Write your name here

Surname	Other names

Edexcel GCE

Centre Number	Candidate Number

Chemistry

Advanced

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

Wednesday 26 January 2011 – Morning
Time: 1 hour 40 minutes

Paper Reference
6CH04/01

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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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 Methods for investigating reaction rates include

A colorimetry.

B measurement of change in volume.

C measurement of change of mass.

D quenching followed by titrating with acid.

Which method would be most suitable to investigate the rate of the following reactions?

(a) $HCOOCH_3(aq) + NaOH(aq) \rightarrow HCOONa(aq) + CH_3OH(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) $(CH_3)_2C{=}CH_2(g) + HI(g) \rightarrow (CH_3)_3CI(g)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 1 = 3 marks)

2 $2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$

This reaction is first order with respect to hydrogen and second order with respect to nitrogen(II) oxide.

By what factor will the initial rate increase if the concentration of hydrogen and nitrogen(II) oxide are both tripled?

☒ **A** 3

☒ **B** 9

☒ **C** 12

☒ **D** 27

(Total for Question 2 = 1 mark)

3 Which reaction has the most positive entropy change for the system, ΔS_{system}?

☒ **A** $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

☒ **B** $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

☒ **C** $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(l)$

☒ **D** $C_4H_{10}(g) \rightarrow C_2H_4(g) + C_2H_6(g)$

(Total for Question 3 = 1 mark)

4 Barium carbonate decomposes in an endothermic reaction when heated to 1500 K.

$$BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$$

What are the signs of the entropy changes at 1500 K?

		ΔS_{system}	$\Delta S_{surroundings}$
☒	**A**	+	+
☒	**B**	+	–
☒	**C**	–	+
☒	**D**	–	–

(Total for Question 4 = 1 mark)

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

5 What are the units of K_c for the following equilibrium?

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

☒ **A** atm

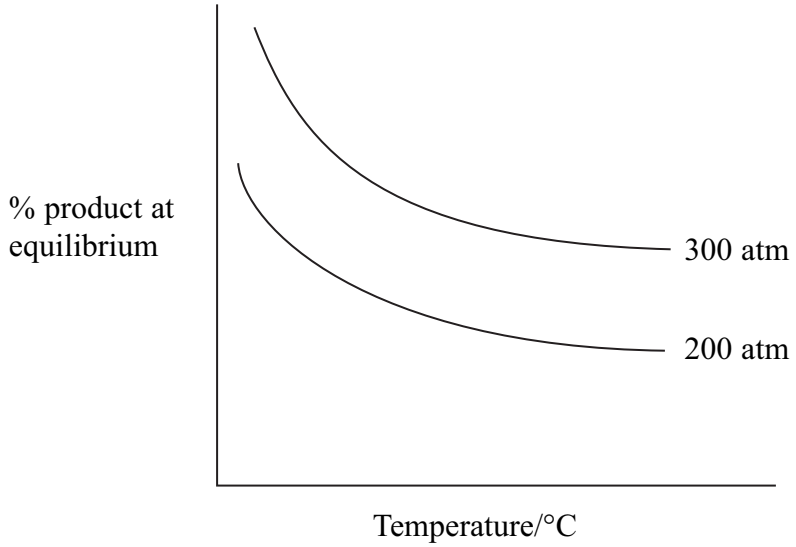
☒ **B** atm^{-1}

☒ **C** $dm^3\,mol^{-1}$

☒ **D** $mol\,dm^{-3}$

(Total for Question 5 = 1 mark)

6 The graph below shows the yield of product in a gaseous equilibrium at different temperatures and pressures.



The forward reaction in the equilibrium is

☒ **A** exothermic, and the number of moles of gas is increasing.

☒ **B** endothermic, and the number of moles of gas is increasing.

☒ **C** exothermic, and the number of moles of gas is decreasing.

☒ **D** endothermic, and the number of moles of gas is decreasing.

(Total for Question 6 = 1 mark)

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

7 Hydrogen cyanide, HCN, reacts with propanal, CH_3CH_2CHO, in the presence of potassium cyanide, KCN.

(a) The mechanism for this reaction is

(1)

☒ **A** nucleophilic addition.

☒ **B** nucleophilic substitution.

☒ **C** electrophilic addition.

☒ **D** electrophilic substitution.

(b) The first stage of the mechanism of this reaction is

(1)

☒ **A** the lone pair of electrons on carbon in CN^- attacking $C^{\delta+}$ of propanal.

☒ **B** the lone pair of electrons on nitrogen in CN^- attacking $C^{\delta+}$ of propanal.

☒ **C** the lone pair of electrons on oxygen in propanal attacking $C^{\delta+}$ of HCN.

☒ **D** the lone pair of electrons on oxygen in propanal attacking $H^{\delta+}$ in HCN.

(c) The product of the reaction is

(1)

☒ **A** 1-hydroxypropanenitrile.

☒ **B** 2-hydroxypropanenitrile.

☒ **C** 1-hydroxybutanenitrile.

☒ **D** 2-hydroxybutanenitrile.

(Total for Question 7 = 3 marks)

8 Which of the following does not have hydrogen bonding in a pure sample, but forms hydrogen bonds with water when it dissolves?

☒ **A** Propane

☒ **B** Propanal

☒ **C** Propanol

☒ **D** Propanoic acid

(Total for Question 8 = 1 mark)

9 Which of the following has both optical and E-Z isomers?

☒ **A** $ClCH_2CHClCH{=}CH_2$

☒ **B** $CH_2{=}CClCH_2CH_2Cl$

☒ **C** $ClCH_2CH{=}CHCH_2Cl$

☒ **D** $CHCl{=}CHCHClCH_3$

(Total for Question 9 = 1 mark)

10 One optically active isomer of 2-chlorobutane reacts with hydroxide ions to form butan-2-ol.

$$C_2H_5CHClCH_3 + OH^- \rightarrow C_2H_5CH(OH)CH_3 + Cl^-$$

The organic product is a **mixture** of enantiomers because

☒ **A** butan-2-ol contains a chiral carbon atom.

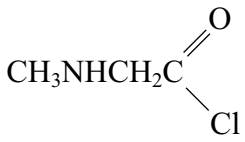
☒ **B** the reaction is a nucleophilic substitution.

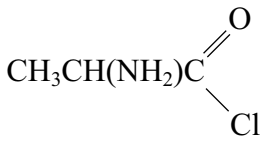
☒ **C** 2-chlorobutane forms a carbocation intermediate.

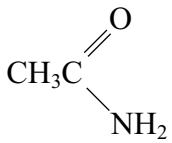
☒ **D** 2-chlorobutane forms a five-bonded transition state.

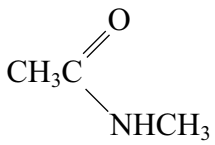
(Total for Question 10 = 1 mark)

11 The organic product of the reaction between ethanoyl chloride and methylamine has the formula

☒ **A** 

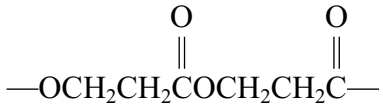
☒ **B** 

☒ **C** 

☒ **D** 

(Total for Question 11 = 1 mark)

12 A section of a polymer is shown below. Which of the following monomers would form this polymer?



☒ **A** $HOCH_2CH_2OH$ and $ClCOCH_2CH_2COCl$

☒ **B** $HOCH_2CH_2OH$ and $HOOCCH_2CH_2COOH$

☒ **C** $ClCH_2CH_2COCl$ alone

☒ **D** $HOCH_2CH_2COOH$ alone

(Total for Question 12 = 1 mark)

13 Which of the following is **not** a reaction of a Brønsted-Lowry acid and base?

☒ **A** $CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$

☒ **B** $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$

☒ **C** $H_2O + HSO_4^- \rightarrow H_2SO_4 + OH^-$

☒ **D** $HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+$

(Total for Question 13 = 1 mark)

14 A buffer solution is made from ammonia and ammonium chloride. When a small amount of acid is added to this buffer

☒ **A** hydrogen ions in the acid combine with chloride ions to make HCl.

☒ **B** hydrogen ions in the acid combine with NH_3 to make NH_4^+.

☒ **C** NH_4^+ ions dissociate to make more NH_3.

☒ **D** the hydrogen ions in the acid prevent dissociation of the NH_4Cl.

(Total for Question 14 = 1 mark)

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

15 Information about four samples of acid is shown below.

Sample 1: 1.0 mol dm^{-3} HCl

Sample 2: 1.0 mol dm^{-3} H_2SO_4

Sample 3: 0.1 mol dm^{-3} HCl

Sample 4: 0.1 mol dm^{-3} CH_3COOH

Which of the following lists shows the samples in order of increasing pH?

☒ **A** 1, 2, 3, 4

☒ **B** 4, 3, 2, 1

☒ **C** 2, 1, 3, 4

☒ **D** 4, 3, 1, 2

(Total for Question 15 = 1 mark)

16 Which reaction has an enthalpy change equal to the enthalpy of hydration of the sodium ion?

☒ **A** $Na^+(g)$ + excess $H_2O(l) \rightarrow Na^+(aq)$

☒ **B** $Na^+(g)$ + 1 mol of $H_2O(l) \rightarrow Na^+(aq)$

☒ **C** $Na^+(s)$ + excess $H_2O(l) \rightarrow Na^+(aq)$

☒ **D** $Na^+(s)$ + 1 mol of $H_2O(l) \rightarrow Na^+(aq)$

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

17 Hydrogen can be manufactured by reacting methane with steam, as shown in the equation below.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H^{\ominus}_{298} = +206.1\,\text{kJ mol}^{-1}$$

Use these values:

the standard entropy of 1 mol of $H_2(g)$ is $(2 \times 65.3) = 130.6\,\text{J mol}^{-1}\,\text{K}^{-1}$
the standard entropy of 1 mol of $H_2O(g)$ is $188.7\,\text{J mol}^{-1}\,\text{K}^{-1}$

You will also need to refer to the data booklet in the calculations which follow.

(a) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{\text{system}}$, for this reaction at 298 K.

(2)

(b) Calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, for this reaction at 298 K. Include a sign and units in your answer.

(2)

(c) Calculate the total entropy change, $\Delta S^{\ominus}_{\text{total}}$, for this reaction at 298 K.

Explain why this value shows that the reaction is not spontaneous at this temperature.

(2)

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(d) The composition of an equilibrium mixture produced at 2.0 atmospheres pressure and at a much higher temperature is shown below.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Amount in equilibrium mixture / mol	0.80	0.80	1.20	3.60

*(i) Write the expression for the equilibrium constant, K_p, of the reaction and calculate its value. Include units in your answer.

(6)

(ii) The total entropy change in J mol^{-1} K^{-1} is related to the equilibrium constant by the equation

$$\Delta S^{\ominus}_{total} = R \ln K_p \quad \text{or} \quad \Delta S^{\ominus}_{total} = 2.3R \log K_p$$

Calculate the total entropy change at the temperature of the reaction.

[R = 8.31 J mol^{-1} K^{-1}]

(1)

(iii) Calculate the temperature at which this equilibrium is reached using your answer to (ii) for $\Delta S^{\ominus}_{\text{total}}$. Assume that ΔH is still +206.1 kJ mol^{-1} and that $\Delta S^{\ominus}_{\text{system}}$ = +225 J K^{-1} mol^{-1}. (This is not the same as the value for $\Delta S^{\ominus}_{\text{system}}$ calculated in (a) which is at 298 K.)

(2)

*(e) Use the magnitude and signs of the entropy changes to explain the effect of a temperature increase on the equilibrium constant of this endothermic reaction.

(2)

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(Total for Question 17 = 17 marks)

18 (a) Calculate the pH of 0.25 mol dm^{-3} hydrochloric acid.

(1)

(b) Propanoic acid, CH_3CH_2COOH, is a weak acid with $K_a = 1.3 \times 10^{-5}$ mol dm^{-3} at 25 °C.

(i) Write the expression for K_a for propanoic acid.

(1)

(ii) Calculate the pH of 0.25 mol dm^{-3} propanoic acid at 25 °C.

(2)

(c) During a titration, 10 cm^3 0.10 mol dm^{-3} sodium hydroxide was added to 10 cm^3 of 0.25 mol dm^{-3} propanoic acid.

(i) Write an equation for the reaction which occurs. State symbols are **not** required.

(1)

(ii) At this point the titration mixture contains 1.5×10^{-3} moles of propanoic acid and 1.0×10^{-3} moles of propanoate ion.

Use your expression for K_a for propanoic acid to calculate the pH of the mixture.

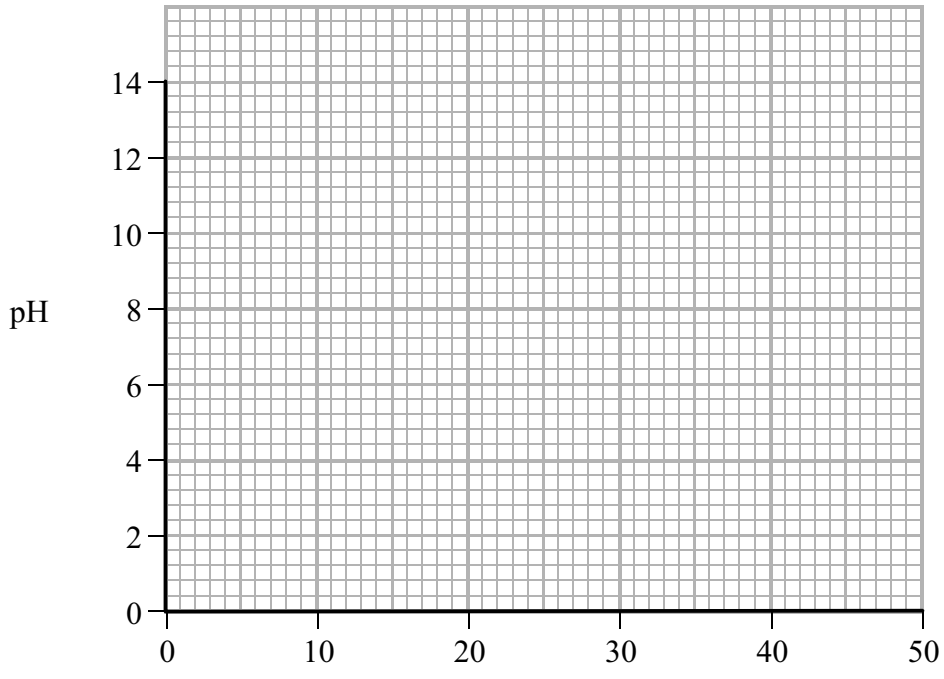
(2)

*(iii) When a further small amount of 0.10 mol dm^{-3} sodium hydroxide is added in the titration, the pH changes very little. Explain why the pH change is small.

(3)

(iv) Draw the titration curve showing the change in pH when 0.10 mol dm^{-3} sodium hydroxide is added to 10 cm^3 of 0.25 mol dm^{-3} propanoic acid until present in excess. The equivalence point is 25 cm^3.

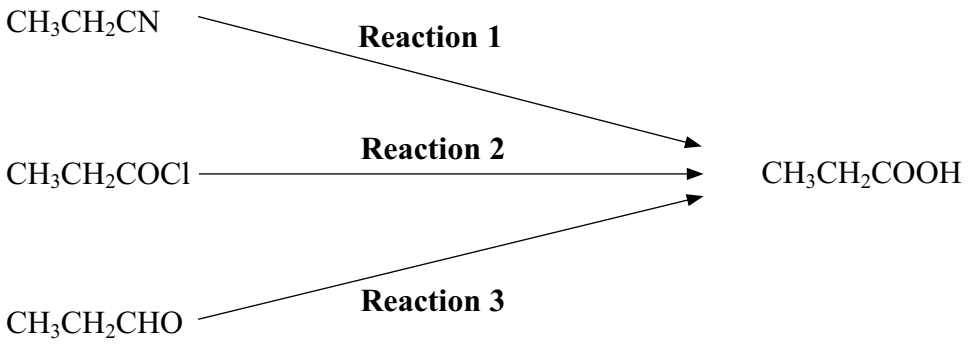
(3)



(v) Explain, referring to your data booklet, whether bromocresol green would be a suitable indicator for this titration.

(2)

(d) Propanoic acid is produced in the reactions shown below.



(i) Suggest a reagent which could be used to carry out **reaction 1**.

(1)

(ii) Write an equation for **reaction 2**. State symbols are **not** required.

(1)

(iii) What would be observed if **reaction 3** was carried out using potassium dichromate(VI) and sulfuric acid?

(1)

(e) What type of reagent would be used to convert propanoic acid to propan-1-ol? Identify a suitable reagent for this reaction.

(2)

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(Total for Question 18 = 20 marks)

19 A student investigated the reaction between iodine and propanone in acidic conditions.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$$

- 50 cm^3 of 0.020 mol dm^{-3} iodine solution was measured into a flask.
- 25 cm^3 of propanone and 25 cm^3 of 1.0 mol dm^{-3} sulfuric acid were measured into a second flask.
- Several 10 cm^3 samples of 0.5 mol dm^{-3} sodium hydrogencarbonate solution were placed in separate conical flasks.
- The mixture of propanone and sulfuric acid was added to the iodine, and a clock started.
- At two minute intervals, 10 cm^3 of the reaction mixture was removed and added to one of the flasks containing sodium hydrogencarbonate solution.
- The contents of this flask were then titrated with 0.01 mol dm^{-3} sodium thiosulfate.

(a) Explain the purpose of adding the reaction mixture to the sodium hydrogencarbonate.

(2)

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(b) What indicator should be used in the titration?

(1)

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*(c) In this experiment the concentration of the iodine was 0.020 mol dm^{-3} and the concentrations of propanone and sulfuric acid were both 1.00 mol dm^{-3}. Why was the iodine solution used much less concentrated than the propanone and sulfuric acid?

(2)

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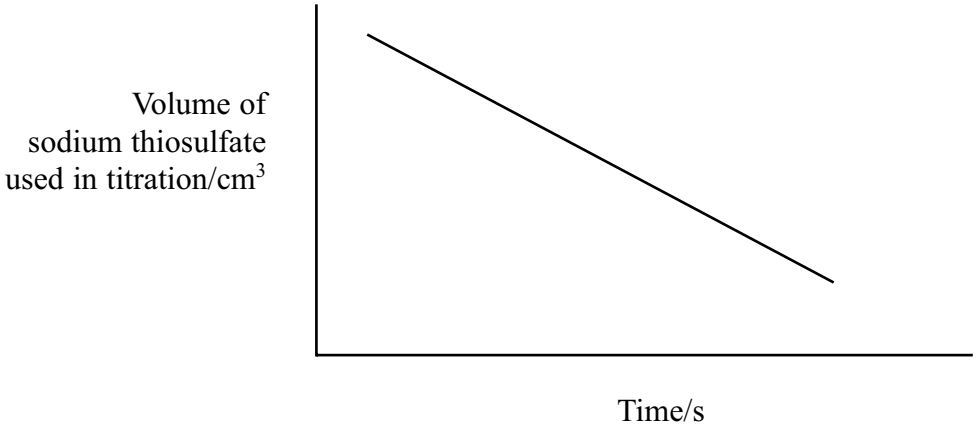
(d) The shape of the graph obtained from the results of the experiment is shown below.



Use the graph to deduce the order of reaction with respect to iodine, explaining your reasoning.

(2)

(e) The solutions used in this experiment could be measured using either measuring cylinders or pipettes.

Give **one** advantage of using a measuring cylinder and **one** advantage of using a pipette.

(2)

(f) In a further investigation, different volumes of sulfuric acid, propanone, iodine and water were mixed. The time taken for the mixture to go colourless was measured.

The experiments were repeated and the results below show average values for the rate of the reaction.

Expt	2 mol dm^{-3} H_2SO_4 /cm^3	2 mol dm^{-3} propanone /cm^3	Water /cm^3	0.01 mol dm^{-3} iodine /cm^3	Rate /mol dm^{-3} s^{-1}
1	20.0	8.0	0	4.0	8×10^{-5}
2	10.0	8.0	10.0	4.0	4×10^{-5}
3	20.0	4.0	4.0	4.0	4×10^{-5}

(i) Explain why water is added in experiments 2 and 3.

(1)

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(ii) Show how you would use the data in the table to deduce the order of reaction with respect to propanone and hydrogen ions. Write the rate equation for the reaction.

(3)

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(Total for Question 19 = 13 marks)

TOTAL FOR SECTION B = 50 MARKS

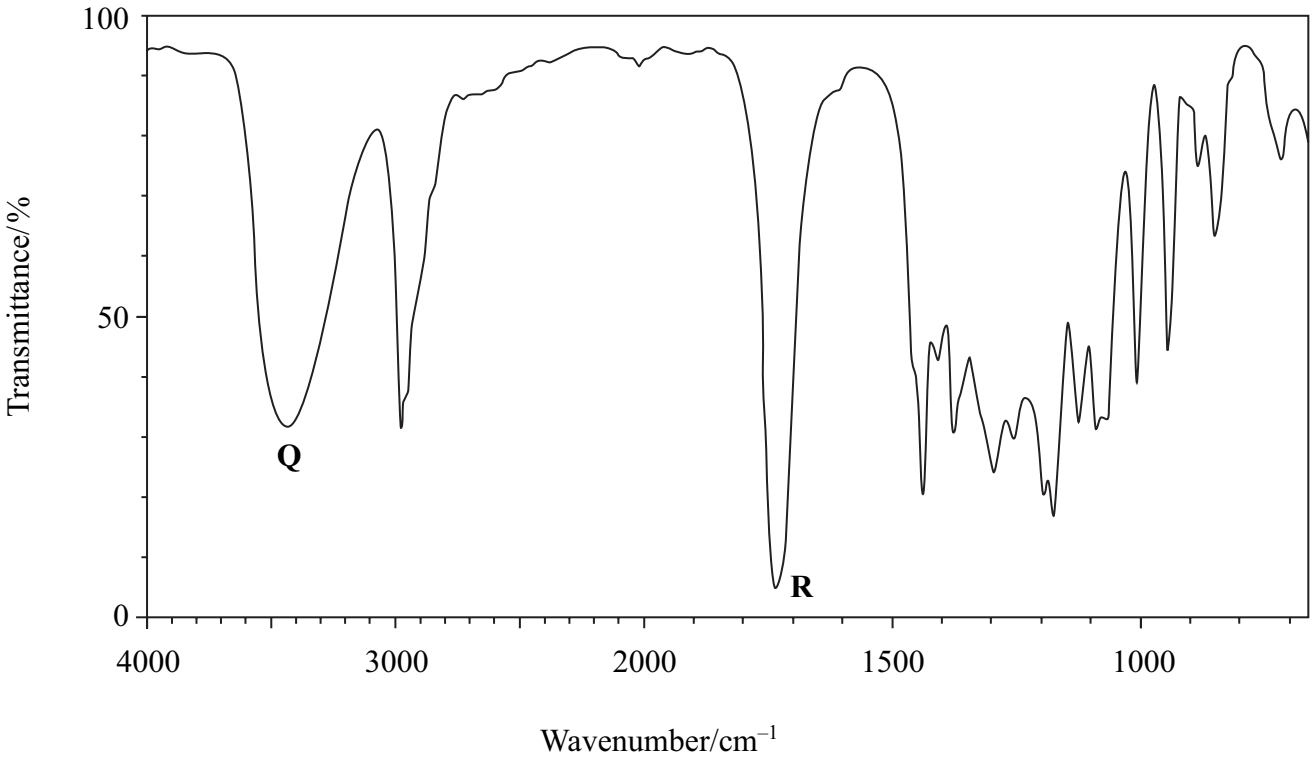
SECTION C

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

20 An organic compound **X** is an ester found in orange peel and has the molecular formula $C_5H_{10}O_3$.

(a) Identify the bonds responsible for the peaks labelled **Q** and **R** in the infrared spectrum of **X** shown below, referring to your data booklet.

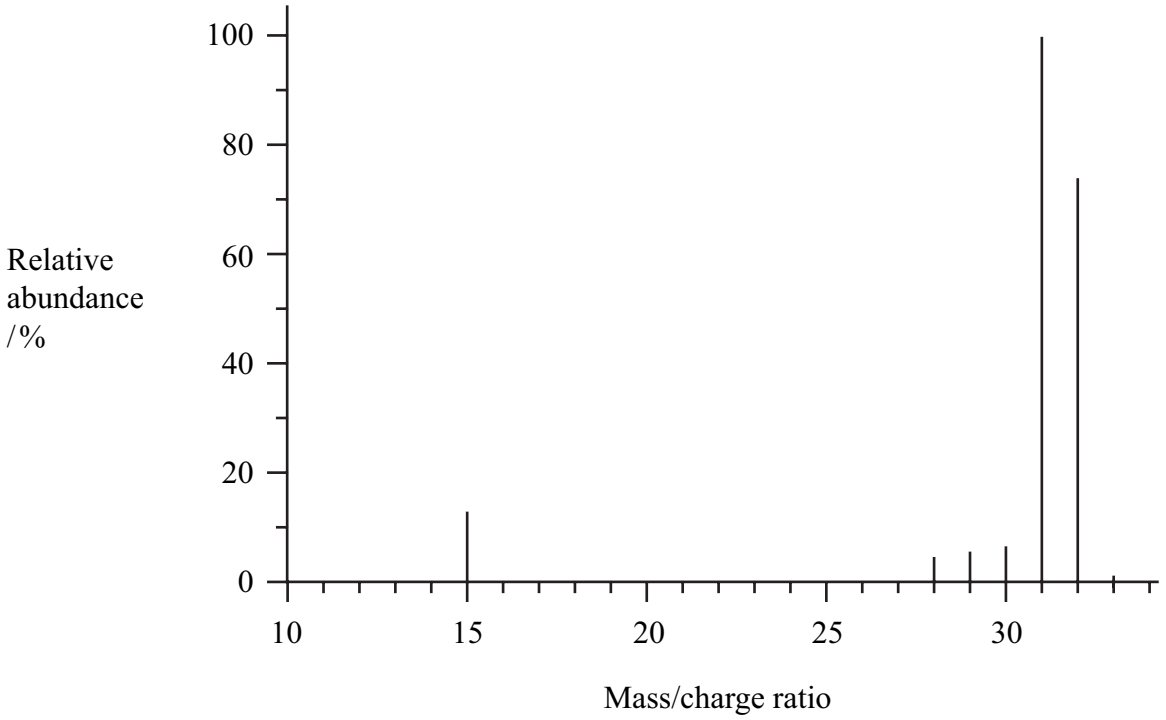
(2)



Q .....

R .....

(b) **X** was heated under reflux with dilute sulfuric acid. The resulting mixture was distilled and a liquid **Y** was collected. The mass spectrum of **Y** is shown below.



(i) Identify **Y**, by name or formula, using the information available. Use **two** pieces of data from the mass spectrum to support your answer.

(2)

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(ii) The identity of **Y** could be confirmed using nmr spectroscopy. Predict the number of peaks in the low resolution proton nmr spectrum of **Y**. Give the chemical shift range for each peak, referring to your data booklet.

(2)

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(c) A second product from the reaction of **X** with hydrochloric acid is **Z**, which has the molecular formula $C_4H_8O_3$.

What can you deduce about **Z** from the results of the following tests?

(i) One mole of **Z** reacts with two moles of phosphorus(V) chloride, PCl_5.

(1)

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(ii) When sodium carbonate solution is added to **Z**, effervescence is seen.

(1)

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(iii) **Z** is warmed gently with potassium dichromate(VI) and sulfuric acid. The organic product of the reaction gives a yellow precipitate with 2,4-dinitrophenylhydrazine (Brady's reagent) but does not react with Tollens' reagent.

(1)

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(iv) **Z** reacts with a solution of iodine in sodium hydroxide to produce a yellow precipitate with an antiseptic smell.

(1)

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(d) Use the results of these tests to deduce the structural formula of **Z** and hence the structural formula of **X**.

(2)

(Total for Question 20 = 12 marks)

21 The equation below shows the type of reaction which can be used in the production of biodiesel from vegetable oils.

$$\begin{array}{l} CH_2OOCR_1 \\ | \\ CHOOCR_2 \\ | \\ CH_2OOCR_3 \end{array} + 3C_2H_5OH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + R_1COOC_2H_5 + R_2COOC_2H_5 + R_3COOC_2H_5$$

(a) (i) Name this type of reaction.

(1)

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(ii) Suggest why water must not be present when this reaction with ethanol is carried out.

(1)

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(b) Give **one** reason why biodiesel is considered a "greener" fuel than diesel produced from crude oil.

(1)

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*(c) The products of the type of reaction shown with ethanol can be separated and identified using gas chromatography (GC).

In chromatography, compounds are separated because of the difference in distribution between a mobile phase and a stationary phase.

Explain why this difference in distribution occurs, and contrast the phases used in gas chromatography (GC) and high performance liquid chromatography (HPLC).

(5)

(Total for Question 21 = 8 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8)
							1.0 H hydrogen 1										(18) 4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									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	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(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

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
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

* Lanthanide series

* Actinide series