

2022

HIGHER SCHOOL CERTIFICATE TRIAL EXAMINATION

Name:	
Class:	

Section I	/20
Section II	/80
Total	/100

Chemistry

General Instructions

- Reading time -5 minutes
- Working time -3 hours
- Write using blue or black pen Black pen is preferred
- Draw diagrams using pencil
- Board-approved calculators may be used
- A data sheet and a Periodic Table are provided at the back of this paper
- Write your name and class at the top of this page

Total marks -100

(Section I) Pages 2-9

20 marks

- Attempt Questions 1-20
- Allow about 35 minutes for this part

(Section II) Pages 10-29

80 marks

- Attempt Questions 21 33
- Allow about 2 hours and 25 minutes for this section

Section I: Multiple Choice Questions (20 marks) Attempt Questions 1-20 Allow about 35 minutes for this section

Use the multiple choice answer sheet for Questions 1-20.

1.	(A)	\bigcirc B	(C)	\bigcirc
2.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
3.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
4.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
5.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
6.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
7.	\bigcirc A	\bigcirc B	(C)	\bigcirc
8.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
9.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
10.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
11.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
12.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
13.	\bigcirc A	\bigcirc B	(C)	\bigcirc
14.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
15.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
16.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
17.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
18.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc
19.	\bigcirc A	\bigcirc B	<u>(C)</u>	\bigcirc
20.	\bigcirc A	\bigcirc B	\bigcirc	\bigcirc

1. Consider the following compound:

What is the systematic name of this compound?

- (A) 5-bromo-2-methylhexan-3-ol
- (B) 2-methyl-5-bromohexan-3-ol
- (C) 2-bromo-5-methylhexan-4-ol
- (D) 5-methyl-2-bromohexan-4-ol
- 2. A salt solution causes red litmus to turn blue. When this solution is vaporised into a flame, a brick red flame colour is observed.

What is a possible identity for this salt?

- (A) Silver nitrate
- (B) Silver acetate
- (C) Calcium nitrate
- (D) Calcium acetate
- 3. Consider the following equilibrium:

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)} \quad \Delta H > 0$$

Which of the following will increase the amount of carbon monoxide at equilibrium?

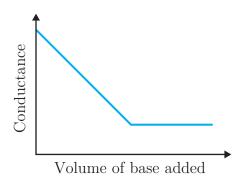
- (A) Adding solid carbon to the reaction mixture
- (B) Decreasing the temperature of the system
- (C) Increasing the volume of the system
- (D) Adding argon gas into the reaction mixture
- 4. Consider the following compound:

$$H - C = C - C - H$$
OH

Which row of the following table correctly describes this compound's water solubility and reactivity with bromine water?

	Water solubility	Reactivity with bromine water
(A)	Soluble	Decolourises
(B)	Soluble	No reaction
(C)	Insoluble	Decolourises
(D)	Insoluble	No reaction

5. A conductometric acid-base titration was carried out and the following conductivity curve was obtained.



Which row of the following table contains an indicator that would be suitable for this titration?

	Indicator	pH range
(A)	Crystal violet	0.0 - 2.0
(B)	Methyl red	4.4 - 6.2
(C)	Cresolphthalein	8.2 - 9.8
(D)	Indigo carmine	11.4 - 13.0

6. How many structural isomers are there for C_5H_{12} ?

- (A) 2
- (B) 3
- (C) 4
- (D) 5

7. The following thermodynamic data applies to the dissolution of an ionic compound in water.

$$\begin{split} \Delta_{\mathrm{sol}} H^{-} &= +111 \text{ kJ mol}^{-1} \\ \Delta_{\mathrm{sol}} S^{-} &= +64 \text{ J mol}^{-1} \text{ K}^{-1} \end{split}$$

Which of the following correctly describes $\Delta_{\rm sol}G^{-}$ and $K_{\rm sp}$ for this ionic compound at 25°C?

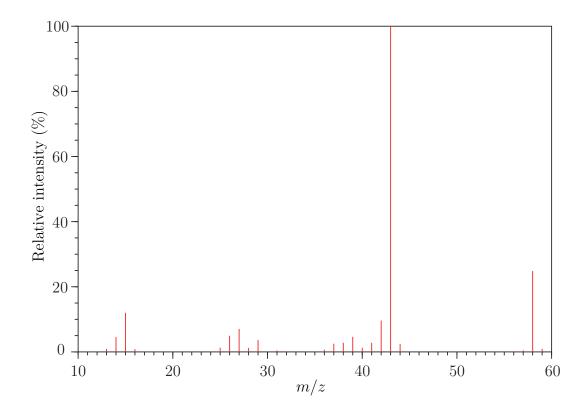
- (A) $\Delta_{\rm sol}G^{-} > 0$ and $K_{\rm sp} < 1$
- (B) $\Delta_{\rm sol}G^{-} > 0$ and $K_{\rm sp} > 1$
- (C) $\Delta_{\rm sol}G^{-} < 0$ and $K_{\rm sp} < 1$
- (D) $\Delta_{\rm sol}G^{-} < 0$ and $K_{\rm sp} > 1$

8. When a 25.00 mL aliquot of a $0.100~{\rm mol\,L^{-1}}$ sulfuric acid solution is titrated with a sodium hydroxide solution, 22.40 mL is required to completely neutralise the acid.

What volume of the same sodium hydroxide solution would be needed to reach the equivalence point if it was titrated with a 25.00 mL aliquot of 0.100 mol L^{-1} acetic acid?

- (A) Less than 11.20 mL
- (B) 11.20 mL
- (C) More than $11.20~\mathrm{mL}$
- (D) Unable to determine unless the concentration of the sodium hydroxide is known

- 9. How does the molecular shape at the carbon atoms change when ethene is converted into polyethylene?
 - (A) Tetrahedral \rightarrow Trigonal pyramidal
 - (B) Trigonal pyramidal \rightarrow Tetrahedral
 - (C) Tetrahedral \rightarrow Trigonal planar
 - (D) Trigonal planar \rightarrow Tetrahedral
- 10. The mass spectrum of propan-2-one is shown below.



Which species is most likely responsible for the base peak on this mass spectrum?

- (A) $CH_3COCH_3^+$
- (B) $C_3H_7^+$
- (C) CH_3CO^+
- (D) $C_2H_5^+$
- 11. A 2.85 g sample of washing powder was analysed for its phosphorus content. The phosphorus was precipitated as ${\rm Mg_2P_2O_7}$ and then filtered. The mass of the precipitate after drying was 0.125 g.

What is the percentage by mass of phosphorus in the washing powder?

- (A) 0.61%
- (B) 1.22%
- (C) 2.45%
- (D) 4.38%

12. The structural formula of aspirin and salicylic acid is shown below.

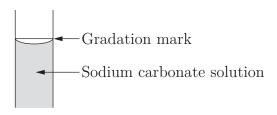


A chemist made the following statements:

- (i) Aspirin contains both a carboxyl and an ester functional group
- (ii) Aspirin can be prepared by a reaction between salicylic acid and methanoic acid
- (iii) Aspirin and salicylic acid would both react with sodium carbonate

Which of the above statement(s) are correct?

- (A) (i) only
- (B) (i) and (ii) only
- (C) (i) and (iii) only
- (D) (i), (ii) and (iii)
- 13. During the preparation of a sodium carbonate primary standard solution, a student filled a volumetric flask to the level shown in the diagram below.



The resultant sodium carbonate solution was used to rinse and fill a conical flask, and then titrated against an unknown acid using a suitable indicator.

Compared to the actual concentration of the acid, the calculated concentration would be:

- (A) Lower
- (B) Higher
- (C) The same
- (D) Different, but higher or lower cannot be predicted
- 14. A quantity of sodium hydroxide is added to 200.0 mL of 0.100 mol L⁻¹ calcium nitrate in order to produce a precipitate.

What mass of sodium hydroxide will cause precipitation to start at 25°C?

- (A) 2.01×10^{-3} g
- (B) 0.0127 g
- (C) 0.0284 g
- (D) 0.0567 g

15. An alcohol with a chemical formula of $C_4H_{10}O$ does not decolourise acidified potassium permanganate (KMnO₄/H⁺).

If this alcohol is mixed with concentrated hydrochloric acid and zinc chloride, how many signals would the organic product of this reaction produce on a ¹H NMR spectrum?

- (A) 1
- (B) 2
- (C) 3
- (D) 4
- 16. A solution containing 15.0 g of sucrose $(C_{12}H_{22}O_{11})$ was allowed to undergo fermentation. During this process, yeast enzymes first hydrolyse sucrose into simple carbohydrates according to the following equation:

$$C_{12}H_{22}O_{11(aq)} + H_2O_{(l)} \xrightarrow{\text{yeast}} 2C_6H_{12}O_{6(aq)}$$

The simple carbohydrates produced are then converted into ethanol and carbon dioxide.

If 4.50 g of ethanol was obtained from this process, what is the percentage yield of ethanol?

- (A) 13.9%
- (B) 27.9%
- (C) 41.8%
- (D) 55.7%
- 17. The table below lists the information from a ¹H NMR spectrum.

Chemical shift (ppm)	Multiplicity	Integration
1.4	Doublet	6
3.8	Septet	1

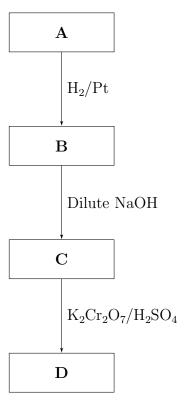
Which compound could have produced this spectrum?

- (A) 2-methylpropanoic acid
- ${\rm (B)\ 2\text{-}bromo\text{-}2\text{-}methylpropane}$
- (C) 1-bromopropane
- (D) 2-bromopropane
- 18. A 20.0 mL solution of $0.50~{\rm mol\,L^{-1}}$ hydrochloric acid was mixed with 20.0 mL of $0.20~{\rm mol\,L^{-1}}$ potassium hydroxide solution.

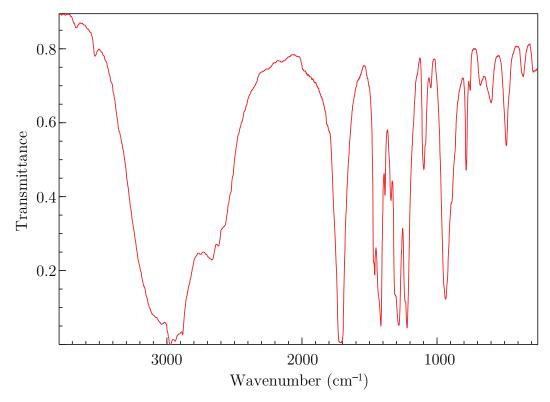
What is the pH of the resultant mixture?

- (A) 0.25
- (B) 0.50
- (C) 0.82
- (D) 2.22

19. Consider the following series of reactions where $\bf A$ to $\bf D$ are different organic compounds.



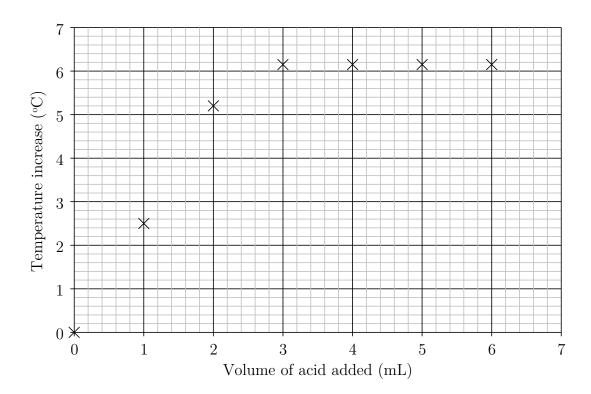
The infrared spectrum of compound $\mathbf D$ is given below.



Based on the above information, a possible identity of compound A is:

- (A) 2-chlorobut-1-ene
- (B) 3-chlorobut-1-ene
- (C) 4-chlorobut-1-ene
- (D) 3-chloro-3-methylbut-1-ene

20. Various volumes of a $1.0~{\rm mol\,L^{-1}}$ unknown acid was mixed with $8.0~{\rm mL}$ of $0.90~{\rm mol\,L^{-1}}$ sodium hydroxide solution and sufficient water was added such that the volume of the resultant solutions are all the same. The graph below shows the change in temperature of each resultant solution.



Which row of the following table shows the minimum volume of acid required to just neutralise the sodium hydroxide solution and the number of acidic protons in a molecule of this acid?

	Minimum volume of acid required (mL)	Number of acidic protons in the acid molecule
(A)	2.4	2
(B)	2.4	3
(C)	3.0	2
(D)	3.0	3

Section II: Short Answer Questions (80 marks) Attempt Questions 21-33

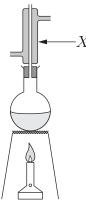
Allow about 2 hours and 25 minutes for this part

Answer the questions in the spaces provided. These spaces provide guidance for the expected length of response.

Show all relevant working in questions involving calculations.

Question 21 (4 marks)

The equipment below can be used to produce methyl ethanoate.



(a)	Write a chemical equation, using structural formulae, for the formation of methyl ethanoate.	2
(b)	Outline how a safety issue in this experiment can be addressed.	1
(c)	Describe the main purpose of apparatus X in this experiment.	1

Question 22 (5 marks)

Consider the following equilibrium reaction occurring in aqueous solution:

$$\begin{split} \left[{\rm Co(H_2O)_6} \right]^{2+}{}_{\rm (aq)} + 4\,{\rm Cl^-}_{\rm (aq)} & \rightleftharpoons \left[{\rm CoCl_4} \right]^{2-}{}_{\rm (aq)} + 6\,{\rm H_2O_{(l)}} \\ {\rm Pink} & {\rm Blue} \end{split}$$

(a)	When this equilibrium mixture is heated, the blue colour of the mixture intensifies.	2
	Explain whether the forward reaction is endothermic or exothermic.	
(b)	Explain any colour changes that would be observed when solid silver nitrate is added to the equilibrium mixture using collision theory.	3

Question 23 (5 marks)

Three different gases were bubbled into water and the subsequent changes in pH were recorded. The results are shown in the table below.

Gas	pH of water
Hydrogen chloride	Decreases
Ammonia	Increases
Boron trichloride	Decreases

Assess the effectiveness of the Arrhenius and Brønsted-Lowry theory of acids and bases at accounting for these observations. Include relevant chemical equations in your answer.

Question 24 (4 marks)

The following equilibrium is established in a 5.0 L container.

$$N_2O_{4(g)} \rightleftharpoons 2 NO_{2(g)}$$

4

The concentration of N_2O_4 is $0.10~{\rm mol}\,L^{-1}$ and the concentration of NO_2 is $0.15~{\rm mol}\,L^{-1}$ in this container at equilibrium. The equilibrium constant for the reaction is 0.225.

The volume of the container is then changed and the system is allowed to reach equilibrium again. The final amount of NO_2 in the container at equilibrium was found to be 0.20 mol. The reaction mixture was maintained at a constant temperature throughout this time.

Calculate the volume that the reaction vessel was changed to.

Question 25 (10 marks)

The reaction pathway below shows how N-methylethanamide can be synthesised in a laboratory. In this process, acetic acid is first converted into acetyl chloride which then undergoes a condensation reaction with methanamine.

a)	At 25°C, the p K_a of acetic acid is 4.76 and the p K_b of methanamine is 3.34.	4
	Show that the equilibrium constant for the following reaction is 7.9×10^5 at 25° C.	
	$CH_3COOH_{(aq)} + CH_3NH_{2(aq)} \rightleftharpoons CH_3COO^{-}_{(aq)} + CH_3NH_{3}^{+}_{(aq)}$	
b)	Propose a reason for why N -methylethanamide cannot be synthesised through a direct condensation reaction between acetic acid and methanamine under standard conditions.	1

(c) The table below shows the boiling points of the organic compounds involved in the final step of the provided reaction pathway.

Compound	Boiling point (°C)
Acetyl chloride	52
Methanamine	-6
N-methylethanamide	202

Explain the differences in boiling points between the three compounds in the table.

Question 26 (8 marks)

A student used the following procedure to determine the identity of an unknown metal carbonate with chemical formula MCO₃, where M is a group 2 metal.

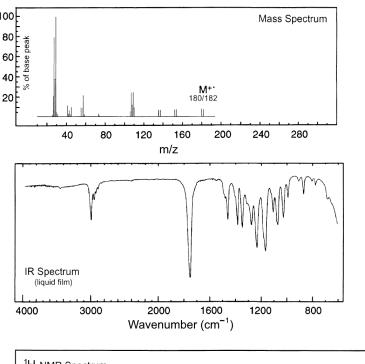
- A solution of NaOH was first prepared by weighing out 2.00 g of NaOH pellets and dissolving them in sufficient water to make a 250.0 mL solution.
- A pure 2.50 g sample of anhydrous MCO₃ solid was mixed with 25.0 mL of 2.00 mol L⁻¹ HCl solution. Sufficient water was added to this mixture to make a 100.0 mL solution.
- The resultant diluted solution was then titrated against 25.0 mL of the NaOH solution. The results are given below:

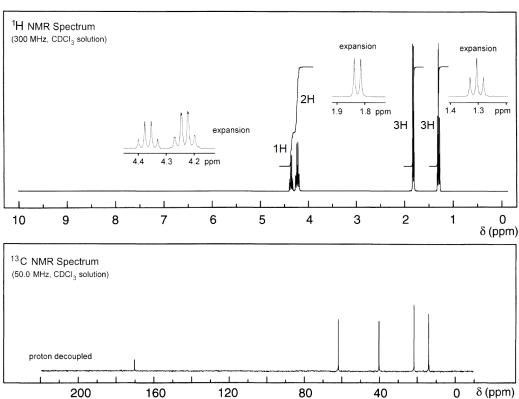
Titration	Titre volume (mL)	
1	20.40	
2	20.10	
3	20.05	
4	20.15	

(<i>a)</i>	Calculate the concentration of excess HCl in the solution that was analysed in the titration as determined by the student using this procedure.	3
(b)	Calculate the molar mass of MCO_3 and hence deduce the identity of M.	3
(b)	Calculate the molar mass of MCO_3 and hence deduce the identity of M.	3
(b)		3
(b)		d)
(b)		3
(b)		q
(b)		25

ou may ass	sume that the studer	nt has rinsed and us	ed all the glassware correctly.	
		• • • • • • • • • • • • • • • • • • • •		
E10 fuel i	s combusted under s	standard conditions,	the following reactions occur:	
C_2H_5C		10 + 211 0	4	
_	$OH_{(l)} + 3O_{2(g)} \rightarrow 2C$	$O_{2(g)} + 3 H_2 O_{(l)}$	$\Delta H = -1367 \text{ kJ mol}^{-1}$	
C_8H_1	$_{8(l)} + \frac{25}{2} O_{2(g)} \rightarrow 8 C$	${\rm CO}_{2(g)} + 9{\rm H}_2{\rm O}_{(l)}$	$\Delta H = -5470 \text{ kJ} \text{mol}^{-1}$	
$\mathrm{C_8H_1}$ late the m	$_{8(l)} + \frac{25}{2} O_{2(g)} \rightarrow 8 C$	${\rm CO_{2(g)}} + 9{\rm H_2O_{(l)}}$ needs to be comple	$\Delta H = -5470 \text{ kJ} \text{mol}^{-1}$ tely combusted to heat 105 g of	wat
$ m C_8H_1$ llate the m $25^{\circ}{ m C}$ to 52	$_{8(l)} + \frac{25}{2} O_{2(g)} \rightarrow 8 C$ ass of E10 fuel that °C, if 40% of the heat	${}^{2}\mathrm{O}_{2(\mathrm{g})} + 9\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$ needs to be comple at released is lost to	$\Delta H = -5470 \text{ kJ} \text{mol}^{-1}$ tely combusted to heat 105 g of the surroundings.	
$ m C_8H_1$ llate the m $25^{\circ}{ m C}$ to 52	$_{8(l)} + \frac{25}{2} O_{2(g)} \rightarrow 8 C$ ass of E10 fuel that °C, if 40% of the heat	${}^{2}\mathrm{O}_{2(\mathrm{g})} + 9\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$ needs to be comple at released is lost to	$\Delta H = -5470 \text{ kJ} \text{mol}^{-1}$ tely combusted to heat 105 g of	
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$ m C_8H_1$ date the m $25^{\circ}{ m C}$ to 52	$_{8(l)} + \frac{25}{2} O_{2(g)} \rightarrow 8 C$ ass of E10 fuel that °C, if 40% of the heat	${}^{2}\mathrm{O}_{2(\mathrm{g})} + 9\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$ needs to be comple at released is lost to	$\Delta H = -5470 \text{ kJ} \text{mol}^{-1}$ tely combusted to heat 105 g of the surroundings.	
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$ m C_8H_1$ date the m $25^{\circ}{ m C}$ to 52	$_{8(l)} + \frac{25}{2} O_{2(g)} \rightarrow 8 C$ ass of E10 fuel that °C, if 40% of the heat	${}^{2}\mathrm{O}_{2(\mathrm{g})} + 9\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$ needs to be comple at released is lost to	$\Delta H = -5470 \text{ kJ} \text{mol}^{-1}$ tely combusted to heat 105 g of the surroundings.	
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$ m C_8H_1$ nlate the m $25^{\circ}{ m C}$ to 52	$_{8(l)} + \frac{25}{2} O_{2(g)} \rightarrow 8 C$ ass of E10 fuel that °C, if 40% of the heat	${}^{2}\mathrm{CO}_{2(\mathrm{g})} + 9\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$ needs to be comple at released is lost to	$\Delta H = -5470 \text{ kJ} \text{mol}^{-1}$ tely combusted to heat 105 g of the surroundings.	
$ m C_8H_1$ nlate the m $25^{\circ}{ m C}$ to 52	$_{8(l)} + \frac{25}{2} O_{2(g)} \rightarrow 8 C$ ass of E10 fuel that °C, if 40% of the heat	${}^{2}\mathrm{CO}_{2(\mathrm{g})} + 9\mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})}$ needs to be comple at released is lost to	$\Delta H = -5470 \text{ kJ} \text{mol}^{-1}$ tely combusted to heat 105 g of the surroundings.	

The spectral data of an unknown organic compound is shown below.





The relative abundance of the isotopes for some common elements is given below.

• ${}^{1}\text{H}: {}^{2}\text{H} = 99.98\%: 0.02\%$

• ${}^{16}\text{O}:{}^{18}\text{O} = 99.8\%:0.2\%$

• ${}^{12}\text{C}$: ${}^{13}\text{C} = 98.9\%$: 1.1%

• ${}^{35}\text{Cl}: {}^{37}\text{Cl} = 75.8\%: 24.2\%$

• ${}^{14}\text{N}:{}^{15}\text{N} = 99.6\%:0.4\%$

• 79 Br: 81 Br = 50.7%: 49.3%

Analyse the spectra above to determine the structural formula of the organic compound.

Note: ¹H NMR chemical shift data has been included on your data sheet.

Question 29 (7 marks)

The concentration of nitrate in a sewage sample was investigated using UV-vis spectroscopy.

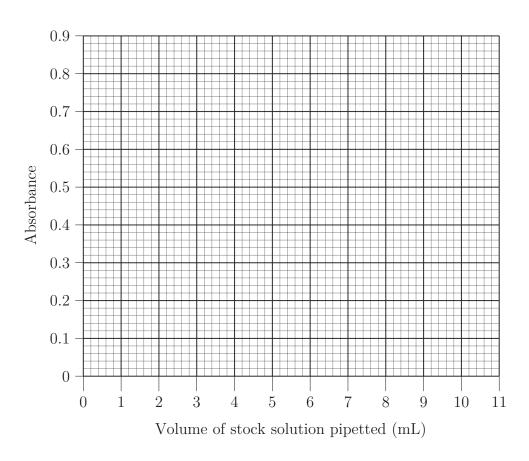
A 2.00 mL sample of the sewage water was pipetted into a 25.0 mL volumetric flask, treated such that all the nitrate is converted into a purple azo dye in a 1 : 1 molar ratio, and then diluted to the mark with distilled water.

Four standard solutions were then made by pipetting 1.00 mL, 2.00 mL, 5.00 mL and 10.0 mL aliquots of a 1.25×10^{-3} mol L⁻¹ potassium nitrate stock solution into separate 25.0 mL volumetric flasks, treating each solution such that all the nitrate in each flask is converted into the same purple azo dye, and then diluting to the mark with distilled water.

The absorbance of the resultant solutions at 520 nm were then measured relative to a blank. The results are shown in the table below.

Solution	Volume of stock solution pipetted (mL)	Absorbance
Blank	0.00	0.000
Standard 1	1.00	0.089
Standard 2	2.00	0.182
Standard 3	5.00	0.440
Standard 4	10.0	0.885
Sample	-	0.520

(a) Construct an appropriate graph of the data.



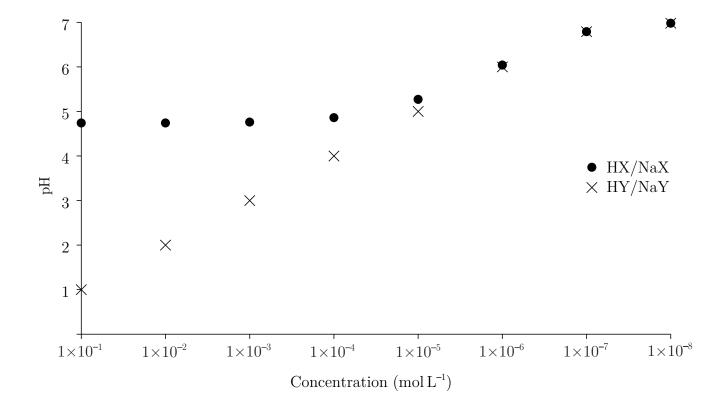
(b)	Determine the concentration of nitrate in the sewage sample in ppm.	3
(c)	Explain how the validity of the investigation would be affected if the azo dye produced from the sample of sewage water was not diluted prior to the absorbance measurement.	2

Question 30 (6 marks)

Two different aqueous solutions containing an acid and a salt were prepared. One solution contains an equimolar mixture of HX and NaX, while the other contains an equimolar mixture of HY and NaY.

To investigate the effect of concentration on the pH of these solutions, each solution was subjected to 10-fold serial dilutions with pure water and the pH of each diluted solution was measured. The results are shown in the table and graph below.

Concentration of acid/salt $(\text{mol } L^{-1})$	pH of HX/NaX mixture	pH of HY/NaY mixture
1.0×10^{-1}	4.74	1.00
1.0×10^{-2}	4.74	2.00
1.0×10^{-3}	4.76	3.00
1.0×10^{-4}	4.86	4.00
1.0×10^{-5}	5.27	5.00
1.0×10^{-6}	6.04	6.00
1.0×10^{-7}	6.79	6.79
1.0×10^{-8}	6.98	6.98



answer.	aations in your

Question 31 (4 marks)

A beaker is known to contain ONE of the following solutions:

- Lead(II) nitrate
- Sodium chloride
- Barium nitrate
- Magnesium nitrate
- Potassium carbonate

A student proposes the following procedure to determine the identity of the solution:

4

- 1. Add sulfuric acid to a sample of the solution.
- 2. Add silver nitrate to a fresh sample of the solution.

Evaluate the effectiveness of the student's proposed procedure at identifying the solution Include any expected observations and relevant net ionic equations in your answer.

Question 32 (6 marks)

Grignard reagents are organometallic compounds with a general chemical formula of R_1 -MgBr where R_1 is an alkyl group. When a carbonyl compound is reacted with a Grignard reagent, the alkyl group of the Grignard reagent is added onto the carbonyl group and an alkoxide ion is formed as shown below:

$$\begin{array}{c}
O \\
\parallel \\
R_2-C-R_3
\end{array}
\xrightarrow{R_1-MgBr}
\begin{array}{c}
O^- \\
\mid \\
R_2-C-R_3
\end{array}$$

where R_2 and R_3 are alkyl groups or hydrogen atoms.

(a) Propose a reagent that could be used to convert an alkoxide ion into an alcohol given that the pK_a of a typical alcohol is approximately 16.

.....

1

5

(b) Using the information above and any other relevant reactions, construct a flowchart to show a reaction pathway that can be used to synthesise the compound below using methanal and a Grignard reagent of your choice as the ONLY starting organic reagents.

$$\begin{array}{c|cccc} H & O & H \\ & & \parallel & \parallel \\ H - C - C - C - H \\ & & \parallel \\ H & & H \end{array}$$

All reagents used must be clearly shown and the structural formula of all intermediates must be drawn.

Question 33 (9 marks)

A student transferred 25.00 mL of an ethanamine solution into a beaker and titrated it against a 0.1100 mol L⁻¹ hydrochloric acid solution. As the titrant was being delivered, changes in pH were monitored using a pH meter immersed in the beaker solution and attached to a data logger. In total, 40.00 mL of hydrochloric acid was added before the recording was stopped.

It was found that the ethanamine solution had an initial pH of 11.80 and the volume of hydrochloric acid required to reach the equivalence point was 22.00 mL.

(a)	Show that the amount of salt produced at the equivalence point is 2.420×10^{-3} mol.	1

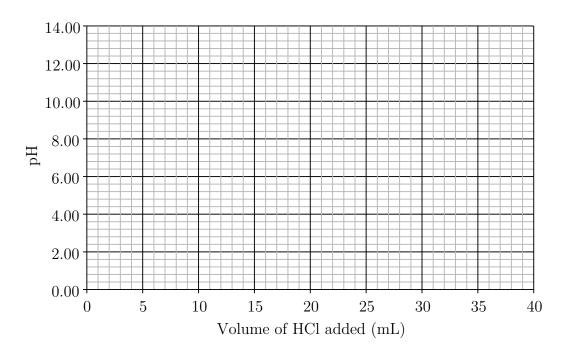
8

(b) The half-equivalence point of a titration occurs when the volume of titrant that has been added is half of what is required to reach the equivalence point. It can be shown that the pOH of the reaction mixture at the half-equivalence point is equal to the pK_b of the weak base being titrated (you are NOT required to prove this).

Using all of the information provided and relevant calculations, draw a titration curve for this titration on the axes below. In particular, you should clearly mark:

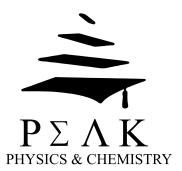
- The initial pH
- The pH and volume added at the half-equivalence point
- The pH and volume added at the equivalence point
- The final pH when 40.00 mL of hydrochloric acid has been added

You may assume that the hydrolysis of the salt produced in part (a) is negligible at the end when 40.00 mL of hydrochloric acid has been added.



If you use this space, clearly indicate which question you are answering.

Section II extra writing space



2022

HIGHER SCHOOL CERTIFICATE TRIAL EXAMINATION SOLUTIONS

Chemistry

General Instructions

- Reading time 5 minutes
- Working time -3 hours
- Write using blue or black pen Black pen is preferred
- Draw diagrams using pencil
- Board-approved calculators may be used
- A data sheet and a Periodic Table are provided at the back of this paper
- Write your name and class at the top of this page

Total marks -100

(Section I) Pages 2-9

20 marks

- Attempt Questions 1-20
- Allow about 35 minutes for this part

(Section II) Pages 10 - 29

80 marks

- Attempt Questions 21 33
- Allow about 2 hours and 25 minutes for this section

Section I: Multiple Choice Questions (20 marks) Attempt Questions 1-20 Allow about 35 minutes for this section

Use the multiple choice answer sheet for Questions 1-20.

1.		\bigcirc B	\bigcirc	\bigcirc
2.	\bigcirc A	\bigcirc B	\bigcirc	
3.	\bigcirc A	$\widehat{\mathbf{B}}$		\bigcirc
4.		\bigcirc B	\bigcirc	\bigcirc
5.	\bigcirc A		<u>(C)</u>	\bigcirc
6.	\bigcirc A		\bigcirc	\bigcirc
7.		\bigcirc B	\bigcirc	\bigcirc
8.	A		©	\bigcirc
9.	\bigcirc A	\bigcirc B	\bigcirc	
10.	\bigcirc A	\bigcirc B		\bigcirc
11.	$\widehat{\mathbf{A}}$		\bigcirc	\bigcirc
12.	A	\bigcirc B		\bigcirc
13.		\bigcirc B	\bigcirc	\bigcirc
14.	\bigcirc A	\bigcirc B	\bigcirc	
15.		\bigcirc B	\bigcirc	\bigcirc
16.	\bigcirc A	\bigcirc B	(C)	
17.	A	\bigcirc B	\bigcirc	
18.	\bigcirc A	\bigcirc B		\bigcirc
19.	A	\bigcirc B		\bigcirc
20.	\widehat{A}		\bigcirc	\bigcirc

Refer to the marking comments uploaded on Discord for explanations to the multiple choice questions.

1. Consider the following compound:

What is the systematic name of this compound?

- (A) 5-bromo-2-methylhexan-3-ol
- (B) 2-methyl-5-bromohexan-3-ol
- (C) 2-bromo-5-methylhexan-4-ol
- (D) 5-methyl-2-bromohexan-4-ol
- 2. A salt solution causes red litmus to turn blue. When this solution is vaporised into a flame, a brick red flame colour is observed.

What is a possible identity for this salt?

- (A) Silver nitrate
- (B) Silver acetate
- (C) Calcium nitrate
- (D) Calcium acetate
- 3. Consider the following equilibrium:

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)} \quad \Delta H > 0$$

Which of the following will increase the amount of carbon monoxide at equilibrium?

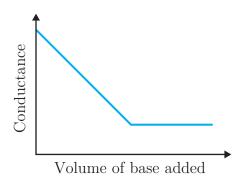
- (A) Adding solid carbon to the reaction mixture
- (B) Decreasing the temperature of the system
- (C) Increasing the volume of the system
- (D) Adding argon gas into the reaction mixture
- 4. Consider the following compound:

$$H - C = C - C - H$$

Which row of the following table correctly describes this compound's water solubility and reactivity with bromine water?

	Water solubility Reactivity with bromine wa		
(A)	onumber Soluble	Decolourises	
(B)	Soluble	No reaction	
(C)	Insoluble	Decolourises	
(D)	Insoluble	No reaction	

5. A conductometric acid-base titration was carried out and the following conductivity curve was obtained.



Which row of the following table contains an indicator that would be suitable for this titration?

	Indicator	pH range
(A)	Crystal violet	0.0 - 2.0
(B)	Methyl red	4.4 - 6.2
(C)	Cresolphthalein	8.2 - 9.8
(D)	Indigo carmine	11.4 - 13.0

- 6. How many structural isomers are there for C_5H_{12} ?
 - (A) 2
 - (B) 3
 - (C) 4
 - (D) 5
- 7. The following thermodynamic data applies to the dissolution of an ionic compound in water.

$$\Delta_{\text{sol}} H^{-} = +111 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{sol}} S^{-} = +64 \text{ J mol}^{-1} \text{ K}^{-1}$$

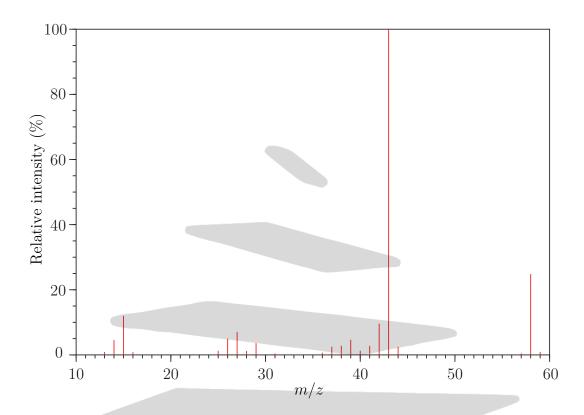
Which of the following correctly describes $\Delta_{\rm sol}G^{\bullet}$ and $K_{\rm sp}$ for this ionic compound at 25°C?

- (A) $\Delta_{\text{sol}}G^{-} > 0$ and $K_{\text{sp}} < 1$
- (B) $\Delta_{\rm sol}G^{-} > 0$ and $K_{\rm sp} > 1$
- (C) $\Delta_{\rm sol}G^{-} < 0$ and $K_{\rm sp} < 1$
- (D) $\Delta_{\rm sol}G^{-} < 0$ and $K_{\rm sp} > 1$
- 8. When a 25.00 mL aliquot of a $0.100~{\rm mol\,L^{-1}}$ sulfuric acid solution is titrated with a sodium hydroxide solution, 22.40 mL is required to completely neutralise the acid.

What volume of the same sodium hydroxide solution would be needed to reach the equivalence point if it was titrated with a 25.00 mL aliquot of 0.100 mol L^{-1} acetic acid?

- (A) Less than 11.20 mL
- (B) 11.20 mL
- (C) More than $11.20~\mathrm{mL}$
- (D) Unable to determine unless the concentration of the sodium hydroxide is known

- 9. How does the molecular shape at the carbon atoms change when ethene is converted into polyethylene?
 - (A) Tetrahedral \rightarrow Trigonal pyramidal
 - (B) Trigonal pyramidal \rightarrow Tetrahedral
 - (C) Tetrahedral \rightarrow Trigonal planar
 - (D) Trigonal planar \rightarrow Tetrahedral
- 10. The mass spectrum of propan-2-one is shown below.



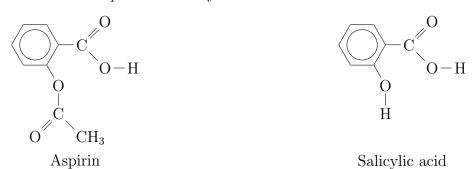
Which species is most likely responsible for the base peak on this mass spectrum?

- (A) $CH_3COCH_3^+$
- (B) $C_3H_7^+$
- (C) CH_3CO^+
- (D) $C_2H_5^+$
- 11. A 2.85 g sample of washing powder was analysed for its phosphorus content. The phosphorus was precipitated as ${\rm Mg_2P_2O_7}$ and then filtered. The mass of the precipitate after drying was 0.125 g.

What is the percentage by mass of phosphorus in the washing powder?

- (A) 0.61%
- (B) 1.22%
- (C) 2.45%
- (D) 4.38%

12. The structural formula of aspirin and salicylic acid is shown below.

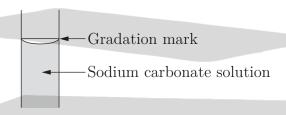


A chemist made the following statements:

- (i) Aspirin contains both a carboxyl and an ester functional group
- (ii) Aspirin can be prepared by a reaction between salicylic acid and methanoic acid
- (iii) Aspirin and salicylic acid would both react with sodium carbonate

Which of the above statement(s) are correct?

- (A) (i) only
- (B) (i) and (ii) only
- (C) (i) and (iii) only
- (D) (i), (ii) and (iii)
- 13. During the preparation of a sodium carbonate primary standard solution, a student filled a volumetric flask to the level shown in the diagram below.



The resultant sodium carbonate solution was used to rinse and fill a conical flask, and then titrated against an unknown acid using a suitable indicator.

Compared to the actual concentration of the acid, the calculated concentration would be:

- (A) Lower
- (B) Higher
- (C) The same
- (D) Different, but higher or lower cannot be predicted
- 14. A quantity of sodium hydroxide is added to 200.0 mL of 0.100 mol L⁻¹ calcium nitrate in order to produce a precipitate.

What mass of sodium hydroxide will cause precipitation to start at 25°C?

- (A) 2.01×10^{-3} g
- (B) 0.0127 g
- (C) 0.0284 g
- (D) 0.0567 g

15. An alcohol with a chemical formula of $C_4H_{10}O$ does not decolourise acidified potassium permanganate (KMnO₄/H⁺).

If this alcohol is mixed with concentrated hydrochloric acid and zinc chloride, how many signals would the organic product of this reaction produce on a ¹H NMR spectrum?

- (A) 1
- (B) 2
- (C) 3
- (D) 4
- 16. A solution containing 15.0 g of sucrose $(C_{12}H_{22}O_{11})$ was allowed to undergo fermentation. During this process, yeast enzymes first hydrolyse sucrose into simple carbohydrates according to the following equation:

$$C_{12}H_{22}O_{11(aq)} + H_2O_{(l)} \xrightarrow{yeast} 2 C_6H_{12}O_{6(aq)}$$

The simple carbohydrates produced are then converted into ethanol and carbon dioxide.

If 4.50 g of ethanol was obtained from this process, what is the percentage yield of ethanol?

- (A) 13.9%
- (B) 27.9%
- (C) 41.8%
- (D) 55.7%
- 17. The table below lists the information from a ¹H NMR spectrum.

Chemical shift (ppm)	Multiplicity	Integration
1.4	Doublet	6
3.8	Septet	1

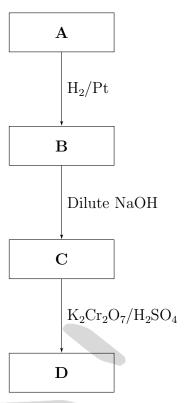
Which compound could have produced this spectrum?

- (A) 2-methylpropanoic acid
- (B) 2-bromo-2-methylpropane
- (C) 1-bromopropane
- (D) 2-bromopropane
- 18. A 20.0 mL solution of $0.50~{\rm mol\,L^{-1}}$ hydrochloric acid was mixed with 20.0 mL of $0.20~{\rm mol\,L^{-1}}$ potassium hydroxide solution.

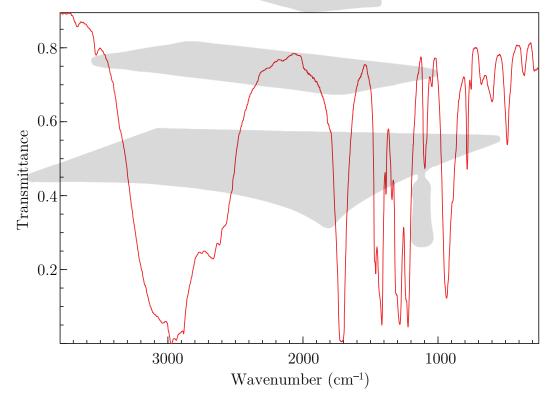
What is the pH of the resultant mixture?

- (A) 0.25
- (B) 0.50
- (C) 0.82
- (D) 2.22

19. Consider the following series of reactions where $\bf A$ to $\bf D$ are different organic compounds.



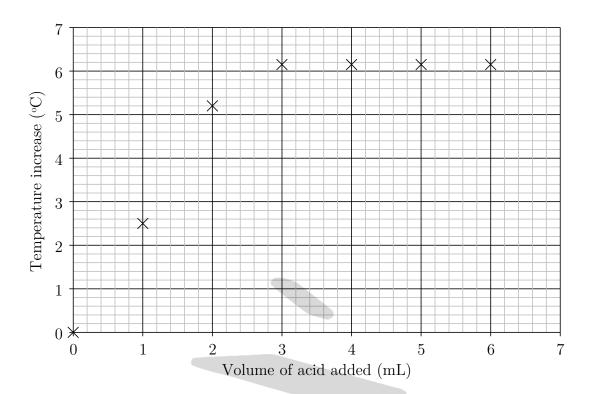
The infrared spectrum of compound ${\bf D}$ is given below.



Based on the above information, a possible identity of compound A is:

- (A) 2-chlorobut-1-ene
- (B) 3-chlorobut-1-ene
- (C) 4-chlorobut-1-ene
- (D) 3-chloro-3-methylbut-1-ene

20. Various volumes of a $1.0~{\rm mol\,L^{-1}}$ unknown acid was mixed with $8.0~{\rm mL}$ of $0.90~{\rm mol\,L^{-1}}$ sodium hydroxide solution and sufficient water was added such that the volume of the resultant solutions are all the same. The graph below shows the change in temperature of each resultant solution.



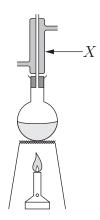
Which row of the following table shows the minimum volume of acid required to just neutralise the sodium hydroxide solution and the number of acidic protons in a molecule of this acid?

	Minimum volume of acid required (mL)	Number of acidic protons in the acid molecule
(A)	2.4	2
(B)	2.4	3
(C)	3.0	2
(D)	3.0	3

Section II: Short Answer Questions (80 marks)

Question 21 (4 marks)

The equipment below can be used to produce methyl ethanoate.

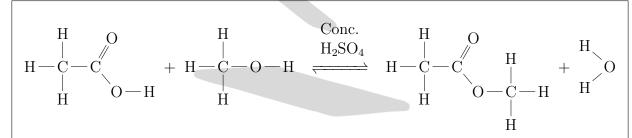


(a) Write a chemical equation, using structural formulae, for the formation of methyl ethanoate.

2

1

1



1 mark — Draws the correct structural formula of the ester or the reactants

1 mark — Writes the correct overall equilibrium equation including the catalyst

(b) Outline how a safety issue in this experiment can be addressed.

An indirect source of heat such as a hot plate and water bath should be used instead of a Bunsen burner since the organic substances in the reaction mixture are flammable.

1 mark - Outlines how a safety issue can be addressed

(c) Describe the main purpose of apparatus X in this experiment.

The reflux condenser allows for higher temperatures to be used for a faster reaction rate while preventing the loss of any volatile substances.

1 mark — Describes the purpose of the condenser in terms of preventing the loss of volatile substances

Question 22 (5 marks)

Consider the following equilibrium reaction occurring in aqueous solution:

$$\begin{split} \left[\mathrm{Co}(\mathrm{H_2O})_6 \right]^{2+}{}_{(aq)} + 4 \, \mathrm{Cl^-}_{(aq)} & \rightleftharpoons \left[\mathrm{CoCl_4} \right]^{2-}{}_{(aq)} + 6 \, \mathrm{H_2O_{(l)}} \\ \mathrm{Pink} & \mathrm{Blue} \end{split}$$

(a) When this equilibrium mixture is heated, the blue colour of the mixture intensifies.

Explain whether the forward reaction is endothermic or exothermic.

At higher temperatures, Le Chatelier's principle predicts the equilibrium will favour the heat absorbing endothermic reaction to decrease the temperature. When the mixture is heated, the blue colour intensifies, indicating that the forward reaction is favoured at higher temperatures. Therefore, the forward reaction must be endothermic.

1 mark — Identifies that the forward reaction is endothermic

1 mark — Explains why the forward reaction is endothermic with reference to the observation and Le Chatelier's principle

(b) Explain any colour changes that would be observed when solid silver nitrate is added to the equilibrium mixture using collision theory.

When $AgNO_3$ is added to this system, it dissociates and the Ag^+ ions precipitate with the Cl^- ions.

$$\mathrm{Ag}^+{}_{(aq)} + \mathrm{Cl}^-{}_{(aq)} \to \mathrm{AgCl}_{(s)}$$

This causes [Cl $^-$] to decrease. Collision theory predicts the forward reaction rate will decrease since there will be less successful collisions between $[Co(H_2O)_6]^{2+}$ and Cl^- ions. As such, the reverse reaction rate will be higher than the forward reaction rate, causing the equilibrium to shift left due to the net reverse reaction that occurs. This causes more $[Co(H_2O)_6]^{2+}$ to form so the pink colour of the mixture will intensify.

1 mark - Explains that the addition of AgNO₃ will cause [Cl⁻] to decrease

1 mark - Explains that the rate of the forward reaction is decreased with collision theory

1 mark – Explains that the equilibrium will shift left so the pink colour intensifies

2

3

Question 23 (5 marks)

Three different gases were bubbled into water and the subsequent changes in pH were recorded. The results are shown in the table below.

Gas	pH of water
Hydrogen chloride	Decreases
Ammonia	Increases
Boron trichloride	Decreases

Assess the effectiveness of the Arrhenius and Brønsted-Lowry theory of acids and bases at accounting for these observations. Include relevant chemical equations in your answer.

Arrhenius proposed that acids are substances that produce H^+ ions in water and bases are substances that produce OH^- ions in water. Brönsted-Lowry proposed that acids are proton donors and bases are proton acceptors. Both theories are effective at accounting for why HCl causes the pH of water to decrease, resulting in an acidic solution. HCl ionises in water to produce H^+ ions as per the Arrhenius theory, or HCl donates a proton to water to form H_3O^+ ions as per the Brönsted-Lowry theory.

$$\begin{split} & HCl_{(g)} \to H^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \\ & HCl_{(g)} + H_{2}O_{(l)} \to H_{3}O^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \end{split}$$

However, the Arrhenius theory is not effective at accounting for why NH₃ produces a basic solution since it does not contain any OH⁻ ions. The Brönsted-Lowry theory is effective at this though as it recognises that ammonia can act as a base by accepting a proton from water to produce OH⁻ ions which leads to an increase in pH.

$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH_{(aq)}^-$$

Both theories are not effective at accounting for why BCl₃ produces an acidic solution since it does not contain any hydrogen/protons that can be ionised or donated. The Lewis theory of acids and bases would be required to account for the acidic properties of BCl₃.

- 2 marks Assesses both theories to be effective at accounting for the acidic nature of HCl and provides at least one chemical equation
- 2 marks Assesses both theories at accounting for the basic nature of NH $_3$ and provides a chemical equation
- 1 mark Assesses both theories to be not effective at accounting for the acidic nature of BCl_3

The following equilibrium is established in a 5.0 L container.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

The concentration of N_2O_4 is $0.10~{\rm mol\,L}^{-1}$ and the concentration of NO_2 is $0.15~{\rm mol\,L}^{-1}$ in this container at equilibrium. The equilibrium constant for the reaction is 0.225.

The volume of the container is then changed and the system is allowed to reach equilibrium again. The final amount of NO_2 in the container at equilibrium was found to be 0.20 mol. The reaction mixture was maintained at a constant temperature throughout this time.

Calculate the volume that the reaction vessel was changed to.

The volume change can cause confusion so a mole ICE table can be used instead.

$$n(N_2O_4)_i = 0.10 \text{ mol L}^{-1} \times 5.0 \text{ L}$$

= 0.50 mol
 $n(NO_2)_i = 0.15 \text{ mol L}^{-1} \times 5.0 \text{ L}$
= 0.75 mol

	N_2O_4	NO_2
Initial (mol)	0.50	0.75
Change (mol)	+0.275	-0.55
Equilibrium (mol)	0.775	0.20

The temperature of the reaction mixture was kept constant so K remains the same.

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$0.225 = \frac{\left(\frac{0.20}{V}\right)^2}{\frac{0.775}{V}}$$

$$= \frac{0.20^2 V}{0.775V^2}$$

$$= \frac{0.20^2}{0.775V}$$

$$\implies V = 0.23 \text{ L}$$

1 mark - Writes the correct expression for K

 $1 \text{ mark} - \text{Determines the correct final equilibrium moles of } N_2O_4 \text{ or equivalent merit}$

2 marks – Makes appropriate substitutions and calculates the correct volume

Answers may also include a concentration ICE table:

	N_2O_4	NO_2
Initial	$\frac{0.50}{V}$	$\frac{0.75}{V}$
Change	$+\frac{0.275}{V}$	$-\frac{0.55}{V}$
Equilibrium	$\frac{0.775}{V}$	$\frac{0.20}{V}$

Question 25 (10 marks)

The reaction pathway below shows how N-methylethanamide can be synthesised in a laboratory. In this process, acetic acid is first converted into acetyl chloride which then undergoes a condensation reaction with methanamine.

(a) At 25°C, the p K_a of acetic acid is 4.76 and the p K_b of methanamine is 3.34.

Show that the equilibrium constant for the following reaction is 7.9×10^5 at 25° C.

$$CH_3COOH_{(aq)} + CH_3NH_{2(aq)} \rightleftharpoons CH_3COO^{-}_{(aq)} + CH_3NH_{3(aq)}^{+}$$

4

$$K = \frac{[\text{CH}_3\text{COO}^-][\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{NH}_2]}$$

Note that when 2 equilibrium equations are added, the equilibrium constant of the overall equation is the product of the K values of the individual equations.

$$CH_{3}COOH_{(aq)} + H_{2}O_{(l)} \rightleftharpoons CH_{3}COO^{-}_{(aq)} + H_{3}O^{+}_{(aq)} \qquad K_{a,1}$$

$$CH_{3}NH_{2(aq)} + H_{2}O_{(l)} \rightleftharpoons CH_{3}NH_{3}^{+}_{(aq)} + OH^{-}_{(aq)} \qquad K_{b,2}$$

$$CH_{3}COOH_{(aq)} + CH_{3}NH_{2(aq)} + 2H_{2}O_{(l)} \rightleftharpoons CH_{3}COO^{-}_{(aq)} + H_{3}O^{+}_{(aq)} + CH_{3}NH_{3}^{+}_{(aq)} + OH^{-}_{(aq)} \qquad K_{3}$$

$$K_{a,1} = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

$$K_{b,2} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

$$K_3 = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{NH}_2]}$$

$$= K_{a,1} \times K_{b,2}$$

However,

$$K_{3} = \frac{[\text{CH}_{3}\text{COO}^{-}][\text{CH}_{3}\text{NH}_{3}^{+}]}{[\text{CH}_{3}\text{COOH}][\text{CH}_{3}\text{NH}_{2}]} \times [\text{H}_{3}\text{O}^{+}][\text{OH}^{-}]$$

$$= K \times K_{w}$$

$$\implies K = \frac{K_{3}}{K_{w}}$$

$$= \frac{K_{a,1} \times K_{b,2}}{K_{w}}$$

$$= \frac{10^{-4.76} \times 10^{-3.34}}{1.0 \times 10^{-14}}$$

$$= 7.9 \times 10^{5}$$

1 mark - Writes a correct expression for K

3 marks - Shows that $K = 7.9 \times 10^5$ with appropriate working out

5

(b) Propose a reason for why N-methylethanamide cannot be synthesised through a direct condensation reaction between acetic acid and methanamine under standard conditions.

The value of K for the reaction in part (a) is very large which indicates the equilibrium favours the right. Therefore, mixing acetic acid with methanamine would just result in a neutralisation reaction that produces a salt instead of an amide.

1 mark – Proposes a reason for why the amide cannot be made through a direct reaction under standard conditions

Note: If the reaction mixture is heated to very high temperatures, then the salt can be decomposed into an amide (though this would no longer be under standard conditions).

(c) The table below shows the boiling points of the organic compounds involved in the final step of the provided reaction pathway.

Compound	Boiling point (°C)
Acetyl chloride	52
Methanamine	-6
N-methylethanamide	202

Explain the differences in boiling points between the three compounds in the table.

Methanamine is a polar molecule that can form strong hydrogen bonds due to its polar amino $(-NH_2)$ group. Acetyl chloride is also polar due to its -COCl group, but it cannot form hydrogen bonds. Instead, it forms weaker dipole-dipole forces. However, acetyl chloride has a much larger molar mass than methanamine and thus stronger dispersion forces which compensates for its lack of hydrogen bonding. Larger molecules contain more electrons which results in a higher probability of temporary dipoles forming and stronger dispersion forces. Ultimately, more energy will be required to overcome the total intermolecular forces of acetyl chloride, giving it a higher BP than methanamine.

N-methylethanamide has the highest BP because it is a polar molecule that contains a highly polar amide (-CONH-) group which allows it to form an extensive network of hydrogen bonds that are very strong and require significant energy to overcome.

4 marks — Explains the differences in BP between methanamine and acetyl chloride in terms of intermolecular forces

1 mark - Explains why N-methylethanamide has the highest BP with reference to H-bonds

3

Question 26 (8 marks)

A student used the following procedure to determine the identity of an unknown metal carbonate with chemical formula MCO₃, where M is a group 2 metal.

- A solution of NaOH was first prepared by weighing out 2.00 g of NaOH pellets and dissolving them in sufficient water to make a 250.0 mL solution.
- A pure 2.50 g sample of anhydrous MCO_3 solid was mixed with 25.0 mL of 2.00 mol L⁻¹ HCl solution. Sufficient water was added to this mixture to make a 100.0 mL solution.
- The resultant diluted solution was then titrated against 25.0 mL of the NaOH solution. The results are given below:

Titration	Titre volume (mL)
1	20.40
2	20.10
3	20.05
4	20.15

(a) Calculate the concentration of excess HCl in the solution that was analysed in the titration as determined by the student using this procedure.

The titration reaction is:

$$\begin{split} \mathrm{HCl_{(aq)}} + \mathrm{NaOH_{(aq)}} &\to \mathrm{NaCl_{(aq)}} + \mathrm{H_2O_{(l)}} \\ n(\mathrm{NaOH}) &= \frac{2.00 \ \mathrm{g}}{(22.99 + 16.00 + 1.008) \ \mathrm{g \, mol^{-1}}} \\ &= 0.0500 \ \mathrm{mol} \\ [\mathrm{NaOH}] &= \frac{0.0500 \ \mathrm{mol}}{0.2500 \ \mathrm{L}} \\ &= 0.200 \ \mathrm{mol} \ \mathrm{L^{-1}} \\ n(\mathrm{NaOH}) \ \mathrm{titrated} &= 0.200 \ \mathrm{mol} \ \mathrm{L^{-1}} \times 0.0250 \ \mathrm{L} \\ &= 5.00 \times 10^{-3} \ \mathrm{mol} \\ n(\mathrm{HCl}) &= 5.00 \times 10^{-3} \ \mathrm{mol} \end{split}$$

These moles came from an average titre of 20.10 mL (discarding the 1st titre).

$$\therefore [HCl] = \frac{5.00 \times 10^{-3} \text{ mol}}{0.02010 \text{ L}}$$
$$= 0.249 \text{ mol L}^{-1}$$

1 mark — Calculates the correct concentration of the NaOH solution

1 mark — Calculates the correct moles of NaOH titrated

1 mark - Calculates the correct concentration of HCl as determined by the student

$$n(\text{HCl}) \, \text{added} = 2.00 \, \, \text{mol} \, \text{L}^{-1} \times 0.0250 \, \, \text{L}$$

$$= 0.0500 \, \, \text{mol}$$

$$n(\text{HCl}) \, \text{leftover} = 0.249 \, \, \text{mol} \, \text{L}^{-1} \times 0.1000 \, \, \text{L}$$

$$= 0.0249 \, \, \text{mol}$$

$$n(\text{HCl}) \, \text{reacted} = n(\text{HCl}) \, \text{added} - n(\text{HCl}) \, \text{leftover}$$

$$= 0.0500 \, \, \text{mol} - 0.0249 \, \, \text{mol}$$

$$= 0.0251 \, \, \text{mol}$$

$$MCO_{3(s)} + 2 \, \text{HCl}_{(aq)} \rightarrow MCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

$$n(\text{MCO}_3) = \frac{0.0251 \, \, \text{mol}}{2}$$

$$= 0.0126 \, \, \text{mol}$$

$$n(\text{MCO}_3) = \frac{2.50 \, \, \text{g}}{M(\text{MCO}_3)}$$

$$M(MCO_3) = 199 \text{ g mol}^{-1}$$

 $\implies M(M) = (199 - (12.01 + 3 \times 16.00)) \text{ g mol}^{-1}$
 $= 139 \text{ g mol}^{-1}$

 $\approx M(\mathrm{Ba})$

 $0.0126 \text{ mol} = \frac{2.50 \text{ g}}{M(\text{MCO}_3)}$

∴ M is Ba.

1 mark - Calculates the correct moles of leftover HCl (or the moles of HCl added)

1 mark - Calculates the correct moles of HCl reacted

1 mark — Calculates the correct molar mass of MCO₃ to THREE significant figures (must have units) and deduces that M is Ba

(c) Explain any discrepancies that will be observed between the value calculated in part (a) and the true concentration of HCl in the solution that was analysed in the titration.

You may assume that the student has rinsed and used all the glassware correctly.

The NaOH solution was prepared as a primary standard, and this will lead to an inaccurate result since NaOH is hygroscopic. The NaOH pellets would have absorbed moisture from the air, so the NaOH solution would be more dilute than what has been calculated. There will be less moles of NaOH than expected, so lower volumes of the HCl solution would be needed to reach the end point, leading to an overestimation of the HCl concentration.

1 mark - Identifies a property of NaOH that makes it an unsuitable primary standard

1 mark — Explains that the HCl concentration has been overestimated

 $\mathbf{2}$

E10 fuel is a mixture that contains approximately 10% ethanol and 90% octane by mass. When E10 fuel is combusted under standard conditions, the following reactions occur:

$$C_2H_5OH_{(l)} + 3 O_{2(g)} \rightarrow 2 CO_{2(g)} + 3 H_2O_{(l)}$$
 $\Delta H = -1367 \text{ kJ mol}^{-1}$
 $C_8H_{18(l)} + \frac{25}{2} O_{2(g)} \rightarrow 8 CO_{2(g)} + 9 H_2O_{(l)}$ $\Delta H = -5470 \text{ kJ mol}^{-1}$

Calculate the mass of E10 fuel that needs to be completely combusted to heat $105~{\rm g}$ of water from $25^{\circ}{\rm C}$ to $52^{\circ}{\rm C}$, if 40% of the heat released is lost to the surroundings.

$$q_{\rm w} = mc\Delta T$$

= 105 g × 4.18 J g⁻¹ K⁻¹ × (52 – 25) K
= 11850.3 J

If there is 40.0% heat loss to the surroundings, then only 60.0% is absorbed by the water.

$$q_{w} = -0.60q(E10)$$

$$\implies q(E10) = \frac{-q_{w}}{0.60}$$

$$= \frac{-11850.3 \text{ J}}{0.60}$$

$$= -19750.5 \text{ J}$$

$$= -19.7505 \text{ kJ}$$

However,

$$\begin{split} q(\text{E10}) &= q(\text{C}_2\text{H}_5\text{OH}) + q(\text{C}_8\text{H}_{18}) \\ &= (\Delta H \times n)_{\text{C}_2\text{H}_5\text{OH}} + (\Delta H \times n)_{\text{C}_8\text{H}_{18}} \\ &= \left(\Delta H \times \frac{m}{M}\right)_{\text{C}_2\text{H}_5\text{OH}} + \left(\Delta H \times \frac{m}{M}\right)_{\text{C}_8\text{H}_{18}} \\ -19.7505 \,\text{kJ} &= \frac{-1367 \,\text{kJ} \,\text{mol}^{-1} \times 0.10 m(\text{E10})}{(2(12.01) + 6(1.008) + 16.00) \,\text{g mol}^{-1}} + \frac{-5470 \,\text{kJ} \,\text{mol}^{-1} \times 0.90 m(\text{E10})}{(8(12.01) + 18(1.008)) \,\text{g mol}^{-1}} \\ \Longrightarrow m(\text{E10}) &= 0.43 \,\text{g} \end{split}$$

1 mark — Calculates the correct energy absorbed by water

1 mark - Calculates the correct energy released by E10 or equivalent merit

2 marks - Makes appropriate substitutions and calculates the correct mass of E10

Answers may also include the following or any other correct approach:

When 1 g of E10 is combusted,

$$\begin{split} n(\mathrm{C_2H_5OH}) &= \frac{0.10 \times 1~\mathrm{g}}{(2(12.01) + 6(1.008) + 16.00)~\mathrm{g\,mol}^{-1}} \\ &= 2.17 \times 10^{-3}~\mathrm{mol} \\ q(\mathrm{C_2H_5OH}) &= -1367~\mathrm{kJ}~\mathrm{mol}^{-1} \times 2.17 \times 10^{-3}~\mathrm{mol} \\ &= -2.97~\mathrm{kJ} \end{split}$$

$$n(C_8H_{18}) = \frac{0.90 \times 1 \text{ g}}{(8(12.01) + 18(1.008)) \text{ g mol}^{-1}}$$

$$= 7.88 \times 10^{-3} \text{ mol}$$

$$q(C_8H_{18}) = -5470 \text{ kJ mol}^{-1} \times 7.88 \times 10^{-3} \text{ mol}$$

$$= -43.1 \text{ kJ}$$

 \therefore The heat of combustion of E10 per gram is given by:

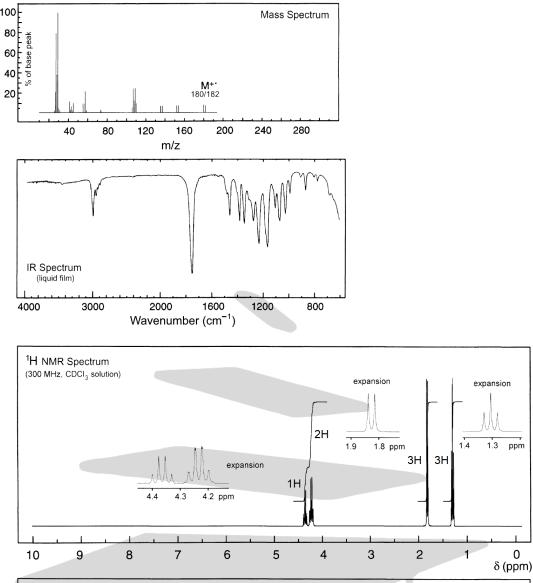
$$\Delta H(E10) = \frac{-2.97 \text{ kJ} + -43.1 \text{ kJ}}{1 \text{ g}}$$

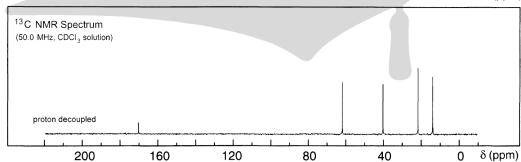
$$= -46.1 \text{ kJ g}^{-1}$$

$$\implies m(E10) = \frac{-19.7505 \text{ kJ}}{-46.1 \text{ kJ g}^{-1}}$$

$$= 0.43 \text{ g}$$

The spectral data of an unknown organic compound is shown below.





The relative abundance of the isotopes for some common elements is given below.

• ${}^{1}\text{H}: {}^{2}\text{H} = 99.98\%: 0.02\%$

• ${}^{16}\text{O}:{}^{18}\text{O} = 99.8\%:0.2\%$

• ${}^{12}\text{C}$: ${}^{13}\text{C} = 98.9\%$: 1.1%

• ${}^{35}\text{Cl}: {}^{37}\text{Cl} = 75.8\%: 24.2\%$

• ${}^{14}\text{N}:{}^{15}\text{N} = 99.6\%:0.4\%$

• 79 Br: 81 Br = 50.7%: 49.3%

Analyse the spectra above to determine the structural formula of the organic compound.

Note: ¹H NMR chemical shift data has been included on your data sheet.

- The two molecular ion peaks at m/z = 180 and 182 which have roughly the same intensity indicates the presence of one Br atom in the molecule (which can exist as 79 Br or 81 Br).
- The molecular mass of the molecular ion containing ⁷⁹Br is 180 amu.

IR

- No absorption above $\approx 3100~{\rm cm}^{-1}$ indicates that there is no O–H or N–H group.
- Strong absorption at $1680 1750 \text{ cm}^{-1}$ indicates a C=O group.

¹H NMR

There are 4 signals on the $^{1}\mathrm{H}$ NMR spectrum, so there are 4 $^{1}\mathrm{H}$ environments and these are summarised in the table below:

δ (ppm)	Integration	Multiplicity	$^{1}{ m H~Neighbours} \ ({ m n}+1~{ m rule})$	Conclusion
1.3	3Н	Triplet (3)	2	A typical CH_3- group with a low δ
				$CH_3 - CH_2 -$ Another CH_3 - group
				that is slightly deshielded
1.82	ЗН	Doublet (2)	1	H
				CH ₃ -C-
4.22	2Н	Quartet (4)	3	A -CH ₂ - group deshielded by an O atom
4.22	211	Quartet (4)	3	$\mathrm{CH_3}\mathrm{-CH_2}\mathrm{-O}$
				A CH group deshielded by C=O and Br
4.36	1H	Quartet (4)	3	H O CH ₃ -C-C- Br

¹³C NMR spectrum

There are 5 signals on the $^{13}\mathrm{C}$ NMR spectrum, so there are 5 C environments which are summarised below:

$\delta \; (\mathrm{ppm})$	Conclusion
13	$ m CH_3 - CH_2 -$
21	$\mathbf{C}\mathrm{H}_{3}\!-\!$
	A carbon deshielded by Br and C=O
40	H O
61	A C $-$ O (ester) environment $ CH_3 - CH_2 - O$
170	A C=O group in an ester (cannot be a carboxylic acid due to the IR spectrum)

From the information above, the fragments that make up the molecule are:

$$\begin{array}{ccc} & H & O \\ & & \parallel & \\ CH_3-C-C- & & CH_3-CH_2-O- \\ & & & \\ Br & & \end{array}$$

The structure is therefore:

The molecular mass of this compound $(C_5H_9O_2Br)$ is:

$$M = (5 \times 12 + 9 \times 1 + 2 \times 16 + 79)$$
 amu = 180 amu

which is consistent with the mass spectrum.

1 mark - Analyses the mass spectrum and identifies the presence of a Br atom

1 mark - Analyses the IR spectrum and identifies the presence of a C=O group

4 marks — Analyses the ¹H NMR spectrum to identify the major structural fragments of the organic compound

1 mark $-\,$ Analyses the $^{13}{\rm C}$ NMR spectra to identify the major structural fragments of the organic compound

1 mark - Determines the correct structural formula of the organic compound



Question 29 (7 marks)

The concentration of nitrate in a sewage sample was investigated using UV-vis spectroscopy.

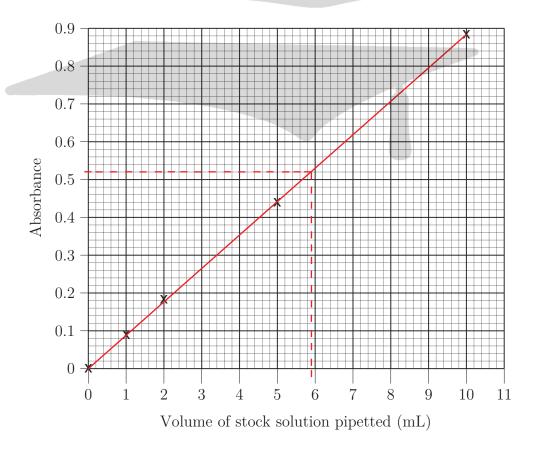
A 2.00 mL sample of the sewage water was pipetted into a 25.0 mL volumetric flask, treated such that all the nitrate is converted into a purple azo dye in a 1 : 1 molar ratio, and then diluted to the mark with distilled water.

Four standard solutions were then made by pipetting 1.00 mL, 2.00 mL, 5.00 mL and 10.0 mL aliquots of a 1.25×10^{-3} mol L⁻¹ potassium nitrate stock solution into separate 25.0 mL volumetric flasks, treating each solution such that all the nitrate in each flask is converted into the same purple azo dye, and then diluting to the mark with distilled water.

The absorbance of the resultant solutions at 520 nm were then measured relative to a blank. The results are shown in the table below.

Solution	Volume of stock solution pipetted (mL)	Absorbance
Blank	0.00	0.000
Standard 1	1.00	0.089
Standard 2	2.00	0.182
Standard 3	5.00	0.440
Standard 4	10.0	0.885
Sample	_	0.520

(a) Construct an appropriate graph of the data.



1 mark - Plots all the data points correctly

1 mark - Draws a line of best fit

(b) Determine the concentration of nitrate in the sewage sample in ppm.

Interpolating from the graph, when A=0.520, $V(\mathrm{KNO_3})=5.90$ mL. This indicates that converting 5.90 mL of the $\mathrm{KNO_3}$ stock solution into the purple azo dye followed by diluting to 25.0 mL would result in a solution with the same absorbance and concentration as the unknown sample analysed.

$$\begin{split} n(\mathrm{NO_3^-}) &= 1.25 \times 10^{-3} \ \mathrm{mol} \, \mathrm{L}^{-1} \times 5.90 \times 10^{-3} \, \, \mathrm{L} \\ &= 7.38 \times 10^{-6} \ \mathrm{mol} \\ m(\mathrm{NO_3^-}) &= 7.38 \times 10^{-6} \ \mathrm{mol} \times (14.01 + 3 \times 16.00) \ \mathrm{g} \, \mathrm{mol}^{-1} \\ &= 4.57 \times 10^{-4} \ \mathrm{g} \\ &= 0.457 \ \mathrm{mg} \\ [\mathrm{NO_3^-}] &= \frac{0.457 \ \mathrm{mg}}{0.0250 \ \mathrm{L}} \\ &= 18.3 \ \mathrm{mg} \, \mathrm{L}^{-1} \\ &= 18.3 \ \mathrm{ppm} \end{split}$$

This is equivalent to the concentration of NO_3^- ions in the diluted sample that was analysed. Removing the dilution factor:

$$[NO_3^-]_{undiluted} = \frac{25.0 \text{ mL}}{2.00 \text{ mL}} \times 18.3 \text{ ppm}$$
$$= 229 \text{ ppm}$$

1 mark – Interpolates the correct volume from the graph (values may vary slightly)

1 mark - Calculates the correct mass of NO₃ or equivalent merit

1 mark - Calculates the correct concentration of NO₃ in ppm

(c) Explain how the validity of the investigation would be affected if the azo dye produced from the sample of sewage water was not diluted prior to the absorbance measurement.

If the sample wasn't diluted from 2.00 mL to 25.0 mL, it's absorbance would have been outside the range of the calibration curve. Extrapolation would then be required which would make the investigation invalid since this assumes that the graph will continue to have the same linear trend at values that were not tested experimentally, which may not necessarily be the case.

1 mark — Identifies that if the sample was not diluted, a larger absorbance value would be obtained

1 mark — Explains that this would make the investigation invalid due to extrapolation being required

3

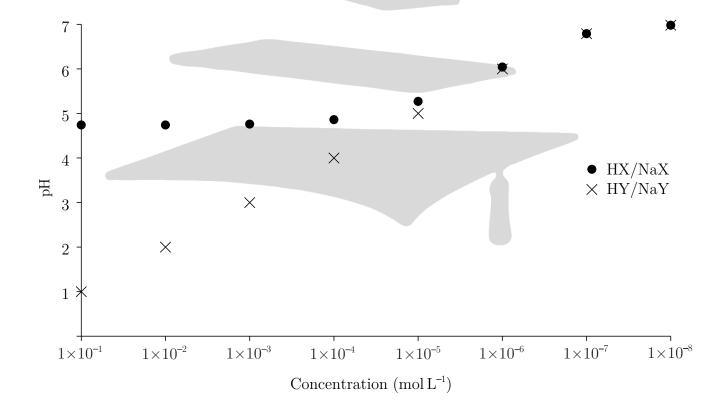
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Question 30 (6 marks)

Two different aqueous solutions containing an acid and a salt were prepared. One solution contains an equimolar mixture of HX and NaX, while the other contains an equimolar mixture of HY and NaY.

To investigate the effect of concentration on the pH of these solutions, each solution was subjected to 10-fold serial dilutions with pure water and the pH of each diluted solution was measured. The results are shown in the table and graph below.

Concentration of acid/salt (mol L^{-1})	pH of HX/NaX mixture	pH of HY/NaY mixture
1.0×10^{-1}	4.74	1.00
1.0×10^{-2}	4.74	2.00
1.0×10^{-3}	4.76	3.00
1.0×10^{-4}	4.86	4.00
1.0×10^{-5}	5.27	5.00
1.0×10^{-6}	6.04	6.00
1.0×10^{-7}	6.79	6.79
1.0×10^{-8}	6.98	6.98



Explain the trends shown in the table and graph. Include relevant chemical equations in your answer.

HY is a strong acid that completely ionises in water to form H_3O^+ ions, whereas HX is a weak acid that only partially ionises in water to form H_3O^+ ions.

$$\begin{split} &HY_{(aq)} + H_2O_{(l)} \to H_3O^+_{(aq)} + Y^-_{(aq)} \\ &HX_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + X^-_{(aq)} \end{split}$$

Therefore, at the same concentration, HY/NaY will have a higher $[H_3O^+]$ and thus a lower pH than HX/NaX since $pH = -\log_{10}[H_3O^+]$.

When the HX/NaX solution is diluted initially, the pH remains relatively constant because it is a buffer containing similar amounts of a weak acid and its conjugate base which can resist changes in pH. As water is added, [HX], $[H_3O^+]$ and $[X^-]$ all decrease due to dilution. Le Chatelier's principle predicts that the equilibrium will shift right, where there are more aqueous particles to counteract the change. This increases the degree of ionisation of HX, causing more H_3O^+ ions to be produced allowing the pH to remain relatively constant.

The HY/NaY solution cannot act as a buffer since it consists of a strong acid and its extremely weak conjugate base. When HY/NaY is diluted 10-fold, $[H_3O^+]$ will simply decrease by a factor of 10, so its pH will incrementally increase by 1.

As the HX/NaX buffer is continuously diluted, the pH begins to change more significantly since the equilibrium has shifted too far to the right and there is insufficient HX remaining that can ionise to counteract the decrease in $[{\rm H}_3{\rm O}^+]$. In very dilute solutions, the degree of ionisation of HX approaches 100% so the pH of HX/NaX converges very closely to that of HY/NaY. Furthermore, the pH of both solutions approach 7 (but can never go above) because water itself undergoes self-ionisation to produce ${\rm H}_3{\rm O}^+$ ions such that $[{\rm H}_3{\rm O}^+]$ can never get lower than 1.0×10^{-7} mol ${\rm L}^{-1}$ regardless of the concentration of the acid.

$$2 H_2 O_{(l)} \rightleftharpoons H_3 O^+_{(aq)} + O H^-_{(aq)}$$

1 mark - Identifies that HX is a weak acid and HY is a strong acid

1 mark — Explains why the pH of HX/NaX does not change significantly when it is initially diluted in terms of it being a buffer

1 mark - Explains why the pH of HY/NaY increases by 1 each time it is diluted 10-fold

1 mark - Explains why the pH of HX/NaX begins to change after several dilutions

1 mark — Explains why the pH of both solutions approach 7 in terms of the self-ionisation of water (or water being a neutral substance)

1 mark - Provides at least TWO relevant chemical equations

A beaker is known to contain ONE of the following solutions:

- Lead(II) nitrate
- Sodium chloride
- Barium nitrate
- Magnesium nitrate
- Potassium carbonate

A student proposes the following procedure to determine the identity of the solution:

- 1. Add sulfuric acid to a sample of the solution.
- 2. Add silver nitrate to a fresh sample of the solution.

Evaluate the effectiveness of the student's proposed procedure at identifying the solution. Include any expected observations and relevant net ionic equations in your answer.

The addition of H_2SO_4 is only partially effective at identifying the solution. If bubbling is observed when H_2SO_4 is added, then the solution must be K_2CO_3 .

$$CO_3^{2-}{}_{(aq)} + 2 H^+{}_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)}$$

However, if a white precipitate is observed instead, then the solution can either be $Pb(NO_3)_2$ or $Ba(NO_3)_2$ and it wouldn't be possible to differentiate the two.

$$\begin{array}{l} {\rm Pb^{2+}}_{(aq)} + {\rm SO_4^{2-}}_{(aq)} \to {\rm PbSO_{4(s)}} \\ {\rm Ba^{2+}}_{(aq)} + {\rm SO_4^{2-}}_{(aq)} \to {\rm BaSO_{4(s)}} \end{array}$$

An additional test would be required to confirm the identity of the solution (e.g. addition of HCl).

If there is no observation after adding H_2SO_4 , then the solution is either NaCl or $Mg(NO_3)_2$. Addition of $AgNO_3$ would be effective at identifying the solution since a white precipitate would form if the solution is NaCl and no observation will be seen if the solution is $Mg(NO_3)_2$.

$$\mathrm{Ag}^+{}_{(\mathrm{aq})} + \mathrm{Cl}^-{}_{(\mathrm{aq})} \to \mathrm{AgCl}_{(\mathrm{s})}$$

2 marks - Evaluates the effectiveness of adding $\rm H_2SO_4$ in terms of it being able to identify $\rm K_2CO_3$ but not being able to differentiate $\rm Pb(NO_3)_2$ and $\rm Ba(NO_3)_2$

1 mark – Evaluates the effectiveness of adding $AgNO_3$ in terms of it being able to differentiate NaCl and $Mg(NO_3)_2$

1 mark - Includes all expected observations and at least TWO net ionic equations

Question 32 (6 marks)

Grignard reagents are organometallic compounds with a general chemical formula of R_1 -MgBr where R_1 is an alkyl group. When a carbonyl compound is reacted with a Grignard reagent, the alkyl group of the Grignard reagent is added onto the carbonyl group and an alkoxide ion is formed as shown below:

$$\begin{array}{c}
O \\
\parallel \\
R_2 - C - R_3
\end{array}
\xrightarrow[R_1]{} R_1 - MgBr \xrightarrow[R_1]{} R_2 - C - R_3$$

where R_2 and R_3 are alkyl groups or hydrogen atoms.

(a) Propose a reagent that could be used to convert an alkoxide ion into an alcohol given that the pK_a of a typical alcohol is approximately 16.

1

H₂O (or any acid)

1 mark - Identifies a reagent that can protonate an alkoxide ion

An explanation is given below:

• Alcohols have a very high pK_a which indicates that they are extremely weak acids. Therefore, alkoxide ions would be strong conjugate bases which can be completely protonated with H_2O (or any acid).

(b) Using the information above and any other relevant reactions, construct a flowchart to show a reaction pathway that can be used to synthesise the compound below using methanal and a Grignard reagent of your choice as the ONLY starting organic reagents.

All reagents used must be clearly shown and the structural formula of all intermediates must be drawn.

Question 33 (9 marks)

A student transferred 25.00 mL of an ethanamine solution into a beaker and titrated it against a 0.1100 mol L⁻¹ hydrochloric acid solution. As the titrant was being delivered, changes in pH were monitored using a pH meter immersed in the beaker solution and attached to a data logger. In total, 40.00 mL of hydrochloric acid was added before the recording was stopped.

It was found that the ethanamine solution had an initial pH of 11.80 and the volume of hydrochloric acid required to reach the equivalence point was 22.00 mL.

(a) Show that the amount of salt produced at the equivalence point is 2.420×10^{-3} mol.

$$ext{HCl}_{(aq)} + ext{C}_2 ext{H}_5 ext{NH}_{2(aq)} o ext{C}_2 ext{H}_5 ext{NH}_3 ext{Cl}_{(aq)}$$

$$n(\text{HCl}) = cV$$

$$= 0.1100 \text{ mol L}^{-1} \times 0.02200 \text{ L}$$

$$= 2.420 \times 10^{-3} \text{ mol}$$

$$n(\text{C}_2 ext{H}_5 ext{NH}_3 ext{Cl}) = n(\text{HCl})$$

$$= 2.420 \times 10^{-3} \text{ mol}$$

1 mark - Shows that the amount of salt produced is 2.420×10^{-3} mol, including a relevant chemical equation

(b) The half-equivalence point of a titration occurs when the volume of titrant that has been added is half of what is required to reach the equivalence point. It can be shown that the pOH of the reaction mixture at the half-equivalence point is equal to the pK_b of the weak base being titrated (you are NOT required to prove this).

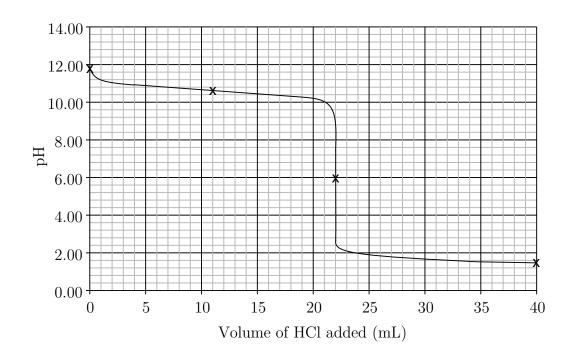
Using all of the information provided and relevant calculations, draw a titration curve for this titration on the axes below. In particular, you should clearly mark:

- The initial pH
- The pH and volume added at the half-equivalence point
- The pH and volume added at the equivalence point
- The final pH when 40.00 mL of hydrochloric acid has been added

You may assume that the hydrolysis of the salt produced in part (a) is negligible at the end when 40.00 mL of hydrochloric acid has been added.

8

1



$$\begin{split} n(\mathrm{C_2H_5NH_2}) &= 2.420 \times 10^{-3} \ \mathrm{mol} \\ [\mathrm{C_2H_5NH_2}]_i &= \frac{2.420 \times 10^{-3} \ \mathrm{mol}}{0.02500 \ \mathrm{L}} \\ &= 0.0968 \ \mathrm{mol} \ \mathrm{L^{-1}} \\ \mathrm{pOH} &= 14.00 - 11.80 \\ &= 2.20 \\ [\mathrm{OH}^-]_\mathrm{eq} &= 10^{-2.20} \ \mathrm{mol} \ \mathrm{L^{-1}} \end{split}$$

Half-equivalence point

$$\mathrm{C_2H_5NH_{2(aq)} + H_2O_{(l)}} \rightleftharpoons \mathrm{C_2H_5NH_3^+}_{(aq)} + \mathrm{OH^-}_{(aq)}$$

	$C_2H_5NH_2$	$\mathrm{C_2H_5NH_3}^+$	OH ⁻
Initial	0.0968	0	0
Change	$-10^{-2.20}$	$+10^{-2.20}$	$+10^{-2.20}$
Equilibrium	0.0905	$10^{-2.20}$	$10^{-2.20}$

$$\begin{split} K_{\rm b} &= \frac{[{\rm C_2H_5NH_3}^+][{\rm OH}^-]}{[{\rm C_2H_5NH_2}]} \\ &= \frac{10^{-2.20}\times 10^{-2.20}}{0.0905} \\ &= 4.4\times 10^{-4} \\ {\rm p}K_{\rm b} &= -{\rm log_{10}}(4.4\times 10^{-4}) \\ &= 3.36 \\ {\rm pOH_{half\,eq\,pt}} &= 3.36 \\ {\rm pH_{half\,eq\,pt}} &= 14.00 - 3.36 \\ &= 10.64 \end{split}$$

$$V(\mathrm{HCl})_{\mathrm{half}\,\mathrm{eq}\,\mathrm{pt}} = \frac{1}{2} \times 22.00 \,\,\mathrm{mL}$$
$$= 11.00 \,\,\mathrm{mL}$$

Equivalence point

$$C_2H_5NH_{3(aq)}^+ + H_2O_{(l)} \rightleftharpoons C_2H_5NH_{2(aq)}^+ + H_3O_{(aq)}^+$$

$$K_{\rm a}K_{\rm b} = K_{\rm w}$$

 $K_{\rm a} \times 4.4 \times 10^{-4} = 1.00 \times 10^{-14}$
 $\implies K_{\rm a} = 2.3 \times 10^{-11}$

The volume of solution at the equivalence point is (25.00 + 22.00) mL = 47.00 mL, so:

$$\begin{split} [C_2 H_5 N H_3^{\ +}]_{eq \ pt} &= \frac{2.420 \times 10^{-3} \ mol}{0.04700 \ L} \\ &= 0.05149 \ mol \ L^{-1} \end{split}$$

	$\mathrm{C_2H_5NH_3}^+$	$C_2H_5NH_2$	$\mathrm{H_{3}O^{+}}$
Initial	0.05149	0	0
Change	-x	+x	+x
Equilibrium	0.05149 - x	x	x

$$K_{\rm a} = \frac{[{\rm C_2H_5NH_2}][{\rm H_3O^+}]}{[{\rm C_2H_5NH_3}^+]}$$
$$2.3 \times 10^{-11} = \frac{x^2}{0.05149 - x}$$

Assume that 0.05149 - x = 0.05149 since $K_{\rm a}$ has a small value.

$$2.3 \times 10^{-11} = \frac{x^2}{0.05149}$$

$$\implies x = 1.1 \times 10^{-6} \text{ mol L}^{-1}$$

$$[H_3O^+] = 1.1 \times 10^{-6} \text{ mol L}^{-1}$$

$$pH = -\log_{10}(1.1 \times 10^{-6} \text{ mol L}^{-1})$$

$$= 5.97$$

Checking the assumption,

$$K_{\rm a} = \frac{\left(1.1 \times 10^{-6}\right)^2}{0.05814 - 1.1 \times 10^{-6}}$$

= $2.3 \times 10^{-11} \implies \text{Valid assumption}$

Final pH

At the end, there are (40.00 - 22.00) mL = 18.00 mL of excess HCl in the solution.

$$n(\text{HCl}) \text{ excess} = 0.1100 \text{ mol L}^{-1} \times 0.01800 \text{ L}$$

= $1.980 \times 10^{-3} \text{ mol}$

Noting that the volume of solution at the end is (25.00 + 40.00) mL = 65.00 mL and assuming that the hydrolysis of the $C_2H_5NH_3^+$ ion is negligible,

$$[H^{+}] = \frac{1.980 \times 10^{-3} \text{ mol}}{0.06500 \text{ L}}$$
$$= 0.03046 \text{ mol L}^{-1}$$
$$pH = -\log_{10}(0.03046)$$
$$= 1.5162$$

3 marks - Calculates the correct p $K_{\rm b}$ of $C_2H_5NH_2$

3 marks - Calculates the correct pH at the equivalence point

1 mark - Calculates the correct final pH

1 mark — Draws a strong acid-weak base titration curve with all the relevant points marked and includes a buffer region