelectronic, so their outer electrons experience equal repulsive shielding from inner shells, Al^{3+} 's are attracted to the nucleus the strongest, so are held closest, so ionic radius is few.

(2) Element: N

Discussion: Generally, ionisation energy increases across a period as nuclear charge increases while electrons experience similar shielding,

so nuclear attraction of outer electrons rises, increasing ionisation energy. N has the arrangement $1s^2 2s^2 2p^3$, so each 2p electron occupies its own orbital. The subsequent element, O, has $1s^2 2s^2 2p^4$, so has a paired orbital with greater spin-pair repulsion which outweighs N's lower nuclear charge. Thus, N has stronger ^{nuclear} attraction of its outer electron, so its ionisation energy is higher than O's.

(3) Element: He.

Discussion: He has arrangement $1s^2$. Thus, its 2 outer-shell electrons in the 1s ~~orbital~~ sub-shell experience very large nuclear attraction as there is no shielding from inner shells. Thus, it has the highest ionisation energy as it ^{requires high energy} ~~is very difficult~~ to overcome the strong attraction between the nucleus and the electrons.

QUESTION THREE

- (a) In the standardisation of a solution of hydrochloric acid, $\text{HCl}(aq)$, students were advised to measure 2.691 g of anhydrous sodium carbonate, $\text{Na}_2\text{CO}_3(s)$, 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, $\text{HCl}(aq)$.

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

✓
✓
✓

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 $\text{HCl}(aq)$ 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 the their procedures.

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

Student A:

$$\text{titre}_{\text{ave.}} = \frac{15.7 + 15.7 + 15.65}{3} = 15.68 \text{ mL}$$

$$[\text{Na}_2\text{CO}_3] = \frac{2.691 \div 106.0}{0.25} = 0.1015 \text{ mol L}^{-1}$$

$$n(\text{Na}_2\text{CO}_3) = 0.1015 \times 0.01 = 0.001015 \text{ mol}$$

$$\therefore n(\text{HCl}) = 0.001015 \text{ mol}$$

$$[\text{HCl}]_A = \frac{0.001015}{0.01568} = 0.06475 \text{ mol L}^{-1} \text{ (4sf)}$$

$$= 0.06475 \text{ mol L}^{-1} \text{ (4sf)}$$

$$= 0.06475 \text{ mol L}^{-1} \text{ (4sf)}$$

Student B:

$$\text{titre ave.} = \frac{19.90 + 20.20}{2} = 20.05 \text{ mL}$$

$$n(\text{Na}_2\text{CO}_3) = 0.001015 \text{ mol}$$

$$\therefore [\text{HCl}]_B = \frac{0.001015}{0.02005} = 0.05065 \text{ mol L}^{-1} \text{ (4 sf)}$$

Validity Source of error:

Transferring the powdered Na_2CO_3 to the flask was likely ~~more~~ inaccurate as residue may be left on the spatula/container. This would make $[\text{Na}_2\text{CO}_3]$ lower than the expected value. Instead, the standard Na_2CO_3 should be standardised itself by titration with another solution of known concentration.

Student A:

~~The~~ The calculated concentration was too low ($0.06475 \text{ mol L}^{-1}$ vs. $0.1040 \text{ mol L}^{-1}$), ^{so invalid.} However, results were accurate with several concordant titres. Thus, experimental technique was likely good, but a mistake was likely made in producing the Na_2CO_3 standard such that its concentration was too low.

Student B:

The calculated $[\text{HCl}]$ was also too low ($0.05065 \text{ mol L}^{-1}$ vs. $0.1040 \text{ mol L}^{-1}$), so invalid. Also, they were inaccurate as no concordant titres (within 0.20 mL) were obtained. This suggests an issue in technique, eg. inability to make the burette go drop-wise, or difficulty determining endpoint.

- (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:

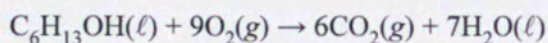
Bond enthalpies / kJ mol ⁻¹			
C-O	358	O-H	463
C=O	745	O=O	498

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.

$$q = mc\Delta T = (300)(4.18)(51.5 - 22.3) = 36617 \text{ J} = 36.62 \text{ kJ}$$

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

$$\Delta_c H = \frac{-36.62}{0.01321}$$

$$= 2772 \text{ kJ mol}^{-1}$$

$$= -2770 \text{ kJ mol}^{-1} \text{ (3 sf)}$$

$$n = \frac{1.35}{102.2}$$

$$n = 0.01321 \text{ mol}$$

Method 2: Using enthalpies of formation

$$\Delta_c H = 6\Delta_f H(\text{CO}_2) + 7\Delta_f H(\text{H}_2\text{O}) - \Delta_f H(\text{C}_6\text{H}_{13}\text{OH})$$

$$= 6(-393) + 7(-286) - (-320)$$

$$= -4040 \text{ kJ mol}^{-1}$$

Method 3: Using bond enthalpies and enthalpies of reaction

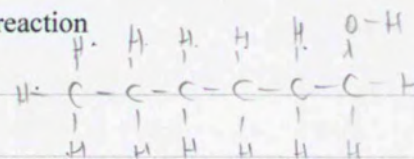
$$-4(\text{C-H}) = -1652$$

$$\therefore (\text{C-H}) = 413$$

$$-(\text{C-C}) + 6(\text{C-H}) = -2826$$

$$(\text{C-C}) = 348$$

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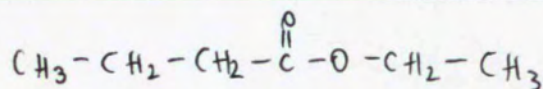
$$\Delta_c H = [5(-348) + 13(-413) + 358 + 463 \times 7] + 320$$

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

In method 1, it is likely that not all energy released actually went toward heating the H_2O , as some would be lost to surroundings (eg. the beaker). Therefore, temperature change is lower than the expected value, so $\Delta_c H$ for method 1 is less negative than the others, as seemingly less energy is released.

In method 3, the bond enthalpies used are likely not the values truly present in hexan-1-ol, as they are derived from averages + the formation of methane and methanol. 'Equivalent' bonds, eg. (C-H), have different enthalpies in different environments, depending on the surrounding molecule. It is likely that the C-C and C-H bonds are actually ~~stronger than~~ weaker than those derived from methane and ethane, as the O-H group in hexan-1-ol draws electron density away from the C's, making the bond weaker. Therefore, method 3 gives a value that is less negative than method 2 as the energy required to break hexan-1-ol's bonds is likely lower than what is calculated. Method 2 gives the most negative $\Delta_c H$, and is likely the most accurate as the exact enthalpy of formation book values are used.

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



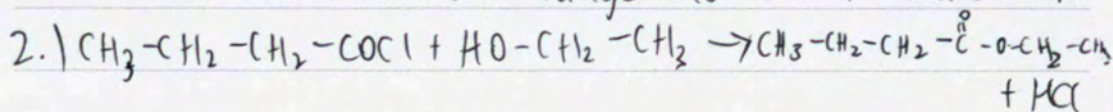
ethyl butanoate

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

In your answer:

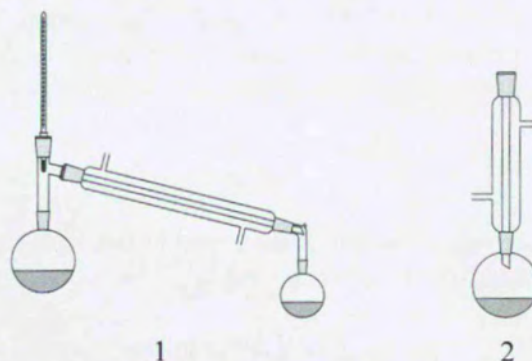
- give structural equations and include clear references to any other reagents or steps which might be required
- compare and contrast the experimental conditions and safety considerations for these reactions.

1.) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{COOH} + \text{HO}-\text{CH}_2-\text{CH}_3 \rightleftharpoons \text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{O}-\text{CH}_2-\text{CH}_3 + \text{H}_2\text{O}$
 for the reaction of a carboxylic acid and an alcohol, an equilibrium is established, yielding lower ester product. ~~H₂SO₄ must~~ ^{Heat with} Concentrated H₂SO₄ must be added which acts as a catalyst (higher rate of reaction) and a dehydrating agent to favour the forward reaction, but conc. acid can be dangerous if it touches skin.



Reaction of an ~~car~~ acid chloride and an alcohol occurs to completion with no catalyst ^{or heat} (as -COCl is highly reactive), so produces a higher yield. However, toxic steamy fumes of HCl are produced, so it should be done in a fume cupboard.

- (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.

Apparatus 2, reflux, should be used for the hydrolysis. This ensures a high yield and rate of reaction as any evaporated ethyl butanoate will be condensed and dripped back into the reaction mixture, allowing for complete ~~esterification~~ hydrolysis of all ethyl butanoate.

*with the ester + dilute H^+ in the flask.

At the end of the reaction, only ethanol and butanoic acid (+ excess $\text{H}_2\text{SO}_4(\text{aq})$) are in the flask. Thus, apparatus 1, distillation, can separate them. The flask should be heated to a temperature $\pm 2^\circ\text{C}$ of ethanol's boiling point, but well below butanoic acid's higher boiling point (around 80°C). Thus, ethanol is evaporated from the mixture, leaving just butanoic acid in the original flask, and condenses. Due to the angle of the condenser, ethanol drips into a new separate flask, not the original reaction mixture.

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.

$$1.80 \times 10^{-10} = [\text{Ag}^+][1.68 \times 10^{-4}]$$

$$[\text{Ag}^+] = \frac{1.80 \times 10^{-10}}{1.68 \times 10^{-4}} \text{ needed to precipitate AgCl}$$

$$2.60 \times 10^{-12} = [\text{Ag}^+]^2 [1.39 \times 10^{-4}]$$

$$[\text{Ag}^+] = 1.368 \times 10^{-4} \text{ mol L}^{-1} \text{ needed to precipitate Ag}_2\text{CrO}_4$$

~~Ag₂CrO₄ precipitates first, as a smaller amount of Ag⁺ is required.~~

AgCl precipitates first

- (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.

$$\text{initial } n(\text{CrO}_4^{2-}) = 0.125 \times 1.39 \times 10^{-4}$$

$$= 1.738 \times 10^{-5} \text{ mol}$$

When AgCl begins to precipitate, $[\text{Ag}^+] = 1.071 \times 10^{-6}$.

$$\therefore \frac{2.60 \times 10^{-12}}{(1.071 \times 10^{-6})^2} = [\text{CrO}_4^{2-}]$$

$$[\text{Cl}^-]_i =$$

$$n(\text{Ag}^+)_{\text{added}} = n(\text{AgCl}(s)) + n(\text{Ag}^+_{\text{rem}})$$

(back)

$$\begin{aligned}
 & 21(\text{Ag}_2\text{CrO}_4) \\
 & = [\text{AgCrO}_4] + [\text{Ag}^+_{\text{aq}}] \\
 & (1.071 \times 10^{-6}) = n(\text{AgCrO}_4) + n(\text{Ag}^+_{\text{aq}}) \\
 & + 3.39 \times 10^{-7} = n(\text{AgCrO}_4) + n(\text{Ag}^+_{\text{aq}})
 \end{aligned}$$

$$1.808 \times 10^{-10} = \left[1.071 \times 10^{-6} - \frac{n(\text{AgCl})}{0.125} \right] \left[1.68 \times 10^{-4} - \frac{n(\text{AgCl})}{0.125} \right]$$

$$n(\text{AgCl}) = 2.113 \times 10^{-5}$$

$$2.60 \times 10^{-12} = \left[1.071 \times 10^{-6} - \frac{n(\text{Ag}_2\text{CrO}_4)}{0.125} \right]^2 \left[1.39 \times 10^{-4} - \frac{n(\text{Ag}_2\text{CrO}_4)}{0.125} \right]$$

$$n(\text{Ag}_2\text{CrO}_4) = 1.283$$

Can not be used to separate

- (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).

AgCl

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.

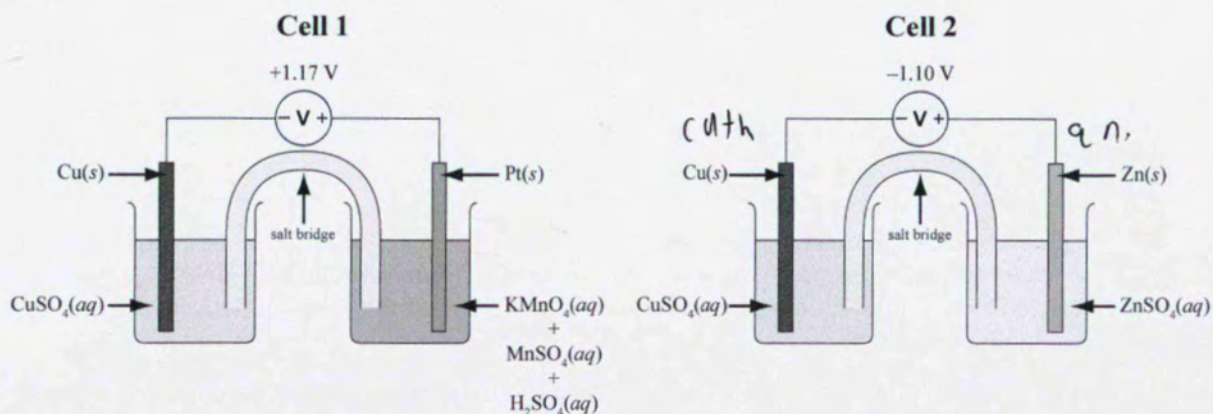
$$\begin{aligned}
 n(\text{AgNO}_3) &= n(\text{AgCl}) + n(\text{Ag}^+_{\text{aq}}) \\
 (0.0168)c &= 0.9922 \times 0.125 + 1.68 \times 10^{-4} + (1.368 \times 10^{-4}) \left(\frac{0.1418}{0.125} \right)
 \end{aligned}$$

$$c = 2.395 \times 10^{-3} \text{ mol l}^{-1} \text{ (4 sf)}$$

- (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.

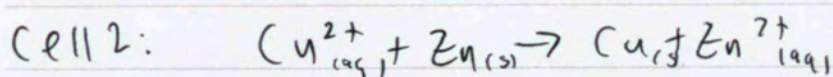
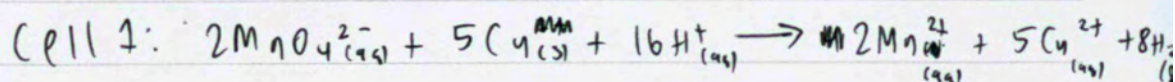
In cell 1, MnO_4^- is spontaneously reduced to Mn^{2+} , which is on the left right (at the cathode) and Cu is spontaneously oxidised to Cu^{2+} , causing mass deposits on the anode. The e^- released in the oxidation of Cu are transferred in the wire to the cathode, where they are gained by MnO_4^- , reducing it to Mn^{2+} .

* (acidity provided by H_2SO_4).

In cell 2, Cu^{2+} is spontaneously reduced to Cu , resulting in mass gain of the cathode, and Zn is spontaneously oxidised to Zn^{2+} , resulting in mass loss of the anode. e^- released in the oxidation of

Zn travel through the wire to the cathode, where they are gained by Cu^{2+} , reducing it to $\text{Cu}(s)$.

In both cases, ions flow in the salt bridge to maintain neutrality in each half cell, and produce a complete circuit for current to flow.



- (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, $\text{H}^+/\text{MnO}_4^-(\text{aq})$.

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

$$1.10 = E^\circ(\text{Cu}^{2+}/\text{Cu}) - (-0.76)$$

$$E^\circ(\text{Cu}^{2+}/\text{Cu}) = 1.86 \text{ V}$$

$$1.17 = E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) - 1.86$$

$$E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = -0.69 \text{ V}$$

Thus, when $\text{Zn}(s)$ is added to $\text{H}^+/\text{MnO}_4^-$, the MnO_4^- spontaneously oxidises Zn to Zn^{2+}

$$E^\circ_{\text{cell}} = -0.69 - (-0.76)$$

$$= 0.07 \text{ V} \Rightarrow E^\circ > 0, \text{ so the reaction is spontaneous}$$

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, $\text{MgCl}_2(s)$, and sodium chloride, $\text{NaCl}(s)$.

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

MgCl_2 will require more energy as its ionic bonds are stronger.

firstly, MgCl_2 ~~extra~~ has larger magnitude of charge (Mg^{2+} vs. Na^+), so the attraction between ions is greater (ionic bond strength is proportional to charge magnitude).

secondly, Mg^{2+} ions are smaller ^{than Na^+} due to the greater nuclear charge than Na^+ , but isoelectronic arrangements (so constant shielding). Therefore, the ionic bonds act over a smaller distance (ionic bond strength is inversely proportional to distance between ions). Also, MgCl_2 has more ions (Cl_2 vs. Cl), so ^{has more ionic bonds to break}. Therefore, MgCl_2 has stronger ionic bonds, so requires more energy to break the crystal into gaseous ions.

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

QUESTION
NUMBER

1biii) In the ~~AA~~ T-shaped molecule, the dipoles ($\delta\text{Br}-\delta\text{F}^-$ due to the electronegativity difference between covalently-bonded molecules) are asymmetrically arranged as the axial dipoles cancel, but the equatorial one does not as it is opposite to lone pairs. Thus, charge distribution is uneven, making BrF_3 polar.

1ci) 20 mL excess:

$$n(\text{HNO}_3) = 0.02 \times 0.13 \\ = 0.0026 \text{ mol}$$

$$[\text{H}_3\text{O}^+] = \frac{0.0026}{0.025 + 0.03498 + 0.02} \\ = 0.1012 \text{ mol L}^{-1}$$

$$\text{pH} = -\log(0.1012) \\ = 0.9950 \text{ (4 sf)}$$

2ai) • Adding $\text{AgNO}_3(\text{s})$ introduces $\text{Ag}^+(\text{aq})$ into solution. This will precipitate with Cl^- in solution, forming white $\text{AgCl}(\text{s})$ precipitate: $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$. This decreases $[\text{Cl}^-]$, shifting equilibrium 2 left to reform it, decreasing $[\text{CoCl}_4]^{2-}$. This increases $[\text{Co}^{2+}]$, shifting equilibrium 1 right, increasing $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

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

QUESTION
NUMBER

Thus, the solution also becomes less blue and more pink (lighter purple).

$$\begin{aligned} 3b) \Delta_c H &= [5(348) + 13(413) + 358 + 463 + 9(498)] \\ &\quad - [12(145) + 14(463)] \\ &= -3010 \text{ kJ mol}^{-1} \end{aligned}$$

4a) ~~find $[CrO_4^{2-}]$ when $AgCl$ precipitates~~

~~for $AgCl$ to precipitate, $[Ag^+] = 4.07 \times 10^{-6} \text{ mol L}^{-1}$~~

find $[Cl^-]$ when Ag_2CrO_4 begins to ppt:

$$[Ag^+] = 1.368 \times 10^{-4} \text{ mol L}^{-1}$$

$$\therefore 1.80 \times 10^{-10} = (1.368 \times 10^{-4})^2 [CrO_4^{2-}]$$

$$[CrO_4^{2-}] = 1.316 \times 10^{-6} \text{ mol L}^{-1}$$

$$[Cl^-]_i = 1.68 \times 10^{-4} \text{ mol L}^{-1}$$

$$\% \text{ ppt: } \frac{(1.68 \times 10^{-4}) - (1.316 \times 10^{-6})}{1.68 \times 10^{-4}} \times 100$$

$$= 99.22\% \text{ (4sf)} \Rightarrow \text{below } 99.9\%$$

$\therefore$ this procedure cannot be used to separate Cl^- from CrO_4^{2-} .

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

QUESTION
NUMBER

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

QUESTION
NUMBER

93102

Outstanding Scholarship

Subject: Chemistry

Standard: 93102

Total score: 26

Q	Score	Marker commentary
1	7	(a) Wrote a balanced chemical equation and discussed entropy changes in the system, surroundings, and total entropy. Addressed reasons for the reaction in water. (b) Lewis diagrams attempted with errors (no brackets), incorrect discussion of F^- ion transfer, but discussed correct shape and polarity of BrF_3 molecules. (c) Two correct pH values calculated correctly, curve attempted, and discussed buffering.
2	6	(a) Addressed equilibrium shifts in the system to both reactants and products (split equations utilised) and addressed the test for water. (b) Incomplete scheme with errors, no correct products, but good discussion of the use of IR and ^{13}C NMR to differentiate compounds. (c) Explained Al and He with good use of chemistry vocabulary, but limited justification against other atoms.
3	7	(a) Calculations completed with mol-ratio errors, and attempts made to discuss accuracy and validity. (b) All three enthalpy values correctly calculated with different reasons for variation in values provided. (c) Drew / named correct ester, discussed two different synthesis routes in depth, addressed multiple safety risks, and discussed both distillation and reflux clearly.
4	6	(a) Completed calculations in (i) and (ii) correctly, with limited attempt made at (iii). (b) Discussed aspects of both electrochemical cells and attempted to answer (ii). (c) Discussed the impact of both the charge and size of the Na^+ and Mg^{2+} ions on the energy requirements.