James Ruse Agricultural High School

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2023

HIGHER SCHOOL CERTIFICATE TRIAL EXAMINATION

Chemistry

General Instructions

- Reading time – 5 minutes
- Working time – 3 hours
- Write using black pen
- Draw diagrams using pencil
- NESA approved calculators may be used
- A formula sheet and data sheet and Periodic Table are provided.
- For questions in Section II, **show all relevant working** in questions involving calculations.

Total marks 100

Section I -20 marks (pages 2-11)

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

Section II -80 marks (pages 14-30)

- Attempt Questions 21–35
- Allow about 2 hours and 25 minutes for this part

This paper MUST NOT be removed from the examination room

Section I

20 marks
Attempt Questions 1-20
Allow about 35 minutes for this section.
Mark your answers on the ANSWER grid in the Answer booklet on page 13.

Select the alternative A, B, C or D that best answers the question. Fill in the response oval completely.

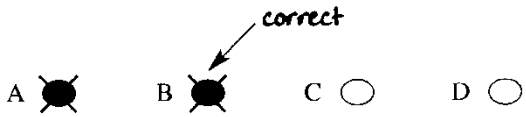
Sample: $2 + 4 =$ (A) 2 (B) 6 (C) 8 (D) 9

A ○ B ● C ○ D ○

If you think you have made a mistake, put a cross through the incorrect answer and fill in the new answer.

A ● B ⊗ C ○ D ○

If you change your mind and have crossed out what you consider to be the correct answer, then indicate the correct answer by writing the word **correct** and drawing an arrow as follows.



1. Which of the reagents will dehydrate an alcohol to an alkene?

   A. Acidified potassium permanganate

   B. Bromine water

   C. Dilute sulfuric acid

   D. Concentrated sulfuric acid

2. Which compound is a functional group isomer of pentan-2-one?

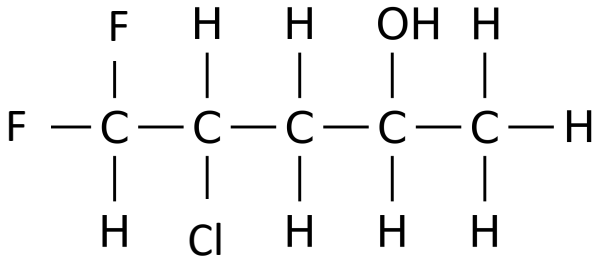
   A. $CH_3CH_2CH_2COCH_3$

   B. $CH_3CH_2CH_2CH_2CHO$

   C. $CH_3CH_2CH_2COOCH_3$

   D. $(CH_3)_2CHCOCH_3$

3. The structure of a compound is shown.



   What is IUPAC preferred name for this compound?

   A. 1,1-difluoro – 2-chloropentan-4-ol

   B. 2- chloro-1,1-difluoropentan-2-ol

   C. 5,5-difluoro- 4 chloropentan-4-ol

   D. 4-chloro-5,5-difluoropentan-2-ol

4. A student was carrying out an experiment to isolate the components of a solution containing iodide, carbonate, and sulfate ions using precipitation reactions.

Which of the following reagents would be invalid for this procedure?

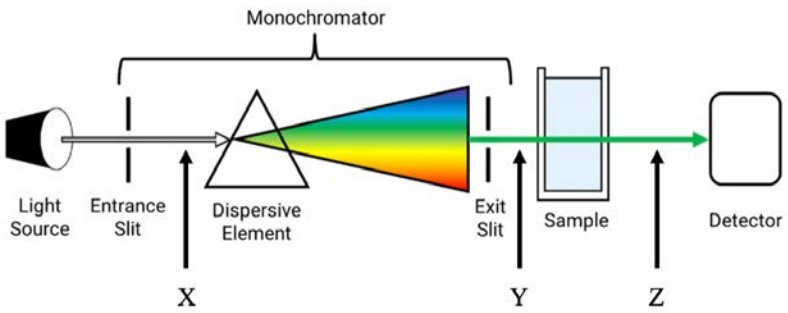
A. Sulfuric acid

B. Silver nitrate

C. Nitric acid

D. Magnesium nitrate

5. The diagram given shows the key components in a UV-Visible spectrophotometer. When the instrument is operated to measure the absorbance of a sample, the intensity of light is recorded at two different locations.



Which pairs of measurements are subtracted to find the light absorption?

A. X – Z

B. X – Y

C. Y – Z

D. Z – Y

6. Which molecule has a linear shape?

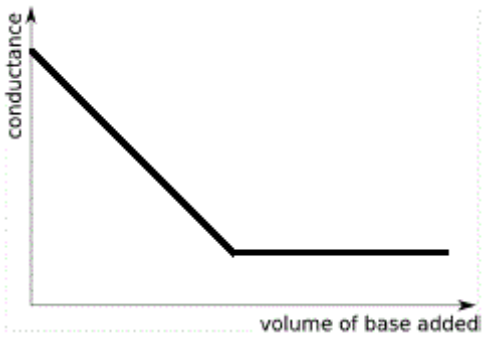
A. Ethyne

B. Ethene

C. Ethane

D. Methane

7. The graph below shows a conductivity titration graph.



Which type of acid-base titration is illustrated with the shape of this graph?

A. Strong acid vs strong base

B. Strong acid vs weak base

C. Strong base vs weak acid

D. Weak acid vs weak base

8. Which of the following would turn pink litmus blue?

A. $CH_3CH_2CH_3$

B. C_2H_5OH

C. CH_3COOCH_3

D. CH_3NH_2

9. Which of the following salt solutions would give a blue grey flame colour?

A. $Pb(NO_3)_2$

B. $CuSO_4$

C. $BaCl_2$

D. $Ca(C_2H_3O_2)_2$

10. Dry ice (solid carbon dioxide) is introduced into a sealed vessel and left to reach equilibrium according to the following equation:

$$CO_2(s) \rightleftharpoons CO_2(g)$$

Which of the following changes to the system is consistent with the shift to the equilibrium?

	Change	*System shifts*
A.	Doubling of reaction volume	left
B.	Increase of reaction temperature	no change
C.	Addition of more gaseous CO_2	left
D.	Addition of more dry ice	right

11. Two solutions of the same concentration Y and Z had pH measurements of 2.00 and 4.00 respectively.

Which statement about solutions Y and Z are correct?

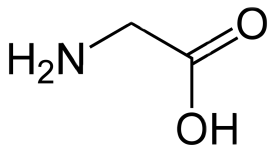
A. The concentration of OH^- in solution Z is 10 times greater than the concentration of OH^- in solution Y.

B. The concentration of OH^- in solution Z is two times greater than the concentration of OH^- in solution Y.

C. The concentration of H^+ in solution Y is two times greater than the concentration of H^+ in Solution Z.

D. The concentration of H^+ in Solution Y is 100 times greater than the concentration of H^+ in Solution Z.

12. Glycine is an amino acid that can undergo condensation polymerization.



What is the molar mass of the polymer formed from 1000 glycine monomer units?

A. 7.5×10^{1} g mol^{-1}

B. 4.3×10^{4} g mol^{-1}

C. 5.7×10^{4} g mol^{-1}

D. 7.5×10^{4} g mol^{-1}

13. A student has three dropper bottles, each containing a solution as shown below:

Bottle	Salt	Concentration mol L^{-1}
A	Sodium carbonate	0.0001
B	Silver sulfate	0.001
C	Lead chloride	0.0005

The student places a plastic sheet on top of a black bench and then combines a drop from two different dropper bottles in order to collect results for the following table:

Solutions	A	B	C
A	NT		
B	NT	NT	
C	NT	NT	NT

NT = no test performed

How many entries in the above table would contain 'No visible reaction'?

A. 0

B. 1

C. 2

D. 3

14. The gas-phase reaction between hydrogen and iodine is shown below:

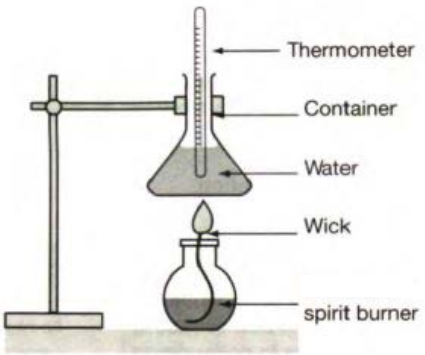
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ K= 46.

0.22 moles of hydrogen gas, 0.63 moles of iodine gas and 2.40 moles of hydrogen iodide were added to a 110 L container.

Which of the following correctly identifies the relationship between Q and K and the equilibrium shift?

	Relationship between Q and K	*System shifts*
A.	Q < K	left
B.	Q < K	right
C.	Q > K	left
D.	Q > K	right

15. The following experiment was set up to measure the temperature change for a heat of combustion reaction.



100.0 mL of water at 308 K was heated by the burning of 1.05 g of ethanol in the spirit burner. Only 45.0% of the energy produced was used to heat the water. The molar heat of combustion of ethanol is -1367 kJ mol^{-1}. What is the final temperature of the water?

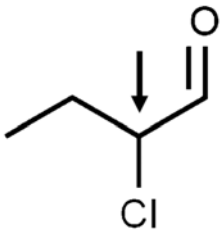
A. 1.46°C

B. 35.0°C

C. 68.5°C

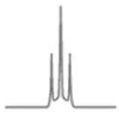
D. 74.5°C

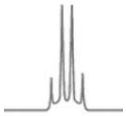
16. A molecule of 2-chlorobutanal is given below:

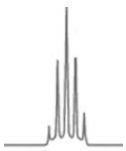


Which of the following shows the splitting pattern observed for the labelled environment in the proton NMR spectrum for this molecule?

A. 

B. 

C. 

D. 

17. An investigation was carried out using gravimetric analysis to determine the identity of an anion species present in a solution. This was achieved by adding 0.04 moles of silver ions, which resulted in the production of 5.52 g of precipitate.

Which of the following is a possible identity for the anion?

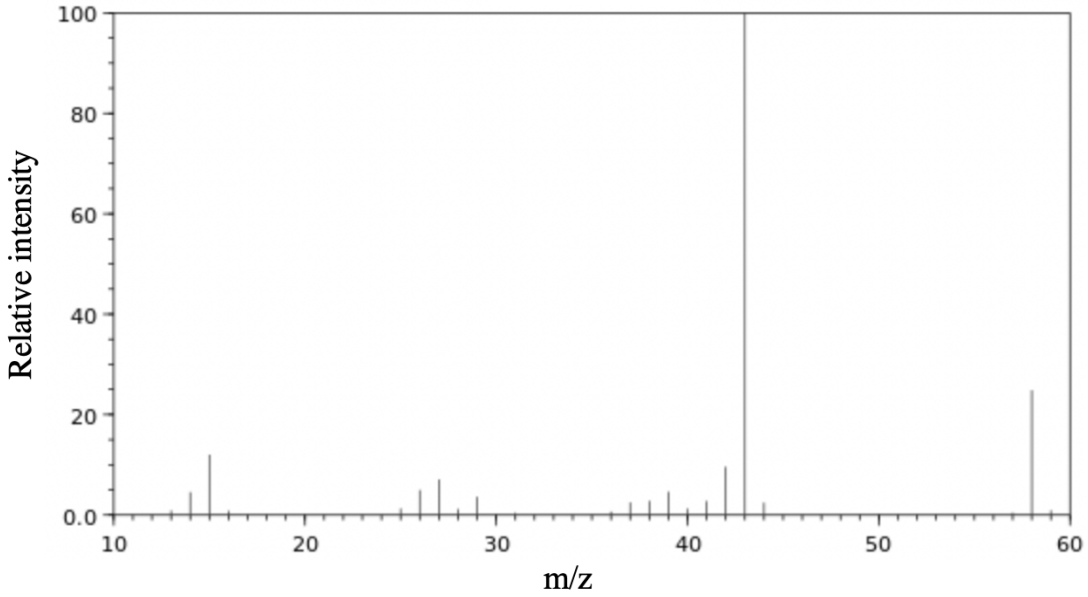
A. CO_3^{2-}

B. Br^-

C. I^-

D. PO_4^{3-}

18. An organic molecule with the chemical formula C_3H_6O is given in the mass spectrum.



Which of the following would give the mass spectrum shown?

A. Propanal

B. Propanone

C. Prop-1-en-1-ol

D. Prop-1-en-2-ol

19. 25.0 mL of a 1.00 mol L^{-1} sodium hydroxide solution in a conical flask is titrated against 1.00 mol L^{-1} hydrochloric acid solution.

What volume of hydrochloric acid must be added to achieve a pH of 1 in the mixture?

A. 25.0 mL

B. 27.5 mL

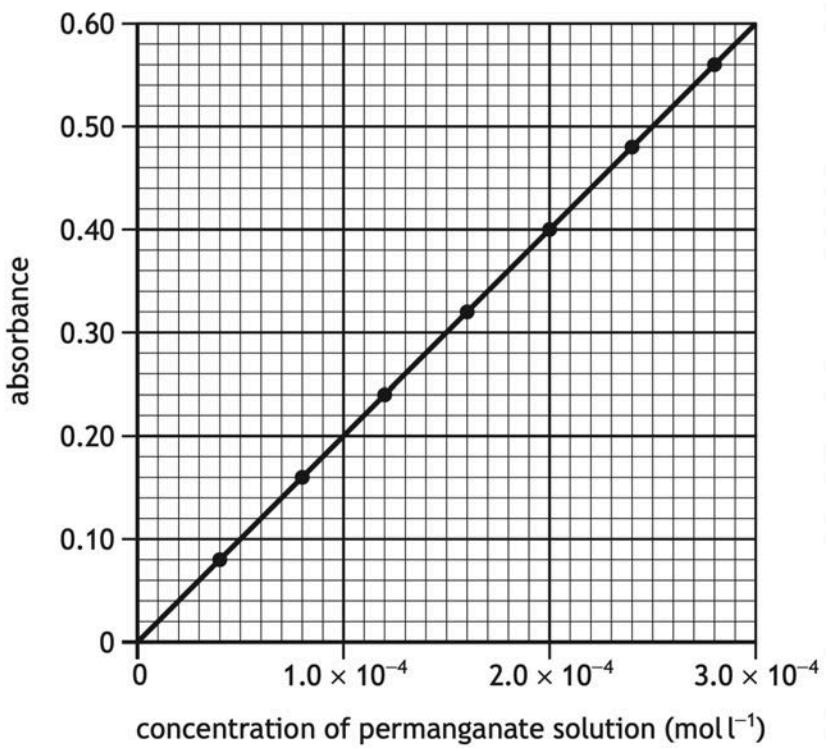
C. 30.0 mL

D. 32.5 mL

20. An investigation was carried out to determine the amount of manganese ions present in a sample of fertiliser. 5.67 g of the fertiliser was weighed out, dissolved in demineralised water and was treated to perform the following chemical reaction:

$$Mn^{2+}(aq) + 4\ H_2O(l) \rightarrow MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$$

The resultant permanganate solution was transferred to a 100 mL volumetric flask that was filled up to the graduated marking using demineralised water. A small amount of this solution was added to a cuvette and analysed using a colorimeter which gave a reading of 0.45 for the absorbance value. This was compared with the calibration curve provided below:



What is the percentage mass of manganese ions in the fertiliser sample?

A. 0.02 %

B. 0.05 %

C. 0.22 %

D. 0.47 %

Section II

80 marks
Attempt Questions 21-35
Allow about 2 hours and 25 minutes for this section

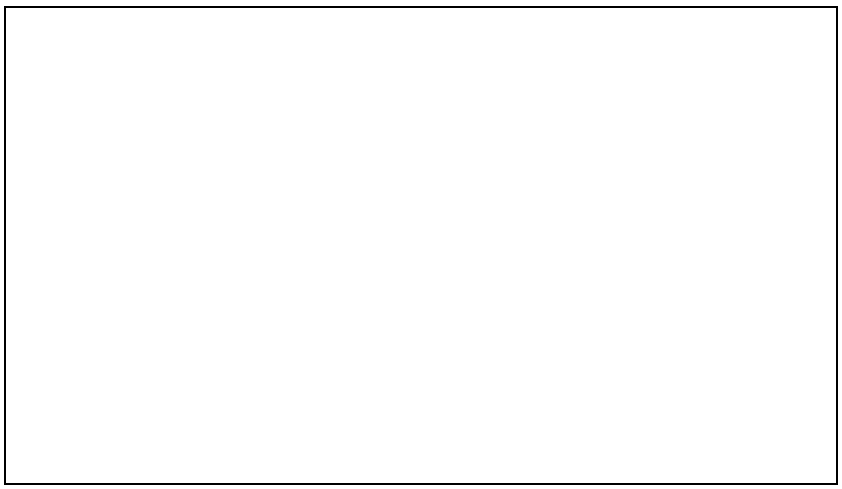
Answer the questions in the spaces provided. These spaces provide guidance for the expected length of response.

Show all relevant working in questions involving calculations.

Extra writing space is provided at the back of this booklet. If you use this space, clearly indicate which question you are answering.

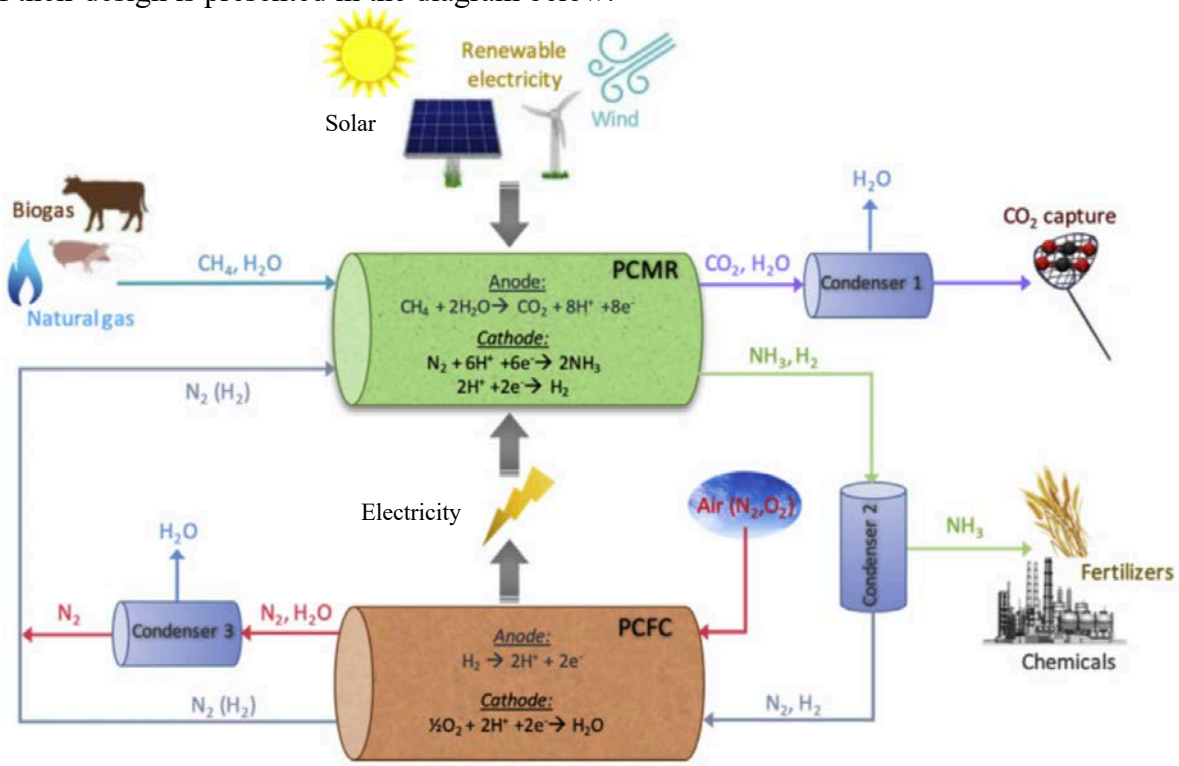
Question 21 (2 marks)

But-2-ene undergoes an addition reaction with water. In the box given, draw the structural formula of the product of this reaction. **2**



Question 22 (4 marks)

A chemist has proposed the integration of an electrochemical cell into the well-established Haber-Bosch process used for the industrial synthesis of ammonia. This would replace the conventional temperature and pressure system used that is driven by the combustion of fossil fuels. An overview of their design is presented in the diagram below:



Using the diagram, explain TWO advantages associated with the use of electrochemical cells in this process. **4**

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Question 23 (4 marks)

Determine how many grams of calcium sulfate will dissolve in 100.0 mL of a 0.0020 mol L^{-1} solution of sodium sulfate. **4**

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Question 24 (4 marks)

Consider the following reaction at equilibrium:

$$N_2O_5(g) \rightleftharpoons NO_3(g) + NO_2(g)$$

Le Chatelier's principle and collision theory can both be used to understand the behaviour of equilibrium systems.

Show how both of these can be used to explain the change that occurs to the system when some $NO_3(g)$ is removed from the system. **4**

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Question 25 (8 marks)

An analytical chemist added 2.56 g of barium hydroxide to 0.250 L of a 0.200 mol L^{-1} of nitric acid in a 400 mL beaker.

(a) Calculate the pH of the resulting solution. Assume the total volume remains unchanged. **4**

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(b) Explain how nitric acid meets the criteria for the Arrhenius and Bronsted-Lowry models of acids. Use equations to support your answer. **4**

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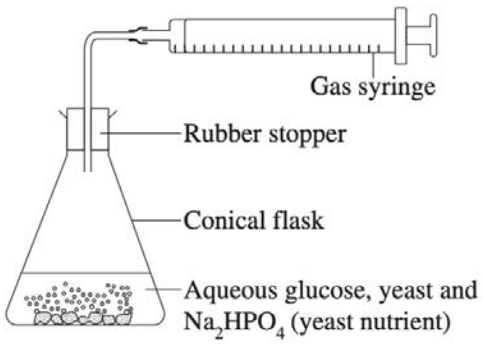
Question 26 (9 marks)

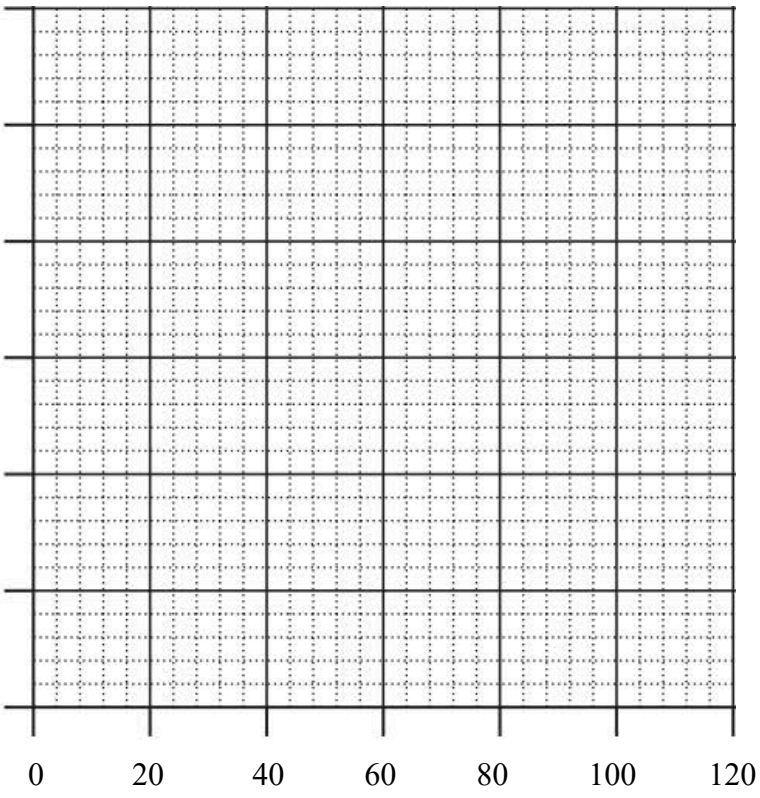
Industrially, ethanol is produced through fermentation of glucose ($C_6H_{12}O_6$) solution.
This reaction can be performed in the school laboratory and the amount of ethanol produced can be determined by measuring the volume of carbon dioxide gas generated.

The following apparatus was set up under standard laboratory conditions (25°C and 100 kPa) and the following data were collected from an experiment.



Hours	Total volume of CO_2 gas produced (mL)
0	0
20	500
40	760
60	900
80	960
100	960
120	960

(a) Plot the results, including a curved line of best fit. **3**



Question 26 continues on page 19

(b) Explain the shape in the graph. **3**

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(c) Calculate the mass of ethanol produced in this reaction. Include a relevant equation in your answer. **3**

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Question 27 (2 marks)

25.00 mL of a straight chain gaseous hydrocarbon was reacted with 200.0 mL of oxygen at 25ºC.
On cooling to 25ºC, the residual mixture of gases had a volume of 137.5 mL.
This was shaken with potassium hydroxide solution to remove the carbon dioxide dropping the final gas volume to 37.50 mL consisting of oxygen only.

Show your relevant working to identify the hydrocarbon. **2**

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Question 28 (4 marks)

Chemists use a variety of spectroscopic techniques to determine different details about the structure of organic compounds.

(a) Draw the structure of 2,4-dimethylpentan-3-one. **1**

(b) Outline the information that could be obtained about this organic compound using.
Infrared spectroscopy. **1**

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(c) Describe the information that could be obtained about this organic compound using:
Carbon-13 NMR spectroscopy. **2**

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Question 29 (5 marks)

The pH in swimming pools is maintained within a range of 7.2 to 7.8 to avoid skin and eye irritation in people.

A common chemical used to maintain this narrow pH range is sodium hydrogen carbonate which is added at regular intervals to swimming pool water.

(a) Which physical property of solid sodium hydrogen carbonate makes it suitable for use in swimming pool water? **1**

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(b) Define the role of a "buffer" in an aqueous environment. **1**

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(c) Justify the use of sodium hydrogen carbonate as a suitable buffer in swimming pools.

Provide relevant chemical equations to support your answer. **3**

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Question 30 (7 marks)

A 0.100 mol L^{-1} ammonium chloride solution has a pH of 4.60.

(a) What is the Ka of this weak acid? **4**

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(b) What is the percent ionisation of this acid? **2**

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(c) Calculate the pKa of the solution. **1**

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Question 31 (7 marks)

A primary straight chained alcohol, a carboxylic acid and an ester made with methanol, are colourless liquids with molar masses of 88 g mol^{-1}.

Identify the compounds and explain the results of physical and chemical tests that could be performed to distinguish between the three liquids. **7**

Question 32 (7 marks)

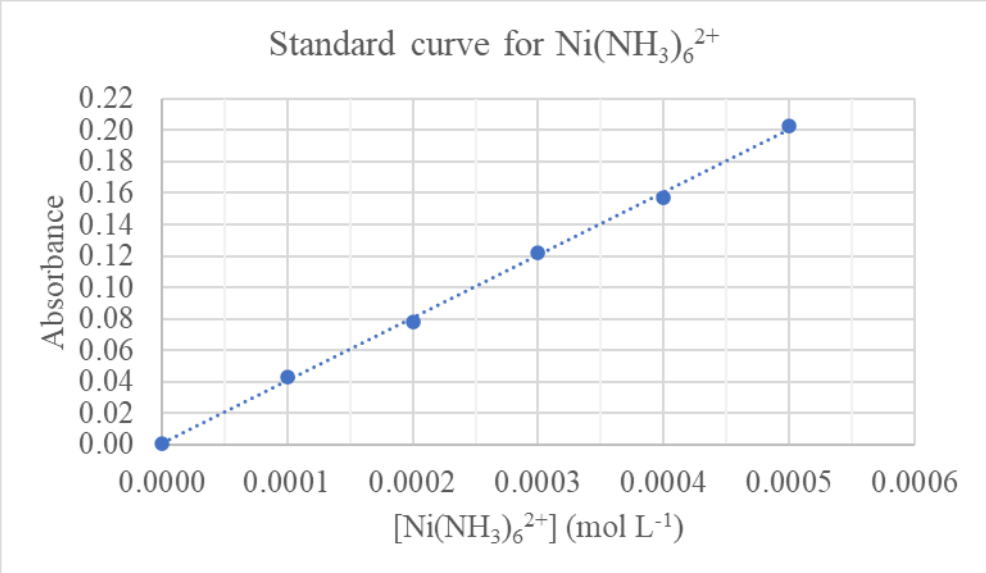
The metal ion complex $Ni(NH_3)_6^{2+}$ can be formed from adding concentrated ammonia to a Ni^{2+} solution, as shown in the following equation:

$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$

The solution formed is a deep blue colour and the absorbance of a $Ni(NH_3)_6^{2+}$ solution can be measured using a colourimeter.

A student made solutions according to the following table in order to produce a standard curve.

Solution	Volume 0.0010 mol L^{-1} Ni^{2+} (mL)	Volume 4.0 mol L^{-1} NH_3 (mL)	Volume H_2O (mL)
1	0	5.0	5.0
2	1.0	5.0	4.0
3	2.0	5.0	3.0
4	3.0	5.0	2.0
5	4.0	5.0	1.0
6	5.0	5.0	0



(a) Explain the purpose of the water in solutions 1– 5. **2**

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Question 32 continues on page 25

The student then made a new solution using 1.0 mL of 0.0070 mol L^{-1} $Ni^{2+}(aq)$, 1.0 mL of 0.40 mol L^{-1} NH_3 and 8.0 mL water. When placed into a colourimeter, an absorbance of 0.17 was recorded.

(b) Calculate the value of K_{eq} for the complexation reaction. **3**

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(c) In making the standard curve, the student treated the reactions as having gone to completion with the Ni^{2+} ion as the limiting agent. When determining the concentration of the unknown Ni^{2+} solution, the system was treated as an equilibrium reaction.

Given that $K_{eq} >> 1$, account for the two different treatments. **2**

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Question 33 (6 marks)

An investigation was carried out using a series of precipitation reactions to determine the concentration of magnesium, silver, and copper ions presents in a sample solution.

A 25.0 mL aliquot of the sample solution was pipetted into a conical flask. That solution was reacted with hydrochloric acid solution until no more precipitate was formed. The precipitate was extracted using gravity filtration, allowed to dry overnight and was found to have a mass of 1.36 g.

The filtrate was collected into a separate conical flask. That solution was treated with a dilute ammonia solution to neutralise the remaining hydrochloric acid. Sodium hydroxide solution was added to the resultant solution until no more precipitate was formed. A mixture of blue and white precipitates was obtained in the conical flask. The precipitates were filtered, dried in an oven, and recorded to have a mass of 2.40 g.

In a separate experiment, a fresh 20.0 mL aliquot of the sample solution was pipetted into a conical flask and titrated with a 0.427 mol L^{-1} solution of sodium carbonate. During this precipitation titration a series of coloured precipitates formed, starting with a pale, yellow silver precipitate, then a blue copper precipitate, followed by a white magnesium precipitate. The titre volume was recorded once a white precipitate had begun to form in the conical flask. The results of the precipitation titration are given in the table:

Titration	*Volume of Na_2CO_3* (mL)
1	41.10
2	39.75
3	39.85
4	39.80

Question 33 continues on page 27

Calculate the concentrations of magnesium, silver, and copper ions in the original sample solution. Include a relevant chemical equation for each precipitation reaction. **6**

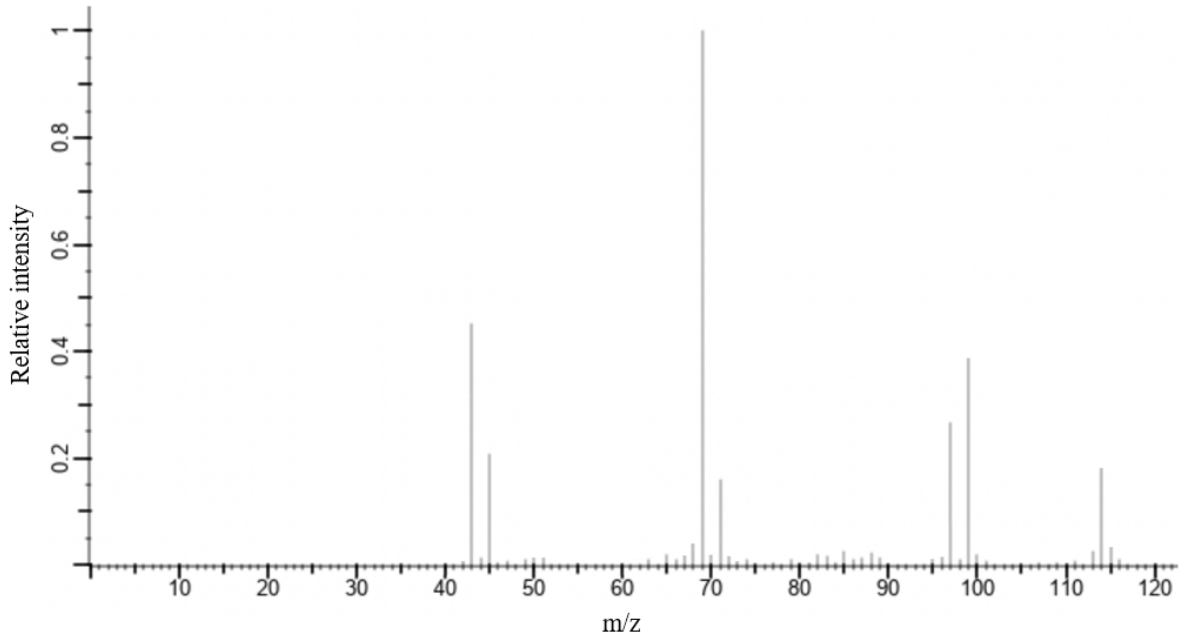
Question 34 (7 marks)

The following information was obtained from the analysis of an unknown organic compound.

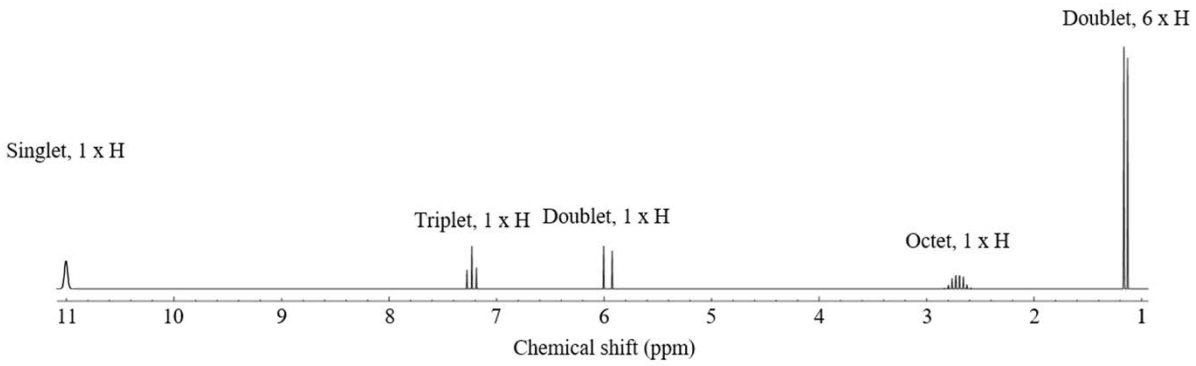
Chemical Reactivity

Chemical Reagent	*Observation*
$NaHCO_3(aq)$	bubbling
$H^+/KMnO_4(aq)$	dark magenta solution
$Br_2(aq)$	colourless solution

Mass Spectrum



Proton NMR (chemical shifts given on page 32)



In the space provided, give the structural formula for the unknown compound that is consistent with all the information provided. Justify your structure with reference to the relevant information from each source of data. **7**

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Question 34 continues on page 30

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Question 35 (4 marks)

Discuss the effects of enthalpy and entropy in the reaction between octane and oxygen in a flame. **4**

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Part B extra writing space
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Type of proton		δ/ppm
$Si(CH_3)_4$	(TMS)	0
$R—CH_3$		0.7–1.3
$R—CH_2—R$		1.2–1.5
$R—CHR_2$		1.5–2.0
$H_3C—CO—$	(aldehydes, ketones or esters)	2.0–2.5
$—CH—CO—$	(aldehydes, ketones or esters)	2.1–2.6
$H_3C—O—$	(alcohols or esters)	3.2–4.0
$—CH—O—$	(alcohols or esters)	3.3–5.1
$R_2—CH_2—O—$	(alcohols or esters)	3.5–5.0
R—OH		1–6
$R_2C=CHR$	(alkene)	4.5–7.0
R—CHO	(aldehyde)	9.4–10.0
R—COOH		9.0–13.0

JRAHS Trial Chemistry answers 2023

1.	A ○	B ○	C ○	D ■
2.	A ○	B ■	C ○	D ○
3.	A ○	B ○	C ○	D ■
4.	A ■	B ○	C ○	D ○
5.	A ○	B ○	C ■	D ○
6.	A ■	B ○	C ○	D ○
7.	A ○	B ■	C ○	D ○
8.	A ○	B ○	C ○	D ■
9.	A ■	B ○	C ○	D ○
10.	A ○	B ○	C ■	D ○
11.	A ○	B ○	C ○	D ■
12.	A ○	B ○	C ■	D ○
13	A ■	B ○	C ○	D ○
14.	A ○	B ■	C ○	D ○
15.	A ○	B ○	C ■	D ○
16.	A ○	B ○	C ■	D ○
17.	A ■	B ○	C ○	D ○
18.	A ○	B ■	C ○	D ○
19.	A ○	B ○	C ■	D ○
20.	A ■	B ○	C ○	D ○

1. Which of the reagents will dehydrate an alcohol to an alkene?

   A. Acidified potassium permanganate

   B. Bromine water

   C. Dilute sulfuric acid

   D. Concentrated sulfuric acid

2. Which compound is a functional group isomer of pentan-2-one?

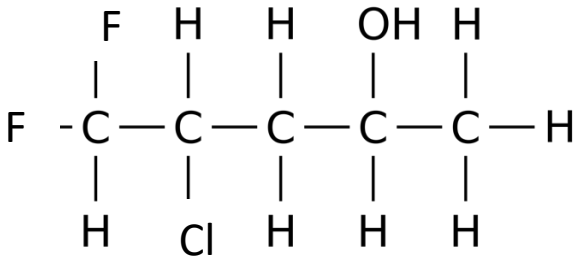
   A. $CH_3CH_2CH_2COCH_3$

   B. $CH_3CH_2CH_2CH_2CHO$

   C. $CH_3CH_2CH_2COOCH_3$

   D. $(CH_3)_2CHCOCH_3$

3. The structure of a compound is shown.



   What is IUPAC preferred name for this compound?

   A. 1,1-difluoro – 2-chloropentan-4-ol

   B. 2- chloro-1,1-difluoropentan-2-ol

   C. 5,5-difluoro- 4 chloropentan-4-ol

   D. 4-chloro-5,5-difluoropentan-2-ol

4. A student was carrying out an experiment to isolate the components of a solution containing iodide, carbonate, and sulfate ions using precipitation reactions.

Which of the following reagents would be invalid for this procedure?

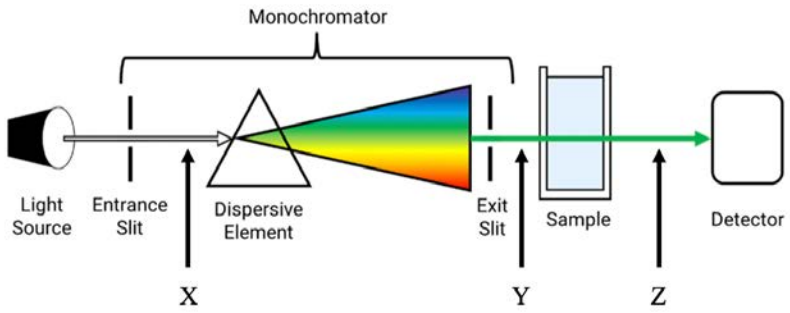
A. Sulfuric acid

B. Silver nitrate

C. Nitric acid

D. Magnesium nitrate

5. The diagram given shows the key components in a UV-Visible spectrophotometer. When the instrument is operated to measure the absorbance of a sample, the intensity of light is recorded at two different locations.



Which pairs of measurements are subtracted to find the light absorption?

A. X – Z

B. X – Y

C. Y – Z

D. Z – Y

6. Which molecule has a linear shape?

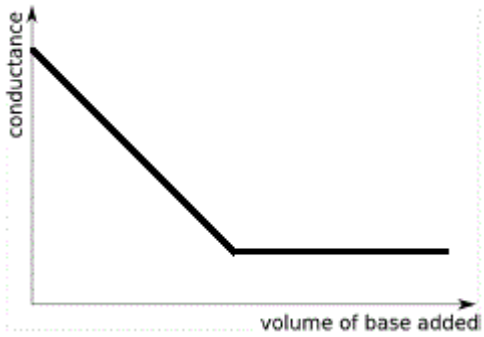
A. Ethyne

B. Ethene

C. Ethane

D. Methane

7. The graph below shows a conductivity titration graph.



Which type of acid-base titration is illustrated with the shape of this graph?

A. strong acid vs strong base

B. strong acid vs weak base

C. strong base vs weak acid

D. weak acid vs weak base

8. Which of the following would turn pink litmus blue?

A. $CH_3CH_2CH_3$

B. C_2H_5OH

C. CH_3COOCH_3

D. CH_3NH_2

9. Which of the following salt solutions would give a blue grey flame colour?

A. $Pb(NO_3)_2$

B. $CuSO_4$

C. $BaCl_2$

D. $Ca(C_2H_3O_2)_2$

10. Dry ice (solid carbon dioxide) is introduced into a sealed vessel and left to reach equilibrium according to the following equation:

$$CO_2(s) \rightleftharpoons CO_2(g)$$

Which of the following changes to the system is consistent with the shift to the equilibrium?

	Change	*System shifts*
A.	Doubling of reaction volume	left
B.	Increase of reaction temperature	no change
C.	**Addition of more gaseous CO_2**	**left**
D.	Addition of more dry ice	right

11. Two solutions of the same concentration Y and Z had pH measurements of 2.00 and 4.00 respectively.

Which statement about solutions Y and Z are correct?

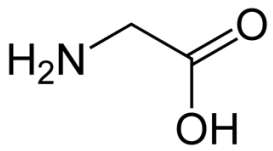
A. The concentration of OH^- in solution Z is 10 times greater than the concentration of OH^- in solution Y.

B. The concentration of OH^- in solution Z is two times greater than the concentration of OH^- in solution Y.

C. The concentration of H^+ in solution Y is two times greater than the concentration of H^+ in Solution Z.

D. The concentration of H^+ in Solution Y is 100 times greater than the concentration of H^+ in Solution Z.

12. Glycine is an amino acid that can undergo condensation polymerization



What is the molar mass of the polymer formed from 1000 glycine monomer units?

A. 7.5×10^{1} g mol^{-1}

B. 4.3×10^{4} g mol^{-1}

C. 5.7×10^{4} g mol^{-1}

D. 7.5×10^{4} g mol^{-1}

13. A student has three dropper bottles, each containing a solution as shown below:

Bottle	Salt	Concentration mol L^{-1}
A	Sodium carbonate	0.0001
B	Silver sulfate	0.001
C	Lead chloride	0.0005

The student places a plastic sheet on top of a black bench and then combines a drop from two different dropper bottles in order to collect results for the following table:

Solutions	A	B	C
A	NT		
B	NT	NT	
C	NT	NT	NT

NT = no test performed

How many entries in the above table would contain 'No visible reaction'?

A. 0

B. 1

C. 2

D. 3

14. The gas-phase reaction between hydrogen and iodine is shown below:

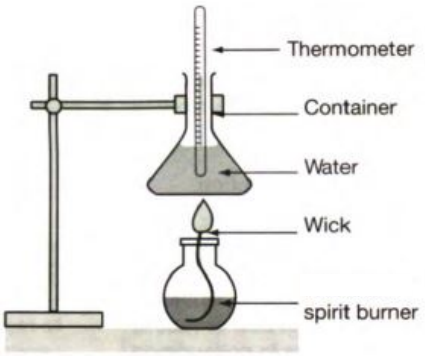
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ K= 46.

0.22 moles of hydrogen gas, 0.63 moles of iodine gas and 2.40 moles of hydrogen iodide were added to a 110 L container.

Which of the following correctly identifies the relationship between Q and K and the equilibrium shift?

	Relationship between Q and K	*System shifts*
A.	Q < K	left
B.	**Q < K**	**right**
C.	Q > K	left
D.	Q > K	right

15. The following experiment was set up to measure the temperature change for a heat of combustion reaction.



100.0 mL of water at 308 K was heated by the burning of 1.05 g of ethanol in the spirit burner. Only 45.0% of the energy produced was used to heat the water. The molar heat of combustion of ethanol is -1367 kJ mol^{-1}. What is the final temperature of the water?

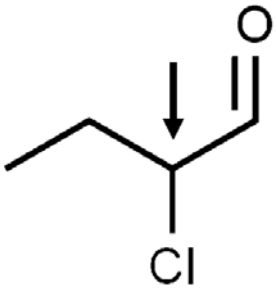
A. 1.46°C

B. 35.0°C

C. 68.5°C

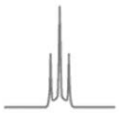
D. 74.5°C

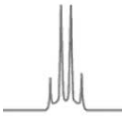
16. A molecule of 2-chlorobutanal is given below:



Which of the following shows the splitting pattern observed for the labelled environment in the proton NMR spectrum for this molecule?

A. 

B. 

C. 

D. 

17. An investigation was carried out using gravimetric analysis to determine the identity of an anion species present in a solution. This was achieved by adding 0.04 moles of silver ions, which resulted in the production of 5.52 g of precipitate.

Which of the following is a possible identity for the anion?

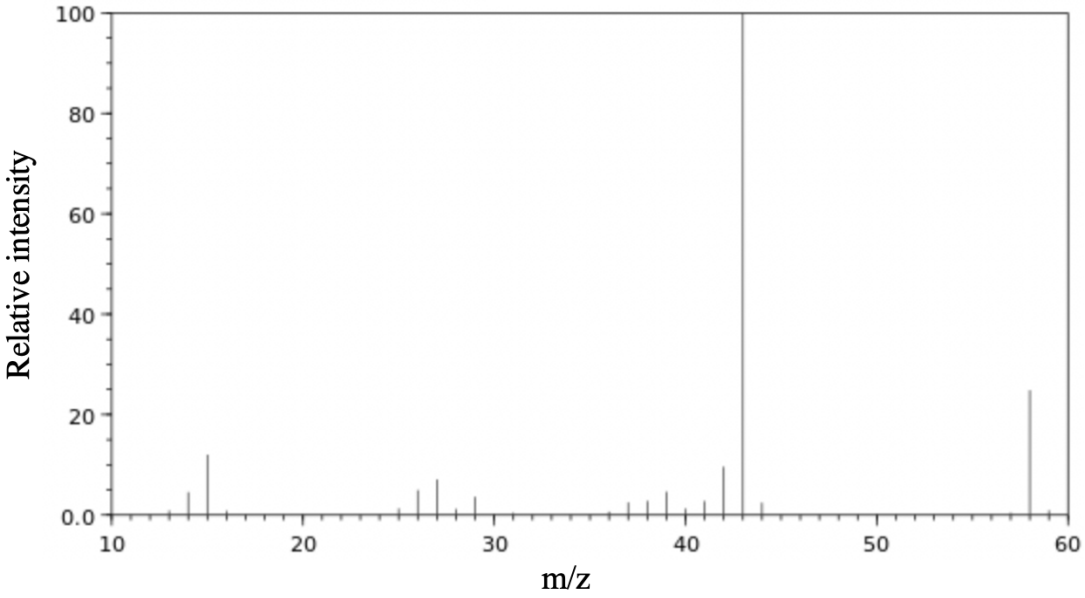
A. **CO_3^{2-}**

B. Br^-

C. I^-

D. PO_4^{3-}

18. An organic molecule with the chemical formula C_3H_6O is given in the mass spectrum.



Which of the following would give the mass spectrum shown?

A. Propanal

B. Propanone

C. Prop-1-en-1-ol

D. Prop-1-en-2-ol

19. 25.0 mL of a 1.00 $molL^{-1}$ sodium hydroxide solution in a conical flask is titrated against 1.00 mol L^{-1} hydrochloric acid solution.

What volume of hydrochloric acid must be added to achieve a pH of 1 in the mixture?

A. 25.0 mL

B. 27.5 mL

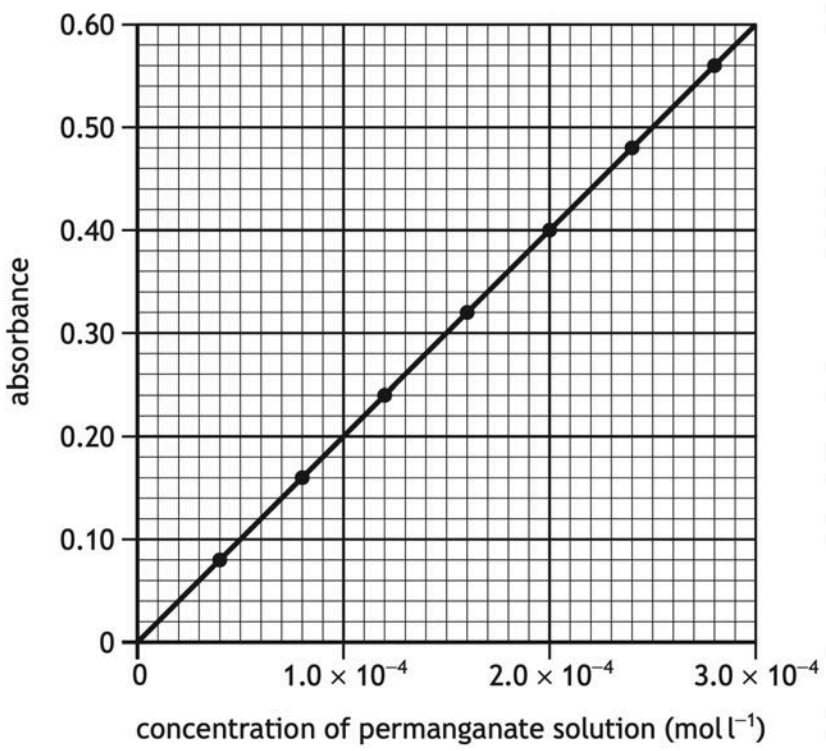
C. 30.0 mL

D. 32.5 mL

20. An investigation was carried out to determine the amount of manganese ions present in a sample of fertiliser. 5.67 g of the fertiliser was weighed out, dissolved in demineralized water and was treated to perform the following chemical reaction:

$$Mn^{2+}(aq) + 4\ H_2O(l) \rightarrow MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$$

The resultant permanganate solution was transferred to a 100 mL volumetric flask that was filled up to the graduated marking using demineralized water. A small amount of this solution was added to a cuvette and analysed using a colorimeter which gave a reading of 0.45 for the absorbance value. This was compared with the calibration curve provided below:



What is the percentage mass of manganese ions in the fertiliser sample?

A. 0.02 %

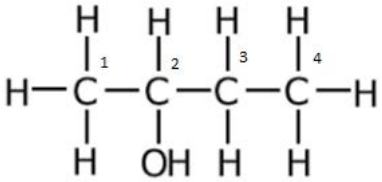
B. 0.05 %

C. 0.22 %

D. 0.47 %

Question 21 (2 marks)

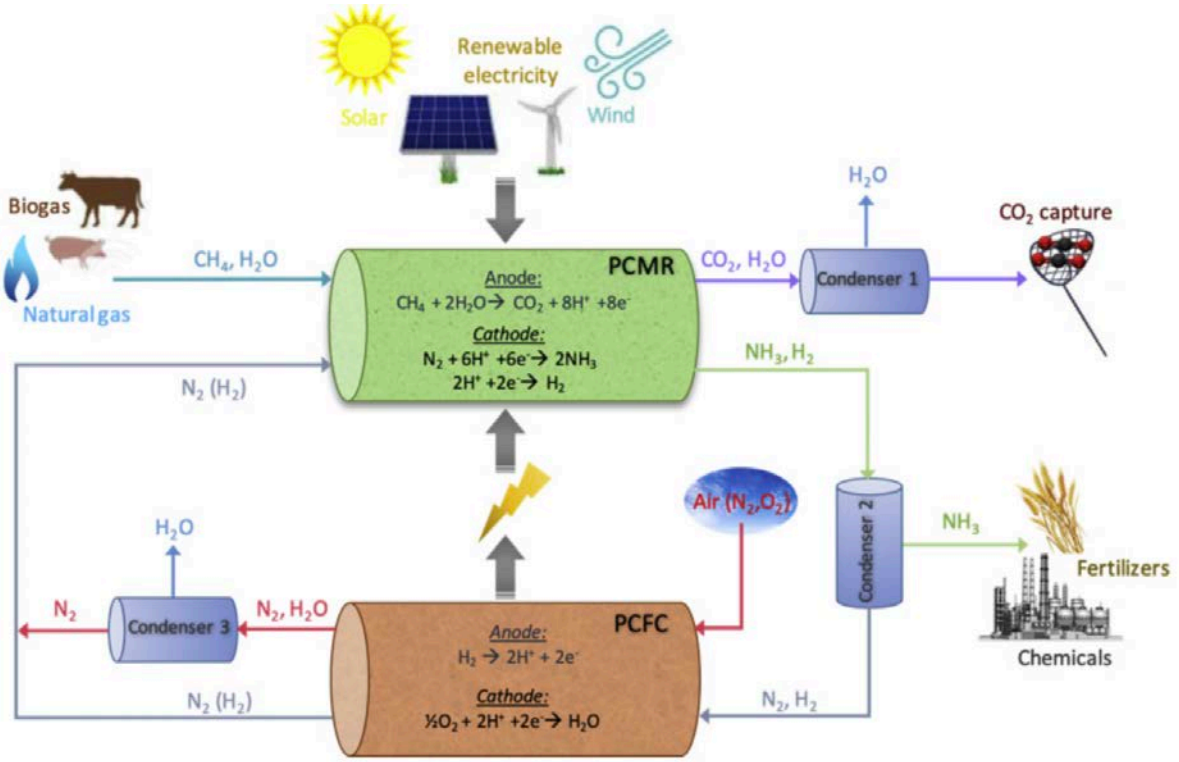
(a) But-2-ene undergoes an addition reaction with water. In the box given, draw the structural formula of the product of this reaction. **2**



Marking Criteria	*Mark(s)*
• One correct structure including chain length and functional group	2
• Some correct structure eg -hydroxyl group, 4 carbons	1

Question 22 (4 marks)

A chemist has proposed the integration of an electrochemical cell into the well-established Haber-Bosch process used for the industrial synthesis of ammonia. This would replace the conventional temperature and pressure system used that is driven by the combustion of fossil fuels. An overview of their design is presented in the diagram below:



Explain TWO advantages associated with using electrochemical cells in this process. **4**

Sample answer:

The introduction of an electrochemical cell in this process provides an avenue to use renewable sources for both energy (e.g. solar and wind) as well as reagents (e.g. biogas). This is advantageous in contrast to the conventional combustion of fossil fuels that generates large amounts of pollution and depletes a finite resource.

The two electrochemical cells used in this method provides a pathway for the recycling of both chemical reagents / products (e.g. unreacted hydrogen and nitrogen gas) and electricity (e.g. PCFC cell generates electricity for the PCMR cell). This is beneficial as reduces the economic costs as less expenses are required for chemical reagents as well as electrical operating costs.

Marking Criteria	*Mark(s)*
• Explains TWO advantages of using electrochemical cells with explicit references made to the diagram provided.	4
• Explains ONE advantage of using electrochemical cells with reference to the diagram provided. • Identifies ONE advantages of using electrochemical cells with reference to the diagram provided.	3
• Explains ONE advantage of using electrochemical cells with reference to the diagram provided **OR** • Identifies TWO advantages of using electrochemical cells with reference to the diagram provided.	2
• Provides some relevant information.	1

Question 23 (4 marks)
Determine how many grams of calcium sulfate will dissolve in 100.0 mL of a 0.0020 mol L^{-1} solution of sodium sulfate. **4**

Marking Criteria	*Mark(s)*
• Correct calculation of mass with correct significant figures (2) • Full working	4
• 4-5 of the following: • Balanced net ionic equation with states • Expression of K_{eq} • Completed ICE table • Calculation of x using quadratic formula • Calculation of moles $CaSO_4$ • Calculation of mass of $CaSO_4$	3

• 2-3 of the above	2
• Some relevant calculation or information	1

Sample answer:

$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

	$CaSO_4$	$[Ca^{2+}]$	$[SO_4^{2-}]$
Initial	-	0	0.002
Change	-	x	x
Equilibrium	-	x	0.002 + x

$K_{sp} = [Ca^{2+}][SO_4^{2-}] = 4.93 \times 10^{-5} = (x)(0.002 + x)$
$x^2 + 0.002x - 4.93 \times 10^{-5} = 0$
$x = 0.00609$ (positive solution since $[Ca^{2+}] = x$)
number of moles $CaSO_4$= cv = $0.00609 \times 0.1 = 0.000609$
mass $CaSO_4$= MM × n = $(40.08 + 32.07 + 4 \times 16.00) \times 0.000609 = 0.083$ g will dissolve.

Question 24 (4 marks)
Consider the following reaction at equilibrium:

$$N_2O_5(g) \rightleftharpoons NO_3(g) + NO_2(g)$$

Le Chatelier's principle and collision theory can both be used to understand the behaviour of equilibrium systems.
Show how both of these can be used to explain the change that occurs to the system when some $NO_3(g)$ is removed from the system. **4**

Marking Criteria	*Mark(s)*
• Demonstrates thorough understanding of Le Chatelier's principle and collision theory in relation to changes in equilibrium systems	4
• 3 of the following • Clear statement of Le Chatelier's principle • Application of Le Chatelier's principle to equilibrium system shown • Outlines collision theory relevant to concentration • Applies collision theory to re-establish equilibrium in system shown discussing forward and reverse reaction rates •	3
• 2 of the above	2
• Some relevant information	1

Sample Answer:

Le Chatelier's principle states that when a system at equilibrium is subjected to a change, the system will shift to partially counteract the change. When $NO_3(g)$, a product, is removed, the position of the system will shift to the right, to form some more $NO_3(g)$ and reach a new equilibrium.
Collision theory accounts for the rate of chemical reactions, based on the number of successful collisions between molecules. When the system was at equilibrium, the rate of the forward and reverse reactions were identical. When some product $NO_3(g)$ is removed, the rate of the reverse reaction decreases (forward reaction rate initially remains the same) as there is less NO_3 to successfully collide with NO_2 to form reactant. This results in the products being formed at the same rate, but reactant being formed more slowly, hance a shift to the right. As this occurs, the rate of the forward reaction decreases and the reverse reaction starts to increase, until they are again equal in order for equilibrium to be reached.

Comments: a number of students wrote ambiguous statements about the forward reaction rate. You need to make it clear that it does not increase to achieve equilibrium.

Question 25 (8 marks)

An analytical chemist added 2.56 g of barium hydroxide to 0.250 L of a 0.200 mol L^{-1} of nitric acid in a 400 mL beaker.

Sample Answer:

$Ba(OH)_2(aq) + 2HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$ Mol Ratio $Ba(OH)_2 : HNO_3 = 1:2$

$M(Ba(OH)_2 = 137.30 + 2(16 + 1.008) = 171.40$ g mol^{-1}

Initial $n(BaOH)_2 = 2.56 / 171.40 = 0.01494$

Initial $n(OH^-) = 2 \times 0.01494 = 0.02987$

Initial $n(HNO_3) = 0.250 \times 0.200 = 0.0500$ mol

Thus HNO_3 is in excess therefore final $n(HNO_3) = 0.0500 - 0.02987 = 0.02013$ mol

$[HNO_3]$ in excess $= 0.02013 / 0.250 = 0.08052$ mol L^{-1}

$pH = -\log_{10}[H^+] = -\log_{10}[0.08052] = 1.094$ pH = 1.09

NB: Strong acid vs Strong Base thus ONE WAY arrow; not equilibrium arrow

Marking Criteria	*Mark(s)*
• Correct calculation of pH of resultant solution showing all working including balanced equation	4
• Correct calculation of pH of resultant solution showing all working without balanced equation OR one error in calculation	3
• Some correct calculations	2

• One correct calculation or balanced equation	1

(b) Explain how nitric acid meets the criteria for the Arrhenius model and Bronsted-Lowry model of acids. **4**

Sample Answer : Nitric acid can be both an Arrhenius and Bronsted-Lowry acid.

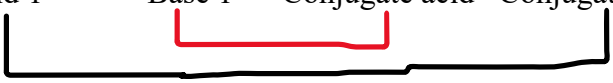
Arrhenius acid ionises in an aqueous solution to produce hydronium ions

$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

A Bronsted-Lowry acid donates a proton to a proton acceptor base and produces conjugate base and acid respectively

$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

Acid 1 Base 1 Conjugate acid Conjugate base



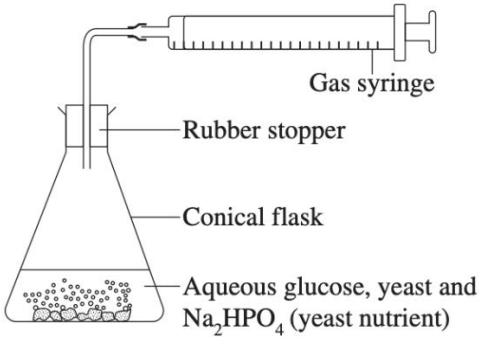
NB : Strong acid ionisation thus ONE Way Arrow; not necessary to mention conjugate acids/bases but better answered did mention this as part of definition for B-L theory. Must have 2 equations as Question states "…relevant equations" plural.

Marking Criteria	*Mark(s)*
• Correct explanations how nitric acid behaves as an Arrhenius and Bronsted Lowry acid with suitable equations and definitions for both.	4
• Correct explanation of nitric acid behaving as Arrhenius and Bronsted-Lowry acid with one suitable equation and both definitions	3
• Correct explanation of nitric acid acting as Arrhenius and B-L acid without equations	2
• Correct definition of either Arrhenius or B-L or one correct equation	1

Question 26 (9 marks)

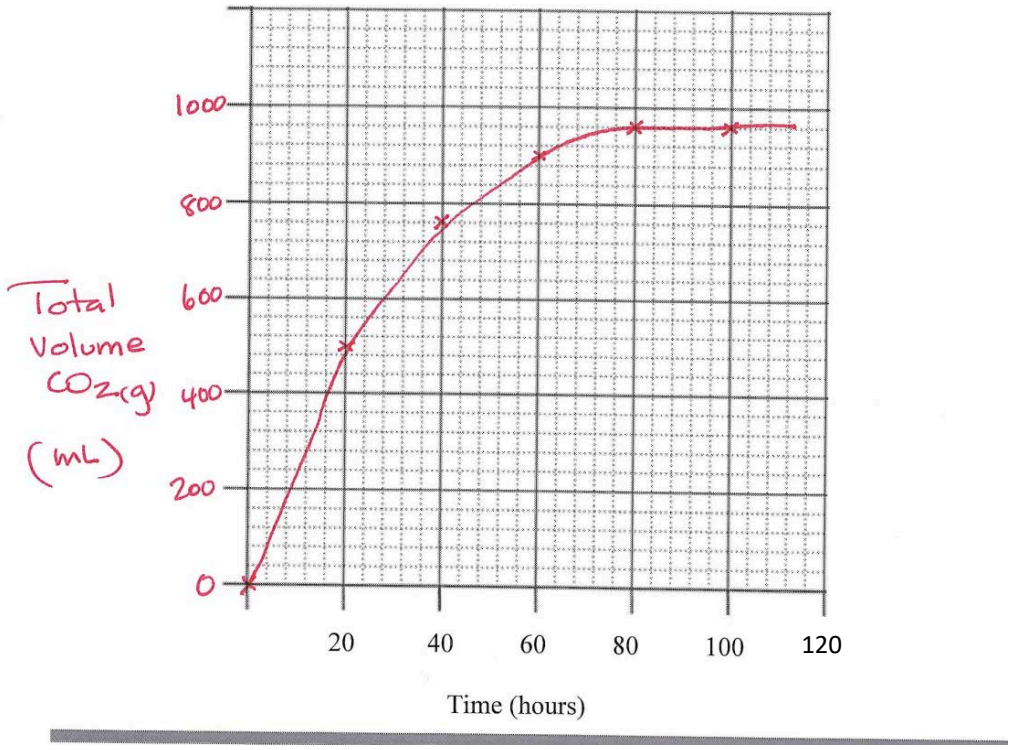
Industrially, ethanol is produced through fermentation of glucose ($C_6H_{12}O_6$).
This reaction can be performed in the school laboratory and the amount of ethanol produced can be determined by measuring the volume of carbon dioxide gas generated.

The following apparatus was set up under standard laboratory conditions (25°C and 100 kPa) and
the following data were collected from an experiment.



Hours	Total volume of CO_2 gas produced (mL)
0	0
20	500
40	760
60	900
80	960
100	960
120	960

(a) Plot the results, including a curved line of best fit. **3**



Marking Criteria	*Mark(s)*
• Correct graphing features including axes label and units, sensible scale, correct plots and curve of best fit	3
• Most graph features correct	2
• 2 correct graph features	1

(b) Explain the shape the graph. **3**

As the reaction proceeds, the volume of carbon dioxide produced increases until the maximum is reached at 960 mL when all the glucose has reacted, or the yeast has been killed by the concentration of ethanol and the graph has a plateau. The rate of production decreases as there are fewer reactants as the reaction proceeds so fewer collisions which is why the graph is a curve and not linear. The curve of the graph is steep at the start then starts to become shallower as the rate decreases.

Marking Criteria	*Mark(s)*
• Explains 2 features in the shape of the graph	3
• Explains one feature in the graph OR outlines 2	2
• Outlines one feature of the graph	1

(c) Calculate the mass of ethanol produced in this reaction. Include a relevant equation in your answer. **3**

$$C_6H_{12}O_6\ (aq) \rightarrow 2CO_2\ (g) + 2C_2H_5OH\ (aq)$$

n CO_2 = V/24.79 = 0.960/24.79 = 0.0387 mol
n C_2H_5OH = 0.0387
mass C_2H_5OH = mol x MM = 0.0387 x (2(12.01) + 6(1.008) + 16) = 1.78 g

Marking Criteria	*Mark(s)*
• Correct mass of ethanol calculated with all relevant calculations and a balanced equation. (must show ethanol as C_2H_5OH)	3
• Some relevant working provided	2
• Some relevant information	1

Question 27 (2 marks)

25 mL of a straight chain gaseous hydrocarbon was reacted with 200 mL of oxygen at 25°C. On cooling to 25°C, the residual mixture of gases had a volume of 137.5 mL.
This was shaken with potassium hydroxide solution to remove the carbon dioxide dropping the final gas volume to 37.5 mL consisting of oxygen only.

Show your relevant working to identify the hydrocarbon.

C_xH_y (g) + O_2 (g) → CO_2 (g) + H_2O (l)
25 mL 200 mL 137.5 mL

V CO_2 = 137.5 – 37.5 = 100 mL
V O_2 used = 200 – 37.5 = 162.5 mL
Therefore ratio C_xH_y : O_2 : CO_2 is
25 : 162.5 : 100
= 1: 6.5 : 4 C_4H_{10} (g) + 6.5 O_2 (g) → 4CO_2 (g) + 5H_2O (l)
The hydrocarbon is butane C_4H_{10}

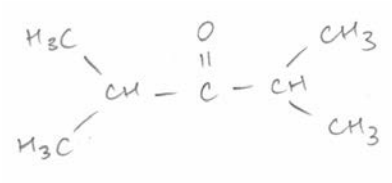
Marking Criteria	*Mark(s)*
• Shows relevant calculations applying Guy Lussac's Law to determine the formula for the hydrocarbon	2
• A relevant calculation	1

Question 28 (4 marks)

Chemists use a variety of spectroscopic techniques to determine different details about the structure of organic compounds.

(a) draw the structure of 2,4-dimethylpentan-3-one. **1**

Sample answer:



Marking Criteria	*Mark(s)*
• Gives the correct structure for 2,4-dimethylpentan-2-one	1

(b) Outline the information that could be obtained about this organic compound using. Infrared spectroscopy. **1**

Sample answer:Infrared spectroscopy provides information regarding the type of functional group present in an organic compound. It would identify that this compound contains a ketone due to the C=O stretch located at 1680 – 1750 cm^{-1}.

Marking Criteria	*Mark(s)*
• Describes the information provided by infrared spectroscopy (functional group identity)	1

(c) Describe the information that could be obtained about this organic compound using: Carbon-13 NMR spectroscopy **2**

Sample answer:

This technique also can be used to obtain information regarding the type of functional group present in an organic compound. It would identify the presence of a ketone due to the presence of a carbon signal at 190 – 220 ppm. It can also identify whether there is symmetry in the organic molecule, where in this case although the compound has 7 carbon atoms, the spectrum would only contain 3 unique signals.

Marking Criteria	*Mark(s)*
• Describes the information provided by carbon-13 NMR spectroscopy for this compound (diagnostic signal and number of signals w/ symmetry)	2
• Provides some relevant information.	1

Question 29 (5 marks)

The pH in swimming pools are maintained within a range of 7.2 to 7.8 to avoid skin and eye irritation in people.

A common chemical used to maintain this narrow pH range is sodium hydrogen carbonate which is added at regular intervals to swimming pool water.

(a) Which physical property of solid sodium hydrogen carbonate makes it suitable for use in swimming pool water? **1**

Sample Answer: Sodium hydrogen carbonate is highly soluble in water.

Marking Criteria	*Mark(s)*
• Identifies a relevant physical property of sodium hydrogen carbonate for use in a swimming pool	1

(b) Define the role of a "buffer" in an aqueous environment. **1**

Sample Answer: A buffer is a soluble chemical which resists a change in pH when a small amount of acid or base is added to an aqueous solution. It allows the system to maintain a narrow pH range.

Marking Criteria	*Mark(s)*
• Correctly defines the role of a buffer in an aqueous system	1

(c) Justify the use of sodium hydrogen carbonate as a suitable buffer in swimming pools.

Provide relevant chemical equations to support your answer. **3**

Sample Answer: Buffers consists of a weak acid and its conjugate base.

Sodium hydrogen carbonate dissolves in water to produce the hydrogen carbonate ion HCO_3^- (aq) and the carbonate ion $CO_3^{2-}(aq)$ react with the addition of small amounts of acid or base to maintain a regular pH in the water in accordance with LeChatelier's Principle.

When an acid is added the following reaction occurs:

$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(aq)$

When a base is added the following reaction occurs:

$HCO_3^-(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + CO_3^{2-}(aq)$

These reactions maintain the pH range of the swimming pool to be within the range of 7.2 to 7.8 which minimizes skin and eye for people using the pools.

NB: Must have 2 Equations showing amphiprotic nature of hydrogen carbonate ion and how this acts as a buffer when small amounts of acid or base are added and TWO way arrows for buffer equilibrium equations.

Marking Criteria	*Mark(s)*
• Justifies the use of sodium hydrogen carbonate as a suitable buffer • Provides relevant equations to support justification	3
• Describes how sodium hydrogen carbonate acts as a buffer • Provides ONE suitable equation	2
• Outlines how sodium hydrogen carbonate acts as a buffer OR • Provides a suitable equation	1

Question 30 (7 marks)

A 0.100 mol $^{L-}$1 ammonium chloride solution has a pH of 4.60.

(a) What is the Ka of this weak acid? **4**

Sample Answer :

Eqn : $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

Determine $[H_3O^+]$ at equilibrium using $[H_3O^+] = 10^{-pH} = 10^{-4.6} = 0.00002511886 = 2.51 \times 10^{-5}$

Construct ICE Table:

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

I	0.100	0	0
C	-s	+s	+s
E	0.1 -s	S	s

As it is a weak acid initially has not dissociated so concentration is 0.1 mol L^{-1}.
Initial concentration of both NH_3 and H_3O^+ is zero.
As acid dissociates the NH_3 and H_3O^+ ions are produced in a1:1 ratio.
This can be represented as s.

Initially no H_3O^+ was present and s = 2.51 X 10^{-5}

So ICE Table becomes

I	0.100	0	0
C	-2.51×10^{-5}	$+2.51 \times 10^{-5}$	$+2.51 \times 10^{-5}$
E	$0.1 - 2.51 \times 10^{-5} = 0.09997488113$	2.51×10^{-5}	2.51×10^{-5}

$Ka = [NH_3][H_3O^+] / [NH_4Cl] = (2.5 \times 10^{-5})^2 / 0.100 = 6.25 \times 10^{-9}$

NB: Must show all working and be careful with rounding up answers to correct place for decimal point.

• Correct calculation of Ka showing all working including ICE table	4
• Mostly correct calculation with one error	3
• Some correct calculations	2
• One correct calculation OR step in the working process	1

(b) What is the percent ionization of this acid? **2**

% dissociation = $[NH_3] / [NH_4Cl] \times 100 = 2.51 \times 10^{-5} / 0.10 \times 100 = 0.0251\%$ dissociated

• Correctly calculates % dissociation of acid showing all working	2

• One correct calculation showing % dissociation	1

(c) Calculate the pKa of the solution. **1**

$pKa = -\log_{10}(Ka) = -\log_{10}(6.25 \times 10^{-9}) = 8.20$

• Correctly calculates pKa value showing all working	1

Question 31 (7 marks)

A primary straight chained alcohol, a carboxylic acid and an ester made with methanol, are colourless liquids with molar masses of 88 g mol^{-1}.

Identify the compounds and explain the results of physical and chemical tests that could be performed to distinguish between the three liquids.

Sample answer
All compounds have molar masses of 88
Primary straight chain alcohol MM pentan-1-ol = 5(12.01) + 12(1.008) + 16 = 88
Carboxylic acid MM butanoic acid = 4(12.01) + 8(1.008) + 2(16) = 88
Ester isomer of butanoic acid made with methanol…methyl propanoate
MM $CH_3OOCCH_2CH_3$ = 88
Physical tests
Measure the boiling points of the three liquids. Methyl propanoate will have the lowest as it has only weak dispersion forces between the molecules. Then pentan-1-ol as it has dispersion forces and also stronger H-bonding between the molecules. Butanoic acid has the highest boiling point as it has more extensive H-bonding between the molecules, this needs to most energy to overcome the intermolecular forces so has the highest boiling point.

Add them to water. The acid is completely soluble in water as it is polar and will hydrogen bond with water. The penta-1-ol is slightly soluble in water as the hydroxyl group will hydrogen bond with water, but the longer alkyl chain inhibits solubility. The ester will not dissolve in water but will form an immiscible layer on top of water as it is non-polar. The ester will have a fruity odour.

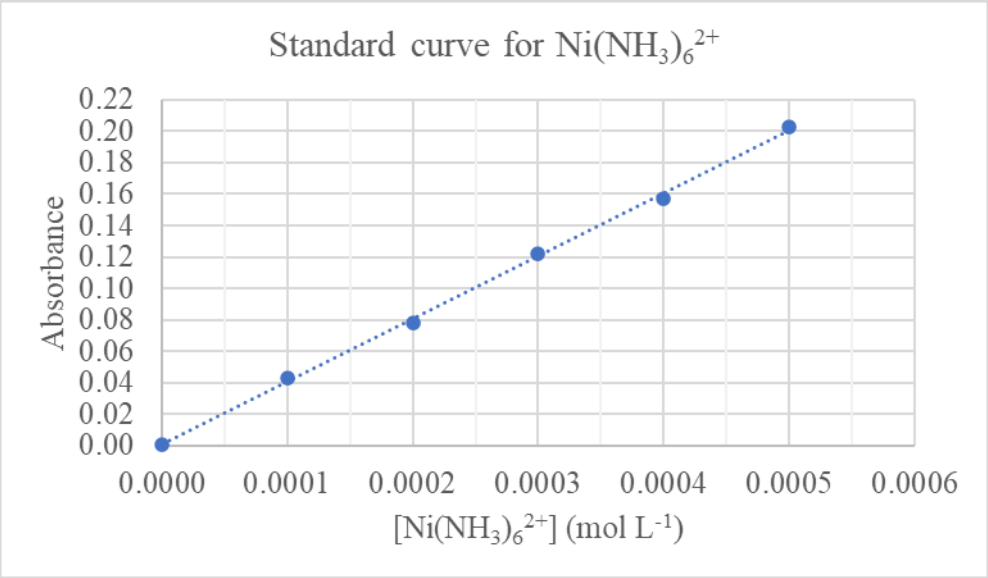
Chemical tests

The alcohol can be oxidised by H^+/MnO_4^-. It will decolourise the permanganate from purple to colourless and become an acid. Neither the acid or the ester will be oxidised.
The acid will react with a carbonate producing bubbles of carbon dioxide. Neither the alcohol or the ester will react with the carbonate.

Marking Criteria	*Mark(s)*
• Identifies the three compounds • Explains at least three physical tests and/or Chemical tests • No incorrect tests given I I I PPC, I I I CCP	7
• Identifies the 3 compounds (I) • Explains two physical tests and /or chemical test (P/C) • Outlines another test (t)	6
• Identifies at least 2 compounds • Explains or outlines a variety of tests • Combinations include: IIIPt√, IIIPPt, IIICt √√, IIIttC, III,ttt, IIPC, IIIPtt, IIPPt,	5
• Identifies at least 2 compounds • Outlines a variety of other tests • Combinations include: IIttp, IIIP, IItp, IItt, IItt√, IIIt, IIItt, IIttt,	4
• A variety of combinations of identifications and tests • Combinations include: Itt√, Ittt, III, IIP, ttt, IPt, III√, IIt, It√, tt√, I√√, P√√, PP or PC, tt√√	3
• Combinations include: P, C, II, tt, t√√, √√	2
• Gives some relevant information	1

Question 32 (7 marks)
The metal ion complex $Ni(NH_3)_6^{2+}$ can be formed from adding concentrated ammonia to a Ni^{2+} solution, as shown in the following equation:
$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$
The solution formed is a deep blue colour and the absorbance of a $Ni(NH_3)_6^{2+}$ solution can be measured using a colourimeter.
A student made solutions according to the following table in order to produce a standard curve below:

Solution	Volume 0.0010 M Ni^{2+} (mL)	Volume 4.0 M NH_3 (mL)	Volume H_2O (mL)
1	0	5.0	5.0
2	1.0	5.0	4.0
3	2.0	5.0	3.0
4	3.0	5.0	2.0
5	4.0	5.0	1.0
6	5.0	5.0	0



(a) Explain the purpose of the water in solutions 1– 5. **2**

The student then made a new solution using 1.0 mL of 0.0070 M Ni^{2+}*(aq)*, 1.0 mL of 0.40 M NH_3 and 8.0 mL water. When placed into a colourimeter, an absorbance of 0.17 was recorded.

Question 1a

Marking Criteria	*Mark(s)*
• Identifies maintaining consistent volume • Relates to validity of method (constant NH_3 concentration)	2
• One of the above	1

Sample answer:

The water is added to ensure that the volume of each of the 6 solutions used to construct the standard curve is 10 mL. This will allow the concentrations of the Ni^{2+} to increase in regular amounts while keeping the concentration of the NH_3 identical in each solution.

Comment: a number of students stated that it improved the validity of the method without demonstrating how it would in this particular system.

(b) Calculate the value of K_{eq} for the complexation reaction. **3**

Marking Criteria	*Mark(s)*
• Calculates equilibrium constant with correct working	3
• 2-3 of the following • Correctly reads from the graph (0.00042 – 0.00043) • Accounts for dilution • Calculates final concentration • Correct expression for K_{eq} •	2
• Some relevant calculations	1

Sample Answer
Initial concentration of $Ni^{2+} = 0.007 \times (1/(1+1+8)) = 0.0007$ mol L^{-1}
Initial concentration $NH_3 = 0.4 \times (1/(1+1+8)) = 0.04$ mol mol L^{-1}

	$[Ni^{2+}]$	$[NH_3]$	$Ni(NH_3)_6^{2+}$
Initial	0.0007	0.04	0
Change	-x	-6x	+x
Equilibrium	0.0007 -x = 0.000275	0.04 -6x = 0.03745	+x = 0.000425

From standard curve, final $[Ni(NH_3)_6^{2+}] = 0.000425$
$K_{eq} = [Ni(NH_3)_6^{2+}]/([Ni^{2+}][NH_3]^6) = 0.000425/(0.000275 \times 0.03745^6) = 5.6 \times 10^8$

(c) In making the standard curve, the student treated the reactions as having gone to completion with the Ni^{2+} ion as the limiting agent. When determining the concentration of the unknown Ni^{2+} solution, the system was treated as an equilibrium reaction.

Given that $K_{eq} >> 1$, account for the two different treatments. **2**

Marking Criteria	*Mark(s)*
• Correctly relates the position of the equilibrium to the initial concentrations • Demonstrates link between position of equilibrium and calculation of complex concentration	2
• One of the above	1

Sample answer:

When forming the solutions for the standard curve, the ammonia concentration was significantly higher (more than 40,000 times higher) than the nickel concentration. This caused the complexation all of the available nickel, particularly as K_{eq} is so high and NH_3 was raised to the power of 6.
In the second experiment, the concentration of ammonia was much lower (only 57 times higher), so the position of the equilibrium was not as far to the right, particularly since $[NH_3]$ was less than 1. This meant that not all of the nickel was complexed, so an equilibrium analysis was necessary.

Comments: In the first experiment, the lowest the NH_3 concentration could be is 1.997 mol L^{-1}. Since K_{eq}= [complex]/[Ni][NH_3]^6 >>1 then [complex]/[Ni] >> 1.997^6 = 63 so almost all the nickel is in the complex, treating the reaction as having gone to completion is reasonable. In the second experiment, the NH_3 concentration was 0.03745. [Complex]/[Ni] >> 0.03745^6 = 2 x 10^{-9}, so we can't say that all of the Ni is used up.
Note that in both situations the K_{eq} is large! You needed to provide a rationalisation for the different treatment based on the data provided, not just whether we knew the standard curve or not.

Question 33 (6 marks)

An investigation was carried out using a series of precipitation reactions to determine the concentration of magnesium, silver, and copper ions presents in a sample solution.

A 25.0 mL aliquot of the sample solution was pipetted into a conical flask. That solution was reacted with hydrochloric acid solution until no more precipitate was formed. The precipitate was extracted using gravity filtration, allowed to dry overnight and was found to have a mass of 1.36 g.

The filtrate was collected into a separate conical flask. That solution was treated with a dilute ammonia solution to neutralise the remaining hydrochloric acid. Sodium hydroxide solution was added to the resultant solution until no more precipitate was formed. A mixture of blue and white precipitates was obtained in the conical flask. The precipitates were filtered, dried in an oven, and recorded to have a mass of 2.40 g.

In a separate experiment, a fresh 20.0 mL aliquot of the sample solution was pipetted into a conical flask and titrated with a 0.427 mol L^{-1} solution of sodium carbonate. During this precipitation titration a series of coloured precipitates formed, starting with a pale, yellow silver precipitate, then a blue copper precipitate, followed by a white magnesium precipitate. The titre volume was recorded once a white precipitate had begun to form in the conical flask. The results of the precipitation titration are given in the table:

Titration	*Volume of Na_2CO_3* (mL)
1	41.10
2	39.75
3	39.85
4	39.80

Calculate the concentrations of magnesium, silver, and copper ions in the original sample solution. Include a relevant chemical equation for each precipitation reaction. **6**

Sample answer:

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

$n(AgCl) = m / MM = 1.36 / (107.9 + 35.45) = 9.49 \times 10^{-3}$ mol $= n(Ag^+)$

$C(Ag^+) = n / V = 9.49 \times 10^{-3} / 0.025 = 0.379$ mol L^{-1}

$2Ag^+(aq) + Cu^{2+}(aq) + 2CO_3^{2-}(aq) \rightarrow Ag_2CO_3(s) + CuCO_3(s)$

$V(\text{avg titre}) = (0.03975 + 0.03985 + 0.03980) / 3 = 0.03980$ L

$n(CO_3^{2-}) = c \times V = 0.427 \times 0.0398 = 0.0170$ mol

$n(Ag^+) = 0.379 \times 0.02 = 0.00759$ mol

$n(Cu^{2+}) = n(CO_3^{2-}) - 2 \times n(Ag^+) = 0.0132$ mol

$C(Cu^{2+}) = n / V = 0.0132 / 0.02 = 0.660$ mol L^{-1}

$Mg^{2+}(aq) + Cu^{2+}(aq) + 4OH^-(aq) \rightarrow Mg(OH)_2(s) + Cu(OH)_2(s)$

$n(Cu^{2+}) = c \times V = 0.660 \times 0.025 = 0.0165$ mol

$m(Cu(OH)_2) = n \times MM = 0.165 \times (63.55 + 2 \times 16.00 + 2 \times 1.008) = 1.61$ g

$m(Mg(OH)_2) = 2.40 - 1.61 = 0.79$ g

$n(Mg(OH)_2) = 0.79 / (24.31 + 2 \times 16.00 + 2 \times 1.008) = 0.0135$ mol $= n(Mg^{2+})$

$C(Mg^{2+}) = n / V = 0.0135 / 0.25 = 0.542$ mol L^{-1}

Marking Criteria	*Mark(s)*
• Correctly calculates the concentrations of magnesium, silver, and copper ions in the original sample solution. • Provides relevant, balanced chemical equations for each precipitation reaction described in the procedure.	6
• Correctly calculates the concentrations of TWO species in the original sample solution (FTE permitted for one concentration) • Provides relevant, balanced chemical equation for at least TWO precipitation reaction described in the procedure.	5
• Correctly calculates the concentrations of ONE species in the original sample solution and part of the second (carbonate concentration) • Provides a balanced chemical equation for ONE precipitation reaction described in the procedure.	4
• Provides the main calculation steps, with a correct calculation for the concentration of ONE species in the original sample solution.	3

• Provides some relevant calculation steps.	2
• Provides some relevant information.	1

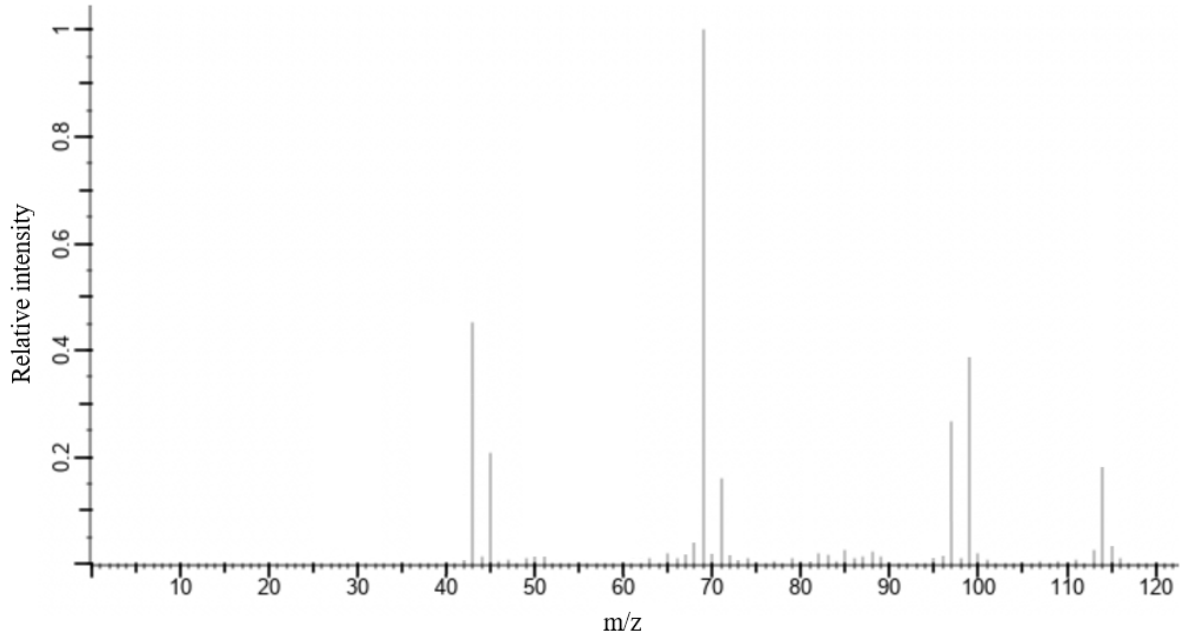
Question 34 (7 marks)

The following information was obtained from the analysis of an unknown organic compound.

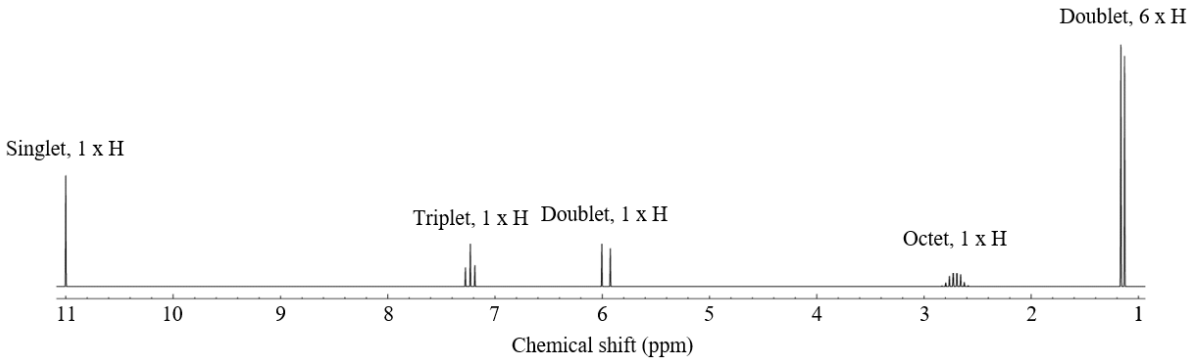
Chemical Reactivity

Chemical Reagent	*Observation*
$NaHCO_3(aq)$	bubbling
$KMnO_4(aq) + H_2SO_4(aq)$	magenta solution
$Br_2(aq)$	colourless solution

Mass Spectrum

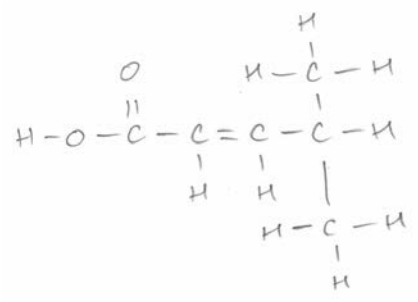


Proton NMR



In the space provided, give the structural formula for the unknown compound that is consistent with all the information provided. Justify your structure with reference to the relevant information from each source of data. **7**

Sample answer:



Structural formula

4-methylpent-2-enoic acid.

Chemical reactivity

The acid base reaction with $NaHCO_3$ to produce bubbles indicates the presence of a carboxylic acid functional group in the unknown organic molecule. The magenta colour observed with the addition of $KMnO_4$ and H_2SO_4 indicates that no reaction has occurred, which means that neither an alcohol nor aldehyde functional group is present. The appearance of a colourless solution with the addition of Br_2 identifies that an addition reaction has taken place and confirms that an alkene is present in the unknown organic molecule.

Mass Spectrum

There is a molecular ion peak at m/z = 114 which gives the molecular mass for the unknown organic compound. As there is a carboxylic acid functional group present with a mass of 45, the remaining mass of 69 accounts for the carbon chain, as well as the alkene double bond. As the proton NMR indicates that there are 10 hydrogen atoms, and 1 is already accounted for in the carboxylic acid, we can conclude that the carbon chain contains 9 hydrogen atoms, and 5 carbon atoms. Using the connectivity details obtained from the proton NMR, we can deduce the structures for each fragment. The base peak at m/z = 69 represents the carbon chain without the carboxylic acid functional group with a structure of $[(CH_3)_2CHCH=CH]^+$. The signal at m/z = 71 has the structure $[CH=CHCOOH]^+$. The fragment at m/z = 97 has lost a hydroxyl group to give $[(CH_3)_2CHCH=CHCO]^+$ whereas the fragment m/z = 99 has lost a methyl group to give $[CH_3CHCH=CHCOOH]^+$. The fragment at m/z = 43 has the structure $[CH_3CHCH_3]^+$ and m/z = 45 is $[COOH]^+$.

Proton NMR

The 1H singlet at ~ 11.0 ppm is characteristic for the single H atom contained in the carboxylic acid functional group that is not adjacent to any other H atoms. There is a 6H doublet at ~ 1.2 ppm which indicates a degree of symmetry in the molecule and represents two CH_3 signals that are directly adjacent to a CH. This pair of signals must be situated beside the 1H octet at ~ 2.7 ppm to give a $CH_3C\underline{H}CH_3$ segment that is also beside one other single H atom. This is likely to be the 1H triplet at ~ 7.2 ppm that is part of the alkene double bond as it is the environment connected to the previous segment which gives a $(CH_3)_2CHC\underline{H}$=CH segment. The 1H doublet at ~ 6.0 ppm is adjacent to the 1H triplet previously mentioned and gives the CH=$\underline{C}$HCOOH segment connected to the carboxylic acid. The coupled signals for the aforementioned 1H doublet and 1H triplet is not possible without an alkene double bond since both environments would otherwise not have enough H atoms.

Marking Criteria	*Mark(s)*
• Gives the correct structural formula for 4-methylpent-2-en-1-oic acid. • Justifies the correct structure with reference to all three sources of data. • Shows a thorough understanding of the interpretation of data from TWO of chemical tests, carbon NMR, and / or mass spectrum. • Refers explicitly to ALL relevant sources of data.	7
• Gives the correct structural formula for 4-methylpent-2-en-1-oic acid. • Justifies the correct structure with reference to all three sources of data. • Shows a thorough understanding of the interpretation of data from TWO of chemical tests, carbon NMR, and / or mass spectrum.	6
• Provides structural formula consistent with analysis. • Shows a detailed understanding of the interpretation of data from ONE of chemical tests, carbon NMR, OR mass spectrum • Shows a sound understanding of the interpretation of data from the remaining sources.	4 – 5
• Shows some understanding of the interpretation of data obtained from chemical tests, carbon NMR, and / or mass spectrum.	2 – 3
• Provides some relevant information.	1

Mass spectrum checklist; provides structures and labels for molecular ion @ 114, base peak @ 69, fragment @ 43, fragment @ 69.

Carbon NMR checklist; interprets splitting patterns for all 5 signals, provides rationale and identity for octet and alkene segments.

Question 35 (4 marks)
Discuss the effects of enthalpy and entropy in the reaction between octane and oxygen in a flame.

Marking Criteria	*Mark(s)*
• Balanced equation with correct states (either SLC or in a flame) • Recognises the H_2O is a gas in the flame • Identifies reaction as exothermic or $\Delta H < 0$ • Identifies release of heat • Correctly deduces ΔS based on equation and/or discussion • Correctly deduces ΔG based on ΔH and ΔS • Correctly identifies spontaneity based on ΔG	4
• 4-6 of above	3
• 2-3 of above (equation can have incorrect states)	2
• Some relevant information	1

Sample Answer:
The reaction between octane and the oxygen in air is:
$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$ at standard conditions.
The reaction is highly exothermic, converting stored chemical potential energy into heat (which can be used to drive combustion engines). This heat energy also converts the water to a gas, as the temperature is higher than standard conditions. This results in 34 moles of gas on the product side, with only 25 moles of gas on the reactant side, indicating an increase in entropy of the system. $\Delta G = \Delta H - T\,\Delta S$ Thus, this reaction is spontaneous due to a decrease in enthalpy and an increase in entropy leading to a $\Delta G < 0$.

Comments: a significant number of students believed that octane was aqueous (it is non-polar). Entropy for a gaseous state is significantly greater than for a liquid state, when marking, the values used were based on the states that you had written (assuming aqueous as liquid for the purposes of carry forward error).