NESA number

Chemistry

2023 TRIAL HSC EXAMINATION

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 formulae sheet, 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 3–10)

- Attempt Questions 1–20
- Answer on the multiple choice grid provided
- Allow about 35 minutes for this section

Section II – 80 marks in Booklet A and B

- Attempt Questions 21– 32
- Allow about 2 hours and 25 minutes for this section in Booklet A and B

Section I
20 marks

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

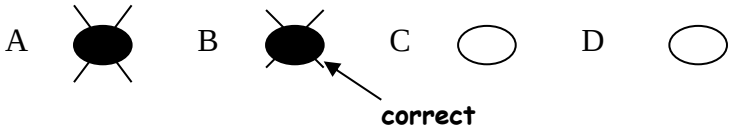
Use the multiple-choice answer sheet.

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

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

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.



Section I

20 marks
Attempt Questions 1–20
Allow about 35 minutes for this section

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

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1. Which one of the following species could be analysed using AAS?

(a) Sr^{2+}
(b) S^{2-}
(c) SO_2
(d) SO_4^{2-}

2. The forward reaction in the equilibrium shown below is endothermic.

$$OCl^- (aq) + H_2O (l) \rightleftharpoons HOCl (aq) + OH^- (aq)$$

Which change increases the concentration of hypochlorous acid (HOCl)?

(a) Adding water.
(b) Adding sodium hypochlorite, NaOCl (s).
(c) Increasing the pH.
(d) Lowering the temperature.

3 Consider the following statements about acid-base indicators. Acid-base indicators

(i) are weak acids or bases.
(ii) are strong acids that change colour as the concentration of hydrogen ions changes.
(iii) must not react with the reactants or products in a titration.
(iv) must be used in large volumes for the best results.

Which of the above statements is/are correct?

(a) i only.
(b) i and ii
(c) i and iii
(d) i, ii, iii and iv

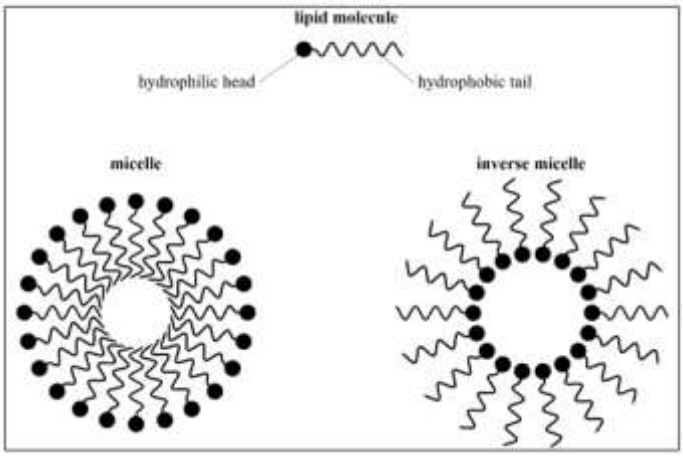
4. Which of the following pairs of compounds will form a precipitate when 0.1 mol L^{-1} solutions of each are mixed?

(a) $AgNO_3$ and $Ba(NO_3)_2$
(b) K_2SO_4 and $Cu(NO_3)_2$
(c) $Ca(NO_3)_2$ and KBr
(d) NaOH and $CuCl_2$

5. How many isomers are there for a molecule with the formula $C_3H_6Cl_2$?

(a) 5
(b) 4
(c) 3
(d) 2

6. Interactions between lipid and solvent molecules can result in the formation of micelles and inverse micelles as shown in the diagrams below.



Which alternative below shows the correct polarity of a solvent which would form each type of micelle?

	Micelle	Inverse micelle
(a)	polar	polar
(b)	polar	non-polar
(c)	non-polar	polar
(d)	non-polar	non-polar

7. Which statement relates most to NMR spectroscopy?

(a) Valence electrons in metal atoms are excited, moving to a higher energy level.
(b) The mass of a charged particle will determine its trajectory in a magnetic field.
(c) Bonds in a molecule can absorb energy, which results in them stretching.
(d) Protons are excited and move to a higher energy spin state.

8. For the equilibrium:

$$2ICl\,(g) \rightleftharpoons I_2\,(g) + Cl_2\,(g)$$

the numerical value of the equilibrium constant K is 4.8×10^{-6} at 25°C.
Which of the following statements is true?
At 25°C at equilibrium

(a) there will be much less I_2 and Cl_2 than ICl.
(b) the will be twice as much ICl as I_2 present.
(c) the pressure of each gas, I_2, Cl_2 and ICl, will all be the same.
(d) there will be much more I_2 and Cl_2 than ICl

9. Which of the following is true for a system at equilibrium?

(a) The number of collisions per unit time between reactants is equal to the number of collisions per unit time between products.

(b) The product of the concentrations of the reactants is equal to the product of the concentrations of the products.

(c) Reactants are reacting to form products at the same rate as products are reacting to form reactants.

(d) All concentrations of reactants and products are equal.

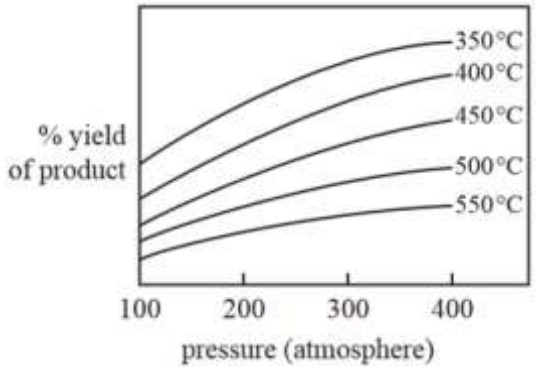
10. The pH of pure water at 50°C ($K_w = 5.5 \times 10^{-14}$) is:

(a) 6.63
(b) 7
(c) 13.2
(d) 13.6

11. The graph below refers to the following gaseous reaction.

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

The effect of increasing pressure and temperature on the equilibrium yield of the products is shown in the graph below.



Which of the following alternatives regarding the chemical system is consistent with the data above?

	Relative numbers of moles of products and reactants	ΔH
(a)	$a + b < c + d$	–
(b)	$a + b < c + d$	+
(c)	$a + b > c + d$	–
(d)	$a + b > c + d$	+

12. Iodine monochloride (ICl) reacts with carbon-carbon double bonds via an addition reaction (one ICl per double bond). If 0.105 g of a molecule of molar mass 304.5 g mol^{-1} reacts with exactly 0.224 g of ICl, how many carbon-carbon double bonds are present in the molecule?

(a) 3
(b) 4
(c) 5
(d) 8

13. Butyl propanoate can be synthesised from 1-butanol and one another reactant.

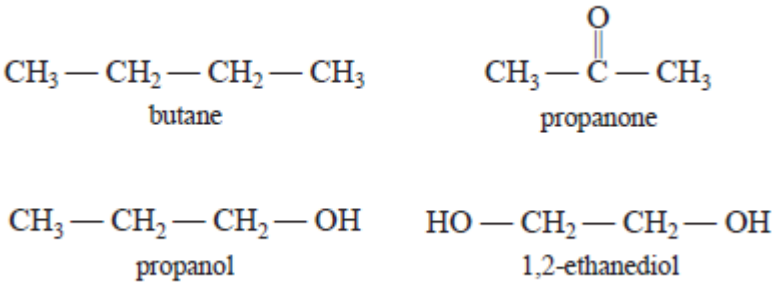
Compared to 1-butanol, the other reactant has:

(a) fewer double bonds
(b) longer carbon chain length
(c) more peaks in its ^{13}C NMR spectrum
(d) the same molecular ion peak in its mass spectrum

14. 100 mL of 0.4 mol/L nitric acid, HNO_3, is added to 100 mL of 0.1 mol/L barium hydroxide, $Ba(OH)_2$. The pH of the resulting solution is

(a) 0.3
(b) 0.7
(c) 0.8
(d) 1.0

15. The four substances below have similar molar masses.



The substance with the highest boiling point is

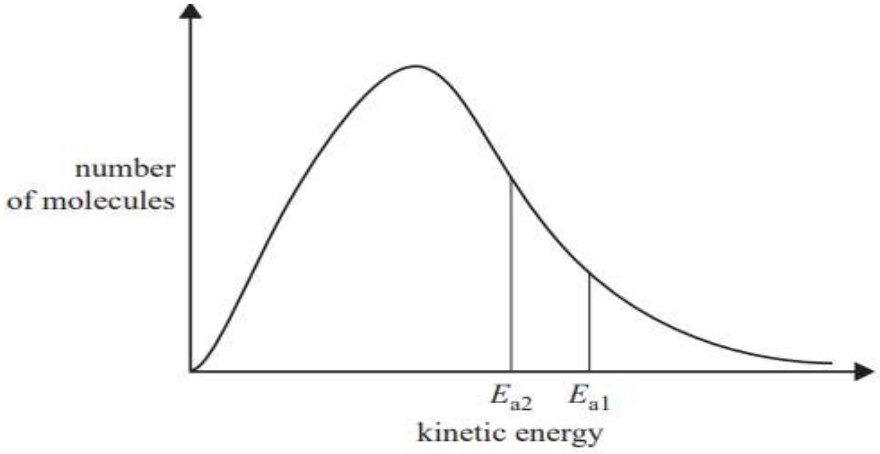
(a) butane
(b) propanol
(c) propanone
(d) 1,2-ethanediol

16. Which one of the following would be classed as a weak, diprotic acid?

(a) $H_2SO_4(aq)$
(b) $H_2CO_3(aq)$
(c) $CH_3COOH(aq)$
(d) $CH_2(OH)CH_2OH(aq)$

17. The diagram below represents the distribution of kinetic energy in a sample of gaseous reactant molecules.

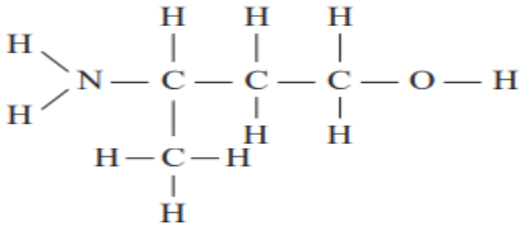
The activation energy E_{a1} has been changed to activation energy E_{a2}. This change increases the reaction rate.



Which of the following gives the most likely cause of the change from E_{a1} to E_{a2} and explains why the reaction rate would increase?

	Cause of the change	***Why the reaction rate increases***
(a)	Catalyst added	Molecules move faster, resulting in more successful collisions
(b)	Catalyst added	Greater proportion of reactants collide with sufficient energy to react
(c)	Temperature increased	Greater proportion of reactants collide with the correct orientation to react
(d)	Concentration of reactants increased	Greater frequency of collisions, resulting in more successful collisions

18. The IUPAC systematic name for the following molecule is



(a) 3-aminobutan-1-ol.
(b) 4-hydroxybutan-2-amine.
(c) 3-methyl-3-aminopropan-1-ol.
(d) 3-hydroxy-1-methylpropan-1-amine.

19. A titration is performed in which a 20.00 mL aliquot of 0.10 mol/L hydrochloric acid solution is titrated with a 0.10 mol/L solution of sodium hydroxide. The pH of the solution in the conical flask is monitored and recorded throughout the titration.

Which of the following graphs shows the expected change in pH during the titration?

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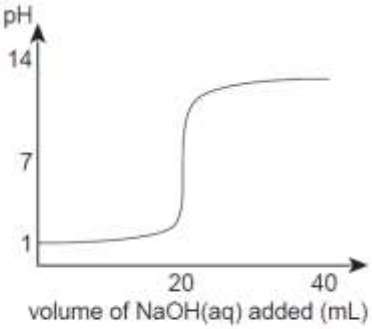
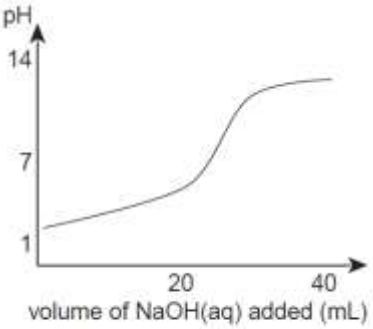


B.



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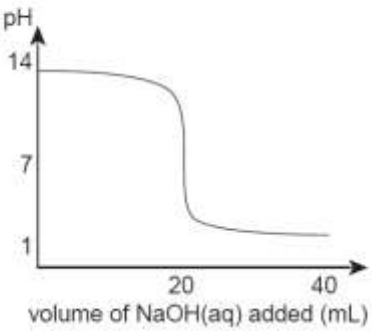
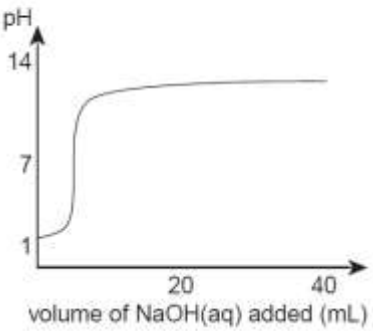
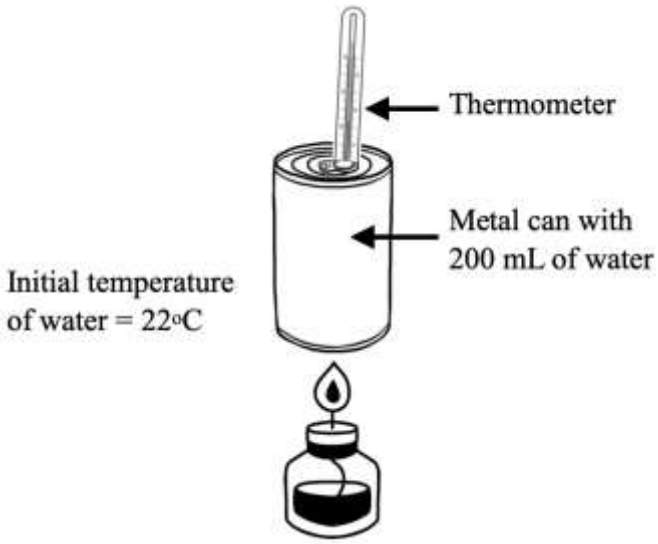


D.



20. A student carried out an experiment, using the apparatus shown, to find the heat of combustion of ethanol.



1.80 g of ethanol was added to a spirit burner. When 1.50g of ethanol was burnt, the temperature of the water increased to 48°C.

Calculate the energy released in kJ.

(a) 21.74 kJ
(b) 18.11 kJ
(c) 4.803 kJ
(d) 4.353 kJ

NESA number

SYDNEY BOYS HIGH SCHOOL

CHEMISTRY
2023 TRIAL HSC EXAMINATION

Section II - Booklet A
Answer questions 21-26

Booklet A Total:

/32

Chemistry

2023 TRIAL EXAMINATION

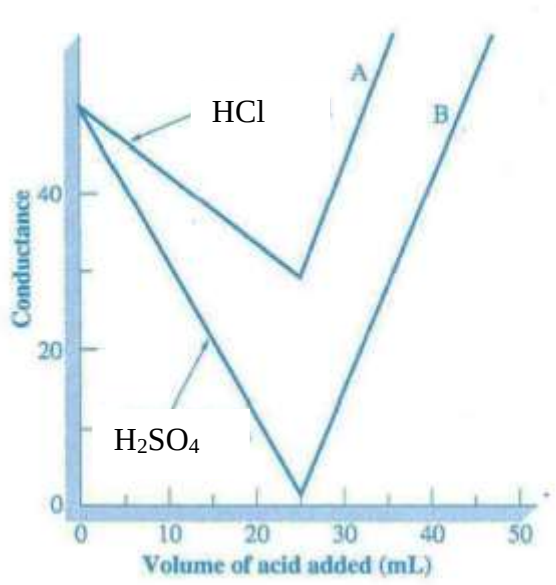
Section II
80 marks

Attempt Questions 21- 32
Allow about 2 hour and 25 minutes for this part

Answer the questions in the spaces provided.
Show all relevant working in questions involving calculations.
Section II

Question 21 (7 marks)

50 mL 0.10 mol/L barium hydroxide solution was titrated with a solution of hydrochloric acid and the electrical conductance measured as a function of volume of acid added. Graph A in the diagram below was obtained.



a) Calculate the concentration of HCl solution added. **2**

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b) Account for the shape of Graph A. **2**

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c) The titration was repeated using sulfuric acid instead of hydrochloric acid. Graph B was obtained. Account for the shape of Graph B. **3**

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Question 22 (7 marks)

A buffer solution has the property of resisting changes in pH even when small amounts of acid or alkali are added to it.

a) Compare the change in pH of a solution containing $CaCl_2$/HCl in a 1:1 mole ratio and a solution containing $NaH_2PO_4^-/Na_2HPO_4$ in a 1:1 mole ratio when a small amount of acid is added to the mixture using equilibrium principles. **5**

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b) Provide reasons why the Arrhenius acid/base theory is inadequate in explaining the differences in behaviour of the substances in part (a). **2**

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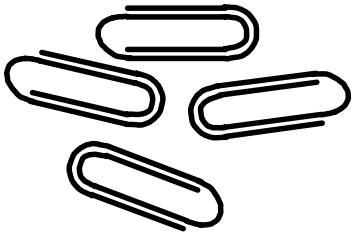
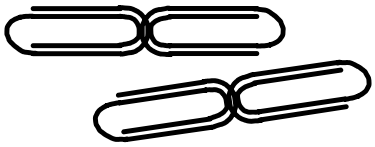
Question 23 (6 marks)

Two students working together set up a simple game involving 40 separate paper clips. Student **X** was responsible for connecting individual paper clips into pairs, whist student **Y** was responsible for taking apart the connected paper clips. Both students remained blindfolded during the game.

Individually separated paper clips



Connected pairs of paper clips



After a while, the amount of individual and connected paper clips became constant.

a) State two ways in which this model relates to the essential features of a dynamic equilibrium reaction? **2**

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b) A third student added another pile of individual paper clips to the game. Student X and Y continued their actions. After a while, the amount of individual and connected paper clips became constant again. **4**

By referring to the collision theory, explain how the addition of more paperclips to the game simulates the effect of concentration on a chemical equilibrium.

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Question 24 (6 marks)

Name of acid	**Formula**	pK_a
Chloroacetic acid	$ClCH_2COOH$	2.85
Hydrofluoric acid	HF	3.17
Cyanic acid	HOCN	3.46
Formic acid	HCOOH	3.74
Hypochlorous	HOCl	7.52

a) From the table above, determine the weakest of these monoprotic acids. **1**

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b) Calculate the % ionisation for a 0.10 mol/L solution of the acid from part a). **3**

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c) Compare the pH of the acid in part a) to a 0.10 mol/L solution of H_2SO_4? **2**

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Question 25 (6 marks)

A stage show requiring a frothing 'blood-like' liquid used dry ice $\left(CO_2(s)\right)$ and iron complexes to produce this effect.

One such iron complex consists of an alkaline solution containing iron (III) chloride and sodium thiocyanate. This produces the following equilibrium reaction:

$$\underset{\text{(yellow)}}{Fe(OH)^{2+} + SCN^-} \rightleftharpoons \underset{\text{(bright red)}}{Fe(SCN)^{2+} + OH^-}$$

a) The numerical value of K at 25°C for this reaction was found to be 2.3×10^{-4}.

i) What does the value of K tell us about the equilibrium concentrations of the $Fe(SCN)^{2+}$ and OH^- ions? **1**

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ii) Predict the colour of the equilibrium solution at 25°C. **1**

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b) If dry ice is added to this solution, the pH changes from about pH 10 to pH 4. Explain why this pH change occurs. **2**

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c) Explain how the addition of dry ice produces the blood-red coloured liquid. **2**

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End of Booklet A

Section II extra writing space.

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NESA number

SYDNEY BOYS HIGH SCHOOL

CHEMISTRY
2023 TRIAL HSC EXAMINATION

Section II - Booklet B
Answer questions 27-33

Booklet B Total:

/48

Question 26 (6 marks)

A solution of an unknown salt is analysed. It is known to contain either Mg^{2+}, Cu^{2+}, or Ca^{2+} as the only cation, and either SO_4^{2-} or Cl^- or CO_3^{2-} as they only anion.

Outline a method that could be used to identify the cation and anion present in the unknown salt solution. Include relevant chemical equations and observations which would confirm the ions present. **6**

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Question 27 (6 marks)

Compound X is a colourless liquid. When drops of sodium hydrogen carbonate solution were added to it, bubbles of colourless gas formed. When a few mL of X was refluxed with methanol and concentrated sulfuric acid, a product more volatile than X was formed. This product had a much more pleasant odour than X.

a) To what class of compound does X belong? Explain. **2**

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b) 0.62g of X was mixed with 100mL of water and titrated with sodium hydroxide solution using phenolphthalein as an indicator. 37.3 mL of 0.223 mol/L sodium hydroxide solution was needed to reach the endpoint. **4**

Calculate the molecular weight of X.

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Question 28 (6 marks)

Nylon 6,6 is a condensation polymer formed from the reaction between hexane-1,6-diamine and hexanedioic acid in a 1:1 mole ratio.

a) Using condensed structural formula, write the chemical equation for the polymerisation reaction. **1**

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The molar masses of some species are shown in the table below.

Species	**Molar mass ($g.mol^{-1}$)**
hexane-1,6-diamine	116.20
hexanedioic acid	146.14
Nylon 6,6	244.31

b) **3**

If 220.0 g of hexanedioic acid and 280.0 g of hexan-1,6-diamine are reacted together in a vessel, what mass of nylon 6,6 is produced if the reaction goes to completion?

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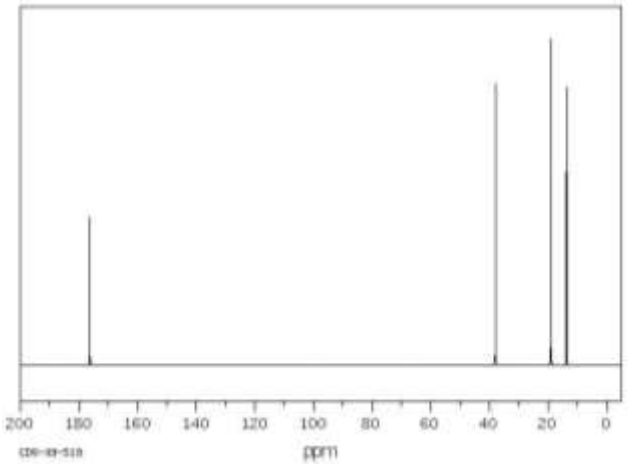
c) Draw a segment of Nylon 6,6 showing 3 amide linkages. **2**

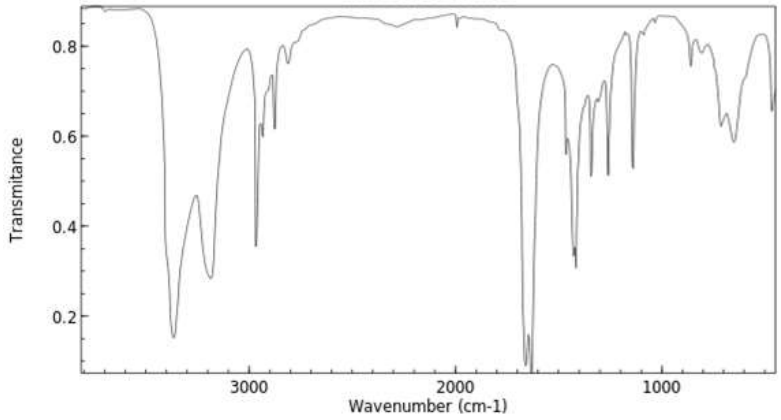
Question 29 (9 marks)

A laboratory assistant came across an unlabelled bottle containing an unknown white crystalline organic solid. The technician carried out several tests on the bottle's contents. The results of the tests are shown.

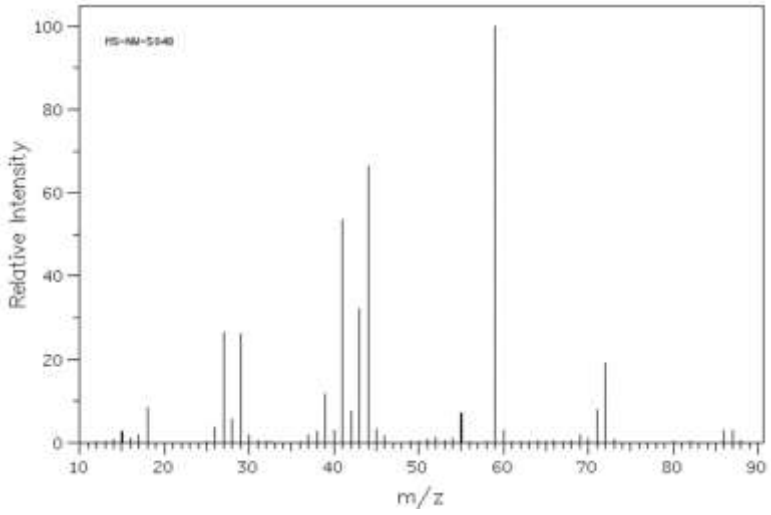
Carbon -13 NMR



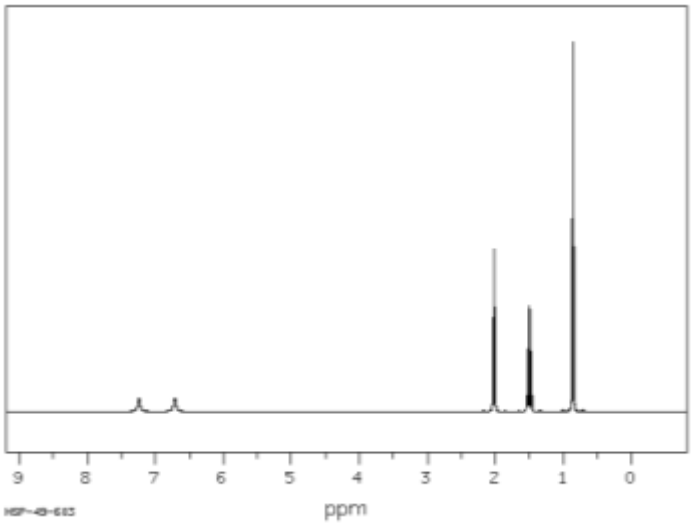
Infrared spectrum



Mass spectrum



Proton NMR



Shift (ppm)	Splitting	Integration
7.24	1	1
6.71	1	1
2.02	3	2
1.50	6	2
0.86	3	3

^{1}H NMR chemical shift data

Type of proton	δ/ppm
$Si(CH_3)_4$ (TMS)	0
R–C**H**$_3$	0.9–1.0
R–C**H**$_2$–R	1.2–1.5
R–C**H**R$_2$	1.5–2.0
R–C≡C–**H** (alkyne)	2.0–3.1
–CO–C**H**$_2$– (aldehydes, ketones or esters)	2.1-2.7
R–C**H**$_2$–NH_2	2.4–3.0
R–C**H**$_2$–X (X = F, Cl, Br, I)	3.0–4.5
–C**H**$_2$–O– (alcohols, ethers or esters)	3.3–4.8
R–O**H**	1–6
R–N**H**$_2$	1–5
R$_2$C=C**H**R (alkene)	4.5–7.0
R–COON**H**–R (amide)	5–9
Ar-**H** (aromatic)	6.9–9.0
R–C**H**O (aldehyde)	9.4–10.0
R–COO**H**	9.0–13.0

a) In the space provided, draw and name the unknown compound that is consistent with all the information provided. Justify your answer with reference to the information provided. **7**

Structure:

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b) For the mass spectrum shown: **2**

i) Identify the mass of the base peak

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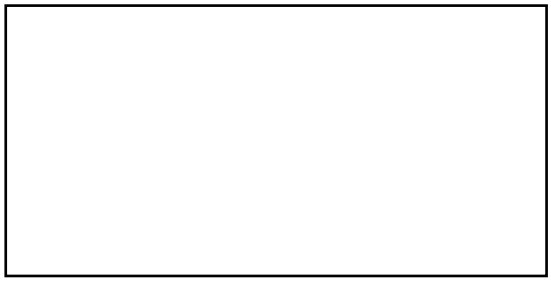
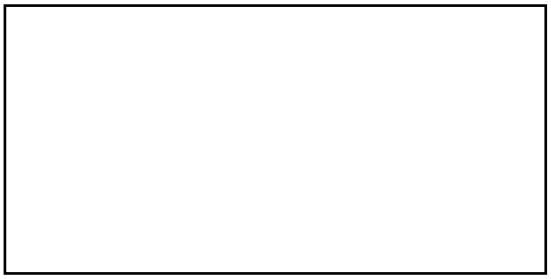
ii) Identify the structure of the fragment that produces the peak at m/z 44.

Question 30 (6 marks)

a) Draw structural formula for both 2-methyl-2-pentanol and for 3-methyl-2-pentanol. **2**





b) Describe, and give the results of, a chemical test to distinguish between these two compounds. **4**

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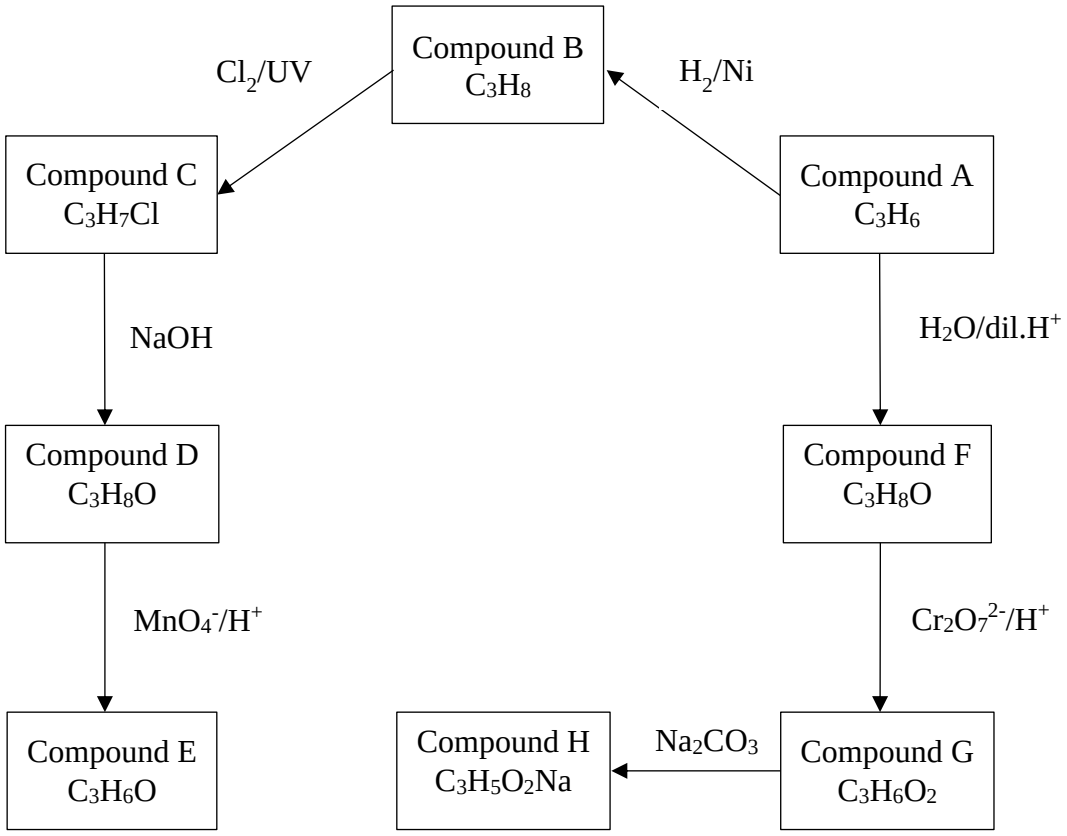
Question 31 (9 marks)

This flowchart shows reactions involving eight different organic compounds A to H.



a) Draw the structures of compounds A to H. **7**
Note: Each compound (A to H) has a unique structure.

Compound A:	Compound B:
Compound C:	Compound D:
Compound E:	Compound F:
Compound G:	Compound H:

b) Using the information provided, justify your identification of Compound D and F. **2**

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Question 32 (6 marks)

The manganese content in a 13.5 g sample of steel was determined by measuring absorbance of permanganate (MnO_4^-) using the following process

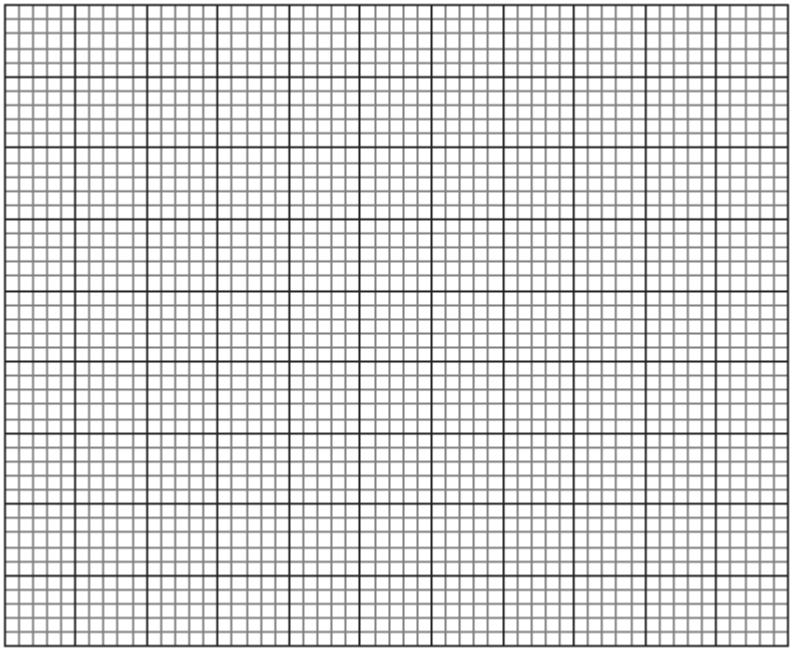
The steel sample was dissolved in nitric acid and the Mn^{2+} (aq) ions produced were oxidised to MnO_4^- by periodate ions, IO_4^- (aq) according to the following equation:

$$2Mn^{2+}(aq) + 5IO_4^-(aq) + 3H_2O(l) \rightarrow 2MnO_4^-(aq) + 5IO_3^-(aq) + 6H^+(aq)$$

The resulting solution was made up to a volume of 250.00 mL. A 20.0 mL aliquot of the solution was diluted to 100.0 mL. The absorbance at 525 nm of the resulting solution was 0.50.

a) Construct a calibration curve using the following data. **3**

Concentration of MnO_4^- (mg/L)	**Absorbance**
0	0
10	0.2
20	0.4
30	0.6
40	0.8
50	1.0



b) Calculate the percentage by mass of manganese in the steel sample. **3**

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End of Booklet B

End of Exam

Section II extra writing space.

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

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NESA number

Chemistry

2023 TRIAL HSC EXAMINATION

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 formulae sheet, 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 3–10)

- Attempt Questions 1–20
- Answer on the multiple choice grid provided
- Allow about 35 minutes for this section

Section II – 80 marks in Booklet A and B

- Attempt Questions 21– 32
- Allow about 2 hours and 25 minutes for this section in Booklet A and B

Section I
20 marks

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

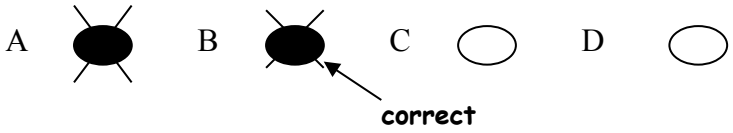
Use the multiple-choice answer sheet.

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

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

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.



Section I

20 marks
Attempt Questions 1–20
Allow about 35 minutes for this section

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

1. Which one of the following species could be analysed using AAS?

(a) Sr^{2+}
(b) S^{2-}
(c) SO_2
(d) SO_4^{2-}

2. The forward reaction in the equilibrium shown below is endothermic.

$$OCl^- (aq) + H_2O (l) \rightleftharpoons HOCl (aq) + OH^- (aq)$$

Which change increases the concentration of hypochlorous acid (HOCl)?

(a) Adding water.
(b) Adding sodium hypochlorite, NaOCl (s).
(c) Increasing the pH.
(d) Lowering the temperature.

3 Consider the following statements about acid-base indicators. Acid-base indicators

(i) are weak acids or bases.
(ii) are strong acids that change colour as the concentration of hydrogen ions changes.
(iii) must not react with the reactants or products in a titration.
(iv) must be used in large volumes for the best results.

Which of the above statements is/are correct?

(a) i only.
(b) i and ii
(c) i and iii
(d) i, ii, iii and iv

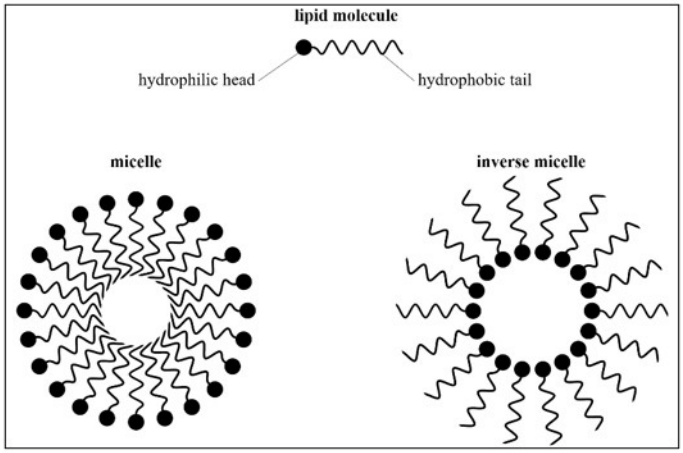
4. Which of the following pairs of compounds will form a precipitate when 0.1 mol L^{-1} solutions of each are mixed?

(a) $AgNO_3$ and $Ba(NO_3)_2$
(b) K_2SO_4 and $Cu(NO_3)_2$
(c) $Ca(NO_3)_2$ and KBr
(d) NaOH and $CuCl_2$

5. How many isomers are there for a molecule with the formula $C_3H_6Cl_2$?

(a) 5
(b) 4
(c) 3
(d) 2

6. Interactions between lipid and solvent molecules can result in the formation of micelles and inverse micelles as shown in the diagrams below.



Which alternative below shows the correct polarity of a solvent which would form each type of micelle?

	Micelle	Inverse micelle
(a)	polar	polar
(b)	polar	non-polar
(c)	non-polar	polar
(d)	non-polar	non-polar

7. Which statement relates most to NMR spectroscopy?

(a) Valence electrons in metal atoms are excited, moving to a higher energy level.
(b) The mass of a charged particle will determine its trajectory in a magnetic field.
(c) Bonds in a molecule can absorb energy, which results in them stretching.
(d) Protons are excited and move to a higher energy spin state.

8. For the equilibrium:

$$2ICl\,(g) \rightleftharpoons I_2\,(g) + Cl_2\,(g)$$

the numerical value of the equilibrium constant K is 4.8×10^{-6} at 25°C.
Which of the following statements is true?
At 25°C at equilibrium

(a) there will be much less I_2 and Cl_2 than ICl.
(b) the will be twice as much ICl as I_2 present.
(c) the pressure of each gas, I_2, Cl_2 and ICl, will all be the same.
(d) there will be much more I_2 and Cl_2 than ICl

9. Which of the following is true for a system at equilibrium?

(a) The number of collisions per unit time between reactants is equal to the number of collisions per unit time between products.

(b) The product of the concentrations of the reactants is equal to the product of the concentrations of the products.

(c) Reactants are reacting to form products at the same rate as products are reacting to form reactants.

(d) All concentrations of reactants and products are equal.

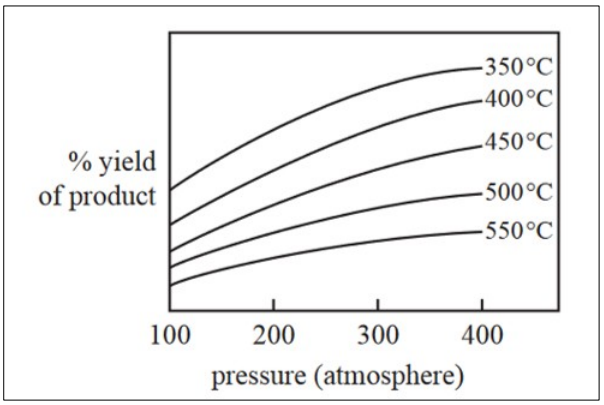
10 The pH of pure water at 50°C ($K_w = 5.5 \times 10^{-14}$) is:
.

(a) 6.63
(b) 7
(c) 13.2
(d) 13.6

11 The graph below refers to the following gaseous reaction.
.

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

The effect of increasing pressure and temperature on the equilibrium yield of the products is shown in the graph below.



Which of the following alternatives regarding the chemical system is consistent with the data above?

	Relative numbers of moles of products and reactants	ΔH
(a)	$a + b < c + d$	–
(b)	$a + b < c + d$	+
(c)	$a + b > c + d$	–
(d)	$a + b > c + d$	+

12. Iodine monochloride (ICl) reacts with carbon-carbon double bonds via an addition reaction (one ICl per double bond). If 0.105 g of a molecule of molar mass 304.5 g mol^{-1} reacts with exactly 0.224 g of ICl, how many carbon-carbon double bonds are present in the molecule?

(a) 3
(b) 4
(c) 5
(d) 8

13. Butyl propanoate can be synthesised from 1-butanol and one another reactant.

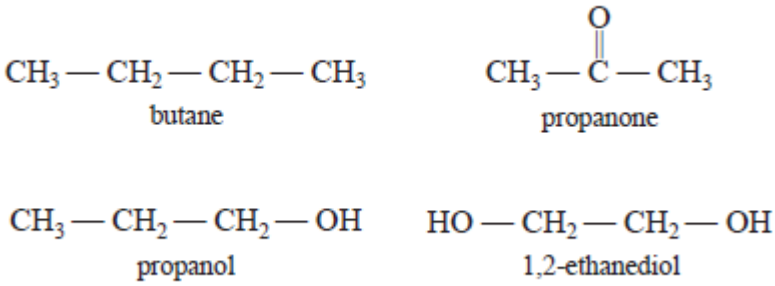
Compared to 1-butanol, the other reactant has:

(a) fewer double bonds
(b) longer carbon chain length
(c) more peaks in its ^{13}C NMR spectrum
(d) the same molecular ion peak in its mass spectrum

14. 100 mL of 0.4 mol/L nitric acid, HNO_3, is added to 100 mL of 0.1 mol/L barium hydroxide, $Ba(OH)_2$. The pH of the resulting solution is

(a) 0.3
(b) 0.7
(c) 0.8
(d) 1.0

15. The four substances below have similar molar masses.



The substance with the highest boiling point is

(a) butane
(b) propanol
(c) propanone
(d) 1,2-ethanediol

16. Which one of the following would be classed as a weak, diprotic acid?

(a) $H_2SO_4(aq)$

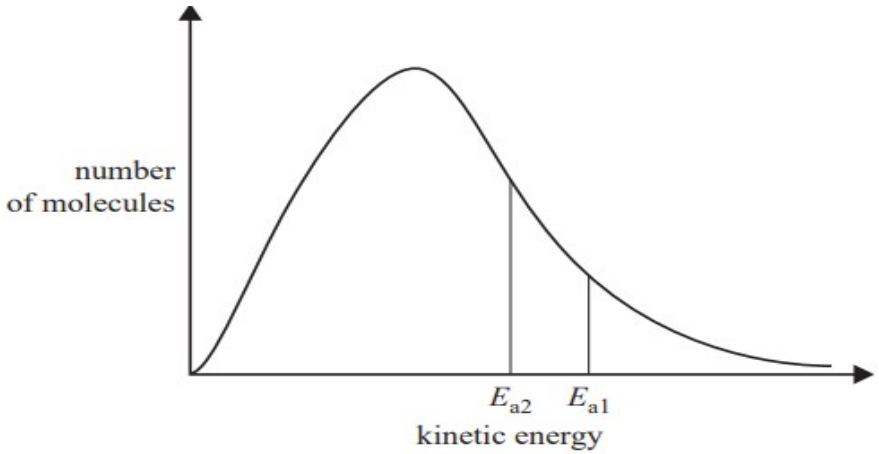
(b) $H_2CO_3(aq)$

(c) $CH_3COOH(aq)$

(d) $CH_2(OH)CH_2OH(aq)$

17. The diagram below represents the distribution of kinetic energy in a sample of gaseous reactant molecules.

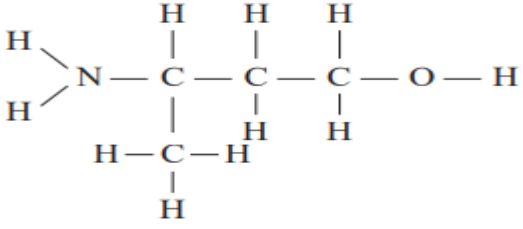
The activation energy E_{a1} has been changed to activation energy E_{a2}. This change increases the reaction rate.



Which of the following gives the most likely cause of the change from E_{a1} to E_{a2} and explains why the reaction rate would increase?

	Cause of the change	***Why the reaction rate increases***
(a)	Catalyst added	Molecules move faster, resulting in more successful collisions
(b)	Catalyst added	Greater proportion of reactants collide with sufficient energy to react
(c)	Temperature increased	Greater proportion of reactants collide with the correct orientation to react
(d)	Concentration of reactants increased	Greater frequency of collisions, resulting in more successful collisions

18. The IUPAC syste



(a) 3-aminobutan-1-ol.

(b) 4-hydroxybutan-2-amine.

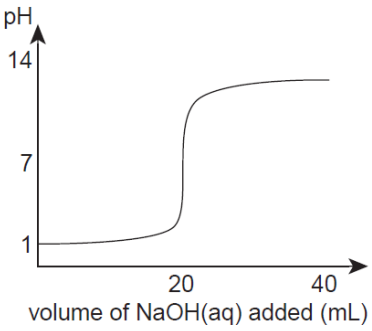
(c) 3-methyl-3-aminopropan-1-ol.

(d) 3-hydroxy-1-methylpropan-1-amine.

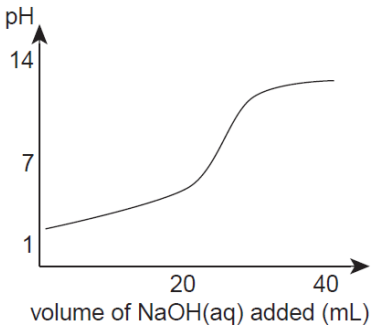
19. A titration is performed in which a 20.00 mL aliquot of 0.10 mol/L hydrochloric acid solution is titrated with a 0.10 mol/L solution of sodium hydroxide. The pH of the solution in the conical flask is monitored and recorded throughout the titration.

Which of the following graphs shows the expected change in pH during the titration? A

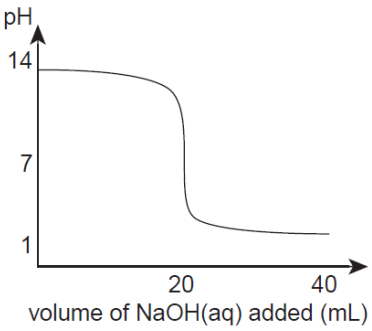
A.



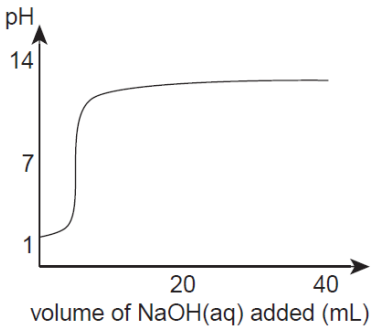
B.



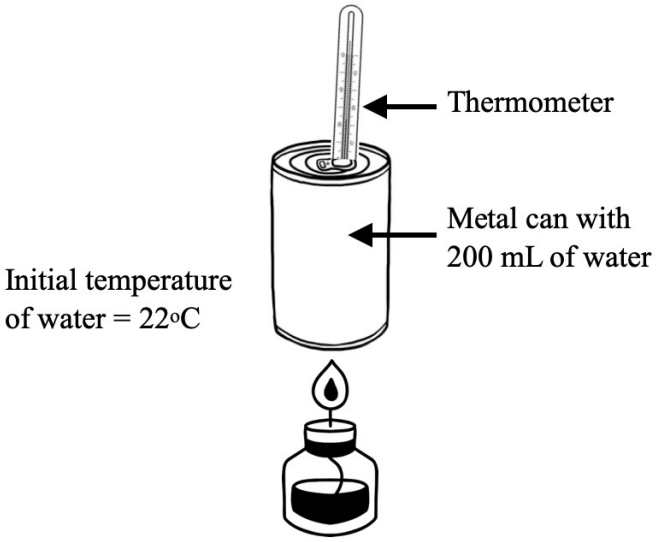
C.



D.



20. A student carried out an experiment, using the apparatus shown, to find the heat of combustion of ethanol.



1.80 g of ethanol was added to a spirit burner. When 1.50g of ethanol was burnt, the temperature of the water increased to 48°C.

Calculate the energy released in kJ.

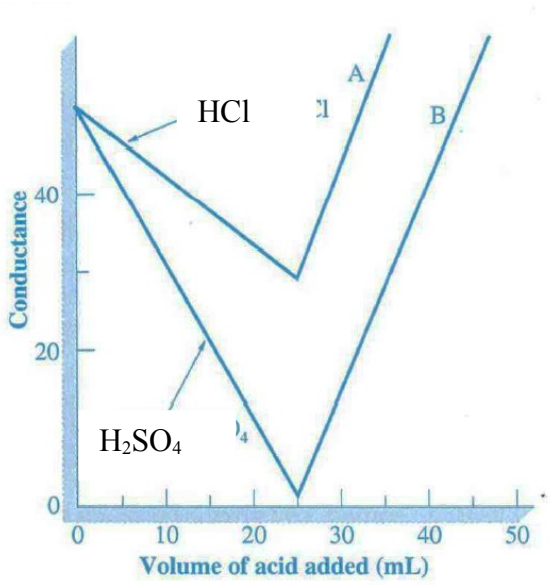
(a) 21.74 kJ
(b) 18.11 kJ
(c) 4.803 kJ
(d) 4.353 kJ

Chemistry Section II

2023 TRIAL EXAMINATION

Question 21 (7 marks)

50 mL 0.10 mol/L barium hydroxide solution was titrated with a solution of hydrochloric acid and the electrical conductance measured as a function of volume of acid added. Graph A in the diagram below was obtained.



a) Calculate the concentration of HCl solution added. **2**

Criteria	**Marks**
Provides correct calculation showing all steps	2
Some relevant steps	1

Sample answer:

$Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$

$n(Ba(OH)_2) = c \times v = 0.1 \times 0.05 = 0.005$ mol
$n(HCl) = 2 \times n(Ba(OH)_2) = 2 \times 0.005 = 0.01$ mol (as reaction ratio is 1:2)
concentration of HCl = $n/V = 0.01/0.025 = 0.40$ mol/L

Markers Note:
Must write a balanced equation as there a 2:1 ratio.
Only use $c_1v_1=c_2v_2$ for dilutions, too easy to miss the ratio.
Put units throughout your answers.
Write formulas and substitute into it.
Annotate your answers, don't just pluck numbers out.

b) Account for the shape of Graph A. **2**

Criteria	Marks
Explains the shape of the titration curve, in terms of ions present and why, at the beginning, as it falls, at equivalence point and as it rises	2
Some relevant information	1

Sample answer:

As barium hydroxide is a strong base, it completely dissociates, producing Ba^{2+} and OH^- ions that are free to move and conduct electric current, so conductivity is high. The curve steadily falls as H^+ ions are added as they react and remove the OH^- ions from solution as H_2O is formed that does not conduct electricity. At equivalence point, conductivity is lowest because the solution only contains Ba^{2+} and Cl^- ions, which are much less mobile that the H^+ or OH^- ions. The curve then rises more steeply as excess HCl is added, dissociates into Cl- and the more highly conductive H^+ ions.

Markers Note:
Many don't know the difference between endpoint and equivalence point.

c) The titration was repeated using sulfuric acid instead of hydrochloric acid. Graph B was obtained. Account for the shape of Graph B. **3**

Criteria	Marks
Explains the shape of the titration curve, in terms of ions present, as it falls, at equivalence point and as it rises	3
Describes the trend in the titration curve and makes an explanation why equivalence point is at zero conductance.	2
Some relevant information	1

Sample answer:

As barium hydroxide is a strong base, it completely dissociates, producing Ba^{2+} and OH^- ions that are free to move and conduct electric current, so conductivity is high. As H_2SO_4 is added, the curve steadily falls as H^+ ions are added because they react and remove the OH^- ions from solution as H_2O is formed that does not conduct electricity. As SO_4^{2-} ion are added they react with the Ba^{2+} ions to form the insoluble $BaSO_4$, removing all Ba^{2+} and SO_4^{2-} ion from solution. The conductivity reaches its lowest level at the equivalence point, when all of the OH^- ions have been neutralised by H^+ and the $BaSO_4$ has precipitated out. At this point, the conductivity would be zero. As excess H_2SO_4 is added, it dissociates, so more ions are released, and conductivity rises again. The initial curve is steeper as H_2SO_4 is diprotic which results in a neutralisation occurring at a faster rate.

Markers Note:
Not penalised twice for missing that $Ba(OH)_2$ is a strong base and completely dissociates. Many didn't recognise that electrically neutral water and $BaSO_4$ produced at the equivalence point.

Question 22 (7 marks)

A buffer solution has the property of resisting changes in pH even when small amounts of acid or alkali are added to it.

a) Compare the change in pH of a solution containing $CaCl_2$/HCl in a 1:1 mole ratio and a solution containing NaH_2PO_4/Na_2HPO_4 in a 1:1 mole ratio when a small amount of acid is added to the mixture using equilibrium principles.

Criteria	Marks
• Makes a general statement summarising the buffering ability of the two pairs of reagents • Compares the reactions of the ions $H_2PO_4^-$, HPO_4^{2-} and Cl^- with water, and relates these to their relative strengths as bases compared with water. • Includes an appropriate equation to illustrate the shift in equilibrium required to maintain the pH when an acid is added.	5
• Compares the reactions of the ions $H_2PO_4^-$, HPO_4^{2-} and Cl^- with water, and relates these to their relative strengths as bases compared with water. • Includes of an appropriate equation to illustrate the shift in equilibrium required to maintain the pH when an acid is added.	4
• Discusses the reactions of the ions $H_2PO_4^-$, HPO_4^{2-} only with water and relates these to their relative strengths as bases compared with water. OR • Discusses the reaction of the Cl^- ion with water and relates this to its relative strength as a base compared with water. AND • Includes an appropriate equation to illustrate the shift in equilibrium required to maintain the pH when an acid is added.	3
• Discusses the reactions of the ions $H_2PO_4^-$, HPO_4^{2-} only with water and relates these to their relative strengths as bases compared with water. OR • Discusses the reaction of the Cl^- ions with water and relates this to its relative strength as a base compared with water. AND • Makes some reference to equilibrium principles to explain the buffering effect.	2
• Provides some relevant information	1

Sample Answer:

The capacity of a solution to resist changes in pH upon addition of an acid relies on the existence of compounds that can react with the acid. Specifically, an acid and a base must be present in the mixture to combine with any added base or acid and preserve the pH. In contrast, a strong acid like HCl, which fully ionises in an aqueous medium, generates a weak conjugate base, Cl^-, that cannot bind to any added acid (proton). Consequently, in the absence of a buffering system, an acid added to the $CaCl_2$/HCl solution will significantly decrease the pH.

The $NaH_2PO_4^-/Na_2HPO_4$ mixture exhibits an equilibrium between $H_2PO_4^-$ and HPO_4^{2-} ions in the presence of water, generating H_3O^+ ions according to the equation below:

$H_2PO_4^-\ (aq) + H_2O\ (l) \leftrightharpoons H_3O^+\ (aq) + HPO_4^{2-}\ (aq)$

In the case of the weak acid $H_2PO_4^-$, the proton remains bound to its conjugate base, the HPO_4^{2-} ion, until it encounters a stronger base, such as the OH^- ion, with which it combines.

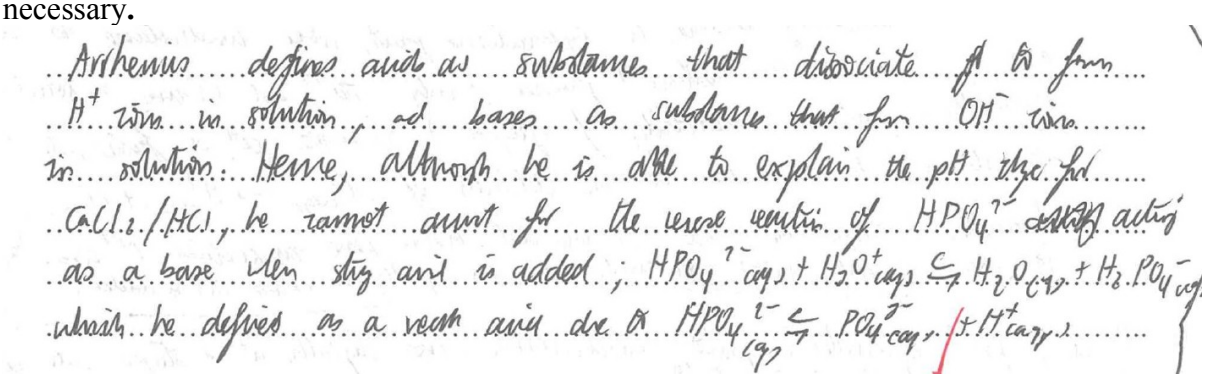
In general, buffer solutions resist changes in pH by having both a weak acid and its conjugate base (or a weak base and its conjugate acid) present in the solution. The acid and its conjugate base can react with added H^+ or OH^- ions to maintain the pH of the solution within a certain range. In this example, the phosphate equilibrium is the only one that can act as a buffer.

Markers Note:
Many failed to recognise that HCl is a strong acid so no equilibrium can be established and that Cl- is an extremely weak conjugate base of HCl which is unable to react with the water to create an equilibrium reaction.
$CaCl_2$ is not a base. Its is a neutral compound as it is formed from a strong acid and a strong base.

b) Provide reasons why the Arrhenius acid/base theory is inadequate in explaining the differences in behaviour of the substances in part (a). **2**

Criteria	Marks
• States that the Arrhenius concept does not relate the idea of strong and weak acids to the position of equilibrium when an acid is placed in water • States that the Arrhenius concept has not considered the role of the solvent in acid-base reactions	2
• Addresses one of the above.	1

Sample Answer:
The Arrhenius theory is insufficient to account for the variation in behaviour because it only defines acids as substances that dissociate in water to produce H^+ ions and bases as substances that dissociate in water to produce OH^- ions. This definition does not encompass all acid-base reactions and fails to explain the behaviour of substances that do not ionise in water or do not produce H^+ or OH^- ions. It does not account for acid/base strength as shown by the relative tendency of the species present to accept or donate protons compared with each other and compared with the solvent. To account for the variation in behaviour, the Brönsted-Lowry definition of acids as proton donors and bases as proton acceptors is necessary.


Arrhenius defines acids as substance that dissociate to form H^+ ions in solution, and bases as substance that form OH^- ions in solution. Hence, although he is able to explain the pH the sol. of $CaCl_2$/HCl, he cannot count for the reverse reaction of HPO_4^{2-} acting as a base when strg acid is added; $HPO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons H_2O(l) + H_2PO_4^-(aq)$ which he defines as a reverse acid rxn of $HPO_4^{2-}(aq) \rightleftharpoons PO_4^{3-}(aq) + H^+(aq)$

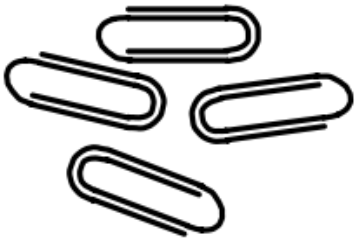
Markers Note:

The question asked for more than 1 reason.

Question 23 (6 marks)

Two students working together set up a simple game involving 40 separate paper clips. Student **X** was responsible for connecting individual paper clips into pairs, whist student **Y** was responsible for taking apart the connected paper clips. Both students remained blindfolded during the game.

Individually separated paper clips



Connected pairs of paper clips

After a while, the amount of individual and connected paper clips became constant.

a) State two ways in which this model relates to the essential features of a dynamic equilibrium reaction? **2**

Criteria	Marks
• States TWO features of a dynamic equilibrium with reference to the game	2
• Provides some relevant information with reference to the game/model	1

Sample Answers:

The connecting of individual paper clips by student X represents the forward reaction and the taking apart of paper clips by student Y represents the reverse reaction. The use of 40 paperclips further represents a closed system and the constant number of both individual and connected paperclips reflect equilibrium concentrations of products and reactants.

Markers Note:
Generally done very well.
Responses must link the features of an equilibrium system to the model/game.

b) A third student added another pile of individual paper clips to the game. Student X and Y continued their actions. After a while, the amount of individual and connected paper clips became constant again. **4**

By referring to the collision theory, explain how the addition of more paperclips to the game simulates the effect of concentration on a chemical equilibrium.

Criteria	Marks
• Identifies addition of paperclips models increase in concentration of	4

reactant/product. • Explains the effect of increased concentration on the rate of reaction in terms of collision theory. • Explains the change in reaction rate over time of both forward and reverse reactions as a result of an increase in concentration with reference to the paper clip game. • Describes why a new equilibrium will be produced	
• Addresses THREE of the above criteria	3
• Addresses TWO of the above criteria	2
• Provides some relevant information	1

Sample Answer:
In general, increasing the concentration of reactants in a chemical reaction increases the rate of the forward reaction, which can lead to the establishment of a new equilibrium.

When the concentration of reactants is increased, there are more reactant molecules present in the system. This means that there are more opportunities for the reactant molecules to collide with each other and react, which increases the rate of the reaction. Thus, an increase in paper clips to the game increases the success and probability of connecting individual paperclips, leading to a higher rate of producing connected paper clips (products).

As the concentration of reactants decreases due to the formation of products, the rate of the forward reaction slows down until it reaches a point where the rate of product formation equals the rate of reactant depletion. At this point, a new equilibrium is established. Thus, as the number of individual paperclips decreases due to the formation of connected paperclips, the rate of the reaction decreases. This will eventually reach a new constant amount of both individual and connected paperclips, reflecting a new equilibrium.

Question 24 (6 marks)

Name of acid	Formula	pK_a
Chloroacetic acid	$ClCH_2COOH$	2.85
Hydrofluoric acid	HF	3.17
Cyanic acid	HOCN	3.46
Formic acid	HCOOH	3.74
Hypochlorous	HOCl	7.52

a) From the table above, determine the weakest of these monoprotic acids. **1**

Criteria	Marks
• Correctly identifies hypochlorous acid	1

Correct answer: Hypochlorous acid
(higher the pKa, weaker the acid)

b) Calculate the % ionisation for a 0.10 mol/L solution of the acid from part a). **3**

Criteria	Marks
• Provides correct calculation showing all steps	3
• Calculates concentration of H_3O^+ with incorrect % ionisation	2
• Calculates Ka	1

Sample answer:
pKa = 7.52 → Ka = $10^{-7.52}$ = 3.01995 x 10^{-8}

$HOCl + H_2O \rightleftharpoons OCl^- + H_3O^+$

	$HOCl + H_2O \rightleftharpoons OCl^-$	+	H_3O^+
I	0.10	0	0
C	-s	+s	+s
E	0.10 -s	s	s

As HOCl is a very weak acid and its Ka is very small 0.1-s ~ 0.1 at equilibrium.

$Ka = [OCl^-][H_3O^+]/[HOCl] = s^2/0.10 = 3.01995 \times 10^{-8}$

$s^2 = 3.01995 \times 10^{-8} \times 0.10$
$s = = 5.50 \times 10^{-5}$
therefore concentration of OCl^- and $H_3O^+ = 5.50 \times 10^{-5}$ mol/L

% ionisation = $[H_3O^+]/[HOCl] = 5.50 \times 10^{-5}/0.10 \times 100 = 0.0550\%$

c) Compare the pH of the acid in part a) to a 0.10 mol/L solution of H_2SO_4? **2**

Criteria	Marks
• Calculates the pH of both HOCl and H2SO4 and provides a final judgement	2
• Calculates only one pH OR • Makes comparison of pH values WITHOUT calculations	1

Answer:

$pH = -\log_{10}[H^+]$
from part b) $[H^+]$ of 0.1 mol/L HOCl = 5.50×10^{-5} mol/L
$pH = -\log_{10}(5.50 \times 10^{-4}) = 4.26$

For 0.1 mol/l of H_2SO_4, [H+] = 0.2 mol/L
$pH = -\log_{10}(0.2) = 0.70$

The pH of 0.1 mol/L HOCl = 4.26 and pH of 0.1 mol/L H_2SO_4 = 0.70. Sulfuric acid is a stronger acid than Hypochlorous acid which is a weak acid.

Question 25 (6 marks)

A stage show requiring a frothing 'blood-like' liquid used dry ice $(CO_2(s))$ and iron complexes to produce this effect.

One such iron complex consists of an alkaline solution containing iron (III) chloride and sodium thiocyanate. This produces the following equilibrium reaction:

$$\underset{\text{(yellow)}}{Fe(OH)^{2+}} + SCN^- \rightleftharpoons \underset{\text{(bright red)}}{Fe(SCN)^{2+}} + OH^-$$

a) The numerical value of K at 25°C for this reaction was found to be 2.3×10^{-4}.
i) What does the value of K tell us about the equilibrium concentrations of the $Fe(SCN)^{2+}$ and OH^- ions? **1**

Criteria	Marks
• Identifies that the concentration of OH^- and $Fe(SCN)^{2+}$ is very low	1

Sample answer:
At equilibrium the concentration of the products, OH^- and $Fe(SCN)^{2+}$ ions is very low as the equilibrium constant K is very small. **1**

ii) Predict the colour of the equilibrium solution at 25°C.

Criteria	Marks
• Identifies that colour at equilibrium	1

Answer:
Yellow or orange

b) If dry ice is added to this solution, the pH changes from about pH 10 to pH 4. **2**
Explain why this pH change occurs.

Criteria	Marks
• Correctly explains the change in pH upon the addition of dry ice in terms of changing $[H^+]/[OH^-]$	2
• Some correct information	1

Sample Answer:

The addition of dry ice (CO_2) causes the pH to drop as it react with water to produce carbonic acid (H_2CO_3) which is weakly acidic. Carbonic acid dissociates to increase $[H^+]$ resulting in the pH change from 10 to 4.

NOTE: Although dry ice is extremely cold, the temperature change is NOT relevant to this question (nor the next). In fact, stating that temperature causes the change in pH and change in colour leads to the two answers contradicting each other.

c) Explain how the addition of dry ice produces the blood-red coloured liquid. **2**

Criteria	Marks

• Correctly explains the change in pH upon the addition of dry ice using appropriate equilibrium theory	2
• Some correct information	1

Sample answer:

As carbonic acid (H_2CO_3) is produced, it will react with the OH^- ions removing them from solution, disturbing equilibrium. According to Le Chatelier's Principle, the system will offset this disturbance by shifting the equilibrium position towards the product side to replace to OH^- ions that reacted. Subsequently more $Fe(SCN)^{2+}$ ions will also be produced which are bright red in colour making the liquid blood-red.

Question 26 (6 marks)

A solution of an unknown salt is analysed. It is known to contain either Mg^{2+}, Cu^{2+}, or Ca^{2+} as the only cation, and either SO_4^{2-} or Cl^- or CO_3^{2-} as they only anion.

Outline a method that could be used to identify the cation and anion present in the unknown salt solution. Include relevant chemical equations and observations which would confirm the ions present. **6**

Marking Criteria	Marks
• Outlines a logical sequence of suitable tests to identify all ions • Includes expected observations for all tests for each possible ion • Includes several balanced chemical equations	6
• Outlines a mostly correct sequence of suitable tests for all ions • Includes expected observations for all tests for each possible ion • Includes a balanced chemical equation	5
• Outlines a sequence of tests for all ions and most of the expected observations • Includes a mostly correct balanced chemical equation	4
• Provides tests that can identify several ions (3 or more) • Includes some expected observations and/or a balanced chemical equation	3
• Outlines one test that could identify a cation OR anion OR • Provides tests that can identify cations and anions OR • Provides a balanced chemical equation and one test that can identify a cation OR anion	2
• Some relevant information	1

Notes: Logical arguments are not chemical identification tests.
You can't identify 2 anions or cations, then say if absent, therefore it must be the other. Need a test to show it.
You can't say it can't be carbonate, because all three are insoluble. Still need to outline a test for carbonate.

Sample answer:

1. Perform a flame test with the sample using a spray bottle:
- if a blue-green flame is observed Cu^{2+} is present ✓
- if a brick-red flame is produce Ca^{2+} is present ✓
- if no visible change in the flame colour is seen ~~produced~~
Mg^{2+} is likely present, to confirm add Need an NH3 test for Mg^{2+}
Na_2CO_3 to a small sample of the solution and a white precipitate $MgCO_3$ should be produced:

$$Mg^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow MgCO_3{}_{(s)}$$ ✓

2. Add dilute HNO_3 ~~acid~~ to a sample and if ~~effervescence~~ bubbling is observed CO_3^{2-} is likely present since acid carbonate reactions produce CO_2 gas:

$$2H^+_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow CO_2{}_{(g)} + H_2O_{(l)}$$ ✓

No reaction will be observed with SO_4^{2-} and Cl^-.

3. If bubbling is not observed after the addition of dilute HNO_3 only SO_4^{2-} or Cl^- can be present.

Add $AgNO_3$ to a sample to produce a white precipitate of either Ag_2SO_4 or $AgCl$:

$$2Ag^+_{(aq)} + SO_4^{2-}_{(aq)} \rightarrow Ag_2SO_4{}_{(aq)}$$ ✓

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(aq)}$$

continued ✓

6. Then add dilute NH_3 solution. If the precipitate redissolves into a colourless solution $AgCl$ was the precipitate and thus Cl^- must be the anion:

$$AgCl_{(s)} + 2NH_3{}_{(aq)} \rightarrow [Ag(NH_3)_2]^+_{(aq)} + Cl^-_{(aq)}$$ ✓

white — colourless

If the precipitate does not redissolve Ag_2SO_4 is likely the precipitate that was formed and SO_4^{2-} is likely the anion. To confirm add $Ba(NO_3)_2$ to a fresh sample and a white precipitate $BaSO_4$ should be produced:

$$Ba^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \rightarrow BaSO_4{}_{(s)}$$ ✓

Question 27 (6 marks)

Compound X is a colourless liquid. When drops of sodium hydrogen carbonate solution were added to it, bubbles of colourless gas formed. When a few mL of X was refluxed with methanol and concentrated sulfuric acid, a product more volatile than X was formed. This product had a much more pleasant odour than X.

a) To what class of compound does X belong? Explain. **2**

Criteria	Marks
• Identifies compound X as a carboxylic acid and correctly explains their reasoning	2
• Correctly identifies class of compound X	1

Sample Answer:

Compound X is a carboxylic acid (alkanoic acid).
When carboxylic acids are reacted with the base $NaHCO_3$, CO_2 is released which is a colourless gas, which can be confirmed with a Limewater Test.
Carboxylic acids react with alcohols to form esters which are sweet smelling and more volatile, lower boiling points, than the carboxylic acids they are synthesised from.

b) 0.62g of X was mixed with 100mL of water and titrated with sodium hydroxide solution using phenolphthalein as an indicator. 37.3 mL of 0.223 mol/L sodium hydroxide solution was needed to reach the endpoint. **4**

Calculate the **molecular weight** of X.

Criteria	Marks
• Calculates the molecular weight of compound X showing all working out • Units of Molecular Weight are AMU (Molar Mass is $gmol^{-1}$) • Correct answer to 2 sig figs	4
• Calculates the molecular weight of compound X showing all working out • Incorrect sig figs or units	3
• Calculates the number of moles of acid neutralised. • Identifies acid:base = 1:1	2
• Calculates the number of moles of base added.	1

Sample answer:

As phenolphthalein indicator used it is a titration between a weak acid and a strong base.
Carboxylic acids are monoprotic

$H^+ + OH^- \rightarrow H_2O$
$n(OH^-) = c \times V = 0.223 \times 0.0373 = 0.0083179$ mol
$n(H^+) = n(OH^-) = 0.0083179$ mol

$MM = m/n = 0.62/0.0083179 = 75$ amu (2 sig fig)

Question 28 (6 marks)

Nylon 6,6 is a condensation polymer formed from the reaction between hexane-1,6-diamine and hexanedioic acid in a 1:1 mole ratio.

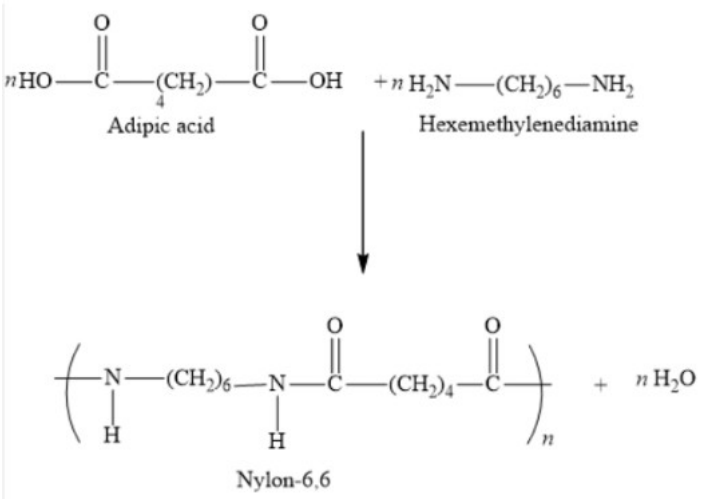
a) Using condensed structural formula, write the chemical equation for the polymerisation reaction. **1**

Criteria	Marks
• Correct equation written	1

Sample answer: NOT n-1, 2n-1 water

hexanedioc acid + 1,6-hexanediamine ⟶ nylon-6,6 + water

$n\text{HOOC-(CH}_2\text{)}_4\text{-COOH} + n\text{H}_2\text{N-(CH}_2\text{)}_6\text{-NH}_2 \longrightarrow \text{-(-OC-(CH}_2\text{)}_4\text{-CONH-(CH}_2\text{)}_6\text{-NH-)}_n\text{-} + n\text{H}_2\text{O}$



Many students drew a DIMER rather than a polymer

The molar masses of some species are shown in the table below.

b) **3**

Species	Molar mass ($g.mol^{-1}$)
hexane-1,6-diamine	116.20
hexanedioic acid	146.14
Nylon 6,6	244.31

If 220.0 g of hexanedioic acid and 280.0 g of hexan-1,6-diamine are reacted together in a vessel, what mass of nylon 6,6 is produced if the reaction goes to completion?

Criteria	Mark
• Correctly calculates the number of moles of each reactant present • Identifies the limiting reagent and uses it to calculate the mass of nylon produced • Correctly calculates the mass of nylon produced	3
• Correctly calculates the number of moles of each reactant present • Calculates the mass of nylon produced without identifying and using the limiting reagent	2
• Correctly calculates the number of moles of each reactant present	1

Sample Answer:

n(hexandioic acid) = = = 1.5054 mol

n(hexan-1,6-diamine) = = = 2.4096 mol

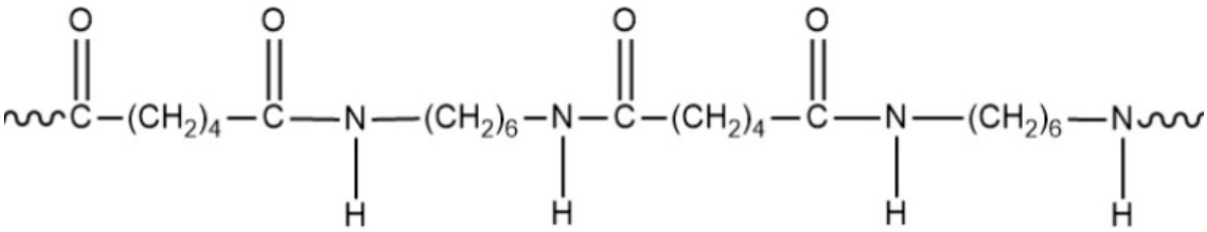
n(hexandioic acid is the limiting reagent (1:1)

∴ n(nylon) = 1.5054 mol
m = n x Mm
= 244.31 g.mol^{-1} x 1.5054 mol
= 367.786 g
= 367.8 g (4.s.f)

c) Draw a segment of Nylon 6,6 showing 3 amide linkages. **2**

Criteria	Marks
• Draws a correct segment of polymer containing 3 amide linkages	2
• Draws a polymer with a correct segment	1

Sample answer:



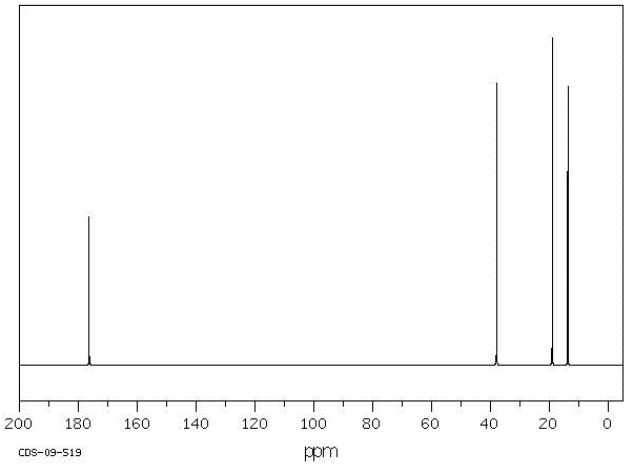
All students that attempted skeletal structures, answered the question incorrectly

Question 29 (9 marks)

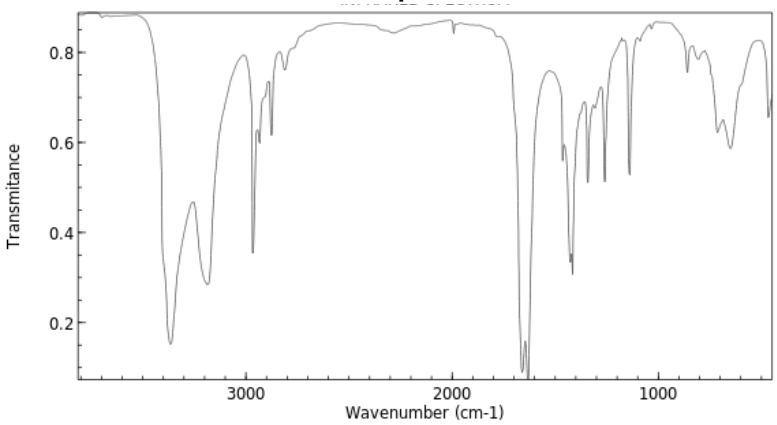
A laboratory assistant came across an unlabelled bottle containing an unknown white crystalline organic solid. The technician carried out several tests on the bottle's contents. The results of the tests are shown.

Shift (ppm)	Splitting	Integration
7.24	1	1
6.71	1	1
2.02	3	2
1.50	6	2
0.86	3	3

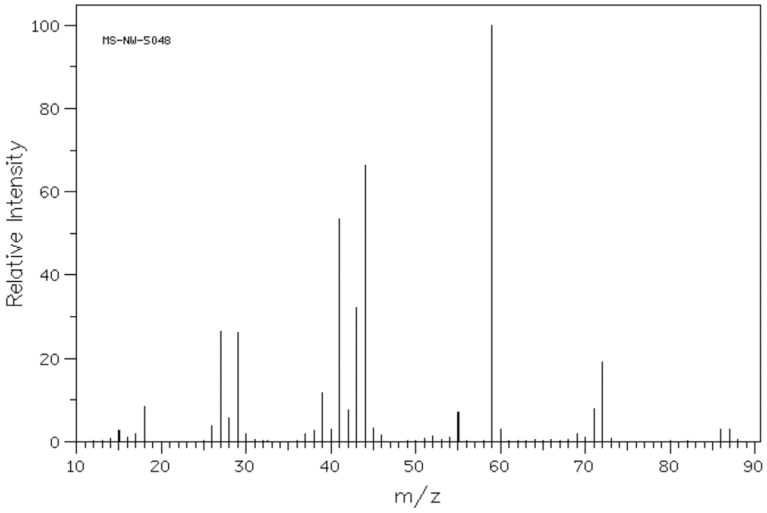
Carbon -13 NMR



Infrared spectrum



Mass spectrum



Proton NMR

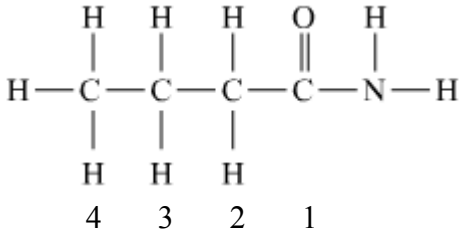
^{1}H NMR chemical shift data

Type of proton	δ/ppm
$Si(C\mathbf{H}_3)_4$ (TMS)	0
R–C$\mathbf{H}_3$	0.9–1.0
R–C$\mathbf{H}_2$–R	1.2–1.5
R–C$\mathbf{H}$$R_2$	1.5–2.0
R–C≡C–**H** (alkyne)	2.0–3.1
–CO–C$\mathbf{H}_2$– (aldehydes, ketones or esters)	2.1-2.7
R–C$\mathbf{H}_2$–NH_2	2.4–3.0
R–C$\mathbf{H}_2$–X (X = F, Cl, Br, I)	3.0–4.5
–C$\mathbf{H}_2$–O– (alcohols, ethers or esters)	3.3–4.8
R–O**H**	1–6
R–N$\mathbf{H}_2$	1–5
R_2C=C**H**R (alkene)	4.5–7.0
R–COON**H**–R (amide)	5–9
Ar-**H** (aromatic)	6.9–9.0
R–C**H**O (aldehyde)	9.4–10.0
R–COO**H**	9.0–13.0

a) In the space provided, draw and name the unknown compound that is consistent with all the information provided. Justify your answer with reference to the information provided. **7**

Criteria	Mark
Demonstrates a comprehensive understanding of the relationship between the features of the spectra and the structure of butanamide. Refers to the relevant spectroscopic data in each of the **four** spectra Correctly names and draws the structure.	7
Demonstrates a comprehensive understanding of the relationship between the features of the spectra and the structure of butanamide. Refers to the relevant spectroscopic data in each of the **three** spectra Correctly names and draws the structure	6
Demonstrates a thorough understanding of the relationship between the features of the spectra and the structure of **an amide**. Refers to the relevant spectroscopic data in each of the three spectra Incorrectly names and/or draws the structure OR Correctly names and/or draws the structure and refers to **two** spectra	5
Demonstrates an understanding of the relationship between the features of the spectra and the structure drawn. Refers to the relevant spectroscopic data in each of the **three or two** spectra to the structure drawn Incorrectly names and/or draws the structure	4
Demonstrates a understanding of the relationship between the features of the spectra and the structure. Refers to the relevant spectroscopic data in each of the **two** spectra	3
Demonstrates some understanding of the interpretation of spectroscopic data	2
Provides some relevant information	1

Name: Butanamide



Name: Butanamide

Carbon-13 NMR

There are 4 peaks representing 4 carbons in 4 different chemical environments.

Peak at 175 ppm arises from a carbonyl carbon from an ester or acid.

Infrared spectrum

Peak at 3350 cm^{-1} is due to N-H groups

Peak at 3150 cm^{-1} is due to C-H groups

Peak at 1650 cm^{-1} is due to C=O carbonyl stretch

Absence of a very broad peak between 2500 and 3000 cm^{-1} indicates that the compound is not a carboxylic acid

Mass spectrum

The base peak is at 59 m/z

The parent ion is at 87 m/z, therefore the molecular mass is 87g/mol

Proton NMR

Triplet at 0.86 ppm arises from H atoms with 2 H atoms on neighbouring C atoms. In this case the H atoms on C4. $\mathbf{H}_3C–CH_2$-

Sextet at 1.5 ppm arises from H atoms with 5 H atoms on neighbouring C atoms. In this case the H atoms on C3. $H_3C–C\mathbf{H}_2$-CH_2-

Triplet at 2.02 ppm arises from H atoms with 2 H atoms on neighbouring C atoms. In this case the H atoms on C2. The are furthest downfield due to their close proximity to the carbonyl group. $H_3C–CH_2$-$C\mathbf{H}_2$-CO-

Singlets at 6.71 and 7.24 arise from the H atoms on the N atom that is part of an amide. -CO-NH_2

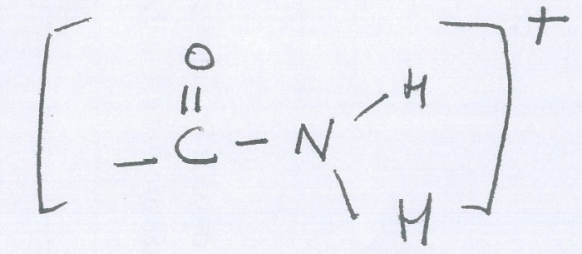
b) For the mass spectrum shown: **2**

i) Identify the mass of the base peak

ii) Identify the structure of the fragment that produces the peak at 44 m/z.

Criteria	Mark
Correctly identifies the base peak at m/z 59 Correctly draws a possible fragment for peak m/z 44 including the positive charge	2
One of the above	1

Sample Answer:
Base peak mass is 59 m/z
Possible fragment for m/z 44:

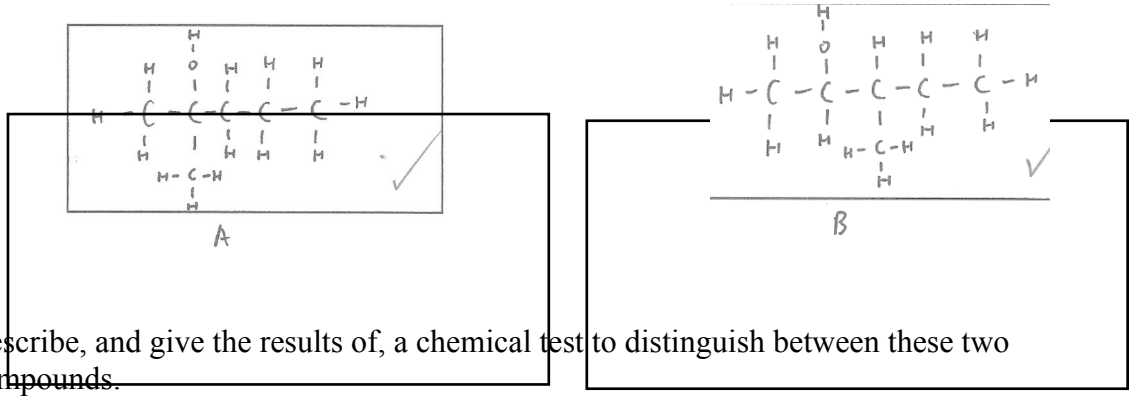


Question 30 (6 marks)

a) 2

Criteria	Mark
Correctly draws both structures	2
Correctly draws only one structures	1

Draw structural formula for both 2-methyl-2-pentanol and for 3-methyl-2-pentanol.



b) 4

Describe, and give the results of, a chemical test to distinguish between these two compounds.

Criteria	Mark
Correctly describes a chemical test for each compound and describes the expected results.	4
Correctly describes a chemical test for one compound and describes the expected results for both compounds OR Correctly describes a chemical test for both compounds and describes the expected results for one compound OR Correctly outlines a chemical test for both compounds and describes the expected results for both compounds	3
Correctly describes a chemical test for one compound and describes the expected results for one compound. OR Correctly describes a chemical test for both compounds OR Describes the expected results for both compounds	2
Correctly describes a chemical test for one compound OR describes the expected results for one compound	1

Sample Answers:

3-methyl-2-pentanol – secondary alcohol

React with - MnO_4^-/H^+ → clear purple solution will change colourless solution as the alcohol undergoes oxidation.

- $Cr_2O_7^{2-}/H^+$ → clear orange solution changes to a clear green solution as the alcohol undergoes oxidation

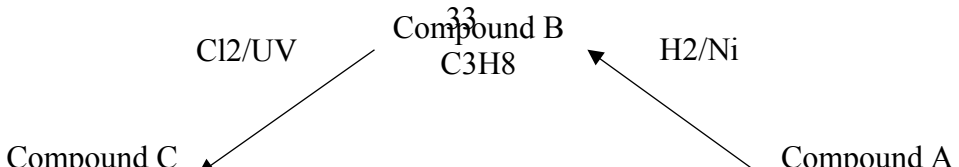
Secondary alcohols undergo oxidation to form ketones.

2-methyl-2-pentanol – tertiary alcohol

React with - MnO_4^-/H^+ → clear purple solution remains unchanged, no reaction
- $Cr_2O_7^{2-}/H^+$ → clear orange solution remains unchanged, no reaction
- $ZnCl_2/HCl$ → fast reaction, 2 layers form

Tertiary alcohols do not undergo oxidation

Question 31 (9 marks)



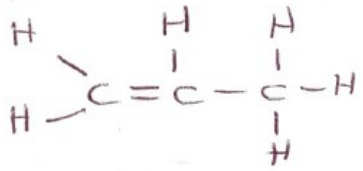
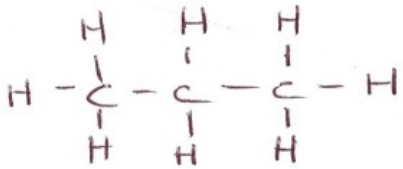
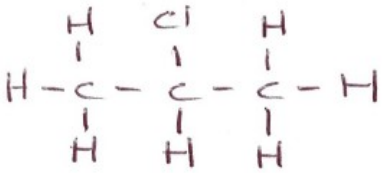
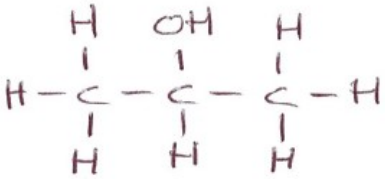
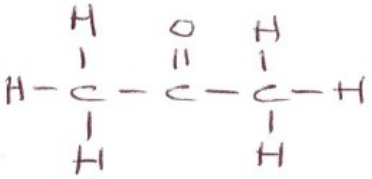
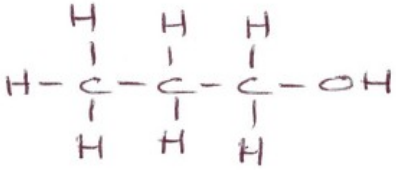
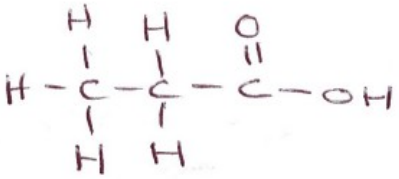
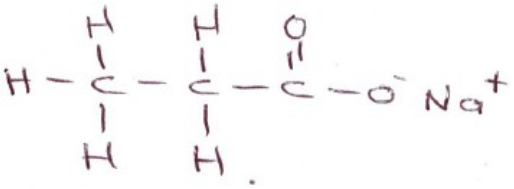
This flowchart shows reactions involving eight different organic compounds A to H.

a) Draw the structures of compounds A to H.
Note: Each compound (A to H) has a unique structure.

Criteria	**Mark**
Correctly draws all 8 compounds	7
Correctly draws 7 compounds	6
Correctly draws 6 compounds	5
Correctly draws 5 compounds	4
Correctly draws 4 compounds	3
Correctly draws 3 compounds	2
Correctly draws 2 compounds	1
Correctly draws 1 compound or incorrectly draws all	0

7

Answers:

Compound A: 	Compound B: 
Compound C: 	Compound D: 
Compound E: 	Compound F: 
Compound G: 	Compound H: 

2

Using the information provided, justify your identification of Compound D and F.

Criteria	**Mark**
Correctly justifies the structures of both Compounds D and F using their reactivities and products formed	2
Correctly justifies either compound D or F OR Provides some relevant information about both	1

Sample Answer:

As Compound F undergoes oxidation with acidified dichromate to form a compound with with 2 oxygens it must be a primary alcohol oxidising to a carboxylic acid.
Compound D undergoes oxidation with acidified permanganate to form a compound with one oxygen atom, a ketone, which does not oxidise further.

Question 32 (6 marks)

The manganese content in a 13.5 g sample of steel was determined by measuring absorbance of permanganate (MnO_4^-) using the following process

The steel sample was dissolved in nitric acid and the $Mn^{2+}(aq)$ ions produced were oxidised to MnO_4^- by periodate ions, $IO_4^-(aq)$ according to the following equation:

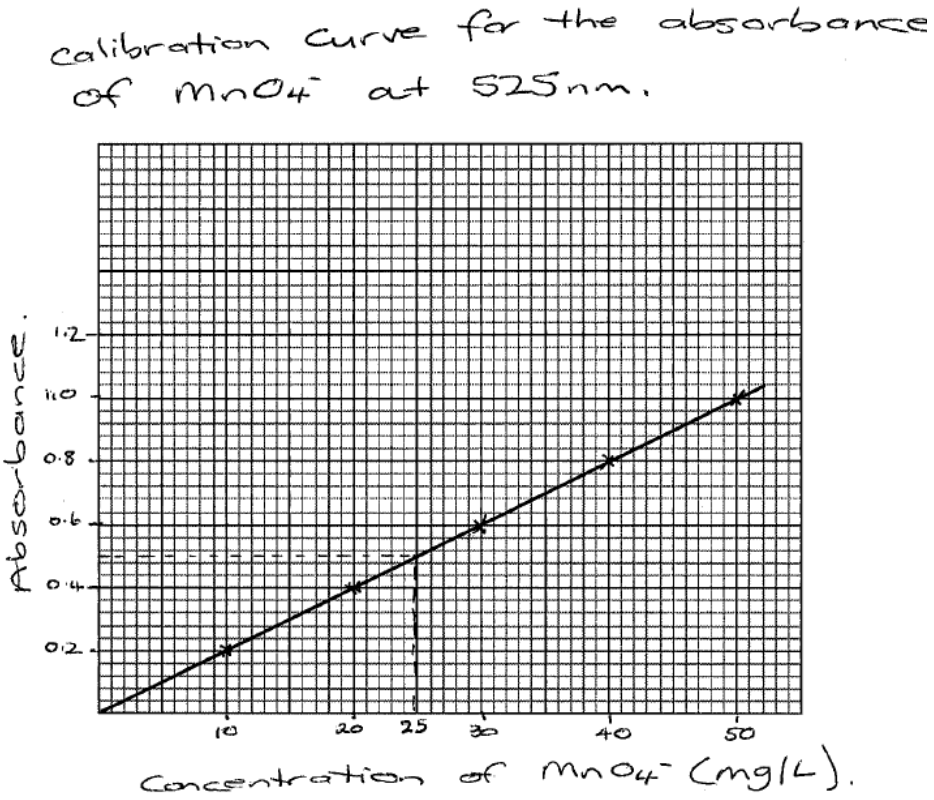
$$2Mn^{2+}(aq) + 5IO_4^-(aq) + 3H_2O(l) \rightarrow 2MnO_4^-(aq) + 5IO_3^-(aq) + 6H^+(aq)$$

The resulting solution was made up to a volume of 250.00 mL. A 20.0 mL aliquot of the solution was diluted to 100.0 mL. The absorbance at 525 nm of the resulting solution was 0.50.

a) Construct a calibration curve using the following data. **3**

Concentration of MnO_4^- (mg/L)	**Absorbance**
0	0
10	0.2
20	0.4
30	0.6
40	0.8
50	1.0

Criteria	**Mark**
Correctly draws calibration curve with the following: - Appropriate Title - Correct scale - Axes labelled with units - Line of best fit drawn through origin - Points plotted correctly	3
3 of the above	2
2 of the above	1



b) Calculate the percentage by mass of manganese in the steel sample. **3**

Criteria	**Mark**
Correctly calculates the percentage of Mn showing all working out	3
Correctly calculates the mass of Mn in the sample showing all working out	2
Calculates the concentration of MnO_4^- (mol/L)	1

Sample Answer:

From graph: concentration = 25 mg/L
In the undiluted sample concentration = 5 x 25 = 125 mg/L (20 ml aliquot was diluted to 100mL)

$$c(MnO_4^-) = \frac{125 \times 10^{-3} gL^{-1}}{118.94\ gmol^{-1}} = 1.0510 \times 10^{-3}\ mol/L$$

$n(MnO_4^-) = 1.0510 \times 10^{-3} \times 0.25 = 2.627 \times 10^{-4}$ mol
Therefore: $n(Mn) = 2.627 \times 10^{-4}$ mol
$m(Mn) = 2.627 \times 10^{-4} \times 54.94 = 0.01443$ g

Therefore: % m (Mn) in steel = 0.01443/13.5 x 100%
= 0.1069 %
= 0.107 % (3 sf)