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 15 June 2011 – Afternoon
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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7/7/5/5/3/

P 3 8 4 8 2 A 0 1 2 4

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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 Which of the following methods would **not** be suitable for measuring the rate of the reaction between methanoic acid and bromine?

$$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$

☒ **A** Colorimetry

☒ **B** Measuring change in electrical conductivity

☒ **C** Quenching samples and titrating with acid

☒ **D** Measuring change in pressure

(Total for Question 1 = 1 mark)

---

2 The equation below shows the hydrolysis of a bromoalkane.

$$RBr + OH^- \rightarrow ROH + Br^-$$

For a particular bromoalkane, the rate equation is

$$\text{rate} = k[RBr]$$

The bromoalkane, RBr, is most likely to be

☒ **A** CH_3Br

☒ **B** CH_3CH_2Br

☒ **C** $(CH_3)_3CCH_2Br$

☒ **D** $(CH_3)_3CBr$

(Total for Question 2 = 1 mark)

---

3 A decrease in the entropy of the system, ΔS_{system}, occurs when

☒ **A** water freezes.

☒ **B** water boils.

☒ **C** water reacts with sodium.

☒ **D** water reacts with ethanoyl chloride.

(Total for Question 3 = 1 mark)

---

4 Methanol is produced in the equilibrium reaction

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -18.3 \text{ kJ mol}^{-1}$$

Addition of more hydrogen to the equilibrium mixture at constant temperature

☒ **A** increases the equilibrium yield of methanol.

☒ **B** decreases the equilibrium yield of methanol.

☒ **C** increases the value of K_p.

☒ **D** decreases the value of K_p.

(Total for Question 4 = 1 mark)

5 The equation for the equilibrium between $NO_2(g)$ and $N_2O_4(g)$ can be written in two ways.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad \text{Equilibrium constant} = K_c$$

or

$$NO_2(g) \rightleftharpoons \tfrac{1}{2}N_2O_4(g) \quad \text{Equilibrium constant} = K'_c$$

Which expression is correct?

☒ **A** $K_c = K'_c$

☒ **B** $K_c = (K'_c)^2$

☒ **C** $K_c = 2(K'_c)$

☒ **D** $K_c = \tfrac{1}{2}K'_c$

(Total for Question 5 = 1 mark)

6 4.0 mol of methanoic acid are reacted with 6.0 mol of ethanol.

$$HCOOH(l) + C_2H_5OH(l) \rightleftharpoons HCOOC_2H_5(l) + H_2O(l)$$

The equilibrium mixture contains 3.0 mol of $HCOOC_2H_5$.

The equilibrium constant, K_c, for the reaction is

☒ **A** 0.33

☒ **B** 1.0

☒ **C** 3.0

☒ **D** 4.0

(Total for Question 6 = 1 mark)

7 A solution of hydrochloric acid has pH 3.0. When it is made 10 times more dilute, the pH is

☒ **A** 0.3

☒ **B** 2.0

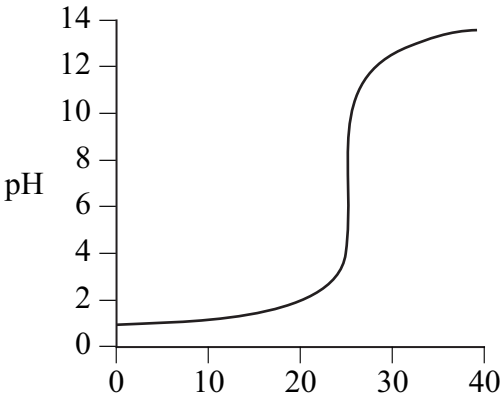
☒ **C** 4.0

☒ **D** 13.0

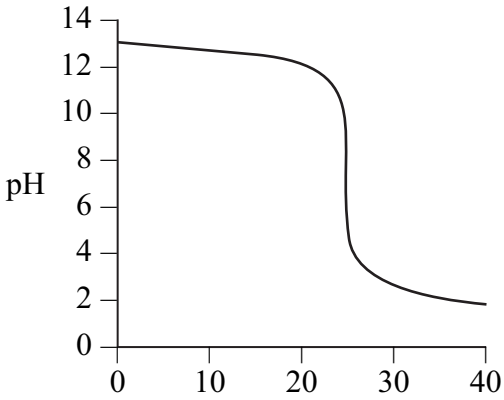
(Total for Question 7 = 1 mark)

8 The titration curves below were obtained using different acids and bases, each with concentration 0.1 mol dm^{-3}.

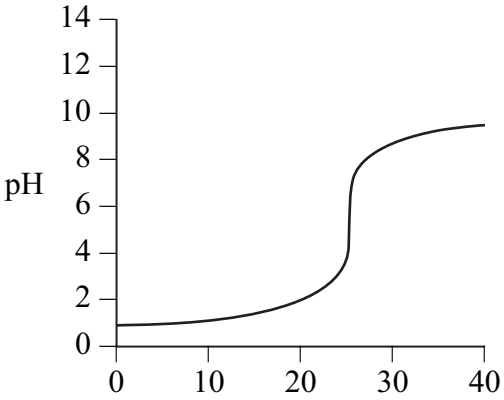
A



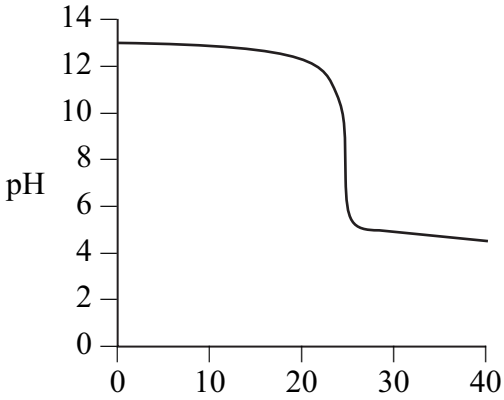
B



C



D



(a) Which curve is produced by adding ammonia to 25 cm^3 of hydrochloric acid?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which curve is produced by adding ethanoic acid to 25 cm^3 of sodium hydroxide?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) An indicator with pK_{In} 8.5 is suitable for the following titrations.

(1)

☒ **A** Titrations **A** and **B** only.

☒ **B** Titrations **A**, **B** and **D** only.

☒ **C** Titration **C** only.

☒ **D** Titrations **A**, **B**, **C** and **D**.

(Total for Question 8 = 3 marks)

9 Ethanoic acid is **not** a product in the reaction of

☒ **A** ethanal with lithium tetrahydridoaluminate.

☒ **B** ethanoyl chloride with water.

☒ **C** ethyl ethanoate with dilute sulfuric acid.

☒ **D** ethanol refluxed with potassium dichromate(VI) and sulfuric acid.

(Total for Question 9 = 1 mark)

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

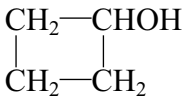
10 This question is about four compounds with molecular formula C_4H_8O.

A $CH_3COCH_2CH_3$

B $CH_3CH_2CH_2CHO$

C $CH_3CH{=}CHCH_2OH$

D



(a) The compounds which react when heated with a mixture of potassium dichromate(VI) and sulfuric acid are

(1)

☒ **A** compounds **A**, **B** and **C**.

☒ **B** compounds **A**, **B** and **D**.

☒ **C** compounds **A**, **C** and **D**.

☒ **D** compounds **B**, **C** and **D**.

(b) The compound which produces a yellow precipitate when heated with a mixture of iodine and sodium hydroxide is

(1)

☒ **A** compound **A**.

☒ **B** compound **B**.

☒ **C** compound **C**.

☒ **D** compound **D**.

(c) There would **not** be a significant peak at mass/charge ratio of 15 in the mass spectrum of

(1)

☒ **A** compound **A**.

☒ **B** compound **B**.

☒ **C** compound **C**.

☒ **D** compound **D**.

(Total for Question 10 = 3 marks)

11 The following tests can be carried out on organic compounds.

A Warm with 2,4-dinitrophenylhydrazine.

B Warm with Fehling's or Benedict's solution.

C Add solid sodium carbonate.

D Add phosphorus(V) chloride, PCl_5.

(a) Which test would give a positive result with propanoic acid but not with propan-1-ol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which test would give a positive result with propanoic acid **and** with propan-1-ol?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) Which test would give a positive result with propanal but not with propanone?

(1)

☒ **A**

☒ **B**

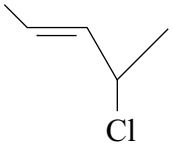
☒ **C**

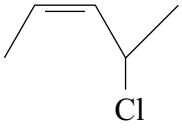
☒ **D**

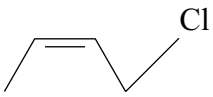
(Total for Question 11 = 3 marks)

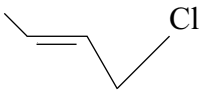
Use this space for any rough working. Anything you write in this space will gain no credit.

12 Which of the following compounds is a *Z* isomer **and** contains a chiral carbon atom?

☒ **A** 

☒ **B** 

☒ **C** 

☒ **D** 

(Total for Question 12 = 1 mark)

13 Which of the following statements about ethanoyl chloride is **not** correct?

☒ **A** It reacts with ammonia to make an amine.

☒ **B** It reacts with an amine to make an amide.

☒ **C** It reacts with an alcohol to make an ester.

☒ **D** It reacts with water to make an organic acid.

(Total for Question 13 = 1 mark)

14 In gas chromatography, mixtures are passed through a long tube containing a liquid as the stationary phase. The mixtures are separated into their components because the components differ in

☒ **A** relative molecular mass.

☒ **B** melting temperature.

☒ **C** volatility.

☒ **D** force of attraction to the liquid.

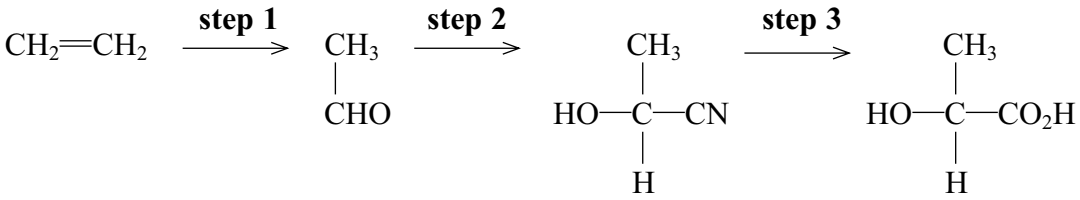
(Total for Question 14 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

15 A sequence of reactions for the production of lactic acid is shown below.



lactic acid

(a) (i) Name the type and mechanism of the reaction in **step 2**.

(2)

.....

(ii) Which **two** substances need to be added to ethanal to carry out the reaction in **step 2**?

(2)

.....

.....

(iii) Give the mechanism for the reaction in **step 2**, using curly arrows to show movements of electron pairs.

(3)

*(iv) The product of **step 2** is not optically active even though it has a chiral carbon atom in its formula. Explain, by reference to the mechanism, the reason for the lack of optical activity.

(2)

(b) What reactant, or combination of reactants, is needed to carry out **step 3**?

(1)

(c) (i) What is the systematic name of lactic acid?

(1)

(ii) Lactic acid molecules can combine to form a biodegradable polymer, poly(lactic acid) or PLA. Draw a section of the polymer with **two** units of the polymer chain and showing all bonds.

(1)

(iii) Suggest why PLA is biodegradable.

(1)

(iv) Lactic acid can be prepared from ethene as shown in the scheme. Lactic acid also forms when milk turns sour.

Suggest **one** reason why it would be advantageous to make lactic acid from milk rather than from ethene.

(1)

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.....

(Total for Question 15 = 14 marks)

16 Nitrogen(IV) oxide, NO_2, is a brown gas which is a pollutant in air. It is produced in the reaction below.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(a) The table below shows the results of a series of experiments to measure the rate of this reaction at 298 K.

Experiment number	Initial concentration / mol dm^{-3}		Initial rate / mol dm^{-3} s^{-1}
	$[O_2(g)]$	$[NO(g)]$	
1	0.0050	0.0125	5.10×10^{-4}
2	0.0100	0.0125	10.2×10^{-4}
3	0.0100	0.0250	40.8×10^{-4}

(i) State, with reasons, the order of reaction with respect to oxygen and the order of reaction with respect to nitrogen(II) oxide, NO.

(2)

.....

.....

.....

.....

(ii) Write the rate equation for the reaction.

(1)

(iii) Calculate the value of the rate constant. Include units in your answer.

(2)

(b) Nitrogen(IV) oxide in air reacts with carbon monoxide in car exhausts. The following two-step reaction mechanism has been suggested.

Step 1: $2NO_2(g) \rightarrow NO(g) + NO_3(g)$ Slow

Step 2: $NO_3(g) + 2CO(g) \rightarrow NO(g) + 2CO_2(g)$ Fast

(i) Write the equation for the overall reaction which takes place.

(1)

(ii) The overall reaction is second order. Suggest a rate equation for this reaction, justifying your answer.

(2)

(Total for Question 16 = 8 marks)

17 Ammonia is manufactured using the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) (i) Calculate $\Delta S^{\ominus}_{system}$ for this reaction at 298 K. Give your answer in J mol^{-1} K^{-1} and include a sign. You will need to refer to your data booklet.

[Note that the standard molar entropy values for gaseous diatomic elements are given for half a mole of molecules, and not per mole of molecules
eg entropy for 1 mol of N_2 is 2 × 95.8 J mol^{-1} K^{-1}.]

(2)

(ii) Using ideas about disorder, explain whether the sign of your answer to (a)(i) is as expected.

(2)

.....

.....

.....

.....

(b) At 700 K, the enthalpy change for this reaction, $\Delta H = -110.2$ kJ mol^{-1}.

(i) Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, at 700 K. Include a sign and units in your answer.

(2)

(ii) Calculate ΔS_{system} for this reaction at 700 K. At this temperature the total entropy change, $\Delta S_{total} = -78.7$ J K^{-1} mol^{-1}. Include a sign and units in your answer.

(1)

(iii) What does the value of ΔS_{total}, which is -78.7 J K^{-1} mol^{-1} at 700 K, indicate about the relative proportions of nitrogen, hydrogen and ammonia at equilibrium?

(1)

.....

.....

.....

(c) A mixture of nitrogen, hydrogen and ammonia is at equilibrium at 150 atm. The partial pressures of nitrogen and ammonia in the mixture are 21 atm and 36 atm respectively.

(i) Write an expression for the equilibrium constant, K_p, for the formation of ammonia, in terms of partial pressures for this reaction, and calculate its value at 700 K. Include units in your answer.

(4)

(ii) In the manufacture of ammonia, pressures of between 100 and 250 atm are used. State and explain **one** advantage, in terms of the yield of ammonia, of using a pressure above 100 atm.

(1)

.....

.....

.....

.....

*(iii) In the manufacture of ammonia, a temperature of about 700 K is used.

For this exothermic reaction how does $\Delta S_{surroundings}$ change as temperature increases?

Explain how this change affects the value of ΔS_{total} and the equilibrium constant as temperature increases.

Hence explain the disadvantage of using a temperature higher than 700 K.

(4)

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(iv) Suggest **one** advantage of using a temperature higher than 700 K.

(1)

.....

.....

(Total for Question 17 = 18 marks)

18 Methanoic acid, ethanoic acid and iodic(I) acid, HIO, are all weak acids.

(a) The values of the acid dissociation constant, K_a, for methanoic and ethanoic acid at 298 K are given below. Iodic(I) acid has a pK_a of 10.64. Complete the table by calculating the value of K_a for iodic(I) acid.

(1)

Acid	K_a / mol dm^{-3}
methanoic acid	1.6×10^{-4}
ethanoic acid	1.7×10^{-5}
iodic(I) acid	

(b) (i) Write the expression for K_a for methanoic acid, HCOOH.

(1)

(ii) Calculate the pH of a solution of methanoic acid with concentration 0.50 mol dm^{-3} at 298 K.

(3)

(iii) State **one** of the assumptions you have made when calculating the pH in (ii).

(1)

.....

.....

.....

.....

.....

(c) The following equilibrium occurs in a mixture of pure methanoic and ethanoic acids.

$$HCOOH + CH_3COOH \rightleftharpoons HCOO^- + CH_3COOH_2^+$$

(i) Give the formulae of the two Brønsted-Lowry acids in this equilibrium.

(1)

.....

.....

(ii) Write an equation showing the products of the equilibrium which is set up when iodic(I) acid is mixed with ethanoic acid.

(1)

$HIO + CH_3COOH \rightleftharpoons$ ..... + ...

(d) A shampoo is buffered by the addition of a mixture of methanoic acid and sodium methanoate.

The pH of this shampoo is 4.9. Calculate the hydrogen ion concentration in the shampoo, and hence the ratio of methanoate ions to methanoic acid.

(2)

(Total for Question 18 = 10 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

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

19 The chemical **X** is an ester with formula $CH_3COOC(CH_3)_3$ which occurs in raspberries and pears. It can be prepared in the laboratory by refluxing ethanoic acid with an alcohol in the presence of a catalyst.

(a) **Name** the alcohol and catalyst which would be used to make **X**.

(2)

Alcohol .....

Catalyst .....

(b) After refluxing, the resulting mixture is distilled to give an impure product containing **X**. The impure product is washed several times with sodium carbonate solution and then dried.

(i) Name the piece of equipment in which the impure product would be washed.

(1)

.....

(ii) What is the purpose of washing the impure product with sodium carbonate solution?

(1)

.....

(iii) Name a suitable drying agent.

(1)

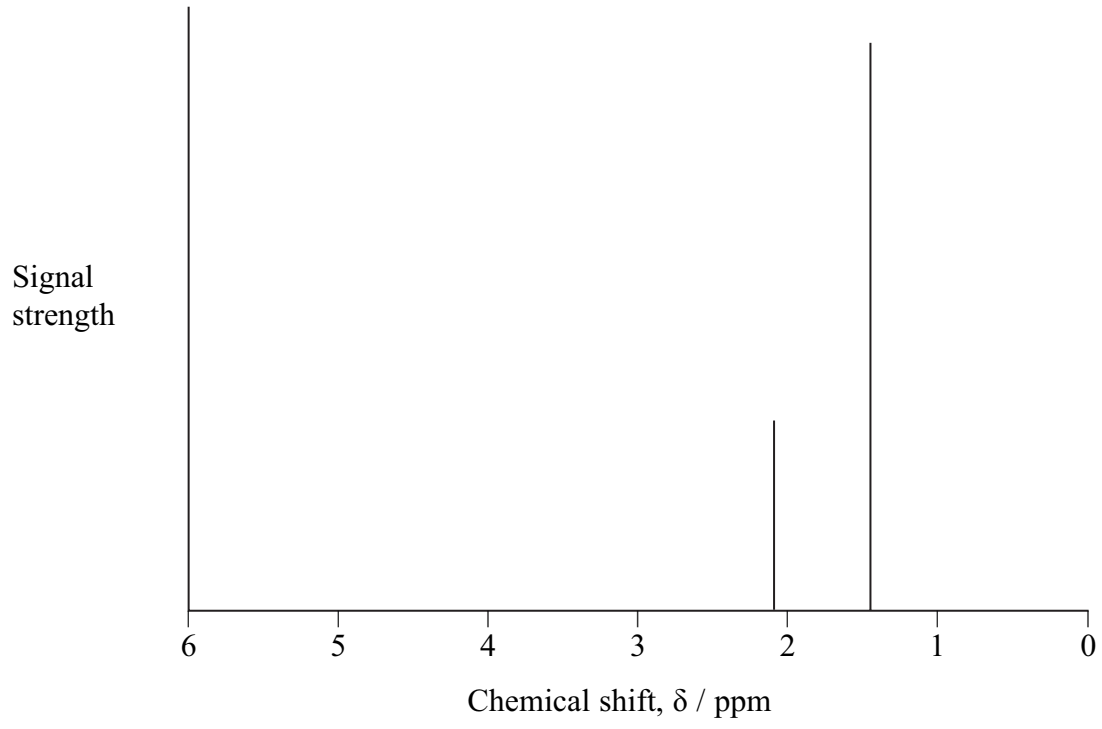
.....

(iv) The impure product is then redistilled and **X**, which has a boiling temperature of 97 °C, is collected. Draw a labelled diagram of the apparatus you would use.

(3)

*(c) **Spectrum 1** is the high resolution proton nmr spectrum of **X**, $CH_3COOC(CH_3)_3$.

Spectrum 1



Explain how **spectrum 1** is consistent with the structure of **X**. You should refer to the number and height of the peaks, the atoms which produce them and their splitting patterns.

(4)

(d) **X** has an isomer, **Y**. **Y** is an ester which can be made from ethanoic acid and 2-methylpropan-1-ol.

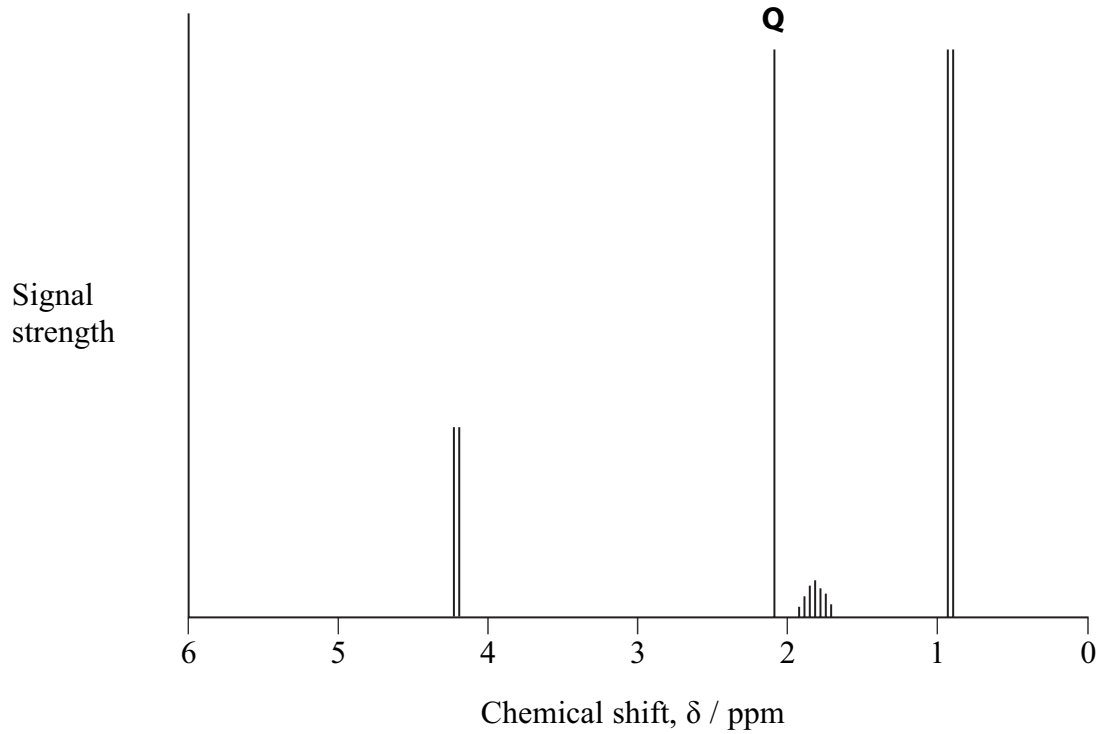
(i) Draw the structural formula of **Y**.

(1)

(ii) **Spectrum 2** is the high resolution proton nmr spectrum of **Y**. On your structural formula in (i), circle the atom or atoms causing the peak labelled **Q** on **spectrum 2**.

(1)

Spectrum 2



(e) **X** has several other structural isomers which have a broad peak at approximately 2960 cm^{-1} in their infrared spectra. Some of the isomers have a chiral carbon atom and all have a higher boiling temperature than **X**. None of them reacts with 2,4-dinitrophenylhydrazine.

*(i) Draw the structure of **one** of the isomers which is optically active, explaining how you use **all** the information in the question.

(5)

(ii) Could the compound you have drawn in (e)(i) be distinguished by infrared spectroscopy from its other isomers with the properties listed above? Explain your answer.

(1)

(Total for Question 19 = 20 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)
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	4.0 He helium 2
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

* 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