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TOP SCHOLAR



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.

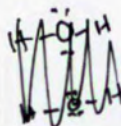
Show ALL working.

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.**

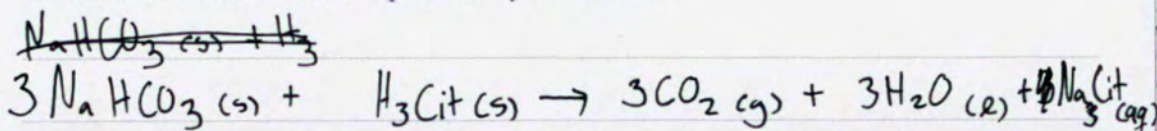


QUESTION ONE

- (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 $\text{NaHCO}_3(s)$ reacts with $\text{H}_3\text{Cit}(s)$, 4 moles of ~~solid~~ ^{particulate} highly ordered unrandomised solid particles react to form 3 moles of highly randomised and disordered gaseous ^{CO_2} particles, and 3 moles of liquid H_2O molecules and 1 mole of aqueous Na_3Cit ions in solution. As the number of particles increases ^{more} and these particles are much more randomly randomised/disordered, there is a greater dispersal of matter and energy in the system. Entropy of the system therefore increases. The temperature of the solution decreases indicating the reaction is endothermic. The temperature of surrounding particles ~~also~~ decreases, so they have less energy and are more less random. There is less dispersal of matter and energy in the surroundings, so entropy of the surroundings decreases. The reaction is spontaneous, so ~~the~~ ΔS is positive, meaning the increase of entropy in the solution outweighs the decrease in the surroundings.

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

As solids, H_3Cit and the ions in NaHCO_3 have restricted movement due to the strong fixed ionic bonds / ^{inter molecular forces} hydrogen bonds holding the ~~same~~ ions/molecules in place. Because of this the particles collide infrequently and with little energy, so there are few collisions, and successful collisions per second, and the ^{rate of} reaction is ~~near~~ effectively 0. Once dissolved in water the Na^+ and HCO_3^- and H_3Cit molecules have more energy and free movement as their respective bonds are broken. There are more successful collisions per second so R.O.R increases and the reaction ^{partially dissociates} H_3Cit reacts with H_2O to form H_3O^+ , which ^{to drive the reaction} is what reacts with HCO_3^- ^{occurs.}

(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:

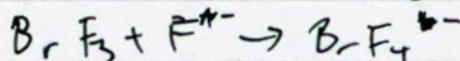
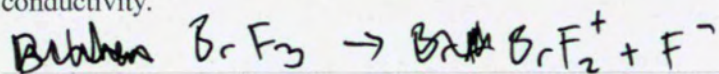


- (i) Predict, with support of Lewis diagrams, the shapes and F-Br-F bond angles for the four different ions which could be produced during autoionisation.

BrF_2^- Lewis diagram: Shape/bond angle: linear, 180°	BrF_4^+ Lewis diagram: Shape/bond angle: axial-equat. equat-equat. seesaw: $<90^\circ$, $<120^\circ$
BrF_2^+ Lewis diagram: Shape/bond angle: bent, $<109.5^\circ$	BrF_4^- Lewis diagram: 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.



When BrF_3 loses and gains and an F^- ion, it forms BrF_2^+ and BrF_4^- respectively, as in (2). The BrF_2^+ and BrF_4^- in (1) could only be produced if an F^+ ion was transferred. It is much more likely for an F^- ion to be transferred than F^+ as F^- is more stable (as it has a full outer shell) and F^- is more easily formed from F .

F is very electronegative, so is more likely to gain electrons than lose them. In BrF_3 the $\text{Br}-\text{F}$ molecule is polar with the electrons orbiting closer to F due to F being more electronegative than Br . It is therefore likely that both the bonded electrons will be transferred with F , rather than Br , in the form of an F^- ion. (2) is more likely than (1) to give the ions responsible for 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.

In BrF_3 there are five electron areas around the central Br atom. To maximise separation and minimise repulsion these will repel into a trigonal bipyramidal arrangement with 90° and 120° bond angles. Two of these electron areas are lone pairs. Lone pair electrons are held closer to the nucleus, so impose greater repulsive forces on other electron areas than bonded electron. To minimise repulsive forces, the lone pairs will therefore occupy the equatorial regions, as these are most separated from the other areas. The final shape will therefore be T-shaped, with two bonds in the axial areas and one in the equatorial with bond angles $< 90^\circ$. Trigonal planar is incorrect as this would have the lone pairs in the axial regions increasing repulsion. The $\text{Br}-\text{F}$ bond is polar as F is more electronegative than Br. It has dipoles as shown: $\text{Br}^{\delta+}-\text{F}^{\delta-}$. Due to the T shape, these polar bonds and their dipoles are arranged asymmetrically around the central Br atom. The dipoles do not cancel, charge distribution is uneven, and BrF_3 is 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 $0.1300 \text{ mol L}^{-1}$ 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.

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

$$\text{Initial } [\text{H}_3\text{O}^+] = \sqrt{\frac{10^{-10.64} \times 10^{-14}}{[\text{CH}_3\text{CH}_2\text{NH}_2]}}$$

$$\text{Initial } n(\text{CH}_3\text{CH}_2\text{NH}_3^+) = n(\text{HNO}_3)_{\text{added at equivalence}} = 0.13 \times 0.03498 = 4.547 \times 10^{-3} \text{ mol}$$

$$\text{Initial } [\text{CH}_3\text{CH}_2\text{NH}_2] = \frac{4.547 \times 10^{-3}}{0.025} = 0.1819 \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = 1.122 \times 10^{-12}$$

$$\text{Initial pH} = 11.95$$

$$\text{pH halfway to equivalence} = 10.64 \quad (17.49 \text{ mL})$$

$$\text{At equivalence } n(\text{CH}_3\text{CH}_2\text{NH}_3^+) = 4.547 \times 10^{-3}$$

$$[\text{CH}_3\text{CH}_2\text{NH}_3^+] = 4.547 \times 10^{-3}$$

$$0.025 + 0.03498$$

$$= 0.0758 \text{ mol L}^{-1}$$

$$[\text{H}_3\text{O}^+] = \sqrt{10^{-10.64} \times 0.0758}$$

$$= 1.318 \times 10^{-6}$$

$$\text{Equivalence pH} = 5.88$$

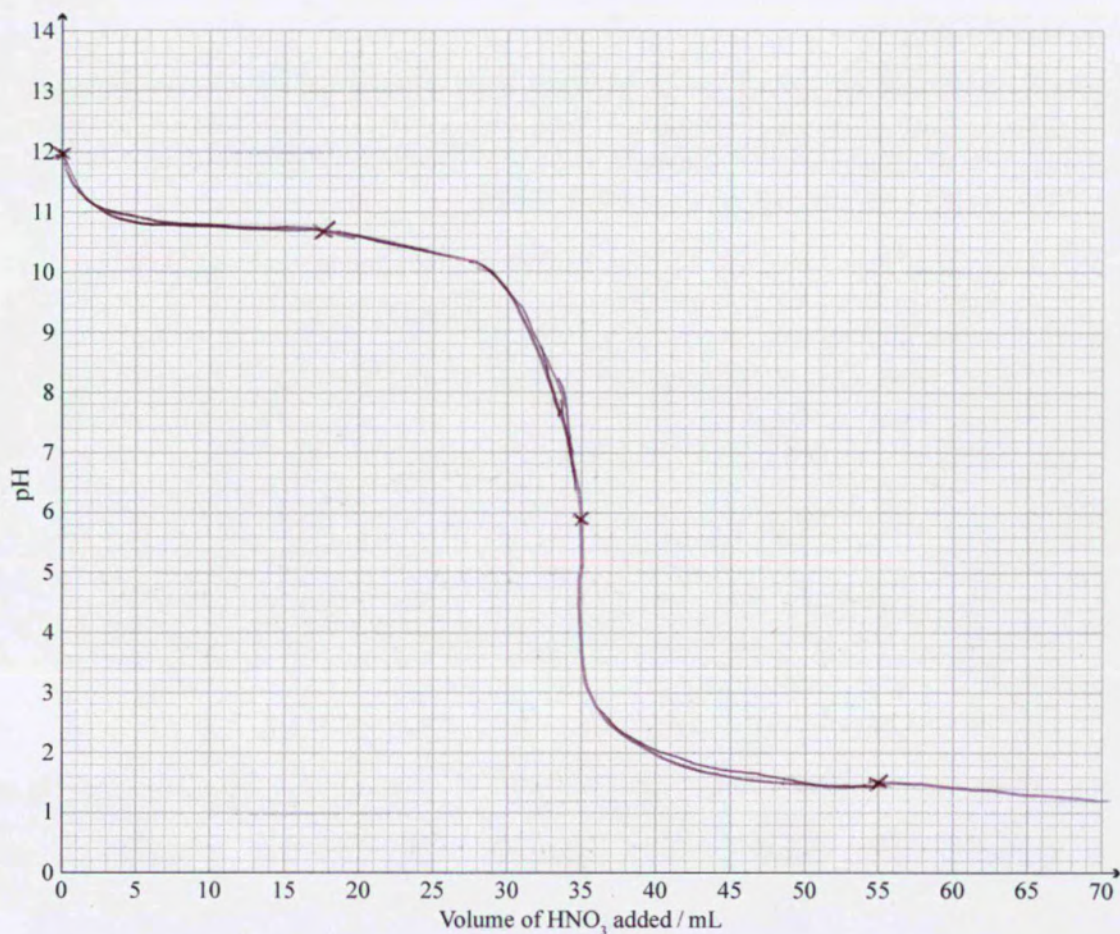
$$\text{After } 54.98 \text{ mL added, } n(\text{HNO}_3) = 0.05498 \times 0.13 - 0.004547$$

$$= 2.6 \times 10^{-3} \text{ mol}$$

$$[\text{H}_3\text{O}^+] = [\text{HNO}_3] = 2.6 \times 10^{-3}$$

$$0.025 + 0.05498$$

$$\text{after } \text{pH} = [\text{H}_3\text{O}^+] = 0.0325 \text{ mol L}^{-1}$$



- (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.

After 18 mL ~~CH_3COOH~~ CH_3COOH CH_3COO^-

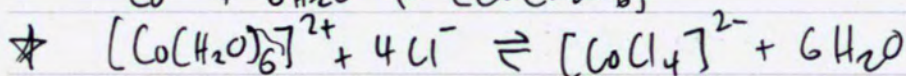
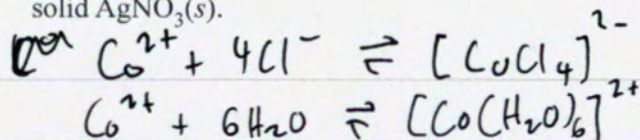
At 18 mL the pH is very close to pK_a , so $\frac{[\text{base}]}{[\text{acid}]}$ is close to (but slightly less than) 1. The solution will have slightly more buffering capacity against strong base but will be proficient against both strong acid and strong base. After 28 mL has been added the pH is more significantly lower than pK_a , so the solution will be a significantly better buffer against strong base than strong acid. However, the solution is still in the buffer zone so will be ~~proficient~~ able to buffer against both to some extent.

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 $\text{AgNO}_3(\text{s})$.



When conc. HCl is added, it fully dissociates in the solution to produce Cl^- ions $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{H}_3\text{O}^+$. An increase in concentration of reactants (Cl^-) in the equilibrium equation causes the equilibrium to shift to favour the forward reaction to remove the added Cl^- . $[\text{CoCl}_4]^{2-}$ therefore increases while $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ decreases as more $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ reacts. The solution turns more blue.

If AgNO_3 is added, it will dissolve to form Ag^+ and NO_3^- ions in solution. This Ag^+ will react with Cl^- to form insoluble AgCl ppt. This decreases $[\text{Cl}^-]$, ~~so for opposite reasoning from before~~ so the equilibrium shifts to favour the backward reaction. $[\text{CoCl}_4]^{2-}$ decreases, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ increases, solution turns more pink.

- (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 chemical paper can be used to detect chloride ions such as in ^{solution} HCl . When in contact with Cl^- ions, $[\text{Cl}^-]$ increases and the equilibrium shifts to produce more Co^{2+} convert $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ to $[\text{CoCl}_4]^{2-}$, so the paper turns from blue to pink. (Using equation * from (i)). If no Cl^- present, paper will remain blue.~~

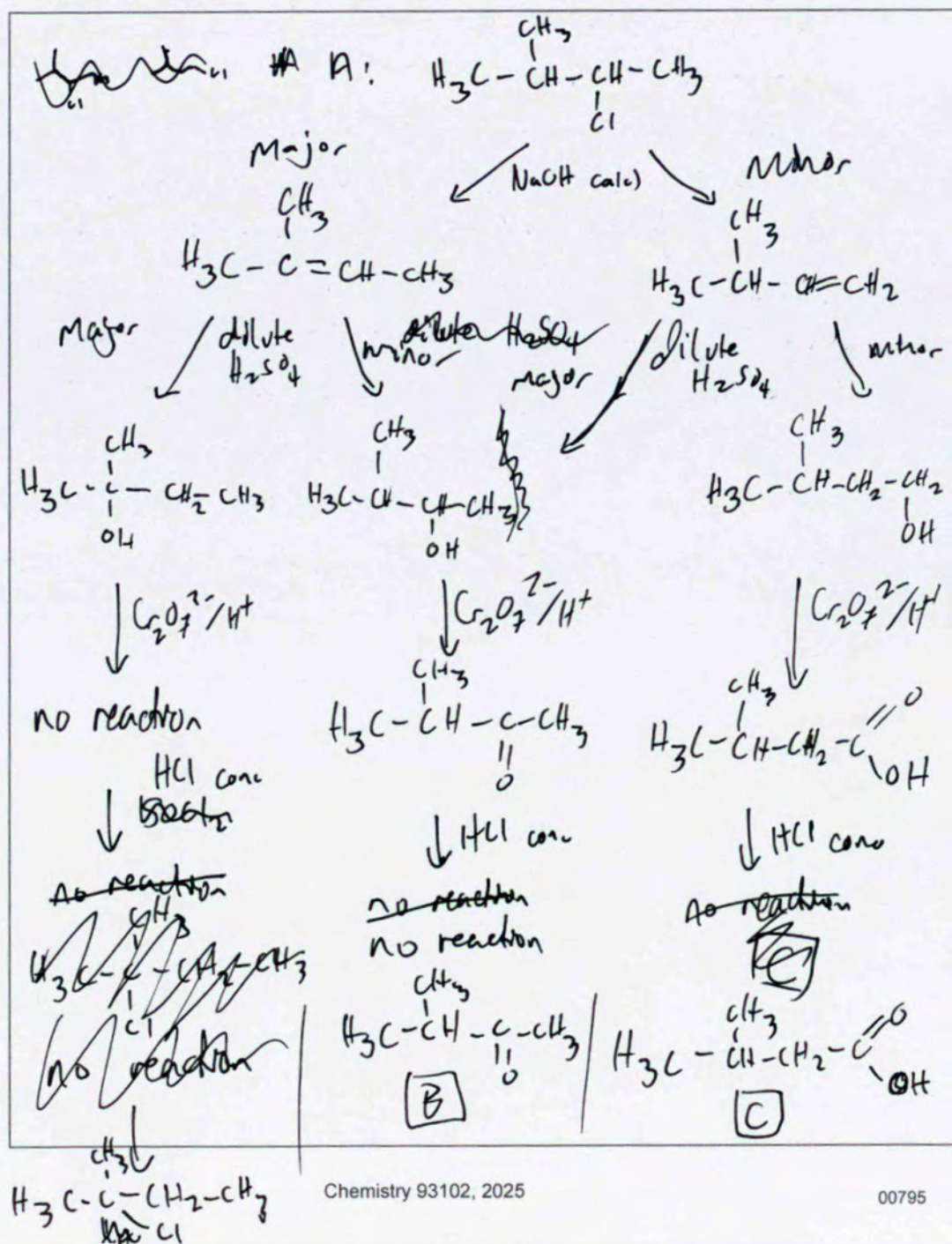
~~The chem~~ The paper can detect H_2O . When in contact with H_2O the equilibrium from (i) will shift to favour the backward reaction, converting blue $[\text{CoCl}_4]^{2-}$ to pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, so the paper turns pink. If no H_2O present it will remain blue. This is evidenced by the ~~ions in the~~ H_2O solution the paper was prepared in being pink due to the ions being surrounded by H_2O . Once the paper is dried there is no H_2O present so the paper turns blue.

(b) Compound A, $C_5H_{11}Cl$, 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 $NaOH(aqc)$. 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.

~~C can be distinguished from the others using IR spectroscopy due to its $\text{C}=\text{O}$ bond in its COOH group. It will show a sharp peak around 1700 cm^{-1} which is absent for A and B.~~

A can be distinguished from B and C due to it not having a $\text{C}=\text{O}$ bond. It will therefore show no strong peak in the $1700\text{--}1730\text{ cm}^{-1}$ range, unlike B and C on the IR. It will also show no peak above 2000 cm^{-1} on the ^{13}C NMR, unlike B and C which have peaks around 210 and 180 ppm respectively. B can be distinguished from C by it having the highest ^{13}C NMR peak due to it having a ketone environment vs C's COOH environment. B can also be distinguished from C with IR, as C has a broad asymmetrical peak around 3000 cm^{-1} from its COOH group while B does not.

HEA:

NAME

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(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.	He
Ions of this Period 3 element have the smallest ionic radius of all ions in this period. Al, Si	
This element exists as a gaseous diatomic molecule, with the highest bond enthalpy of any of the diatomic molecules.	N ₂

Shortest length

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

(1) Element: B

Discussion: ~~He, O, F, and Ne~~ have 4, 5 and 6 electrons in the 2p subshell respectively, and therefore have paired ~~at~~ electrons (as they have more than 3). The general trend of ionisation energy across a period is increasing as nuclear charge increases while the electron shielding effect and ~~distance from~~ atomic radius stays roughly constant. This trend is disrupted for B. Be has arrangement $1s^2 2s^2$, while B has $1s^2 2s^2 2p^1$. This addition of an electron to a new subshell increases the shielding effect and radius for B compared to Be. This outweighs its greater nuclear charge and means its ionisation energy decreases ~~disrupting the trend~~.

(2) Element: He

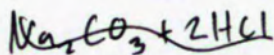
Discussion: Ionisation energy increases in general across a period, as described above. Ionisation energy decreases down a group as

Successive elements have their outermost e^- s in higher principal energy levels, leading to much more electron shielding and higher atomic radii. This outweighs the greater nuclear charge, decreasing ionisation energy. The effect down a group is much more significant than the effect across a period. The element with highest ionisation energy is that with lowest ~~group~~ ^{period} and greatest highest group, i.e. He.

(3) Element: ~~N₂~~

Non-polar Discussion: Bond enthalpy is determined by the length of the bond and the number of e^- it ~~stores~~ has (single, double triple bond). Triple bonds have much higher enthalpies than doubles which are higher than singles. Bond length is proportional to atomic radius. The element with the smallest atomic radius that forms triple bonded, diatomic molecules is ~~N₂~~, so the ^{gaseous} element is N.

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 their procedures.

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

$$\text{Student A: Avg titre} = \frac{15.7 + 15.7 + 15.65}{3} = 15.68 \text{ mL}$$

$$n(\text{Na}_2\text{CO}_3) = \frac{2.691}{106.0}$$

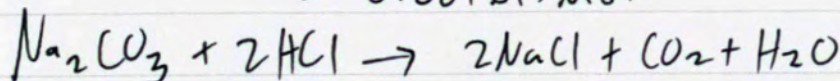
$$= 0.02539 \text{ mol}$$

$$[\text{Na}_2\text{CO}_3] = \frac{0.02539}{0.25}$$

$$= 0.1015 \text{ mol L}^{-1}$$

$$10 \text{ mL } n(\text{Na}_2\text{CO}_3) = 0.1015 \times 0.01$$

$$= 0.001015 \text{ mol}$$



$$n(\text{HCl}) = 2 \times 0.001015$$

$$= 2.031 \times 10^{-3}$$

$$[\text{HCl}] = \frac{2.031 \times 10^{-3}}{0.01568} = 0.1295 \text{ mol L}^{-1}$$

$$\text{Student B: Avg titre} = \frac{19.90 + 20.20 + 20.55}{3}$$

$$= 20.22 \text{ mL}$$

$$[\text{HCl}] = \frac{2.031 \times 10^{-3}}{0.02022}$$

$$= 0.1005 \text{ mol L}^{-1}$$

Student A differs from teacher by 24.5%.
 while student B differs by only 3.41%.
 so student B's results are more accurate. However,
 her findings are less valid as she had a greater
 variation/range in her titration values than student A, so
 it is possible the result was due to chance.

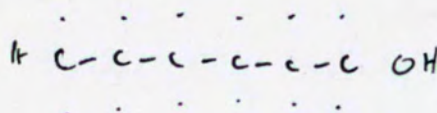
Student A was less accurate but his titrations
 were very consistent, giving his results more validity.
 Error may have ~~arose~~ arose from parallax (not
 reading burette at right angles), not consistently
 using bottom of ^{or pipette} meniscus for measurements, or misjudging
 the endpoint of the titration. Student B while had
 more random error, while student A a systematic error
 (e.g. making his Na_2CO_3 solution too concentrated by misreading
 the scale).

- (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

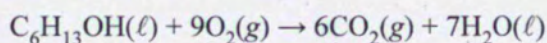
Enthalpies of reaction / kJ mol ⁻¹	
C(g) + 4H(g) → CH ₄ (g)	Δ _r H° -1652
2C(g) + 6H(g) → C ₂ H ₆ (g)	Δ _r H° -2826



The specific heat capacity of water is 4.18 J g⁻¹ °C⁻¹.

M(C₆H₁₃OH(l)) = 102.2 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.

$$n = \frac{1.35}{102.2} = 0.01321 \text{ mol}$$

$$Q_{\text{water}} = E = m_c \Delta T = 300 \times 4.18 \times (51.5 - 22.3)$$

$$\text{Energy released } E = 36.616 \text{ kJ}$$

$$\Delta_c H = \frac{-36.616}{0.01321} = -2771.900 = -2772 \text{ kJ mol}^{-1}$$

Method 2: Using enthalpies of formation

$$\begin{aligned} \Delta_c H &= \Delta_c H = \sum \Delta_f \text{ products} - \sum \Delta_f \text{ reactants} \\ &= -320 - 6(-393) - 7(-286) \\ &= -4640 \text{ kJ mol}^{-1} \end{aligned}$$

Method 3: Using bond enthalpies and enthalpies of reaction

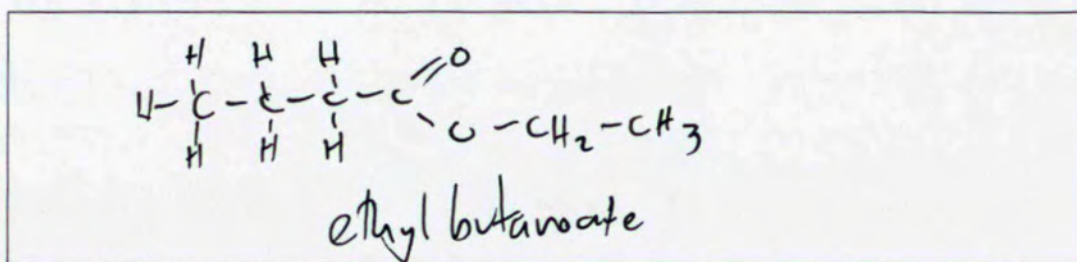
$$\begin{aligned} \Delta_c H &= \Delta_r H = \sum \text{bonds broken} - \sum \text{bonds formed} \\ \text{enthalpy bonds broken} &= \left(\frac{1652}{4}\right) \times 13 + \left(\frac{2826}{2} - \frac{6}{4}(1652)\right) \times 5 + 398 + 463 \\ &= 4445 + 47712412 \\ \text{enthalpy bonds formed} &= 12 \times 745 + 14 \times 463 \\ &= 15422 \end{aligned}$$

$$\Delta_c H = -3010$$

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

~~The~~ Method 1 ~~the~~ likely underestimates the enthalpy of combustion as much of the energy released is radiated into the surroundings and not absorbed by the water. This means the temperature rises by less than expected and $\Delta_c H$ is ~~less~~ calculated to be lower than the true energy released. Method 3 likely underestimates the true value as it doesn't account for the enthalpy change associated with the changing intermolecular forces and states of particles, only the change in intramolecular bonds. It ~~underest~~ There are ^{likely stronger} ~~weaker~~ intermolecular forces in the products than reactants so more energy is released than accounted for by calculating change in bond enthalpies. Nine gaseous moles of O_2 are reduced to only six gaseous moles of CO_2 . Method 2 calculates the correct $\Delta_c H$ as it accounts for this ^{change} as ^{intermolecular} forces are ^{and the state of the substance.} taken into $\Delta_c H$.

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

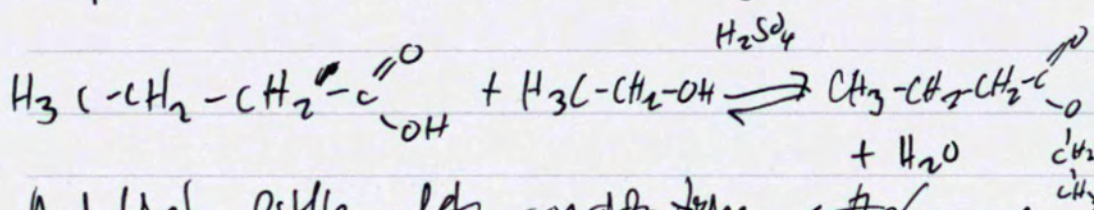


- (ii) Outline two different reactions that could be used to prepare this ester in a chemistry laboratory.

In your answer:

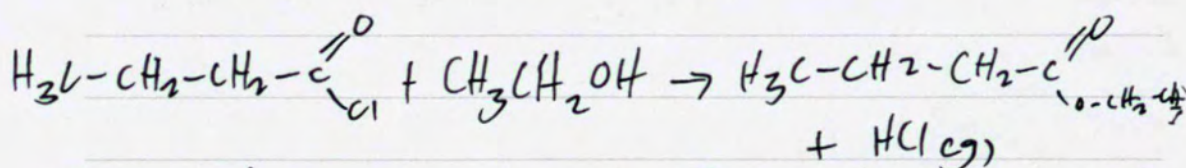
- give structural equations and include clear references to any other reagents or steps which might be required
- compare and contrast the experimental conditions and safety considerations for these reactions.

1st method: React butanoic acid with ethanol in the presence of conc. H_2SO_4 catalyst and reflux



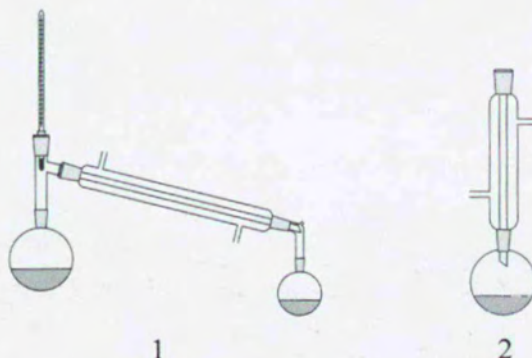
Relatively little safety considerations as the gentle handling of H_2SO_4 . Can acquire final product via distillation

2nd method: React butanoyl chloride with ethanol



This reaction occurs violently at room temperature with no catalyst. Much more dangerous as reaction mixture fizzes and releases dangerous ^{acidic} HCl fumes. However greater yield as reaction not an equilibrium.

- (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.

The acid hydrolysis will occur under reflux using 2. This allows the rate of reaction to be increased while not allowing volatile ^{or reactants} products like ethanol to escape the vessel as they are condensed and returned. Once the reaction is complete, ethanol and butanoic acid can be separated by distillation using 1. Butanoic acid has a higher boiling point than ethanol, so by heating the mixture to just above ethanol's boiling point ($\sim 100^\circ\text{C}$) the ethanol will evaporate while the butanoic acid does not. It will then condense into a separate container allowing them to be separated.

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, KCl(aq) , and $1.39 \times 10^{-4} \text{ mol L}^{-1}$ potassium chromate, $\text{K}_2\text{CrO}_4\text{(aq)}$. Small crystals of silver nitrate, $\text{AgNO}_3\text{(s)}$, 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.

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

AgCl

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

$$[\text{Ag}^+] = 1.071 \times 10^{-6} \text{ mol L}^{-1}$$

Ag_2CrO_4

$$2.60 \times 10^{-12} = [\text{Ag}^+]^2 \times [\text{CrO}_4^{2-}] \times 1.39 \times 10^{-4}$$

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

a lower $[\text{Ag}^+]$ is required for AgCl to ppt.
than for Ag_2CrO_4 , so AgCl is the first
solid to precipitate

- (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.

CrO_4^{2-} Cr^{2+} remains in solution

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

$$K_s[\text{Cl}^-] = 1.80 \times 10^{-10}$$

$$\begin{aligned} &= \frac{1.80 \times 10^{-10}}{1.368 \times 10^{-4}} \\ &= 1.316 \times 10^{-6} \text{ mol L}^{-1} \end{aligned}$$

$$\frac{1.316 \times 10^{-6}}{1.39 \times 10^{-4}} = 9.466 \times 10^{-3}$$

$$= 0.009466$$

$$= 0.9466\%$$

Percentage precipitated = $1 - 0.009466 = 99.05\%$
 $99.05 < 99.9$, cannot 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).

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.

$$n(\text{Cl}^-) = 0.125 \times 1.68 \times 10^{-4}$$

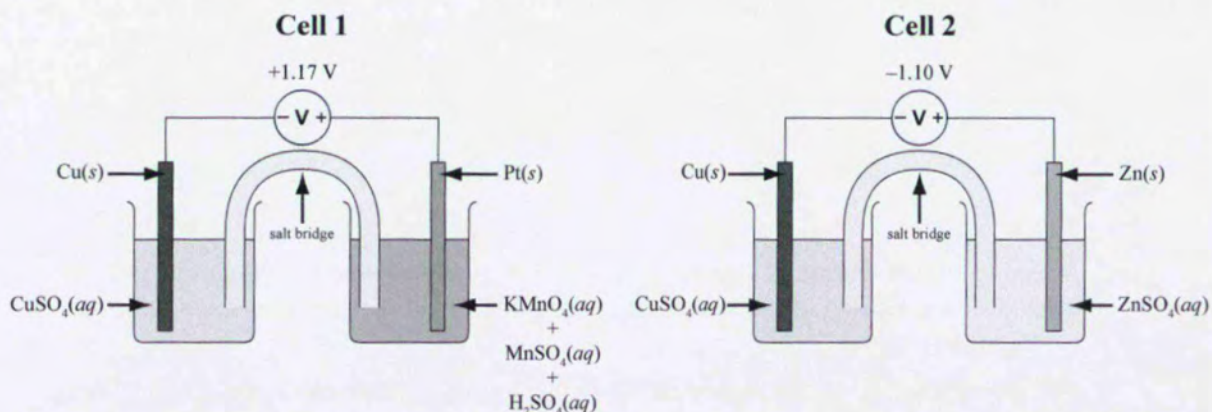
$$= 2.1 \times 10^{-5} \text{ mol}$$

$$n(\text{Ag}^+) \text{ precipitated} = 2.1 \times 10^{-5} \times 99$$

- (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, the Cu anode loses mass over time while the ~~the cathode~~ in the right half cell fades ~~as~~ from purple to colourless over time. In the left half cell Cu is ^{oxidized} ~~reduced~~ to Cu²⁺ at the cathode, each Cu atom loses two electrons. These electrons travel according to their natural flow along the wire toward the cathode, indicated by the positive voltage. At the cathode they reduce MnO_4^- to Mn^{2+} colourless ^{purple} Mn^{2+} ions in solution. ~~Each Mn^{2+} ion gains an electron~~ This causes the color change. Electrons are transferred from left to right, from Cu to MnO_4^- , through the wires. The charge in each half cell is kept neutral by the salt bridge.

As the left cell becomes positively charged, ~~K⁺~~ ^{SO₄²⁻} ions enter from the salt bridge, and vice versa with K⁺ ions in the right cell. In cell 2, the Cu cathode ~~anode~~ gains mass while the Zn anode ^{over time} loses mass. ~~Cu²⁺ is reduced to Cu(s) at the cath~~ ^{At the anode} Zn(s) is oxidised to Zn²⁺ losing two e⁻ that travel down the wire ^{according to} their natural flow to the cathode, where they reduce Cu²⁺ to Cu(s), which is deposited on the cathode. Again, ions in the salt bridge ensure each cell remains neutral as electrons are transferred from the right cell to the left.

- (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, Zn(s), was added to a beaker containing a solution of acidified potassium permanganate, $\text{H}^+/\text{MnO}_4^-(\text{aq})$.

Cell 1 $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$
 $E^\circ(\text{cell}) = E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) - E^\circ(\text{Cu}^{2+}/\text{Cu}) = 1.17 \text{ V}$
~~as it is spontaneous $E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) > E^\circ(\text{Cu}^{2+}/\text{Cu})$~~

Cell 2, ~~the cell Zn~~
 ~~$E^\circ(\text{Cu}^{2+}/\text{Cu}) > E^\circ(\text{Zn}^{2+}/\text{Zn})$ as Cu^{2+} is reduced spontaneously~~
~~Therefore $E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) > E^\circ(\text{Zn}^{2+}/\text{Zn})$~~
 ~~$\text{H}^+/\text{MnO}_4^-$ spontaneously reduces Zn^{2+} to Zn~~

Cell 2: $E^\circ(\text{Cu}^{2+}/\text{Cu}) - E^\circ(\text{Zn}^{2+}/\text{Zn}) = 1.10 \text{ V}$
 ~~$E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) - E^\circ(\text{Zn}^{2+}/\text{Zn}) =$~~
 ~~$= E^\circ(\text{Mn}^-/\text{Mn}^{2+})$~~ $E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$
 $E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = 1.51 \text{ V}$

$E^\circ \text{Cell} = E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) - E^\circ(\text{Zn}^{2+}/\text{Zn})$
 $= 1.51 - (-0.76)$
 $= 2.27$

Question Four continues on the next page.

Zn loses mass, solution turns purple to colourless as MnO_4^- spontaneously ~~oxidises Zn to Zn²⁺~~

- (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.

The energy required is determined by the strength of ~~and number~~ of the ionic bonds. The strength of an ionic bond is proportional to the charge on the ions and inversely proportional to the length of the bond (which is determined by atomic radii). Cl^- ions have the same charge and radius in both MgCl_2 and NaCl . ~~but~~ Mg^{2+} has a greater charge than Na^+ . It also has a smaller atomic radius, ~~as both elements have the same~~ as the ions are isoelectronic, but Mg^{2+} has a greater nuclear charge so it holds its outermost electrons more tightly. (while sodium is equivalent). The MgCl_2 ionic bonds are therefore stronger so more energy is required to break them apart as they are shorter and have greater charge, so more they are stronger than in NaCl . More energy required to break ~~them~~ apart an MgCl_2 crystal than an NaCl crystal.

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