Write your name here

Surname	Other names

Pearson Edexcel
International Advanced Level

Centre Number | Candidate Number

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Tuesday 14 June 2016 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH04/01

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided – *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets – *use this as a guide as to how much time to spend on each question.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

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5/6/3/3/1/

P 4 6 6 6 4 A 0 1 2 8

PEARSON

SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 Consider the reaction

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

This is an example of

☐ **A** acylation.

☐ **B** hydrolysis.

☐ **C** neutralization.

☐ **D** substitution.

(Total for Question 1 = 1 mark)

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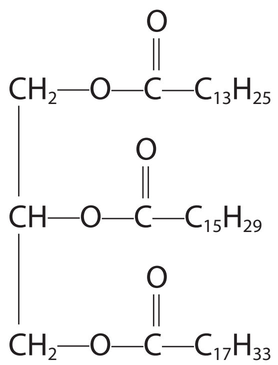
2 The formula of a compound present in some vegetable oils is shown below.



Which alcohol is produced when this oil is hydrolysed?

☐ **A** Methanol

☐ **B** Ethanol

☐ **C** Propan-1-ol

☐ **D** Propane-1,2,3-triol

(Total for Question 2 = 1 mark)

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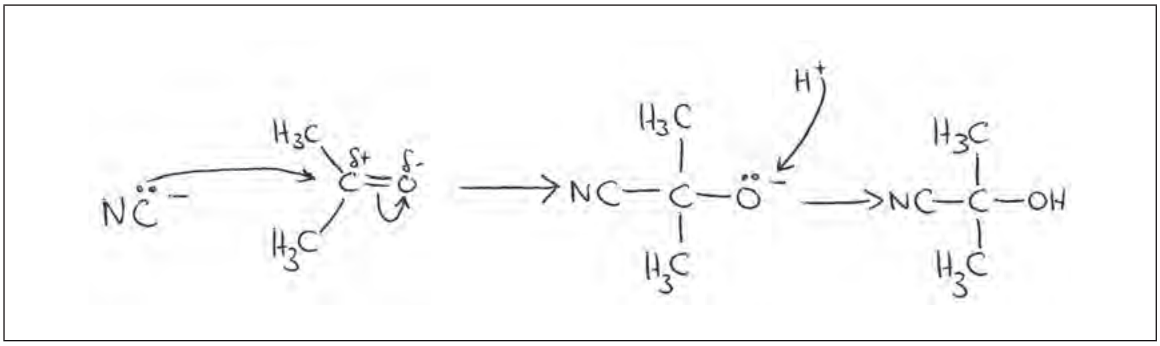
3 This question is about the reaction of cyanide ions with a ketone.

(a) A student wrote the reaction mechanism shown below.



What is the error in this mechanism?

(1)

☒ **A** The direction of the curly arrow from the cyanide ion.

☒ **B** The direction of the curly arrow from the hydrogen ion.

☒ **C** The dipole on the atoms in the carbonyl bond.

☒ **D** The structure of the intermediate ion.

(b) The mechanism for the reaction between cyanide ions and ketones has similarities to the mechanism for the reaction between hydroxide ions and **primary** halogenoalkanes.

Both mechanisms

(1)

☒ **A** involve initial attack by a nucleophile.

☒ **B** result in the formation of optical isomers.

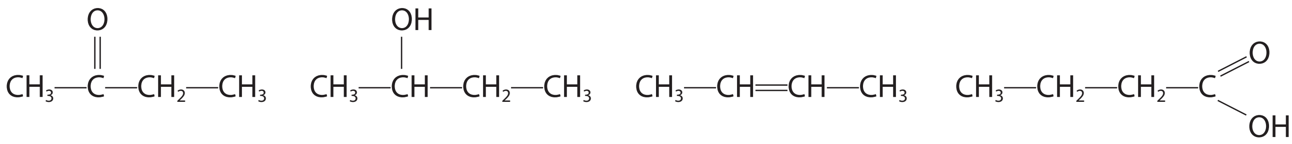
☒ **C** involve attack from above or below a planar structure.

☒ **D** produce a racemic mixture.

(Total for Question 3 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

4 All of the following molecules have four carbon atoms.



P **Q** **R** **S**

(a) Which of these molecules would react with sodium?

(1)

- ☒ **A** Q only
- ☒ **B** S only
- ☒ **C** Q and S only
- ☒ **D** P and R only

(b) Which of these molecules would give a positive result for the iodoform test?

(1)

- ☒ **A** P only
- ☒ **B** Q only
- ☒ **C** P and Q only
- ☒ **D** R and S only

(c) Which of these molecules would give a positive result when tested with 2,4-dinitrophenylhydrazine?

(1)

- ☒ **A** P only
- ☒ **B** Q only
- ☒ **C** R only
- ☒ **D** P and S only

(d) Which of these molecules would be oxidized by ammoniacal silver nitrate (Tollen's reagent)?
(1)

- ☒ **A** P only
- ☒ **B** Q only
- ☒ **C** R only
- ☒ **D** None of P, Q, R or S

(e) Which of these molecules would be reduced with lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether to form a **primary** alcohol?
(1)

- ☒ **A** P
- ☒ **B** Q
- ☒ **C** R
- ☒ **D** S

(Total for Question 4 = 5 marks)

---

5 Which of the following compounds reacts with phosphorus(V) chloride to form propanoyl chloride?

- ☒ **A** $CH_3CH_2CH_2OH$
- ☒ **B** $CH_3CH_2CH_2CH_2OH$
- ☒ **C** CH_3CH_2COOH
- ☒ **D** $CH_3CH_2CH_2COOH$

(Total for Question 5 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

6 Chromatography is a chemical technique used to analyse mixtures.

(a) A component of a mixture will move more quickly through a gas chromatography column if it has

(1)

☒ **A** higher molar mass.

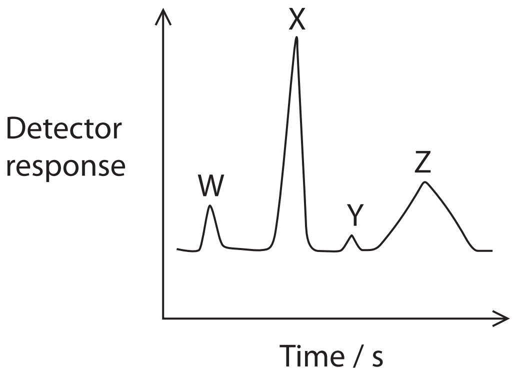
☒ **B** stronger interactions with the stationary phase.

☒ **C** lower adsorption to the stationary phase.

☒ **D** lower volatility.

(b) A mixture of four substances was separated using HPLC. The separation was carried out using a polar stationary phase and a non-polar mobile phase.

The chromatogram produced is shown below.



Which of the four substances is likely to be the **least** polar?

(1)

☒ **A** W

☒ **B** X

☒ **C** Y

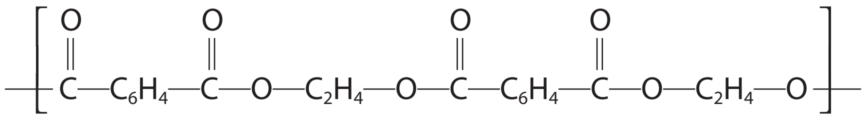
☒ **D** Z

(Total for Question 6 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

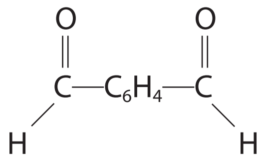
7 Polyesters are condensation polymers.

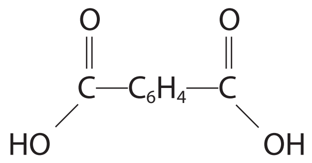
(a) PET, polyethylene terephthalate, is an example of a polyester.
Part of this polymer is shown below.

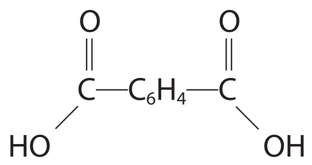


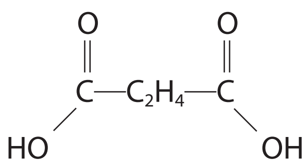
Which of the following could be the monomers of this polymer?

(1)

☒ **A**  and HO—C_2H_4—OH

☒ **B**  and C_2H_4

☒ **C**  and HO—C_2H_4—OH

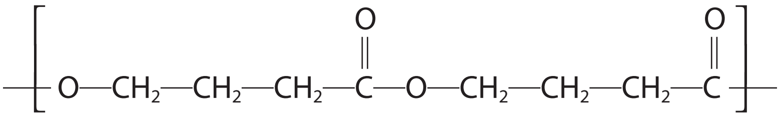
☒ **D** HO—C_6H_4—OH and 

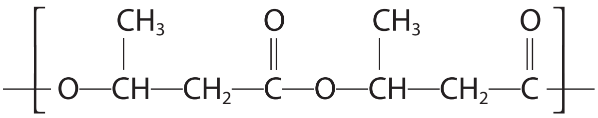
Use this space for any rough working. Anything you write in this space will gain no credit.

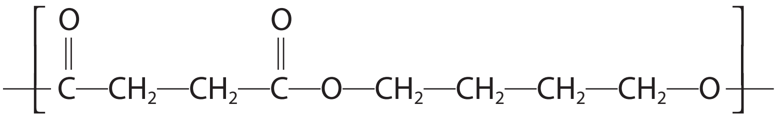
(b) Another polyester, PHB, is made from a single monomer, 3-hydroxybutanoic acid.

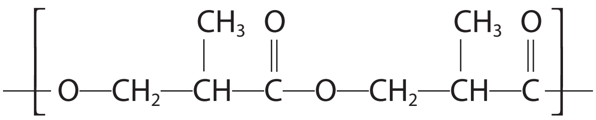
Which of the following correctly represents a section of this polymer?

(1)

☒ **A** 

☒ **B** 

☒ **C** 

☒ **D** 

(Total for Question 7 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

8 Buffers are vital in the maintenance of a relatively stable pH in the human body.
One of these is the carbonic acid-hydrogencarbonate buffer.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

(a) Given the formula above, calculate the pH of a solution at 38°C when

$pK_a = 6.1$ $[HCO_3^-] = 3.51 \times 10^{-4}$ mol dm^{-3} $[H_2CO_3] = 3.15 \times 10^{-5}$ mol dm^{-3}

(1)

☒ **A** 5.05

☒ **B** 5.14

☒ **C** 7.05

☒ **D** 7.15

(b) Carbonic acid is formed by dissolving carbon dioxide in water.
This equilibrium is represented by the following equation.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

If carbon dioxide is removed from this equilibrium mixture, the pH will

(1)

☒ **A** decrease.

☒ **B** increase.

☒ **C** remain approximately constant because the concentration of the hydrogencarbonate ions changes to compensate.

☒ **D** remain approximately constant because the concentration of the carbonic acid changes to compensate.

(Total for Question 8 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

9 The Ostwald Process is a method for making nitric acid. The equation for the first stage of this process is

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H = -905 \text{ kJ mol}^{-1}$$

(a) Which of the following would both **decrease** the equilibrium yield of nitrogen monoxide?

(1)

☒ **A** Increasing both the pressure and the temperature.

☒ **B** Decreasing both the pressure and the temperature.

☒ **C** Decreasing the pressure and increasing the temperature.

☒ **D** Increasing the pressure and decreasing the temperature.

(b) For this stage of the process, the catalyst is an alloy of platinum and rhodium. A pressure of between 4 and 10 atm and a temperature of 1150 K are used. Unreacted reactants are recycled.

Which one of the following changes will affect the value of the equilibrium constant, K_p?

(1)

☒ **A** Increasing the surface area of the platinum-rhodium catalyst.

☒ **B** Increasing the pressure above 10 atm.

☒ **C** Not recycling unreacted reactants.

☒ **D** Decreasing the temperature below 1150 K.

(Total for Question 9 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

10 An equilibrium can be established when a solute dissolves in two different solvents which are immiscible. The equilibrium constant, known as the partition coefficient, indicates the distribution of the solute between the two solvents.

This question is about ammonia dissolving in water and in trichloromethane when the equilibrium is

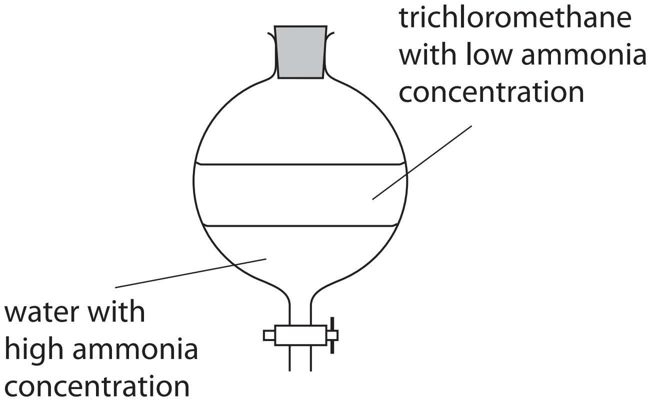
$$NH_3(\text{trichloromethane}) \rightleftharpoons NH_3(aq)$$

Ammonia is more soluble in water than in trichloromethane.

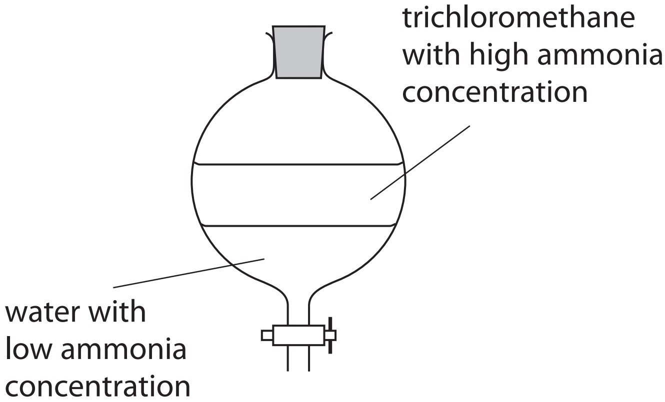
The density of trichloromethane is 1.48 g cm^{-3}. The density of water is 1.00 g cm^{-3}.

(a) Which of the following diagrams is correct for this system of equilibrium?

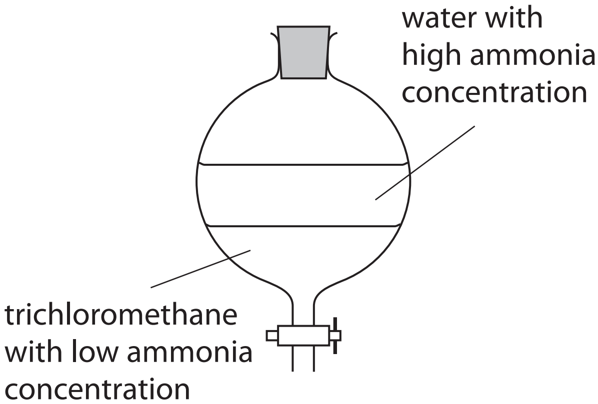
(1)



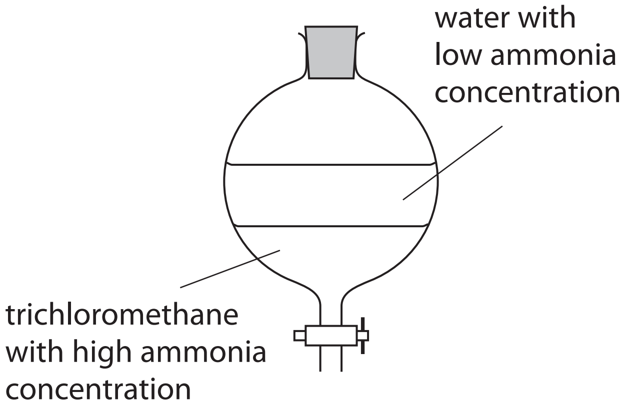
☒ **A**



☒ **B**



☒ **C**



☒ **D**

(b) At 25°C when ammonia is dissolved in a mixture of water and trichloromethane, the equilibrium concentration of ammonia in water is 1.02 mol dm^{-3} and in trichloromethane is 0.045 mol dm^{-3}.

$$NH_3\text{(trichloromethane)} \rightleftharpoons NH_3\text{(aq)}$$

What is the value of the equilibrium constant for this system?

(1)

- ☒ **A** 0.0441
- ☒ **B** 0.975
- ☒ **C** 1.065
- ☒ **D** 22.7

(Total for Question 10 = 2 marks)

TOTAL FOR SECTION A = 20 MARKS

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SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

11 Carbonic acid is a weak acid which dissociates in two stages.

Stage 1 $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$ $K_{a1} = 4.17 \times 10^{-7}$ mol dm^{-3}

Stage 2 $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$ $K_{a2} = 4.79 \times 10^{-11}$ mol dm^{-3}

(a) Write the K_a expressions for

(2)

Stage 1 K_{a1} =

Stage 2 K_{a2} =

(b) A solution of carbonic acid has an initial concentration of 0.100 mol dm^{-3}.

$$K_{a1} = 4.17 \times 10^{-7} \text{ mol dm}^{-3}$$

(i) Use K_{a1} to calculate the equilibrium concentration, in mol dm^{-3}, of the hydrogencarbonate ions, HCO_3^-. Give your answer to **three** significant figures.

(2)

(ii) Use your answer to (b)(i) to calculate the pH of this solution.

(1)

*(iii) State the **three** assumptions you have made in your calculations in (b)(i) and (b)(ii).

(3)

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(c) Carbonic acid forms two types of salt: carbonates and hydrogencarbonates.

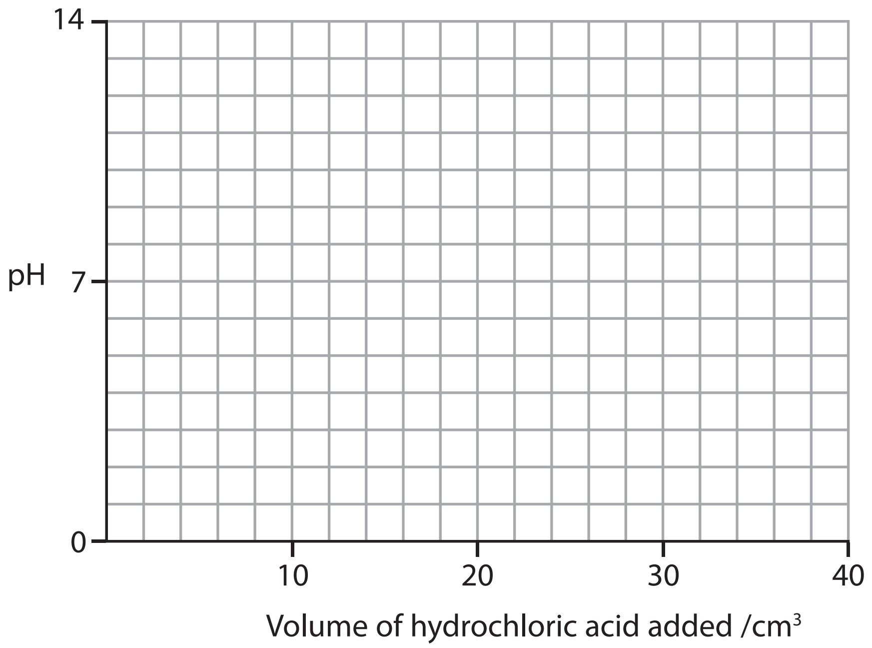
A solution of sodium carbonate is titrated with hydrochloric acid.

On the grid below, sketch the likely shape of the titration curve during this reaction given that:

- carbonates require **two** moles of H^+ ions per mole of carbonate for complete reaction
- 10 cm^3 of sodium carbonate with a concentration of 0.100 mol dm^{-3} is used
- the sodium carbonate solution has a pH of 11.3
- 40 cm^3 of hydrochloric acid with a concentration of 0.100 mol dm^{-3} is added
- pK_{a1} = 6.4 and pK_{a2} = 10.3

Clearly label any equivalence points in the sketch.

(5)



(Total for Question 11 = 13 marks)

12 This is a question about entropy changes.

(a) Consider the reaction between solid ammonium carbonate and pure ethanoic acid. The equation for this reaction is

$$(NH_4)_2CO_3(s) + 2CH_3COOH(l) \rightarrow 2CH_3COONH_4(s) + H_2O(l) + CO_2(g)$$

(i) State what you would observe as this reaction occurs.

(1)

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*(ii) Predict the sign of the entropy change of the system, $\Delta S^{\ominus}_{\text{system}}$.
Fully justify your answer. No calculation is required.

(2)

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(b) The rhombic allotrope of sulfur reacts with fluorine to produce sulfur hexafluoride:

$$S(s,\ rhombic)\ +\ 3F_2(g)\ \rightarrow\ SF_6(g) \qquad \Delta H_f^{\ominus} = -1209\ kJ\ mol^{-1}$$

(i) Use the standard molar entropies on pages 2, 3 and 29 of the Data Booklet to calculate the standard molar entropy change of the system ($\Delta S^{\ominus}_{system}$) for this reaction. Include a sign and units in your answer.

Note that the standard molar entropies of the elements are given **per atom** so that the standard molar entropy of fluorine, $S^{\ominus}[\frac{1}{2}F_2(g)] = +158.6\ J\ mol^{-1}\ K^{-1}$.

(2)

(ii) Use the value of the standard enthalpy change of formation ($\Delta H_f^{\ominus}$) given above to calculate the entropy change of surroundings ($\Delta S^{\ominus}_{surroundings}$) for this reaction at 298 K. Include a sign and units in your answer.

(2)

(iii) Use your answers to (b)(i) and (b)(ii) to calculate the total entropy change ($\Delta S^{\ominus}_{total}$) for the formation of one mole of sulfur hexafluoride.
Include a sign and units in your answer.

(1)

(iv) What would be the effect, if any, of an increase in temperature on the value of $\Delta S^{\ominus}_{total}$ calculated in (b)(iii)? Justify your answer and state any assumptions that you have made.

(3)

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(c) The equations for dissolving two sulfates are shown below.

$$MgSO_4(s) + aq \rightleftharpoons Mg^{2+}(aq) + SO_4^{2-}(aq) \qquad \Delta S^{\ominus}_{total} = +20\ J\ mol^{-1}\ K^{-1}$$

$$BaSO_4(s) + aq \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad \Delta S^{\ominus}_{total} = -190\ J\ mol^{-1}\ K^{-1}$$

(i) Compare the values of the total entropy changes for dissolving these two sulfates and show that they are consistent with the trend in the solubility of Group 2 sulfates.

(2)

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(ii) The values of the total entropy change and the equilibrium constant of a reaction are related by the following equation.

$$\Delta S_{total} = R \ln K$$

Calculate the value of the equilibrium constant, K, for the dissolving of magnesium sulfate at 298 K.

$$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

(1)

(Total for Question 12 = 14 marks)

13 This is a question about using the Landolt Iodine Clock to study the reaction kinetics of iodate(V) ions reacting with hydrogensulfate(IV) ions.

Reaction 1 $IO_3^-(aq) + 3HSO_3^-(aq) \rightarrow I^-(aq) + 3HSO_4^-(aq)$

One version of this clock involves the iodide ions formed reacting rapidly with the iodate(V) ions in acid solution to form iodine:

Reaction 2 $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$

The iodine is immediately reduced to iodide by the hydrogensulfate(IV) ions:

Reaction 3 $I_2(aq) + HSO_3^-(aq) + H_2O(l) \rightarrow 2I^-(aq) + HSO_4^-(aq) + 2H^+(aq)$

Once all of the hydrogensulfate(IV) ions have been used up, then the iodine reacts with starch to produce a blue-black complex.

(a) What would be the problem if the amount of hydrogensulfate(IV) ions were in excess?

(1)

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(b) Why is it important that **Reaction 2** and **Reaction 3** are very much faster than **Reaction 1**?

(1)

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....

(c) A series of experiments is carried out in which different volumes of the iodate(V) ions solution are used.

(i) Why is it important that the temperature is kept constant?

(1)

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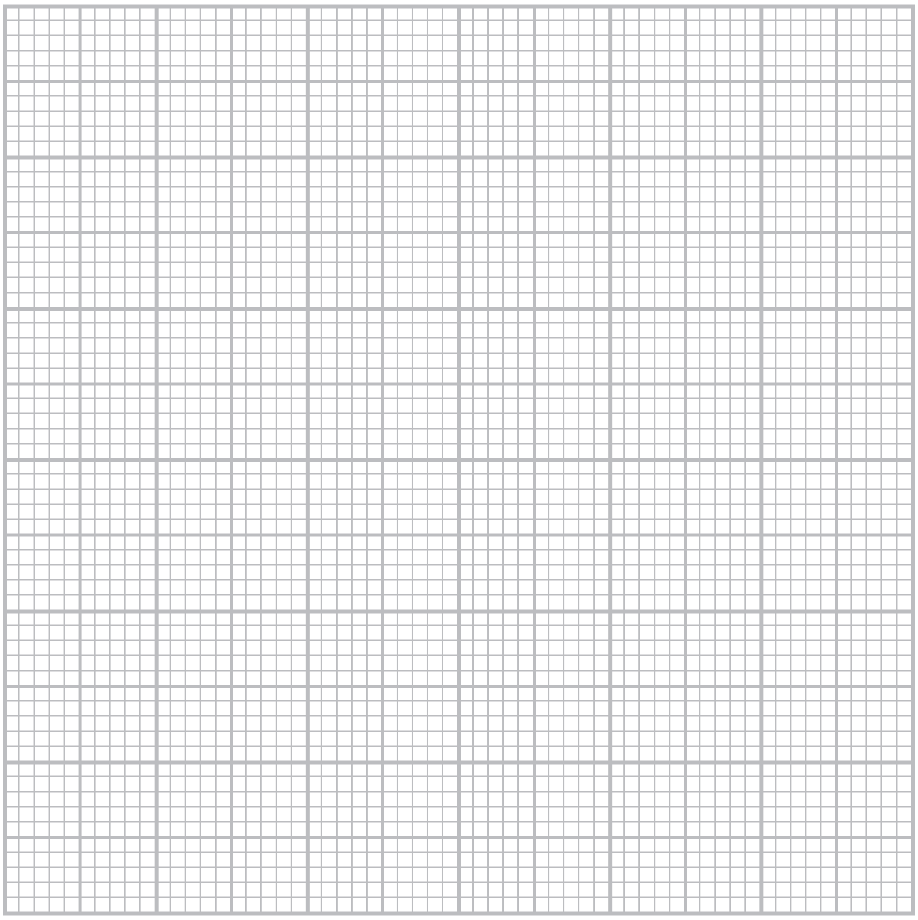
(ii) It is assumed that the initial rate of reaction is proportional to 1/time taken for the blue-black complex to form.

The following results are obtained.

Complete the table and use the results to plot a graph of 1000/time on the vertical axis, against the volume of iodate(V) ions on the horizontal axis.

(5)

Volume of $IO_3^-(aq)$ / cm^3	10.0	8.0	6.0	5.0	4.0	2.0
Time taken, t / s	180	200	300	357	444	900
1000 t / s^{-1}	5.56	5.00	3.33	2.80	2.25	



(iii) Suggest a suitable piece of apparatus for measuring the volume of the solution containing iodate(V) ions.

(1)

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(iv) If the total volume of the reaction mixture is kept constant, the volume of the iodate(V) ion solution may be used instead of the concentration to plot the graph.

Explain why this is possible

(1)

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(v) Deduce the order of the reaction with respect to iodate(V) ions.

Justify your answer.

(2)

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(vi) **Reaction 1** is first order with respect to hydrogensulfate(IV) ions.
Outline how you would show this.

(1)

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(vii) Write the rate equation for **Reaction 1**.
State the units of the rate constant.

(2)

Rate equation:

Units of rate constant ....

(d) The Landolt Iodine Clock can be used to determine the activation energy of **Reaction 1** using the equation:

$$\ln \text{rate} = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$$

(i) State the experimental measurements you would make to provide the numerical data for the calculation of the activation energy.

(1)

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(ii) Describe how you would use your experimental measurements to obtain a value for the activation energy.

You should include

- how the data are processed
- the graph you would plot and its expected shape
- how the activation energy of the reaction can be calculated from the graph produced.

(6)

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(Total for Question 13 = 22 marks)

TOTAL FOR SECTION B = 49 MARKS

DO NOT WRITE IN THIS AREA

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

14 Butanedione has two carbonyl groups. It is a volatile yellow-green liquid and its colour is due to electron delocalisation.

Butanedione can be reduced to butane-2,3-diol which does not have this electron delocalisation.

(a) Identify a suitable reagent for this reduction and complete the equation for the reaction.

(3)

Reagent ....

$CH_3COCOCH_3$ + ... [H] $\rightarrow$

butanedione butane-2,3-diol

(b) Suggest what you would see when this reaction occurs.

(1)

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(c) (i) A mixture of butanedione and butane-2,3-diol can be separated by distillation.

State which compound will have the higher boiling temperature. Justify your answer.

(1)

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(ii) Explain why both compounds are soluble in water.

(1)

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(d) Butane-2,3-diol shows a type of stereoisomerism that butanedione does not. State this type of stereoisomerism and describe how it arises.

(2)

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(e) Butane-2,3-diol can be esterified using excess propanoic acid.

(i) Suggest an alternative reagent to propanoic acid which would react with butane-2,3-diol to form the same ester.

State **two** of the ways in which the esterification reaction will be different with the use of your chosen reagent.

(3)

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(ii) Draw the **skeletal** formula of the ester produced from butane-2,3-diol and **excess** propanoic acid.

(2)

(f) Use the Data Booklet to state **two** differences between the infrared spectra of butanedione and butane-2,3-diol. Include the wave numbers of the relevant groups or bonds.

(2)

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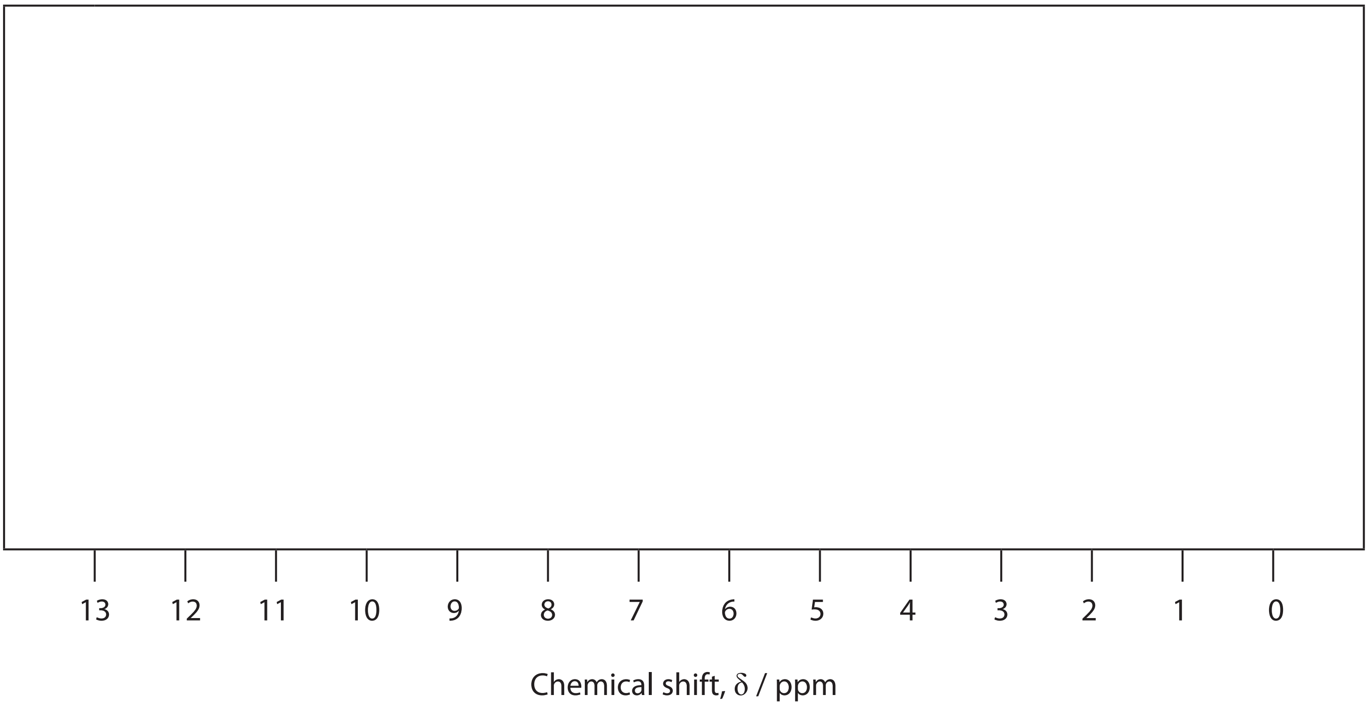
*(g) Use chemical shift data from the Data Booklet to sketch the **high** resolution proton nmr spectrum for propanoic acid. The peaks do not overlap.

Explain the number of peaks, their splitting pattern and the ratio of the areas under each set of peaks.

(5)



(h) State the type of radiation that is used to create the nmr spectrum.

(1)

(Total for Question 14 = 21 marks)

TOTAL FOR SECTION C = 21 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

Key

relative atomic mass **atomic symbol** name atomic (proton) number

1 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (8) (18)
							1.0 **H** hydrogen 1										4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12											27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 **Ce** cerium 58	141 **Pr** praseodymium 59	144 **Nd** neodymium 60	[147] **Pm** promethium 61	150 **Sm** samarium 62	152 **Eu** europium 63	157 **Gd** gadolinium 64	159 **Tb** terbium 65	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	232 **Th** thorium 90	[231] **Pa** protactinium 91	238 **U** uranium 92	[237] **Np** neptunium 93	[242] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[245] **Bk** berkelium 97	[251] **Cf** californium 98	[254] **Es** einsteinium 99	[253] **Fm** fermium 100	[256] **Md** mendelevium 101	[254] **No** nobelium 102	[257] **Lr** lawrencium 103