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## **2022** BORED OF STUDIES TRIAL EXAMINATION

5th October

# Chemistry

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### **General Instructions**

- Reading time – 5 minutes
- Working time – 3 hours
- Write using black pen
- Draw diagrams using pencil
- Calculators approved by NESA may be used
- A formulae sheet, data sheet and Periodic Table are provided

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### **Total Marks: 100**

#### **Section I – 20 marks** (pages 2–12)

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

#### **Section II – 80 marks** (pages 13–38)

- Attempt Questions 21–38
- Allow about 2 hours and 25 minutes for this section

## Section I

20 marks

Attempt Questions 1–20

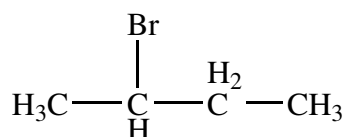
Allow about 35 minutes for this section

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

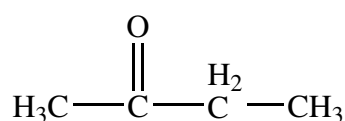
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1 Which of the following compounds, when added, would decolourise bromine water?

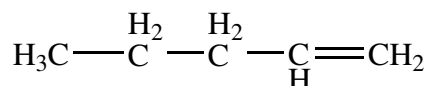
A.



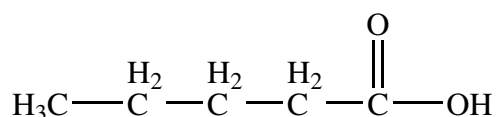
B.



C.



D.



2 The combustion of octane is a non-equilibrium reaction that is commonly used as an energy source to power cars.

Which of the following options correctly describes enthalpy, entropy and Gibbs free energy values of this reaction?

	<i>Enthalpy</i>	<i>Entropy</i>	<i>Gibbs free energy</i>
A.	$\Delta H > 0$	$\Delta S > 0$	$\Delta G < 0$
B.	$\Delta H > 0$	$\Delta S < 0$	$\Delta G > 0$
C.	$\Delta H < 0$	$\Delta S > 0$	$\Delta G < 0$
D.	$\Delta H < 0$	$\Delta S < 0$	$\Delta G < 0$

3 Which of the following compounds has the greatest molar solubility in water at 25 °C?

- A. Lead(II) chloride
- B. Lead(II) sulfate
- C. Calcium sulfate
- D. Barium hydroxide

4 A 0.100 mol L<sup>-1</sup> solution of ethanoic acid has a pH of 2.960.

What percentage of the total unionised ethanoic acid and ethanoate ion concentration consists of unionised ethanoic acid?

- A. 98.9%
- B. 1.01%
- C. 33.8%
- D. 66.2%

5 How many <sup>1</sup>H NMR and <sup>13</sup>C NMR peaks will appear in 2-hydroxypropane-1,2,3-tricarboxylic acid (citric acid)?

	<i>Number of peaks in <sup>1</sup>H NMR</i>	<i>Number of peaks in <sup>13</sup>C NMR</i>
A.	3	3
B.	4	4
C.	3	4
D.	4	3

6 Calcite is a mineral that is primarily composed of calcium carbonate.

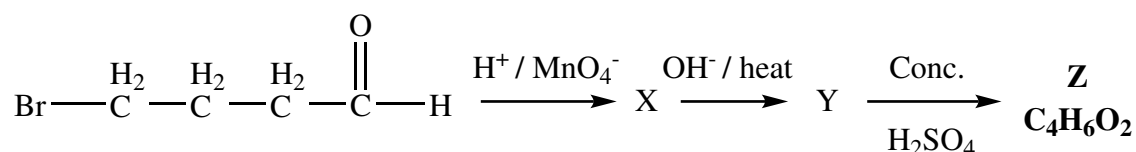
A sample of 12.95 g of calcite containing 95% calcium carbonate was heated to produce calcium oxide and carbon dioxide. No calcium is present in the impurity.

What is the mass of calcium oxide produced after the reaction concludes?

- A. 6.89 g
- B. 5.21 g
- C. 4.78 g
- D. 0.689 g

- 7 Which of the following compounds is an isomer of ethyl propanoate?
- A. Butanal
  - B. Pentan-3-one
  - C. Butanoic acid
  - D. 2-methylbutanoic acid
- 8 A chemist reacts hydrogen chloride with pure oxygen to form chlorine gas and water vapour in an equilibrium reaction.
- If the chemist replaces pure oxygen with air from the atmosphere, whilst keeping the total pressure constant, how will it likely affect the equilibrium?
- A. Decreases forward rate of reaction and increases the yield of chlorine gas
  - B. Increases forward rate of reaction and increases the yield of chlorine gas
  - C. Decreases forward rate of reaction and decreases the yield of chlorine gas
  - D. Increases forward rate of reaction and decreases the yield of chlorine gas
- 9 A 450 mL solution of  $0.15 \text{ mol L}^{-1}$  nitric acid was mixed with 250 mL of  $0.10 \text{ mol L}^{-1}$  barium hydroxide in a beaker. What is the pOH of the solution in the beaker?
- A. 1.60
  - B. 12.40
  - C. 12.39
  - D. 1.61
- 10 Soaps and detergents are vital materials used in everyday life to clean and wash clothing and glassware. What are their roles in removing grease from surfaces?
- A. They are emulsifiers and will increase cohesive forces.
  - B. They are emulsifiers and will decrease cohesive forces.
  - C. They are stabilisers and will increase cohesive forces.
  - D. They are stabilisers and will decrease cohesive forces.

- 11 The following chemical pathway was used to produce a compound Z with chemical formula  $C_4H_6O_2$ . Compound Z then underwent polymerisation to produce a polymer that had a molar mass of  $1.03 \times 10^5 \text{ g mol}^{-1}$ .



What is the approximate number of carbon atoms that make up this polymer?

- A. 1200
- B. 946
- C. 3782
- D. 4800

**The following information applies to both question 12 and 13.**

A student attempts to determine the enthalpy of neutralisation for the reaction between hydroiodic acid (HI) and sodium hydroxide (NaOH). The student mixes 90.0 mL of equimolar  $1.00 \text{ mol L}^{-1}$  solutions of HI and NaOH into a copper calorimeter and records a temperature increase of 4.43 K.

- 12 What is the empirical molar enthalpy of neutralisation?
- A.  $-37.0 \text{ kJ mol}^{-1}$
  - B.  $-18.5 \text{ kJ mol}^{-1}$
  - C.  $-37.0 \times 10^3 \text{ kJ mol}^{-1}$
  - D.  $-18.5 \times 10^3 \text{ kJ mol}^{-1}$
- 13 The student repeated the same experiment with the same volume, concentrations and equipment, but with hydrobromic acid (HBr) and potassium hydroxide (KOH) instead.

The empirical molar enthalpy of neutralisation would be

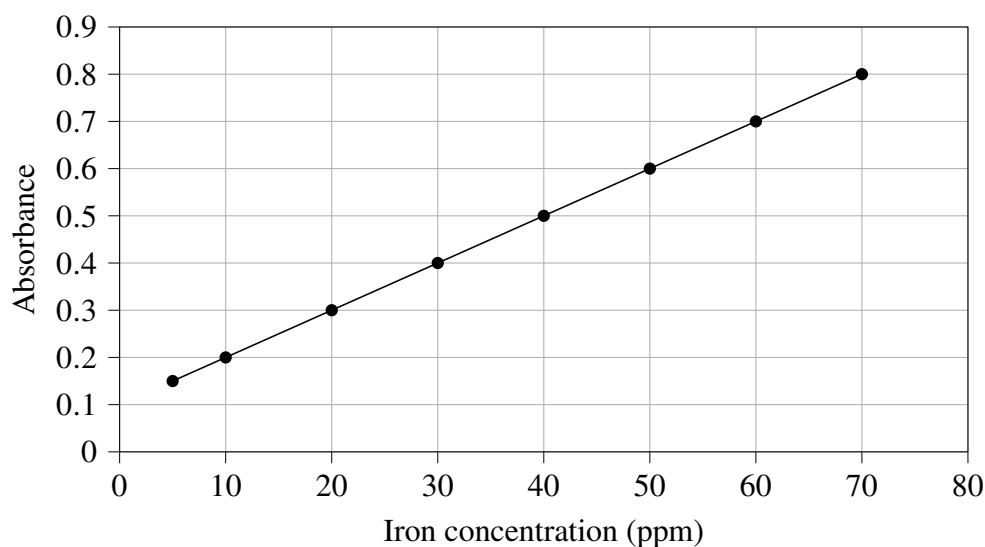
- A. more negative than the original experiment.
- B. less negative than the original experiment.
- C. approximately the same as the original experiment.
- D. different from the original experiment, but more or less negative cannot be predicted.

**The following information applies to both question 14 and 15.**

Atomic absorption spectroscopy was used to analyse a set of standard solutions of iron. The results are presented in the table and its corresponding calibration curve below.

<i>Concentration of iron (ppm)</i>	5	10	20	30	40	50	60	70
<i>Absorbance</i>	0.15	0.20	0.30	0.40	0.50	0.60	0.70	0.80

This calibration curve was used by a student to determine the iron concentration in nearby lakes at two separate sites. The results of this analysis and the concentrations found are given below.



This calibration curve was used by a student to determine the iron concentration in nearby lakes at two separate sites. The results of this analysis and the concentrations found are given below.

<i>Sample location</i>	<i>Absorbance</i>	<i>Concentration (ppm)</i>
Site A	0.35	25
Site B	0.90	80

**14** Which of the following statements correctly describes the validity and reliability of the data collected at Site A and B?

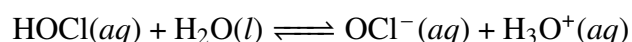
- A. The data at Site A is valid and reliable, while the Site B data is invalid and unreliable.
- B. The data at Site A is valid and unreliable, while the Site B data is invalid and unreliable.
- C. The data at both Site A and B is invalid and unreliable.
- D. The data at both Site A and B is valid and reliable.

- 15 The student was also asked to use the same calibration curve to analyse the iron content of a 200 mg iron supplement tablet using the following process.

The tablet was crushed, dissolved and made up to a volume of 200 mL. 10.0 mL of this solution was further diluted to 100.0 mL. The absorbance of this resulting solution was 0.45.

What is the percentage by mass of iron in the tablet?

- A. 3.5%
  - B. 0.18%
  - C. 35%
  - D. 18%
- 16 Hypochlorous acid (HOCl) is a weak acid which ionises to form the hypochlorite and hydronium ions in water in an equilibrium reaction:



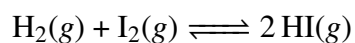
Which of the following salts can increase the degree of ionisation of hypochlorous acid, when added into reaction?

- A. Sodium chloride
  - B. Sodium nitrate
  - C. Ammonium nitrate
  - D. Sodium acetate
- 17 Throughout history, the definition of an ‘acid’ and a ‘base’ has constantly evolved to holistically encompass the properties of certain substances with each other.

Which of the following contains an acid and a base, one of which cannot be explained by Arrhenius theory, yet both of which can be explained by Bronsted-Lowry theory?

- A.  $\text{Na}_2\text{O}$  and  $\text{Ba}(\text{OH})_2$
- B.  $\text{C}_3\text{H}_9\text{N}$  and  $\text{NaOH}$
- C.  $\text{C}_{17}\text{H}_{35}\text{COONa}$  and  $\text{C}_6\text{H}_8\text{O}_7$  (citric acid)
- D.  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose) and  $\text{CH}_3\text{CONH}_2$

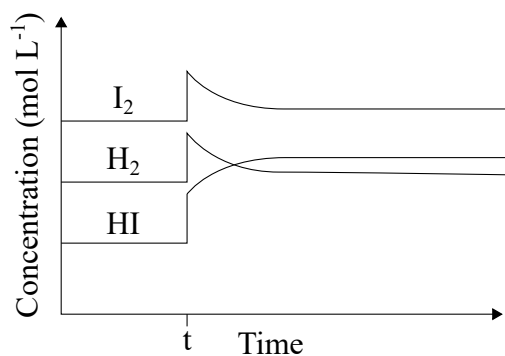
- 18 Hydrogen iodide (HI) can be formed from the reversible reaction of iodine and hydrogen gas:



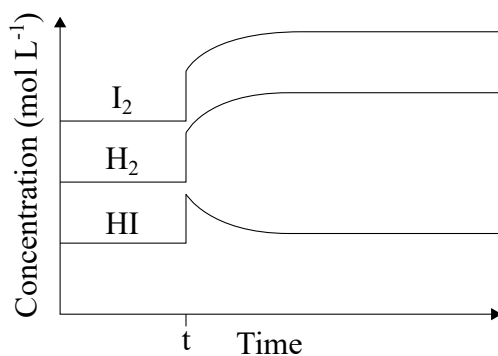
A system of HI, H<sub>2</sub> and I<sub>2</sub> was initially at equilibrium. At time t, the pressure of the system was increased by compressing the system.

Which of the following graphs best represents the changes in concentration of the equilibrium mixture?

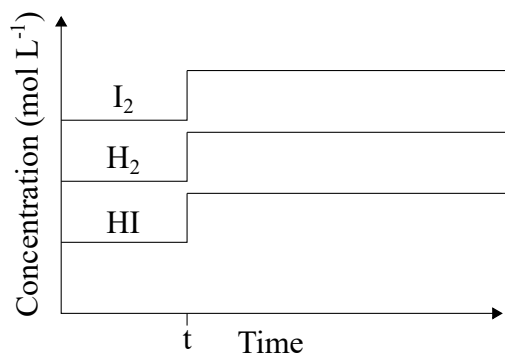
A.



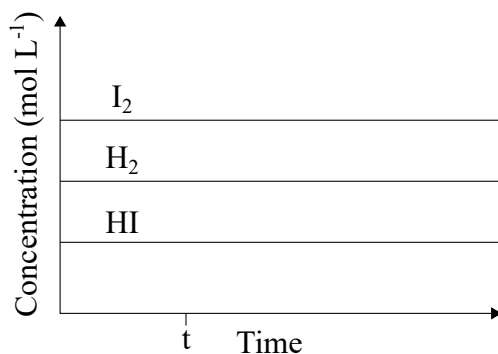
B.



C.



D.





- 19 A student prepared two solutions in separate beakers by mixing different chemicals.

In Beaker A, 50 mL of  $0.01 \text{ mol L}^{-1} \text{ HNO}_3$  was mixed with 50 mL of  $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$ .

In Beaker B, 50 mL of  $0.01 \text{ mol L}^{-1} \text{ KH}_2\text{PO}_4$  was mixed with 50 mL of  $0.01 \text{ mol L}^{-1} \text{ K}_2\text{HPO}_4$ .

5 mL of  $0.01 \text{ mol L}^{-1} \text{ NaOH}$  was added to each beaker.

Which of the following correctly describes the effect on the pH after adding the NaOH to each beaker?

	<i>pH in beaker A</i>	<i>pH in beaker B</i>
A.	Increases	Remains relatively stable
B.	Remains relatively stable	Increases
C.	Decreases	Remains relatively stable
D.	Decreases	Decreases

- 20 In a titration of standardised sodium hydroxide with hydrochloric acid, the following procedure was used:

1. A burette was first rinsed three times with distilled water, then three times with sodium hydroxide. The burette was then filled with the sodium hydroxide.
2. A conical flask was rinsed three times with distilled water.
3. A pipette was rinsed three times with distilled water. Hydrochloric acid was pipetted into the conical flask immediately after rinsing.
4. Three drops of phenolphthalein were added to the conical flask and titrated with the sodium hydroxide.

Based on the above procedure, the calculated concentration of hydrochloric acid from the titration is most likely to be

- A. approximately the same as the actual concentration.
- B. below the actual concentration.
- C. above the actual concentration.
- D. different from the actual concentration, but above or below cannot be predicted.

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Username: .....

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## Chemistry

### Section II Answer Booklet 1

80 marks

Attempt Questions 21–38

Allow about 2 hours and 25 minutes for this section

Booklet 1 – Attempt Questions 21–31 (40 marks)

Booklet 2 – Attempt Questions 32–38 (40 marks)

#### Instructions

- Write your student number, username and name on the top right of this page.
- 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.
- If you require extra writing space, please ask for a writing booklet. If you use a writing booklet, clearly indicate which questions you are answering.

Please turn over

**Question 21** (5 marks)

An ester is produced from a 10.0 g sample of propan-1-ol.

During its production from propan-1-ol, only inorganic reactants were used but there were no carbon-carbon bonds broken.

- (a) The ester was produced using reflux. Outline the purpose of refluxing. 2

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- (b) Calculate the maximum possible mass of the ester produced. Show the relevant reaction scheme. 3

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**Question 22** (3 marks)

The table below shows the boiling points of straight chain alcohols and esters of similar carbon atom numbers.

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<i>Alcohol</i>	<i>Boiling point (°C)</i>	<i>Ester</i>	<i>Boiling point (°C)</i>
CH <sub>3</sub> CH <sub>2</sub> OH	78	CHCOOCH <sub>3</sub>	32
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	97	CH <sub>3</sub> COOCH <sub>3</sub>	57
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	118	CH <sub>3</sub> CH <sub>2</sub> COOCH <sub>3</sub>	80
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> OH	138	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	102
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> OH	157	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub>	126

Explain the trends in boiling point in the table with reference to intermolecular forces.

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**Question 23** (3 marks)

The solubility of radium sulfate ( $\text{RaSO}_4$ ) in water at  $25^\circ\text{C}$  is  $2.1 \times 10^{-3} \text{ g L}^{-1}$ . Find the value of  $K_{\text{sp}}$ , given the molar mass of  $\text{RaSO}_4$  is  $322.06 \text{ g mol}^{-1}$ . **3**

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**Question 24** (3 marks)

A student mixed 20 mL of  $0.0100 \text{ mol L}^{-1}$  barium chloride with 20 mL of  $0.0200 \text{ mol L}^{-1}$  silver nitrate. **3**

Determine whether a precipitate will form. Justify your answer.

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**Question 25** (5 marks)

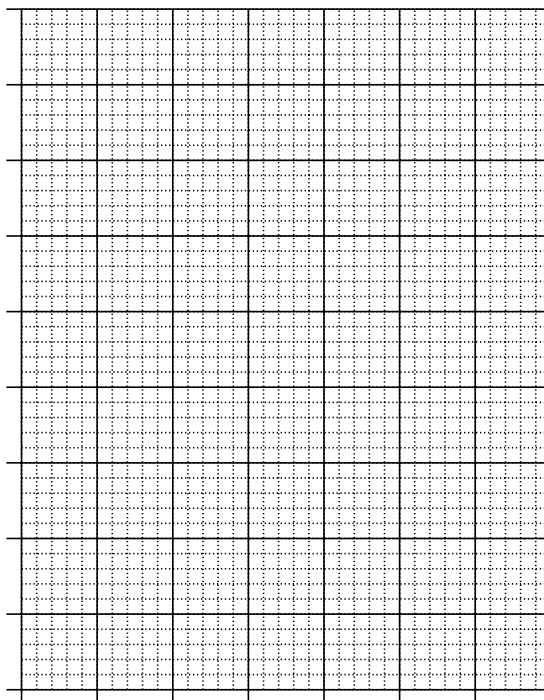
A student was provided with a spirit burner containing an unknown alcohol and was asked to determine the identity of this alcohol.

The student performed an experiment to determine the heat of combustion of this alcohol using 250.0 mL of water in a calorimeter. The spirit burner initially weighed 120.00 g. After the experiment, it weighed 119.06 g.

The following temperature data was collected.

<i>Time (min)</i>	0	0.5	1	2	3	4	5	6
<i>Temperature of water (°C)</i>	20.0	22.0	24.0	28.0	32.0	36.0	32.0	28.0

- (a) By graphing the temperature over time, calculate the experimental heat of combustion in  $\text{kJ g}^{-1}$  for this unknown alcohol. **3**



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**Question 25 continues on page 18**

Question 25 (continued)

- (b) The heat of combustion experiment the student performed is prone to heat loss. Assume that 40% of the heat was lost to the surroundings. 2

Given that the molar heat of combustion of this unknown alcohol is  $-1370 \text{ kJ mol}^{-1}$ , determine the identity of the unknown alcohol. Justify your answer using a calculation.

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**End of Question 25**

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**Question 26** (3 marks)

The  $pK_a$  for nitrous acid ( $\text{HNO}_2$ ) is 3.16 at  $25^\circ\text{C}$ .

**3**

Calculate the pH of a solution of  $0.200\text{ mol L}^{-1}$  of sodium nitrite.

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**Question 27** (5 marks)

Hydrocyanic acid ( $\text{HCN}$ ) is a weak acid with  $K_a = 6.2 \times 10^{-10}$  at temperature  $298\text{ K}$ .

A student prepared a solution in a laboratory mixing  $100\text{ mL}$  of  $0.10\text{ mol L}^{-1}$   $\text{HCN}$  with  $100\text{ mL}$  of  $0.10\text{ mol L}^{-1}$   $\text{KCN}$ .

(a) Calculate the pH of the solution.

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(b) Explain how the solution can be considered appropriate as a buffer.

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**Question 28** (4 marks)

A 1.0 L vessel at temperature of 300 K is filled with 0.10 mol of nitrogen monoxide gas, 0.050 mol of hydrogen gas and 0.10 mol of water vapour. The reaction of the gases reaches an equilibrium.

- (a) Write down the chemical equation of the equilibrium reaction in the vessel. 1

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- (b) At equilibrium, the concentration of the nitrogen monoxide is  $0.062 \text{ mol L}^{-1}$ . Calculate the value of the equilibrium constant of the reaction based on your chemical equation written in part (a). 3

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**Question 29** (3 marks)

- Explain why a titration between ammonia and butanoic acid is better monitored using a pH probe rather than chemical indicators. 3

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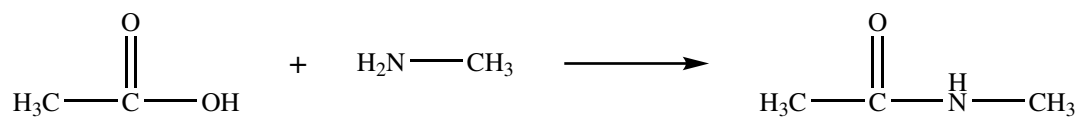
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**Question 30** (3 marks)

The  $pK_b$  of methanamine is 3.34 and the  $pK_a$  of acetic acid is 4.76.

**3**

Explain why the following reaction cannot be conducted directly with good yield. Show all calculations.



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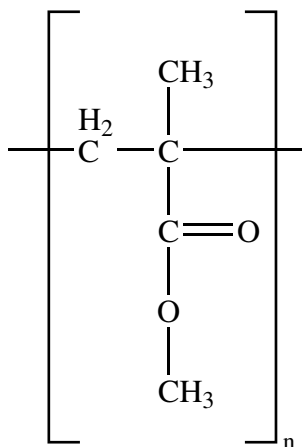
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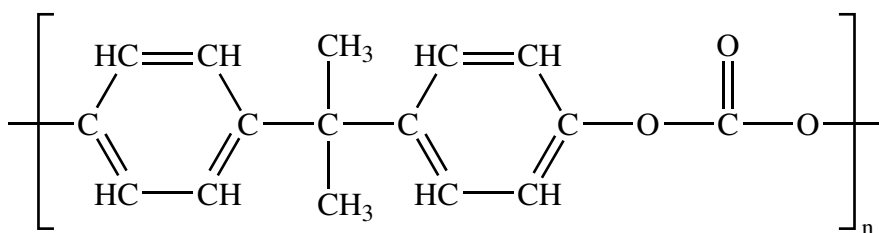
**Question 31** (3 marks)

The chemical structures of two polymers are provided below.

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polymethyl methacrylate



polycarbonate

Which polymer is more brittle than the other? Justify your answer.

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## Chemistry

### Section II Answer Booklet 2

#### Booklet 2 – Attempt Questions 32–38 (40 marks)

#### Instructions

- Write your student number, username and name on the top right of this page.
- 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.
- If you require extra writing space, please ask for a writing booklet. If you use a writing booklet, clearly indicate which questions you are answering.

**Please turn over**

**Question 32** (5 marks)

The fermentation of compound A ( $C_6H_{12}O_6$ ) produces a main target product compound B ( $C_2H_6O$ ). This process also produces several by-products with the following chemical formulae, where  $a$  and  $b$  are unknown integers:

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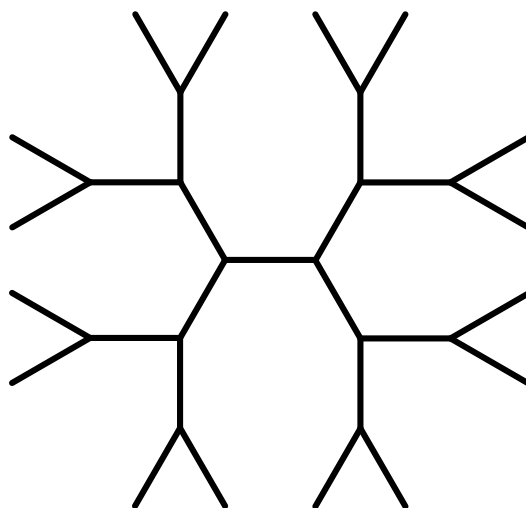
- Compound C ( $C_2H_aO_2$ )
- Compound D ( $C_3H_bO_3$ )
- Compound E ( $C_4H_6O_4$ )

Compound C, D and E underwent chemical tests with acidified  $KMnO_4$  and aqueous  $NaHCO_3$ .

The results are shown in the following table.

<i>Compound</i>	<i>Colour after addition of acidified <math>KMnO_4</math> solution</i>	<i>Observation after addition of aqueous <math>NaHCO_3</math> solution</i>
C	Purple	Bubbles produced
D	Colourless	No change
E	Purple	Bubbles produced

Compound D and compound E each have two peaks in their  $^{13}C$  NMR spectra. Also, they react with each other to form a two-dimensional polymer with the following geometric structure.



**Question 32 continues on page 25**



Question 32 (continued)

Draw the following chemical structures. Justify your answers.

Compound B

Compound C

Compound D

Compound E

Polymer formed from reaction of D and E

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**End of Question 32**

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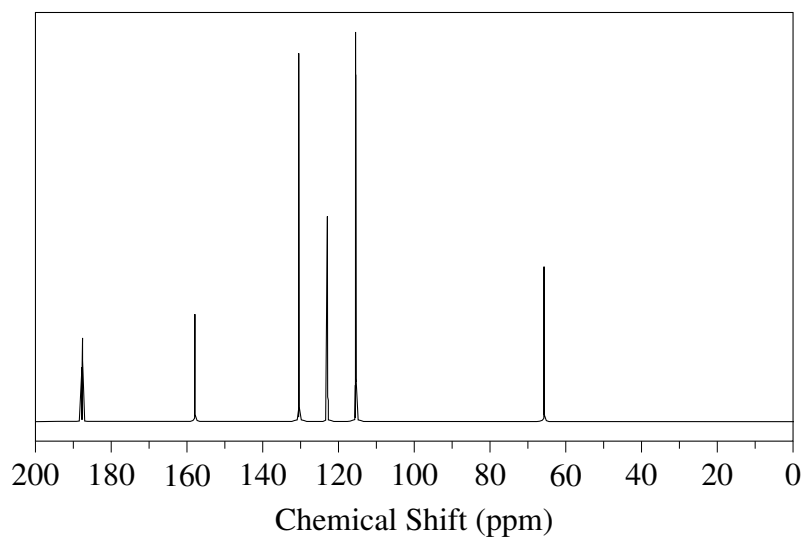
**Question 33** (5 marks)

A chemist obtained  $^{13}\text{C}$  NMR and proton NMR spectral data of an unknown compound as shown below.

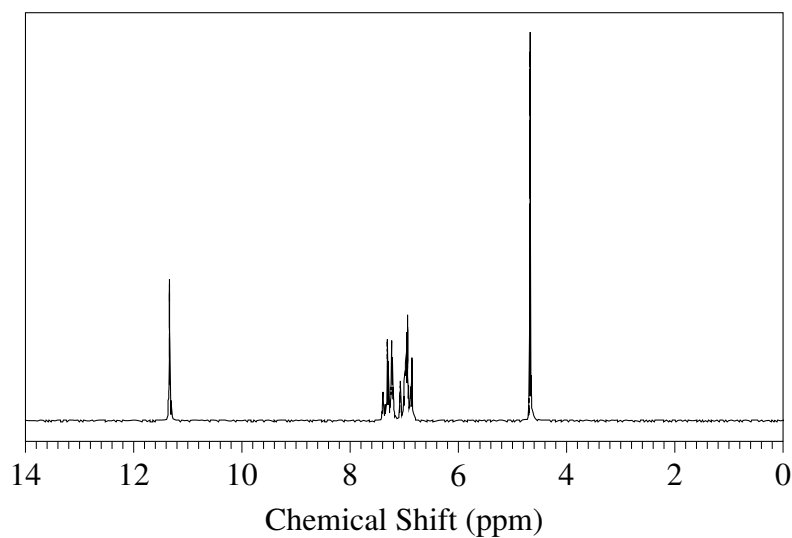
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The chemist is aware that the compound has the molecular formula  $\text{C}_8\text{H}_8\text{O}_3$ .

**Carbon-13 NMR**



**Proton NMR**



**Question 33 continues on page 27**

Question 33 (continued)

For the proton NMR spectrum, the following additional information is provided.

<i>Chemical shift (ppm)</i>	<i>Multiplicity</i>	<i>Number of hydrogens</i>
4.67	Singlet	2
6.91	Doublet	2
7.01	Triplet	1
7.28	Triplet	2
11.34	Singlet	1

With reference to the data provided, draw the structure of the compound. Justify your answer.

**End of Question 33**

**Please turn over**

**Question 34** (5 marks)

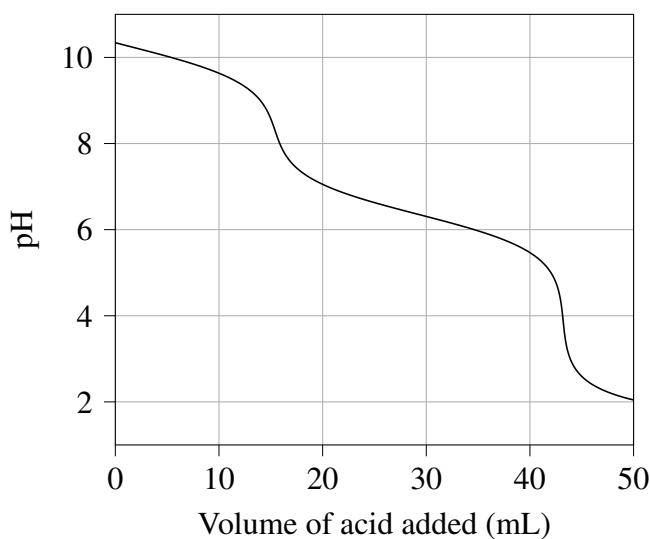
A student has a 1500 mL sample of freshly prepared sodium hydroxide solution. They titrate 25.00 mL of the solution against 0.1006 mol L<sup>-1</sup> hydrochloric acid using phenolphthalein indicator. The titres are recorded as below.

5

<i>Titre</i>	<i>Volume of HCl(aq) added (mL)</i>
1	27.02
2	26.62
3	26.65
4	26.59

After the titrations, 1351 mL of the sample remains in the bottle.

The student then accidentally left the bottle of sodium hydroxide open to the air for a long period of time. The student then takes 25.00 mL from this bottle and titrates it against 0.0998 mol L<sup>-1</sup> hydrochloric acid. The solution was monitored by a pH meter, which showed the following graph.



**Question 34 continues on page 29**

Question 34 (continued)

Explain how the bottle of sodium hydroxide being left open affected the results of the subsequent titration. Include relevant calculations in your answer.

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**End of Question 34**

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**Question 35** (5 marks)

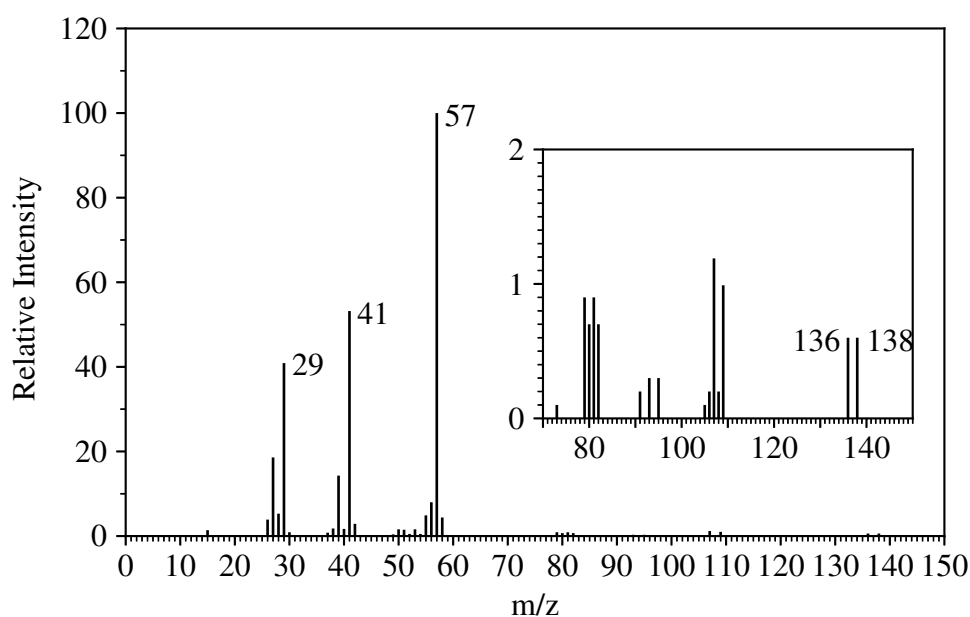
The flowchart shown on the next page shows seven distinct chemical compounds A, B, C, D, E, F and G. Each arrow represents one of the following reagents and conditions:

5

- Reaction with concentrated  $\text{H}_2\text{SO}_4$
- Reaction with ethanolic KOH
- Reaction with  $\text{H}_2$  through a palladium on carbon catalyst
- Reaction with an elemental halogen under UV light

The boiling point of compound G is higher than the boiling point of compound B.

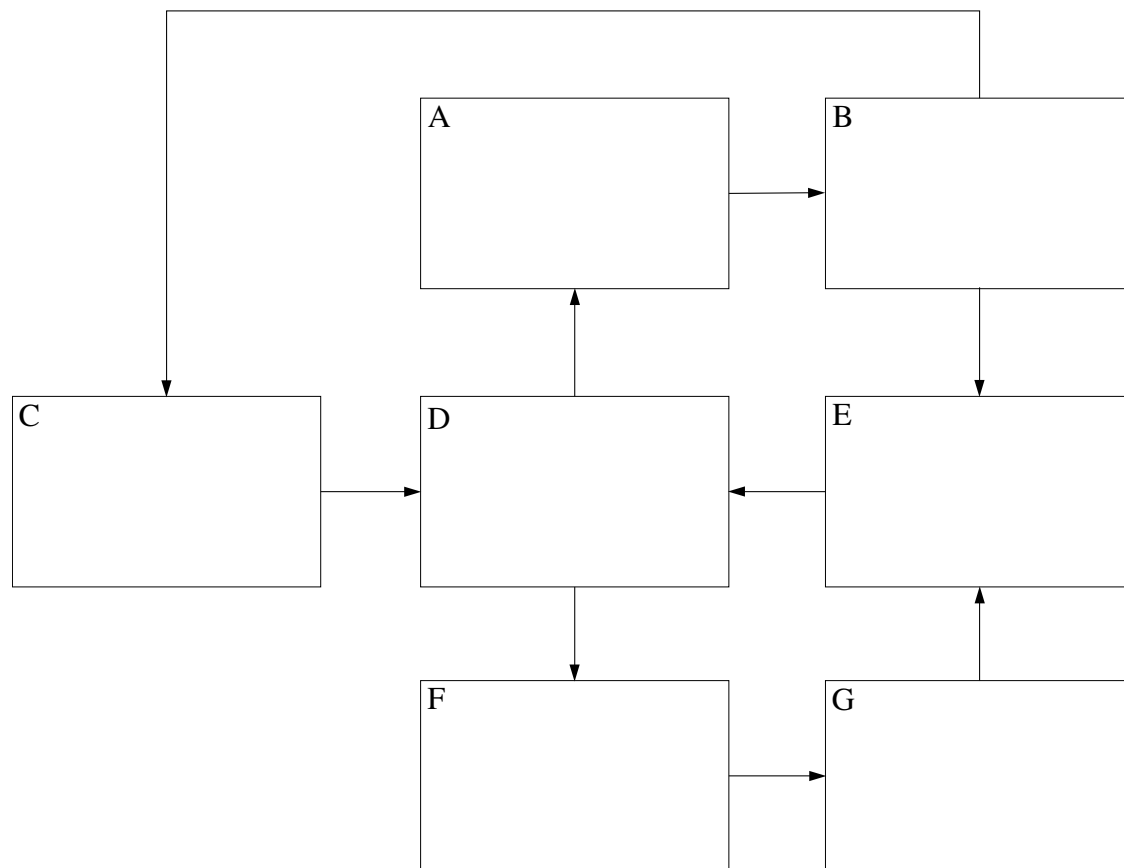
The mass spectrum of one of the seven compounds is shown below.



**Question 35 continues on page 31**

Question 35 (continued)

Complete the flow chart by drawing the structural formulae for the compounds A, B, C, D, E, F and G.

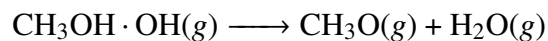
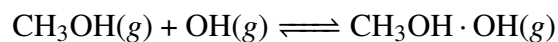


**End of Question 35**

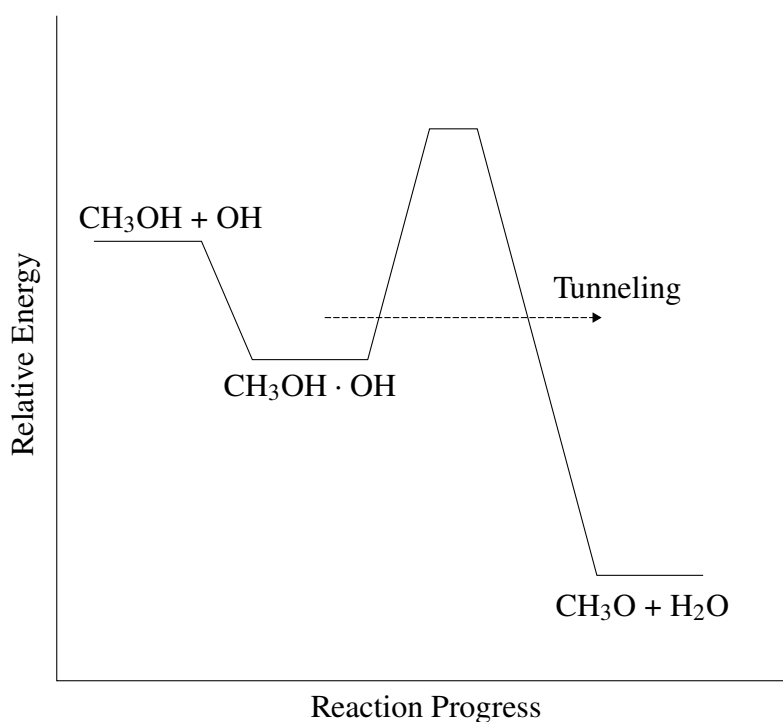
**Please turn over**

**Question 36** (5 marks)

A reaction sequence between methanol and a hydroxy species (OH) is shown in the chemical equations below.



The following diagram shows the relative energy of the different species on the pathway to the formation of products.



The arrow in the diagram represents “tunnelling effects”, which enable reactants that do not have sufficient activation energy to cross the barrier at a low rate.

The reaction is carried out in an inert atmosphere of helium gas.

Assume the concentration of each mentioned species, except the helium gas, is low.

**Question 36 continues on page 33**



## Question 36 (continued)

- (a) Explain why the formation of the final products can be seen as irreversible but the formation of the  $\text{CH}_3\text{OH} \cdot \text{OH}$  gas must be considered as reversible. **1**

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- (b) By considering collision theory and other effects, explain how the rate of formation of  $\text{CH}_3\text{O}$  gas is affected by the temperature of the reactants and the pressure of helium gas. **4**

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**End of Question 36**

**Please turn over**

**Question 37** (7 marks)

A student is given unknown compounds A, B and C. The following information is known about the compounds:

7

- There are exactly four distinct elements amongst the three compounds
- Compound A contains two ions in a 1:1 molar ratio
- Compound B contains an element that compound C does not
- Addition of aqueous ammonia to 1.000 g of compound A dissolved in water leads to the formation of 0.7794 g of compound B as a precipitate, which is then converted to compound C as a solid after heating.

The student performs two different sets of titrations on:

- 1.000 g of compound A dissolved in neutral aqueous buffer
- 0.7794 g of compound B dissolved in neutral aqueous buffer

Each of the precipitation titrations used a barium nitrate solution which reacts with various neutral buffered solutions to form a precipitate with  $K_{sp} = 1.08 \times 10^{-10}$ . The buffer acts only as a proton donor or acceptor.

The average volume of  $0.1000 \text{ mol L}^{-1}$  barium nitrate solution that must be added to reach the equivalence point in the titration is given by  $V_{eq}$  in the table below.

<i>Compound which titration was performed on</i>	$V_{eq}$ (mL)
<b>Compound A</b>	46.56
<b>Compound B</b>	15.52

Assume all reactions give a 100% yield.

**Question 37 continues on page 35**

Do NOT write in this area.

Question 37 (continued)

Identify the chemical formulas for compounds A, B and C. Justify your answer.

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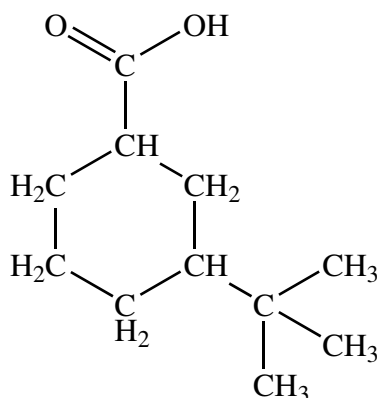
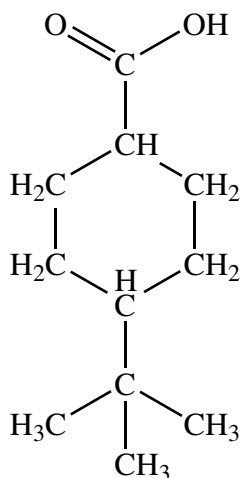
**End of Question 37**

**Please turn over**

**Question 38** (8 marks)

A HSC student has samples of two structurally similar carboxylic acids shown below.

8



The student has access to chemicals, laboratory equipment and instruments encountered or discussed in the HSC course (this includes the relevant spectrometers, any chemical reagents and any glassware), with the exception of pH meters and pH indicators.

**Question 38 continues on page 37**

Do NOT write in this area.

Question 38 (continued)

Propose a method the student could use to determine the difference in  $pK_a$  between the two acids as accurately as possible. Include qualitative descriptions of how calculations may be carried out by hand and calculator to find the difference in  $pK_a$ .

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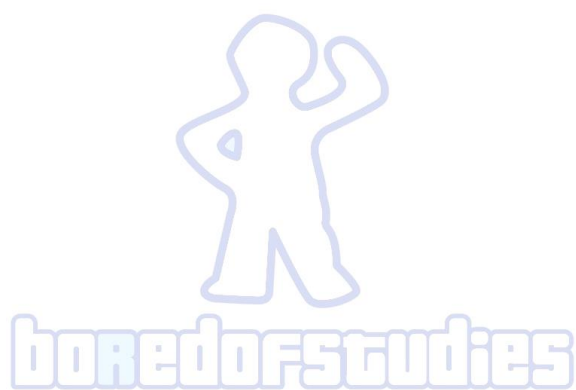
**End of paper**

## Section II extra writing space

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

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**Do NOT write in this area.**



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**2022**

**BORED OF STUDIES TRIAL EXAMINATION**

# Chemistry

# Marking Guidelines

## Section I

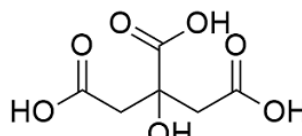
### Multiple-choice answer key

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

### Multiple-choice explanations

Question	Ans	Explanation				
1	C	Bromine water tests for C=C bonds in alkenes by decolourising from orange-brown to colourless. Only (C) has this type of bond.				
2	C	Enthalpy is negative since combustion is exothermic.  Entropy is positive since in the equation $\text{C}_8\text{H}_{18}(l) + 12.5\text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(l)$  There is an increase in particle number from 13.5 to 17. $\Delta G = \Delta H - T\Delta S$ $\Delta G = (-ve) - (+ve)(+ve)$ $\Delta G = -ve - (+ve)$ $\Delta G = -ve - ve$ $\Delta G = -ve$				
3	D	Since each compound has a different number of ions when dissolved in water, the molar solubility needs to be calculated based off the $K_{sp}$ values given on the data sheet. Let $x$ be the concentration of the salt dissolves in a 1 L saturated solution.  <table><tr><td>Lead (II) chloride: <math>4x^3 = 1.70 \times 10^{-6}</math> <math>x = 0.0075 \text{ mol L}^{-1}</math> (3sf)</td><td>Lead (II) sulfate: <math>x^2 = 2.53 \times 10^{-8}</math> <math>x = 0.000159 \text{ mol L}^{-1}</math> (3sf)</td></tr><tr><td>Calcium sulfate: <math>x^2 = 4.93 \times 10^{-5}</math> <math>x = 0.00702 \text{ mol L}^{-1}</math> (3sf)</td><td>Barium hydroxide: <math>4x^3 = 2.55 \times 10^{-4}</math> <math>x = 0.0399 \text{ mol L}^{-1}</math> (3sf)</td></tr></table> Therefore, barium hydroxide has the highest molar solubility	Lead (II) chloride: $4x^3 = 1.70 \times 10^{-6}$ $x = 0.0075 \text{ mol L}^{-1}$ (3sf)	Lead (II) sulfate: $x^2 = 2.53 \times 10^{-8}$ $x = 0.000159 \text{ mol L}^{-1}$ (3sf)	Calcium sulfate: $x^2 = 4.93 \times 10^{-5}$ $x = 0.00702 \text{ mol L}^{-1}$ (3sf)	Barium hydroxide: $4x^3 = 2.55 \times 10^{-4}$ $x = 0.0399 \text{ mol L}^{-1}$ (3sf)
Lead (II) chloride: $4x^3 = 1.70 \times 10^{-6}$ $x = 0.0075 \text{ mol L}^{-1}$ (3sf)	Lead (II) sulfate: $x^2 = 2.53 \times 10^{-8}$ $x = 0.000159 \text{ mol L}^{-1}$ (3sf)					
Calcium sulfate: $x^2 = 4.93 \times 10^{-5}$ $x = 0.00702 \text{ mol L}^{-1}$ (3sf)	Barium hydroxide: $4x^3 = 2.55 \times 10^{-4}$ $x = 0.0399 \text{ mol L}^{-1}$ (3sf)					



4	A	<p>Since the pH is 2.960 then <math>[H_3O^+] = 10^{-2.960} \text{ mol L}^{-1}</math>.</p> <table><tr><td></td><td colspan="4"><math>CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)</math></td></tr><tr><td>I</td><td>0.100</td><td>-</td><td>0</td><td>0</td></tr><tr><td>C</td><td><math>-10^{-2.960}</math></td><td>-</td><td><math>+10^{-2.960}</math></td><td><math>+10^{-2.960}</math></td></tr><tr><td>E</td><td><math>0.100 - 10^{-2.960}</math></td><td>-</td><td><math>10^{-2.960}</math></td><td><math>10^{-2.960}</math></td></tr></table> <p><math display="block">\% \text{ unionised} = \frac{CH_3COOH_{\text{equilibrium}}}{CH_3COOH_{\text{initial}}} = \frac{0.100 - 10^{-2.960}}{0.100} \times 100\%</math><math display="block">= 98.9\% \text{ (3sf)}</math></p>		$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$				I	0.100	-	0	0	C	$-10^{-2.960}$	-	$+10^{-2.960}$	$+10^{-2.960}$	E	$0.100 - 10^{-2.960}$	-	$10^{-2.960}$	$10^{-2.960}$
	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$																					
I	0.100	-	0	0																		
C	$-10^{-2.960}$	-	$+10^{-2.960}$	$+10^{-2.960}$																		
E	$0.100 - 10^{-2.960}$	-	$10^{-2.960}$	$10^{-2.960}$																		
5	B	<p>The structure of citric acid is as below.</p>  <p>Citric acid</p> <p>Due to symmetry, there are 4 carbon environments and 4 hydrogen environments.</p>																				
6	A	<p><math>CaCO_3(s) \rightarrow CaO(s) + CO_2(g)</math> <math>m(CaCO_3) = 12.95 \times 0.95 = 12.3025 \text{ g}</math></p> <p><math display="block">n(CaCO_3) = \frac{m}{MM} = \frac{12.3025}{40.08 + 12.01 + 16.00 \times 3} = 0.1229... \text{ mol}</math></p> <p><math>n(CaO) = n(CaCO_3) = 0.1229... \text{ mol}</math> <math>m(CaO) = 0.1229 \times (40.08 + 16.00) = 6.89 \text{ g (3sf)}</math></p>																				
7	D	<p>Ethyl propanoate has the formula <math>C_5H_{10}O_2</math>. By drawing each structure, the only one that has the formula <math>C_5H_{10}O_2</math> is 2-methylbutanoic acid.</p>																				
8	C	<p><math>4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)</math></p> <p>Less oxygen is present in air from the atmosphere as it is a mixture of gases including nitrogen and carbon dioxide. Therefore, a decrease in <math>[O_2]</math> leads to a lower reaction rate as less molecules are present which lowers the number of collisions. There is a decrease in yield as the equilibrium will shift left by Le Chatelier's Principle due to the lower <math>[O_2]</math>.</p>																				
9	B	<p><math>n(HNO_3) = cv = 0.15 \times 0.450 = 0.0675 \text{ mol}</math> <math>n(Ba(OH)_2) = cv = 0.10 \times 0.250 = 0.0250 \text{ mol}</math></p> <p><math>n(H^+) = 0.0675 \text{ mol}</math> <math>n(OH^-) = 2 \times 0.0250 = 0.0500 \text{ mol}</math></p>																				

		<p>Since <math>n(\text{H}^+) &gt; n(\text{OH}^-)</math> then <math>\text{H}^+</math> is in excess.</p> <p><math>n(\text{H}^+) \text{ excess} = 0.0675 - 0.0500 = 0.0175 \text{ mol}</math></p> <p><math>c(\text{H}^+) \text{ excess} = \frac{n}{v} = \frac{0.0175}{0.700} = 0.025 \text{ mol L}^{-1}</math></p> <p><math>\text{pH} = -\log_{10} 0.025 = 1.60205 \dots</math>  <math>\text{pOH} = 14 - 1.60205 \dots = 12.39794 = 12.40</math></p>
10	B	<p>Soaps are surfactants which decreases the surface tension, thus decreasing cohesive forces. Soaps also form micelles in their cleaning action, forming emulsions.</p>
11	D	<p>Oxidation of the first compound gives 4-bromobutanoic acid. That is substituted with <math>\text{OH}^-</math> to give 4-hydroxybutanoic acid. Concentrated <math>\text{H}_2\text{SO}_4</math> will dehydrate it and give <math>\text{CH}=\text{CH}-\text{CH}_2-\text{COOH}</math>.</p> <p>There is no possibility of that to undergo condensation polymerisation. It instead undergoes addition polymerisation and so the final polymer contains all the atoms from the monomer.</p> <p><math>MM(Z) = 4 \times 12.01 + 6 \times 1.008 + 2 \times 16.00 = 86.088 \text{ g mol}^{-1}</math></p> <p>Let <math>N</math> be the number of monomers that make up the polymer.  <math>86.088 \times N = 1.03 \times 10^5</math>  <math>N = 1197.67 \dots</math></p> <p>Since each monomer has 4 carbon atoms, the approximate number of carbon atoms in the polymer is <math>4N</math>, which is closest to 4800.</p>
12	A	<p>Since HI and NaOH are a strong acid and base respectively, the net ionic reaction is:</p> <p><math>\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})</math></p> <p><math>n(\text{H}^+) = n(\text{HI}) = cv = 0.09 \times 1.00 = 0.09 \text{ mol}</math>  <math>n(\text{OH}^-) = n(\text{NaOH}) = cv = 0.09 \times 1.00 = 0.09 \text{ mol}</math>  <math>n(\text{H}_2\text{O}) = n(\text{H}^+) = n(\text{OH}^-) = 0.09 \text{ mol}</math></p> <p><math>q = mc\Delta T = (90 + 90) \times 4.18 \times 4.43 = 3333.132 \text{ J} = 3.33132 \text{ kJ}</math></p> <p><math>\Delta H_c = -\frac{q}{n} = -\frac{3.33132}{0.09} = -37.0 \text{ kJ mol}^{-1} \text{ (3sf)}</math></p>
13	C	<p>Since HBr and KOH are also strong acids/bases, their net ionic reaction is the same as the reaction in Q12. Thus, the enthalpy of neutralisation is approximately the same.</p>

14	B	<p>For reliability of the data there needs to be at least 3 different trials that produce consistent results. Since there is only one data point for each site, none of the data is reliable for either site.</p> <p>Validity relies on the experimental setup and accuracy of assumptions in the graph. For Site A the 0.35 absorbance is within the graph's sample data points for the 5-70 ppm concentration and so it is valid to assume the line of best fit can be used to estimate the concentration in this solution.</p> <p>For Site B the 0.90 absorbance is outside the graph's data points and so it is invalid to assume that the relationship for the line of best fit will continue by extrapolation, as the trend may be different.</p>
15	C	<p><math>A = 0.45</math>, so from the graph:  <math>[\text{Fe}] = 35 \text{ ppm} = 35 \text{ mg L}^{-1}</math></p> <p>Converting this into <math>\text{mol L}^{-1}</math>:</p> $c(\text{Fe})_{\text{diluted}} = \frac{0.035}{55.85} = 0.0006266 \dots \text{mol L}^{-1}$ $n(\text{Fe})_{\text{diluted}} = 0.0006266 \dots \times 0.1 = 0.00006266 \dots \text{mol}$ $c_1 v_1 = c_2 v_2$ $n(\text{Fe})_{\text{initial}} = 0.00006266 \dots \times \frac{0.2}{0.01} = 0.001253 \text{ mol}$ $m(\text{Fe})_{\text{initial}} = n \times MM = 0.001253 \times 55.85 = 0.070 \text{ g}$ $\% m(\text{Fe})_{\text{initial}} = \frac{70}{200} \times 100\% = 35\%$
16	D	<p>The compounds are all salts which can form solutions that have acidic, neutral, or basic pH.</p> <p><math>\text{NaCl}</math> and <math>\text{NaNO}_3</math> are neutral salts due to having a strong acid and strong base as conjugates.</p> <p><math>\text{NH}_4\text{NO}_3</math> is an acidic salt as it comes from the reaction of a weak base and strong acid. Adding <math>\text{NH}_4\text{NO}_3</math> will increase <math>[\text{H}_3\text{O}^+]</math> and so the equilibrium will shift left. This will decrease ionisation as more of the neutral acid <math>\text{HOCl}</math> molecule will form.</p> <p><math>\text{NaCH}_3\text{COO}</math> is a basic salt as it comes from the reaction of a strong base and weak acid. Adding <math>\text{NaCH}_3\text{COO}</math> will produce <math>\text{OH}^-</math> which reacts with <math>\text{H}_3\text{O}^+</math> removing it from the solution and therefore decreasing <math>[\text{H}_3\text{O}^+]</math>. The equilibrium shifts right by Le Chatelier's Principle and so more ions are formed. This increases the degree of ionisation.</p>

17	C	<p><math>\text{Na}_2\text{O}</math> is neither an acid nor a base, so (A) is incorrect.</p> <p><math>\text{C}_3\text{H}_9\text{N}</math> (amine) and <math>\text{NaOH}</math> are both bases, not an acid and a base, so (B) is incorrect</p> <p>Glucose is neutral, so (D) is incorrect.</p> <p><math>\text{C}_{17}\text{H}_{35}\text{COONa}</math> contains <math>\text{C}_{17}\text{H}_{35}\text{COO}^-</math>, which is a Bronsted-Lowry base and not an Arrhenius base. Citric acid contains 3 carboxylic acid groups, and thus is an Arrhenius acid. Hence, (C) is correct.</p>
18	C	<p>The number of moles of gas on either side of the equation are equal in ratio 2:2. Therefore an increase in pressure will NOT lead to a shift in the equilibrium as no side is favoured.</p> <p>However, the act of compressing the system will reduce volume and so the concentrations of each species will rise in <math>c = \frac{n}{v}</math> and then plateau due to the lack of equilibrium shift.</p>
19	A	<p>Beaker A does not form a buffer and so adding a base to it will lead to pH increase. Beaker B contains a buffer solution and so adding a base will lead to a minimal pH change as the solution will resist the pH change.</p>
20	B	<p>Step 1: The step is correct</p> <p>Step 2: The step is correct</p> <p>Step 3: The pipette must be rinsed with the hydrochloric acid solution before being pipetted, as the distilled water in the pipette will dilute the acid.</p> <p>Step 4: The step is correct</p> <p>The actual concentration of <math>\text{HCl}</math> will be greater than the concentration of <math>\text{HCl}</math> in the pipette/conical flask.</p>

## Section II

### Question 21 (a)

Criteria	Marks
• Gives TWO reasons for reflux	2
• Provides some relevant information	1

**Sample answer:**

Heating increases the speed of the reaction by allowing more reactants to have the required collisional energy to overcome the activation energy barrier. Cooling using a condenser is needed to prevent the loss of the reaction mixture, since all the compounds in esterification including the reactants and the ester are volatile.

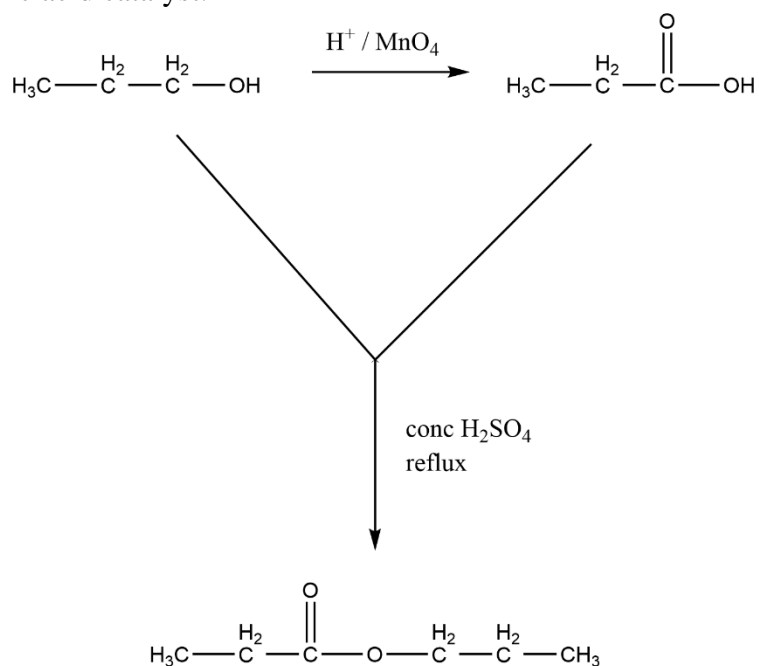
### Question 21 (b)

Criteria	Marks
• Provides correct calculations and a relevant reaction scheme	3
• Provides some relevant steps	2
• Provides some relevant information	1

**Sample answer:**

Esters are made of alcohols and carboxylic acids. Therefore, the ester is made of propanoic acid and propanol.

Propanol may be converted to propanoic acid with acidified potassium permanganate solution. Esterification reaction between propanol and propanoic acid to form propyl propanoate using concentrated sulfuric acid catalyst.



$$n(\text{C}_3\text{H}_8\text{O}) = \frac{m}{MM} = \frac{10}{3 \times 12.01 + 8 \times 1.008 + 16.00} = 0.1664 \dots \text{ mol}$$

Mass of ester is maximised when propanoic acid and propanol react in the stoichiometric 1:1 ratio so would want to oxidise half of the propanol.

$$n(\text{C}_6\text{H}_{12}\text{O}_2) = \frac{0.1664 \dots}{2} = 0.08321 \dots$$

$$m(\text{C}_6\text{H}_{12}\text{O}_2) = 0.08321 \dots \times (6 \times 12.01 + 12 \times 1.008 + 2 \times 16.00) = 9.67 \text{ g (3 sf)}$$

## Question 22

Criteria	Marks
• Explains patterns in the boiling points	3
• Explains most of the patterns in the boiling points	2
• Explains a pattern in the boiling points	1

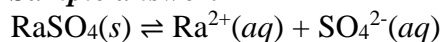
### *Sample answer:*

Alcohols have higher boiling points than the esters due to hydrogen bonding. The boiling points of both alcohols and esters increase with the number of carbon atoms due to increase in dispersion forces. The difference in boiling points between alcohols and esters decreases with increasing carbon atoms because dispersion forces become the predominant intermolecular force.

## Question 23

Criteria	Marks
• Provides correct calculations • Provides a relevant chemical equation	3
• Provides some relevant steps	2
• Provides some relevant information	1

### *Sample answer:*



First converting the solubility from grams to moles per litre:

$$[\text{RaSO}_4] = \frac{2.1 \times 10^{-3}}{322.06} = 6.521 \dots \times 10^{-6} \text{ mol L}^{-1}$$

$$[\text{Ra}^{2+}] = [\text{SO}_4^{2-}] = 6.521 \dots \times 10^{-6} \text{ mol L}^{-1}$$

$$K_{sp} = [\text{Ra}^{2+}][\text{SO}_4^{2-}] = 6.521 \dots \times 10^{-6} \times 6.521 \dots \times 10^{-6} = 4.3 \times 10^{-11} \text{ (2 sf)}$$

### Question 24

Criteria	Marks
<ul style="list-style-type: none"><li>Provides correct calculations</li><li>Provides a relevant chemical equation</li></ul>	3
<ul style="list-style-type: none"><li>Provides some relevant steps</li></ul>	2
<ul style="list-style-type: none"><li>Provides some relevant information</li></ul>	1

**Sample answer:**

$$n(\text{BaCl}_2) = cv = 0.0100 \times 0.0200 = 0.000200 \text{ mol}$$

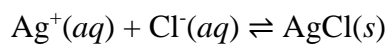
$$n(\text{Cl}^-) = 2 \times 0.000200 = 0.000400 \text{ mol}$$

$$n(\text{AgNO}_3) = cv = 0.0200 \times 0.0200 = 0.000400 \text{ mol}$$

$$n(\text{Ag}^+) = 0.00400 \text{ mol}$$

$$[\text{Ag}^+] = \frac{n}{v} = \frac{0.000400}{0.04} = 0.0100 \text{ mol L}^{-1}$$

$$[\text{Cl}^-] = \frac{n}{v} = \frac{0.000400}{0.04} = 0.0100 \text{ mol L}^{-1}$$



$$Q = [\text{Ag}^+][\text{Cl}^-] = 0.0100 \times 0.0100 = 1.00 \times 10^{-4} \text{ (3 sf)}$$

From the data sheet  $K_{sp} = 1.77 \times 10^{-10}$ .

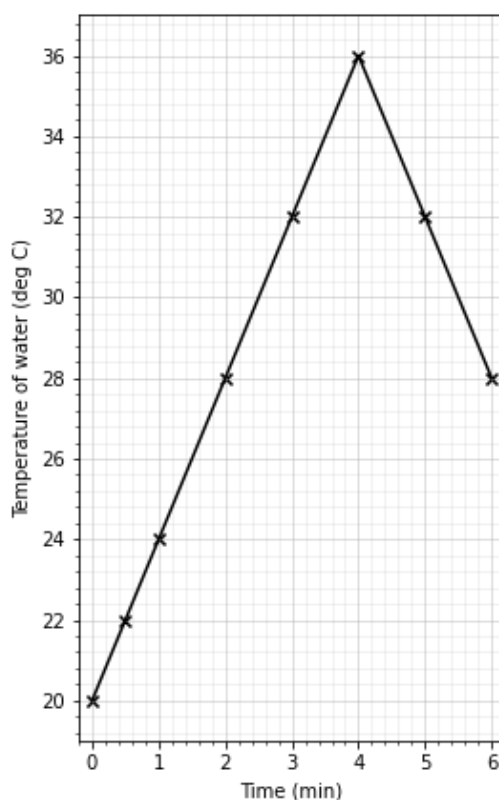
Since  $Q > K_{sp}$  then a precipitate forms.

**Question 25 (a)**

Criteria	Marks
<ul style="list-style-type: none"><li>Provides graph with<ul style="list-style-type: none"><li>correctly labelled axes including units</li><li>correctly plotted points</li><li>correct line(s) of best fit</li></ul></li><li>Correctly calculates the experimental heat of combustion</li></ul>	3
<ul style="list-style-type: none"><li>Provides a substantially correct graph and substantially correct calculations</li></ul>	2
<ul style="list-style-type: none"><li>Provides some relevant information</li></ul>	1

*Sample answer:*

**Temperature of water over time**



The maximum temperature is 36°C and the change in temperature is  $36 - 20 = 16^{\circ}\text{C}$ .

The energy supplied to water is:  $q = mc\Delta T = 250 \times 4.18 \times 16 = 16720 \text{ J}$

The mass of alcohol consumed is  $120.00 - 119.06 = 0.94 \text{ g}$

Heat of combustion is:

$$-\frac{q}{m} = -\frac{16720}{0.94} = -177887 \text{ J g}^{-1} = -17.8 \text{ kJ g}^{-1} \text{ (3 sf)}$$



**Question 25 (b)**

Criteria	Marks
<ul style="list-style-type: none"><li>Provides correct calculations</li><li>Identifies the unknown alcohol as ethanol</li></ul>	2
<ul style="list-style-type: none"><li>Provides some relevant information</li></ul>	1

**Sample answer:**

The proportion of heat not lost to the surroundings is 60%.

The true heat of combustion is:

$$\frac{17.8}{0.6} = 29.7 \text{ kJ g}^{-1}$$

This is approximately equivalent to  $1370 \text{ kJ mol}^{-1}$  so:

$$MM = \frac{1370}{29.7} = 46.1 \text{ g mol}^{-1}$$

The general formula for an alcohol is  $\text{C}_n\text{H}_{2n+1}\text{OH}$  which has molar mass of:

$$MM = 12.01n + (2n + 1)1.008 + 16.00 + 1.008 = 14.026n + 18.016$$

Solving for  $n$ :

$$14.026n + 18.016 = 46.1$$

$$n = 2.00$$

Therefore, the alcohol is ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ).

### Question 26

Criteria	Marks
<ul style="list-style-type: none"> <li>Provides correct calculations</li> <li>Provides a relevant chemical equation</li> </ul>	3
<ul style="list-style-type: none"> <li>Provides some relevant steps</li> </ul>	2
<ul style="list-style-type: none"> <li>Provides some relevant information</li> </ul>	1

**Sample answer:**

$$pK_a = 3.16$$

$$K_a = 10^{-3.16}$$

$$K_w = K_a K_b$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-3.16}} = 1.445 \dots \times 10^{-11}$$

	$\text{NO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{OH}^-(aq)$			
I	0.2	-	0	0
C	-x	-	+x	+x
E	0.2 - x	-	x	x

$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = \frac{x^2}{0.2 - x} = 1.445 \dots \times 10^{-11}$$

Nitrite is a weak base so  $x \ll 0.2$ , which means  $0.2 - x \approx 0.2$ .

$$x = \sqrt{0.2 \times 1.445 \dots \times 10^{-11}} = 1.700 \dots \times 10^{-6} \text{ mol L}^{-1}$$

$$\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10} x = -\log_{10} 1.700 \dots \times 10^{-6} = 5.77 \dots$$

$$\text{pH} = 14 - 5.77 \dots = 8.23$$

**Question 27 (a)**

Criteria	Marks
• Provides correct calculations	3
• Provides some relevant steps	2
• Provides some relevant information	1

**Sample answer:**

$$n(\text{HCN})_{\text{initial}} = cv = 0.10 \times 0.1 = 0.01 \text{ mol}$$

$$n(\text{CN}^-)_{\text{initial}} = cv = 0.10 \times 0.1 = 0.01 \text{ mol}$$

$$c(\text{HCN})_{\text{diluted}} = \frac{n}{v} = \frac{0.01}{0.2} = 0.05 \text{ mol L}^{-1}$$

$$c(\text{CN}^-)_{\text{diluted}} = \frac{n}{v} = \frac{0.01}{0.2} = 0.05 \text{ mol L}^{-1}$$

	$\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CN}^-(aq) + \text{H}_3\text{O}^+(aq)$			
I	0.05	-	0.05	0
C	-x	-	+x	+x
E	0.05 - x	-	0.05 + x	x

$$K_a = \frac{[\text{CN}^-][\text{H}_3\text{O}^+]}{[\text{HCN}]} = \frac{[\text{H}_3\text{O}^+](0.05 + x)}{0.05 - x} = 6.2 \times 10^{-10}$$

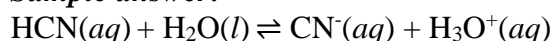
Since HCN is a weak acid then  $x \ll 0.05$ , which means  $0.05 \pm x \approx 0.05$ .

$$[\text{H}_3\text{O}^+] = 6.2 \times 10^{-10}$$

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = 9.21$$

**Question 27 (b)**

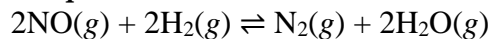
Criteria	Marks
• Provides a relevant chemical equation	2
• Explains how the buffer is able to resist a change in pH	
• Provides some relevant information	1

**Sample answer:**

On the addition of an acid such as HCl, the increased  $\text{H}_3\text{O}^+$  is consumed by the reverse reaction by Le Chatelier's principle. The solution resists the pH change and can be referred to as a buffer.

**Question 28 (a)**

Criteria	Marks
<ul style="list-style-type: none"> <li>Provides the correct chemical equation</li> </ul>	1

*Sample answer:***Question 28 (b)**

Criteria	Marks
<ul style="list-style-type: none"> <li>Provides correct calculations</li> </ul>	3
<ul style="list-style-type: none"> <li>Provides some relevant steps</li> </ul>	2
<ul style="list-style-type: none"> <li>Provides some relevant information</li> </ul>	1

*Sample answer:*

	$2\text{NO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{N}_2(g) + 2\text{H}_2\text{O}(g)$			
I	0.1	0.05	0	0.1
C	$-2x$	$-2x$	$+x$	$+2x$
E	$0.1 - 2x$	$0.05 - 2x$	$x$	$0.1 + 2x$

$$0.1 - 2x = 0.062$$

$$x = 0.019$$

$$K = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2[\text{H}_2]^2} = \frac{0.019(0.1 + 2 \times 0.019)^2}{(0.1 - 2 \times 0.019)^2(0.05 - 2 \times 0.019)^2} = 6.5 \times 10^2 \text{ (2 sf)}$$

**Question 29**

Criteria	Marks
<ul style="list-style-type: none"> <li>Provides a correct explanation</li> </ul>	3
<ul style="list-style-type: none"> <li>Describes features of the acid, base and pH throughout the titration</li> </ul>	2
<ul style="list-style-type: none"> <li>Provides some relevant information</li> </ul>	1

*Sample answer:*

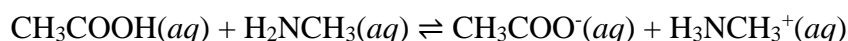
Ammonia and butanoic acid are weak base and weak acid respectively. The change in pH is therefore gradual throughout the titration. The indicator will change colour gradually and therefore the equivalence point cannot be accurately determined, so will need to observe the entire shape of the pH curve.

### Question 30

Criteria	Marks
<ul style="list-style-type: none"><li>Provides correct calculations of a relevant equilibrium constant</li><li>Provides a relevant chemical equation</li></ul>	3
<ul style="list-style-type: none"><li>Describes some relevant steps</li></ul>	2
<ul style="list-style-type: none"><li>Provides some relevant information</li></ul>	1

**Sample answer:**

The acid-base reaction between the reactants almost fully consumes the reactant material, which becomes unavailable for the desired reaction. This evidenced by the calculation below.



$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{NCH}_3^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{NCH}_3]} = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{H}_3\text{NCH}_3^+][\text{OH}^-]}{[\text{H}_2\text{NCH}_3][\text{H}^+][\text{OH}^-]}$$

$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{H}_3\text{NCH}_3^+][\text{OH}^-]}{[\text{H}_2\text{NCH}_3]K_w} = \frac{K_a K_b}{K_w} = \frac{10^{-4.76} \times 10^{-3.34}}{10^{-14}} = 7.94 \times 10^5 \text{ (3 sf)}$$

Since  $K \gg 1$  then the position of the equilibrium lies far away from the reactants.

### Question 31

Criteria	Marks
<ul style="list-style-type: none"><li>Explains why polymethyl methacrylate is more brittle than polycarbonate</li></ul>	3
<ul style="list-style-type: none"><li>Identifies relevant features of polymethyl methacrylate</li></ul>	2
<ul style="list-style-type: none"><li>Provides some relevant information</li></ul>	1

**Sample answer:**

Polymethyl methacrylate has more bulky side chains. This means that it is more difficult for the polymer chains to move into the most suitable positions and therefore instead bonds will need to stretch more than in polycarbonate. Therefore, the polymethyl methacrylate is more brittle than polycarbonate because the bonds will break earlier.

### Question 32

Criteria	Marks
<ul style="list-style-type: none"><li>• Draws the correct chemical structures</li><li>• Justifies the correct structures showing an understanding of the chemical tests and spectroscopic data</li></ul>	5
<ul style="list-style-type: none"><li>• Draws the most of the correct chemical structures</li><li>• Justifies the correct structures showing an understanding of the chemical tests and spectroscopic data</li></ul>	3-4
<ul style="list-style-type: none"><li>• Provides some correct chemical structures</li></ul>	2
<ul style="list-style-type: none"><li>• Provides some relevant information</li></ul>	1

#### *Sample answer:*

For the compounds to be identified:

- **Unlikely** to contain an alcohol if the solution remains purple upon the addition of acidified  $\text{KMnO}_4$  (an oxidant that would oxidise primary and secondary alcohols under standard conditions).
- **Likely** to contain a carboxylic acid if bubbles form upon the addition of  $\text{NaHCO}_3$  (effervescence with the addition of  $\text{NaHCO}_3$  to a carboxylic acid is indicative of the production of carbon dioxide gas).

Compound B:

The target product of fermentation is ethanol.

Compound C:

Using the previous lines of thought, it must be a carboxylic acid with 2 carbons and no further oxygens, so it must be ethanoic acid.

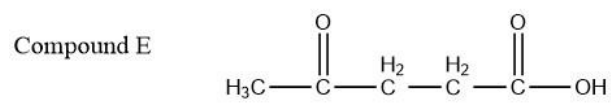
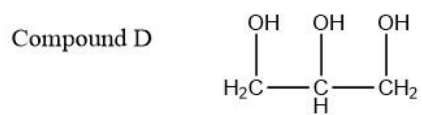
Compound E:

A carboxylic acid with 4 carbons. However, only two  $\text{C}^{13}$  NMR peaks indicate symmetry. Since there are 4 oxygens, the compound can be deduced to be butanedioic acid.

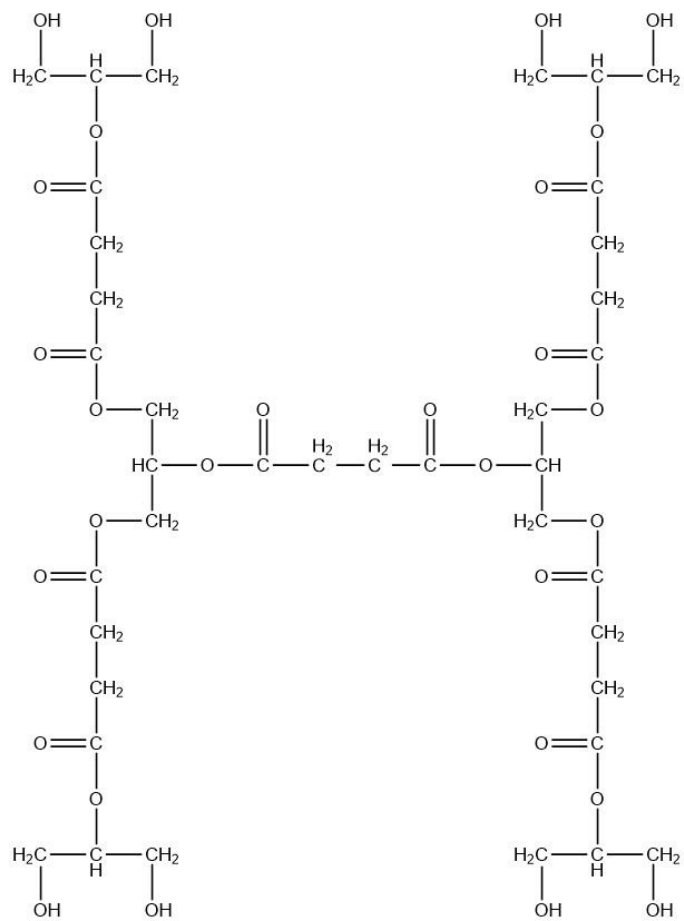
Compound D:

It is not a carboxylic acid. However, it reacts with butanedioic acid to form a polymer, which suggests that it contains an alcohol. This is further justified by the decolourisation of acidified  $\text{KMnO}_4$  solution (which would decolourise upon oxidising a primary or secondary alcohol). A linear polymer is formed when reacting butanedioic acid with a diol, so 3 -OH groups must be present. Since there are two  $\text{C}^{13}$  NMR peaks, compound D must be propane-1,2,3-triol.

The structures are provided below:



Polymer



### Question 33

Criteria	Marks
<ul style="list-style-type: none"> <li>Writes the correct structural formula (naming not required)</li> <li>Justifies the correct structure showing an extensive understanding of the interpretation of spectroscopic data</li> <li>Refers explicitly to the relevant spectroscopic data</li> </ul>	5
<ul style="list-style-type: none"> <li>Writes the correct structural formula for an isomer (naming not required)</li> <li>Justifies the structure showing a thorough understanding of the interpretation of spectroscopic data</li> <li>Refers to relevant spectroscopic data</li> </ul>	4
<ul style="list-style-type: none"> <li>Shows a sound understanding of the interpretation of spectroscopic data</li> <li>Uses relevant information presented in the question to justify the structure of the chemical</li> <li>Provides a structural formula consistent with analysis</li> </ul>	3
<ul style="list-style-type: none"> <li>Shows some understanding of the interpretation of spectroscopic data</li> </ul>	2
<ul style="list-style-type: none"> <li>Provides some relevant information</li> </ul>	1

#### Sample answer:

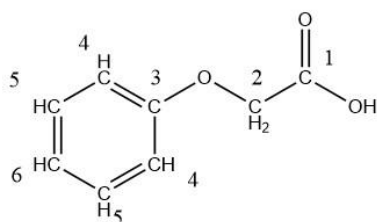
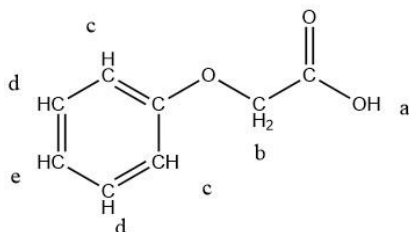
The carbon-13 peaks near 120 ppm indicate a possible structure containing a benzene ring. The carbon-13 peak near 190 indicates the likely presence of C=O. The carbon-13 peak near 66 ppm indicates the likely presence of a C-O-C bond.

The benzene ring is likely monosubstituted because there are 5 protons near 7 ppm. It is likely these are attached to the benzene ring. The extremely high proton NMR peak likely indicates a carboxylic acid.

Therefore, the structure and spectral assignments are:

- From lowest to highest, proton NMR: b, c, e, d, a
- From lowest to highest, carbon-13 NMR: 2, 4, 6, 5, 3, 1

The structure is provided below showing the above assignments.



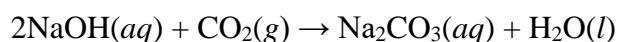


### Question 34

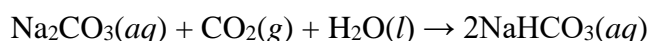
Criteria	Marks
• Provides the correct calculations of the amount of water evaporated and the amount of carbon dioxide absorbed	5
• Provides most correct steps	3-4
• Provides some relevant information	1-2

#### *Sample answer:*

The subsequent titration displays two equivalence points and there is likely the presence of a diprotic base. CO<sub>2</sub> absorption likely occurred according to the following reaction:



From the reaction equation it can be seen that 2NaOH is consumed to form one Na<sub>2</sub>CO<sub>3</sub>. The titration graph displays a greater volume addition between the first and second equivalence points. Up to the first equivalence point, clearly some other base than Na<sub>2</sub>CO<sub>3</sub>(aq) is present. However, it could not be NaOH(aq) because then there would be three equivalence points. This base is actually NaHCO<sub>3</sub> formed from the following acid base reaction:



Between the start and first equivalence point, conversion of Na<sub>2</sub>CO<sub>3</sub> to NaHCO<sub>3</sub> occurs. This corresponds to the amount of Na<sub>2</sub>CO<sub>3</sub> present. From the graph, the volume of acid added to get to the first equivalence point is approximately 16 mL.

$$n(\text{Na}_2\text{CO}_3) = 0.0998 \times 0.016 = 0.00160 \dots \text{ mol}$$

$$[\text{CO}_3^{2-}] = \frac{0.0016 \dots}{0.025} = 0.0639 \dots \text{ mol L}^{-1}$$

Between first and second equivalence point, the conversion of NaHCO<sub>3</sub> to H<sub>2</sub>CO<sub>3</sub>/CO<sub>2</sub> occurs. This corresponds to the amount of NaHCO<sub>3</sub> present *at the first equivalence point* (i.e, total NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>). From the graph, the volume of acid added to get to the second equivalence point is 43 mL. The volume of additional acid from first to second equivalence point is given by 43 – 16 = 27 mL.

$$n(\text{Na}_2\text{CO}_3) + n(\text{NaHCO}_3) = 0.0998 \times 0.027 = 0.00269 \dots \text{ mol}$$

$$n(\text{NaHCO}_3) = 0.00269 \dots - 0.00160 \dots = 0.00109 \dots \text{ mol}$$

$$[\text{HCO}_3^-] = \frac{0.00109 \dots}{0.025} = 0.0439 \dots \text{ mol L}^{-1}$$

Water evaporation occurred by the increase of second equivalence point. Without water evaporation, second equivalence point should not change because 2NaOH converted to Na<sub>2</sub>CO<sub>3</sub> which both consumes 2 protons in titration (Na<sub>2</sub>CO<sub>3</sub> is converted to 2NaHCO<sub>3</sub>, both of which consume two protons in titration).

Now consider the *entire* container. The  $n(\text{H}^+)_{\text{neutr}}$  the container should be able to consume can be calculated from the original titration.

$$v_{\text{titre}} = \frac{26.62 + 26.65 + 26.59}{3} = 26.62 \text{ mL}$$

$$[\text{NaOH}] = 0.1006 \times \frac{0.02662}{0.025} = 0.1071 \dots \text{ mol L}^{-1}$$

$$n(\text{H}^+)_{\text{neutr}} = n(\text{NaOH}) = 0.1071 \dots \times 1.351 = 0.1447 \dots \text{ mol}$$

$$[\text{H}^+]_{\text{neutr}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] = 0.0439 \dots + 2 \times 0.0639 \dots = 0.1716 \dots \text{ mol L}^{-1}$$

$$v_{\text{final}} = \frac{n(\text{H}^+)_{\text{neutr}}}{[\text{H}^+]_{\text{neutr}}} = \frac{0.1447 \dots}{0.1716 \dots} = 0.843 \dots \text{ L}$$

$$v_{\text{evap}} = 1351 - 843 \dots = 508 \text{ mL (3 sf)}$$

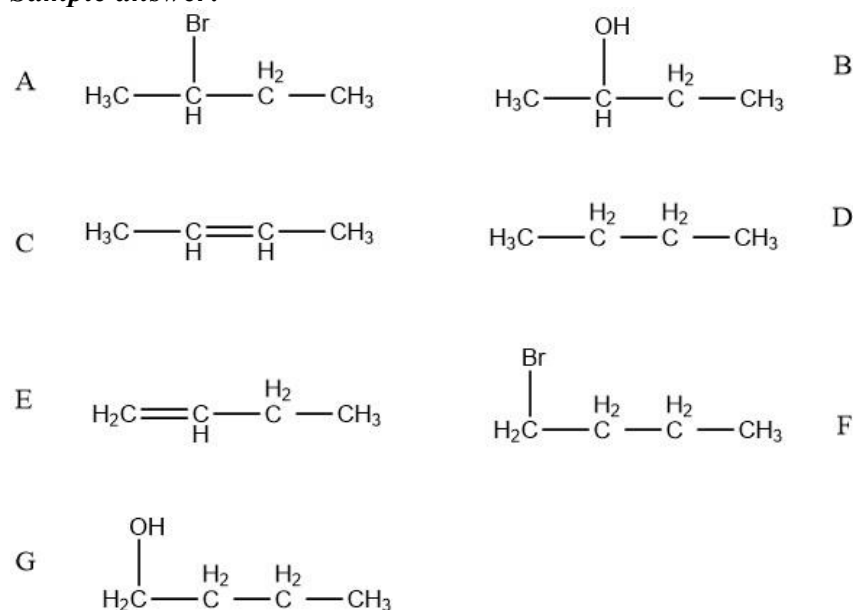
Amount of  $\text{CO}_2$  absorbed is

$$v_{\text{final}} \times ([\text{HCO}_3^-] + [\text{CO}_3^{2-}]) = 0.843 \times (0.0439 \dots + 0.0639 \dots) = 0.0909 \text{ mol (3sf)}$$

### Question 35

Criteria	Marks
• Draws correct structural formulae for all compounds	5
• Draws substantially correct structural formulae demonstrating an understanding of most reactions	3-4
• Draws structural formulae demonstrating an understanding of some different reactions	1-2

**Sample answer:**



**Question 36 (a)**

Criteria	Marks
<ul style="list-style-type: none"> <li>Provides a correct reason</li> </ul>	1

**Sample answer:**

The final products consist of two species which are relatively unlikely to collide and therefore react because the concentration is low, while the complex is one species and with sufficient energy can easily decompose (no collision required).

OR

The activation energy of the reverse reaction for final product formation is much higher than the activation energy for the formation of reactants from the intermediate complex.

**Question 36 (b)**

Criteria	Marks
<ul style="list-style-type: none"> <li>Shows a comprehensive understanding of how pressure and temperature affect the rate of formation of CH<sub>3</sub>O gas</li> </ul>	4
<ul style="list-style-type: none"> <li>Shows an understanding on how some aspects of pressure and temperature may affect the rate of formation of CH<sub>3</sub>O gas</li> </ul>	2-3
<ul style="list-style-type: none"> <li>Provides some information about how pressure and/or temperature may affect the rate of formation of CH<sub>3</sub>O gas</li> </ul>	1

**Sample answer:**

At high temperature (both low and high pressure), tunnelling is less important because the complex has sufficient energy to overcome the barrier to become products. Therefore, the greater the temperature, the greater the rate of product formation, because the easier it is to overcome the energy barrier.

At high pressure and low temperature, collisions reduce the energy of the complex and therefore slow the conversion back to reactants. On the other hand, conversion to products is therefore much more likely as tunnelling still operates and therefore the rate is higher than at higher (but not too much higher) temperatures.

The rate decreases with increasing temperature because conversion of complex to reactants becomes more likely than tunnelling to form products.

At low pressure and low temperature, reduction of energy of the complex by collisions is less likely. There is also not enough energy to readily overcome the activation barrier and too much energy for the complex to be more stable. Therefore, the rate at low temperature and low pressure is expected to be relatively less (or similar) to high temperatures. The rate is expected to be *much less* than at high pressures and low temperatures.

### Question 37

Criteria	Marks
<ul style="list-style-type: none"> <li>Determines the identity of all unknown species</li> <li>Provides correct working</li> </ul>	7
<ul style="list-style-type: none"> <li>Determines the identity of most unknown species</li> <li>Provides most correct working</li> </ul>	5-6
<ul style="list-style-type: none"> <li>Determines the identity of some unknown species</li> <li>Provides some correct working</li> </ul>	3-4
<ul style="list-style-type: none"> <li>Provides some relevant steps</li> </ul>	2
<ul style="list-style-type: none"> <li>Provides some relevant information</li> </ul>	1

#### Sample answer:

Since the precipitate is  $\text{BaSO}_4$  in the precipitometric titration (from the  $K_{\text{sp}}$ ), then A is likely a sulfate, and given the 1:1 molar ratio, having formula  $\text{MSO}_4$  for some unknown element M.

$$n(\text{Ba}^{2+}) = n(\text{SO}_4^{2-}) = n(\text{M}^{2+}) = 0.100 \times 0.04656 = 0.004656$$

$$MM(\text{MSO}_4) = \frac{m(\text{MSO}_4)}{n(\text{MSO}_4)} = \frac{1.000}{0.004656} = 214.8 \text{ g mol}^{-1}$$

$$MM(\text{M}) = MM(\text{MSO}_4) - MM(\text{SO}_4) = 214.8 - (32.07 + 4 \times 16.00) = 118.7 \text{ g mol}^{-1}$$

Hence, the element M is Sn and subsequently the identity of compound A is  $\text{SnSO}_4$ .

Note that the ratio of  $V_{\text{eq}}$  between compound B and A is  $\frac{15.52}{46.56} = \frac{1}{3}$  and therefore the precipitate contains one-third of the amount of sulfate from before.

Hence, compound B has the formula  $\text{Sn}_3\text{SO}_4\text{X}$  for some unknown X. The associated ions are  $\text{Sn}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{X}^{4-}$ . Ammonia acts as a base (there would be too many elements were it a part of compound B) so possibilities for X include  $\text{OH}^-$  and  $\text{O}^{2-}$  and these need to add to a charge of -4.

$$n(\text{B}) = 0.100 \times 0.01552 = 0.001552$$

$$MM(\text{B}) = \frac{m(\text{B})}{n(\text{B})} = \frac{0.7794}{0.001552} = 502.19 \dots \text{ g mol}^{-1}$$

$$MM(\text{X}) = MM(\text{B}) - 3MM(\text{Sn}) - MM(\text{SO}_4) = 502.19 \dots - 3 \times 118.7 - (32.07 + 4 \times 16.00) = 50.02 \dots \text{ g mol}^{-1}$$

$$MM(\text{OH}^-) = 16.00 + 1.008 = 17.008 \text{ g mol}^{-1}$$

$$MM(\text{O}^{2-}) = 16.00 \text{ g mol}^{-1}$$

The logical combination is two hydroxides and one oxide to match molar mass of X as well as its charge of -4. Hence, the identity of compound B is  $\text{Sn}_3(\text{OH})_2\text{OSO}_4$ .

B contains an element C does not. This is consistent with the water evaporation and that C does not have hydrogen. Hence, the identity of compound C is  $\text{Sn}_3\text{O}_2\text{SO}_4$ .

### Question 38

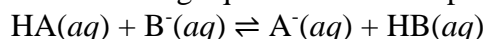
Criteria	Marks
<ul style="list-style-type: none"> <li>Provides a correct method to determine the difference in <math>pK_a</math></li> <li>Shows in detail how calculations can be performed to calculate the difference in <math>pK_a</math></li> </ul>	8
<ul style="list-style-type: none"> <li>Provides a correct method to determine the difference in <math>pK_a</math></li> <li>Shows how calculations can be performed to calculate the difference in <math>pK_a</math></li> </ul>	6-7
<ul style="list-style-type: none"> <li>Provides a portion of a correct method to determine the difference in <math>pK_a</math></li> </ul>	4-5
<ul style="list-style-type: none"> <li>Provides some relevant steps towards the determination of the difference in <math>pK_a</math></li> </ul>	2-3
<ul style="list-style-type: none"> <li>Provides some relevant information</li> </ul>	1

#### Sample answer:

Represent the  $pK_a$ 's of the first carboxylic acid as  $HA$  with  $pK_{a1}$  and the second carboxylic acid as  $HB$  with  $pK_{a2}$ .

Set up an equilibrium system by mixing the two acids and adjusting the pH (such as by adding an appropriate amount of  $NaOH$ ) so that the amounts of  $HA$ ,  $A^-$ ,  $HB$  and  $B^-$  are appreciable.

The following equilibrium is set up:



$$K = \frac{[A^-][HB]}{[HA][B^-]} = \frac{[H^+][A^-][HB]}{[HA][H^+][B^-]} = \frac{K_{a1}}{K_{a2}}$$

$$pK = -\log_{10} \left( \frac{K_{a1}}{K_{a2}} \right) = -\log_{10} K_{a1} - (-\log_{10} K_{a2}) = pK_{a1} - pK_{a2}$$

The relative amounts of protonated and deprotonated forms of each species only need to be determined. This can be done using NMR, such as  $^1H$  NMR on the  $-CH-COOH$ , the chemical shift of which can be expected to differ based on whether the carboxylic acid is protonated or deprotonated.

For each acid, obtain the proton NMR shift for both the protonated and deprotonated forms. For the acid mixture, a single peak will be observed for each species  $HA/A^-$  ( $HA$  and  $A^-$  show up as a single peak) and  $HB/B^-$  ( $HB$  and  $B^-$  show up as a single peak). The chemical shifts in the NMR data can then be used to determine the relevant concentrations and subsequently determine the difference in  $pK_a$ .

**Remark:** Whilst not required in the response, the following is provided to elaborate on the actual calculation.

The peak is the weighted average, with the weights being the concentrations. Let  $\delta_x$  refer to the chemical shift of species  $x$ .

With some manipulation:

$$\delta_{\text{HA/A}^-} = \frac{[\text{HA}]}{[\text{HA}] + [\text{A}^-]} \times \delta_{\text{HA}} + \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} \times \delta_{\text{A}^-} = \frac{\delta_{\text{HA}} + \delta_{\text{A}^-} \frac{[\text{A}^-]}{[\text{HA}]}}{1 + \frac{[\text{A}^-]}{[\text{HA}]}}$$

$$\frac{\delta_{\text{HA}} - \delta_{\text{HA/A}^-}}{\delta_{\text{HA/A}^-} - \delta_{\text{A}^-}} = \frac{[\text{A}^-]}{[\text{HA}]}$$

Similarly

$$\frac{\delta_{\text{HB}} - \delta_{\text{HB/B}^-}}{\delta_{\text{HB/B}^-} - \delta_{\text{B}^-}} = \frac{[\text{B}^-]}{[\text{HB}]}$$

Since  $\delta_{\text{HA/A}^-}$ ,  $\delta_{\text{HA}}$ ,  $\delta_{\text{A}^-}$ ,  $\delta_{\text{HB/B}^-}$ ,  $\delta_{\text{HB}}$  and  $\delta_{\text{B}^-}$  can be obtained from the NMR then  $\frac{[\text{A}^-]}{[\text{HA}]}$  and  $\frac{[\text{B}^-]}{[\text{HB}]}$  can be calculated.

This subsequently gives the value of  $K$  and therefore the value of  $pK$  which provides the desired difference in  $pK_a$ 's.

Acid/base can be added to obtain multiple values for the difference in  $pK_a$ 's which can then be averaged to get an empirical value.