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)

Monday 19 January 2015 – 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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6/6/6/6/2/

P 4 5 0 4 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 Sulfuryl chloride, SO_2Cl_2, decomposes in a first order reaction.

The half-life for this reaction is 2300 s.

In an experiment, the initial concentration of sulfuryl chloride is 1.0 mol dm^{-3}.

What is the concentration, in mol dm^{-3}, of sulfuryl chloride after 4600 s?

☒ **A** 0.75

☒ **B** 0.50

☒ **C** 0.25

☒ **D** 0.125

(Total for Question 1 = 1 mark)

2 Which classes of halogenoalkane can react with alkali by an S_N2 mechanism?

☒ **A** Primary and secondary.

☒ **B** Secondary and tertiary.

☒ **C** Primary and tertiary.

☒ **D** Primary, secondary and tertiary.

(Total for Question 2 = 1 mark)

3 Which of the following is the correct order of **decreasing** entropy?

	Highest entropy	Middle entropy	Lowest entropy
☒ **A**	ice at 0 °C	water at 0 °C	steam at 120 °C
☒ **B**	ice at 0 °C	steam at 120 °C	water at 100 °C
☒ **C**	steam at 100 °C	water at 0 °C	ice at –20 °C
☒ **D**	steam at 100 °C	ice at –20 °C	water at 100 °C

(Total for Question 3 = 1 mark)

4 Ethanol burns in excess oxygen to produce carbon dioxide and water.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

The standard molar entropies of the reactants and products at 298 K are given in the table below.

Substance	$S^{\ominus}$/J mol^{-1} K^{-1}
$C_2H_5OH(l)$	161
$O_2(g)$	205
$CO_2(g)$	214
$H_2O(l)$	70

The value of $\Delta S^{\ominus}_{system}$ for this reaction, in J mol^{-1} K^{-1}, is

☒ **A** –138

☒ **B** –82

☒ **C** +82

☒ **D** +138

(Total for Question 4 = 1 mark)

5 Nitrogen reacts with hydrogen to form ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.2 \text{ kJ mol}^{-1}$$

What is the value of $\Delta S^{\ominus}_{surroundings}$, in J mol^{-1} K^{-1}, for this reaction at 25 °C?

☒ **A** –3688

☒ **B** –309.4

☒ **C** +309.4

☒ **D** +3688

(Total for Question 5 = 1 mark)

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

6 The signs of $\Delta H^{\ominus}_{reaction}$ and $\Delta S^{\ominus}_{system}$ for four different gaseous reactions are shown in the table. Which reaction must be thermodynamically feasible at **all** temperatures?

	$\Delta H^{\ominus}_{reaction}$	$\Delta S^{\ominus}_{system}$
☒ **A**	negative	negative
☒ **B**	negative	positive
☒ **C**	positive	negative
☒ **D**	positive	positive

(Total for Question 6 = 1 mark)

7 Use the data in the table to calculate the enthalpy change of solution of calcium chloride, $CaCl_2$.

Lattice energy of calcium chloride	–2258 kJ mol^{-1}
Hydration enthalpy of Ca^{2+}	–1650 kJ mol^{-1}
Hydration enthalpy of Cl^-	–364 kJ mol^{-1}

The enthalpy change of solution of calcium chloride, in kJ mol^{-1}, is

☒ **A** –244

☒ **B** –120

☒ **C** +120

☒ **D** +244

(Total for Question 7 = 1 mark)

8 The expression that relates ΔS_{system} to the equilibrium constant, K, for a reaction is

☒ **A** $\Delta S_{system} = R\ln K + \Delta H/T$

☒ **B** $\Delta S_{system} = R\ln K - \Delta H/T$

☒ **C** $\Delta S_{system} = T\ln K + \Delta H/R$

☒ **D** $\Delta S_{system} = T\ln K - \Delta H/R$

(Total for Question 8 = 1 mark)

9 Dinitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At equilibrium, when the temperature is 400 K, the equilibrium partial pressures are shown in the table below.

Formula	Equilibrium partial pressure / atm
N_2O_4	0.365
NO_2	4.18

The numerical value for the equilibrium constant, K_p, is

☒ **A** 0.0209

☒ **B** 11.5

☒ **C** 31.4

☒ **D** 47.9

(Total for Question 9 = 1 mark)

10 A buffer solution is 0.1 mol dm^{-3} with respect to ethanoic acid and 0.05 mol dm^{-3} with respect to sodium ethanoate.

K_a for ethanoic acid = 1.7×10^{-5} mol dm^{-3}

The pH of this buffer solution is

☒ **A** 2.88

☒ **B** 4.47

☒ **C** 4.77

☒ **D** 5.07

(Total for Question 10 = 1 mark)

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

11 The equation for the reaction between a weak acid, HX, and sodium hydroxide is

$$HX(aq) + NaOH(aq) \rightarrow NaX(aq) + H_2O(l)$$

The pH of the solution of the salt NaX is most likely to be

- ☒ **A** 5.5
- ☒ **B** 7.0
- ☒ **C** 8.5
- ☒ **D** 13.0

(Total for Question 11 = 1 mark)

12 When a small amount of hydrochloric acid is added to a buffer solution, the change in pH is very small.

What is the best explanation for this?

- ☒ **A** The dissociation of the acid in the buffer solution is small.
- ☒ **B** The concentration of the buffer solution only changes a little.
- ☒ **C** The ratio of the concentration of acid to conjugate base in the buffer solution does not change.
- ☒ **D** The ratio of the concentration of acid to conjugate base in the buffer solution only changes a little.

(Total for Question 12 = 1 mark)

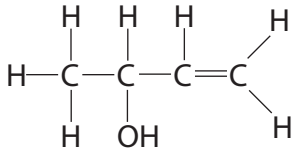
13 How many **structural** isomers have the formula C_5H_{12}?

- ☒ **A** 2
- ☒ **B** 3
- ☒ **C** 4
- ☒ **D** 5

(Total for Question 13 = 1 mark)

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

14 What types of stereoisomerism (if any) can exist in molecules of the following substance?



☒ **A** *E-Z* isomerism only.

☒ **B** *E-Z* and optical isomerism.

☒ **C** Neither *E-Z* nor optical isomerism.

☒ **D** Optical isomerism only.

(Total for Question 14 = 1 mark)

15 An organic compound gave a pale yellow precipitate when warmed with a solution of iodine in sodium hydroxide. It also gave steamy fumes when tested with phosphorus(V) chloride.

The organic compound consistent with these results is

☒ **A** $BrCH_2CH_2CH_2COOH$

☒ **B** $BrCH_2CH_2COCH_3$

☒ **C** $HOCH_2CH_2CH_2COOH$

☒ **D** $HOCH_2CH_2COCH_3$

(Total for Question 15 = 1 mark)

16 Which type of radiation is used in nmr spectroscopy?

☒ **A** Infrared

☒ **B** Microwaves

☒ **C** Radio waves

☒ **D** Ultraviolet

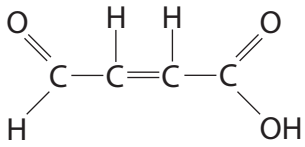
(Total for Question 16 = 1 mark)

17 Which of these gases is normally used as the mobile phase in gas chromatography?

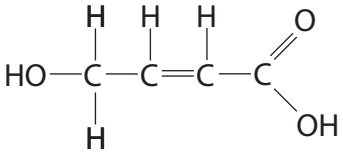
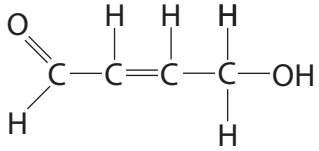
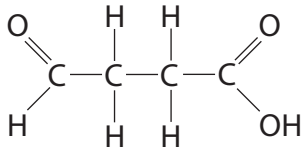
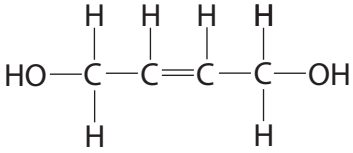
- ☒ **A** Argon
- ☒ **B** Chlorine
- ☒ **C** Radon
- ☒ **D** Steam

(Total for Question 17 = 1 mark)

18 The molecule shown below was reacted with excess lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether, followed by the addition of acid.



The product of the reaction is

- ☒ **A** 
- ☒ **B** 
- ☒ **C** 
- ☒ **D** 

(Total for Question 18 = 1 mark)

19 The molecule $CH_3CH_2CONHCH_2CH_3$ can be made in a single step at room temperature from

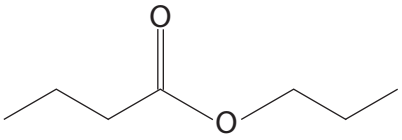
- ☒ **A** CH_3COCl and $CH_3CH_2CH_2NH_2$
- ☒ **B** CH_3CH_2COCl and $CH_3CH_2NH_2$
- ☒ **C** CH_3COOH and $CH_3CH_2CH_2NH_2$
- ☒ **D** CH_3CH_2COOH and $CH_3CH_2NH_2$

(Total for Question 19 = 1 mark)

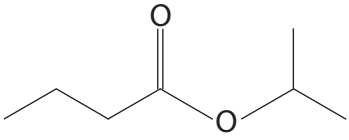
20 The products of the hydrolysis of an ester were propan-2-ol and 2-methylpropanoic acid.

The ester was

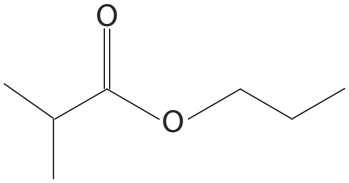
☒ **A**



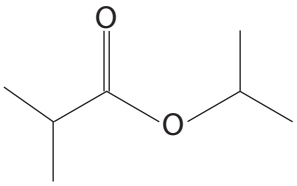
☒ **B**



☒ **C**



☒ **D**



(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

21 (a) Iodine reacts with propanone, CH_3COCH_3, in the presence of a catalyst of dilute hydrochloric acid.

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

Students carried out a rate investigation of this reaction. In each set of experiments, the initial concentration of one substance was varied and the initial concentrations of the other two substances were kept constant.

First set of experiments

The initial concentration of propanone was varied.

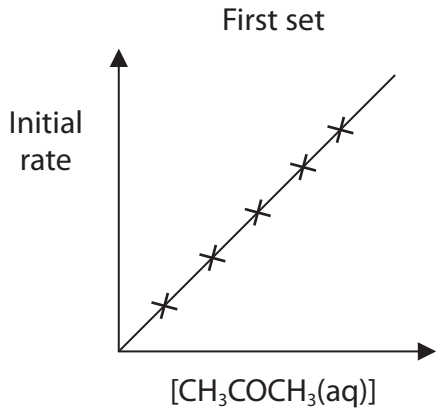
Second set of experiments

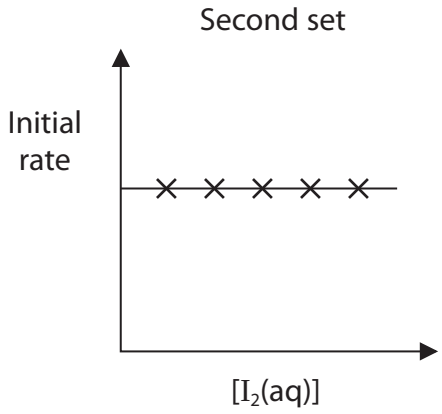
The initial concentration of iodine was varied.

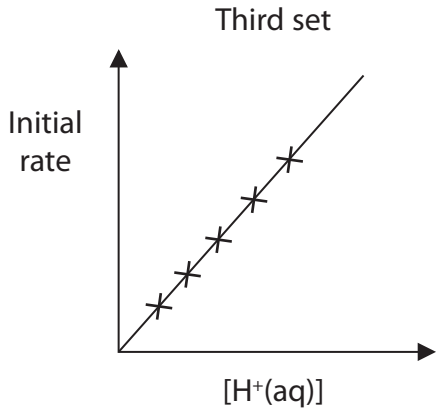
Third set of experiments

The initial concentration of hydrochloric acid was varied.

The results of each set of experiments are shown in the graphs below.







(i) For the second set of experiments, state a practical method for following the progress of this reaction. Indicate which substance is being monitored by your method.

(2)

*(ii) Use the graphs to deduce the orders of reaction with respect to propanone, iodine and H^+ ions. Explain your reasoning.

(4)

(iii) Write the rate equation for the reaction.

(1)

(iv) In one of the experiments, the following data were collected:

$[CH_3COCH_3(aq)] = 0.667 \text{ mol dm}^{-3}$

$[I_2(aq)] = 1.67 \times 10^{-3} \text{ mol dm}^{-3}$

$[H^+(aq)] = 0.667 \text{ mol dm}^{-3}$

Initial rate $= 8.80 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

Use the data to calculate the value for the rate constant.
Include units in your answer.

(2)

(v) Use the rate equation to suggest a possible rate-determining step in the mechanism for the reaction between iodine and propanone in the presence of dilute hydrochloric acid.

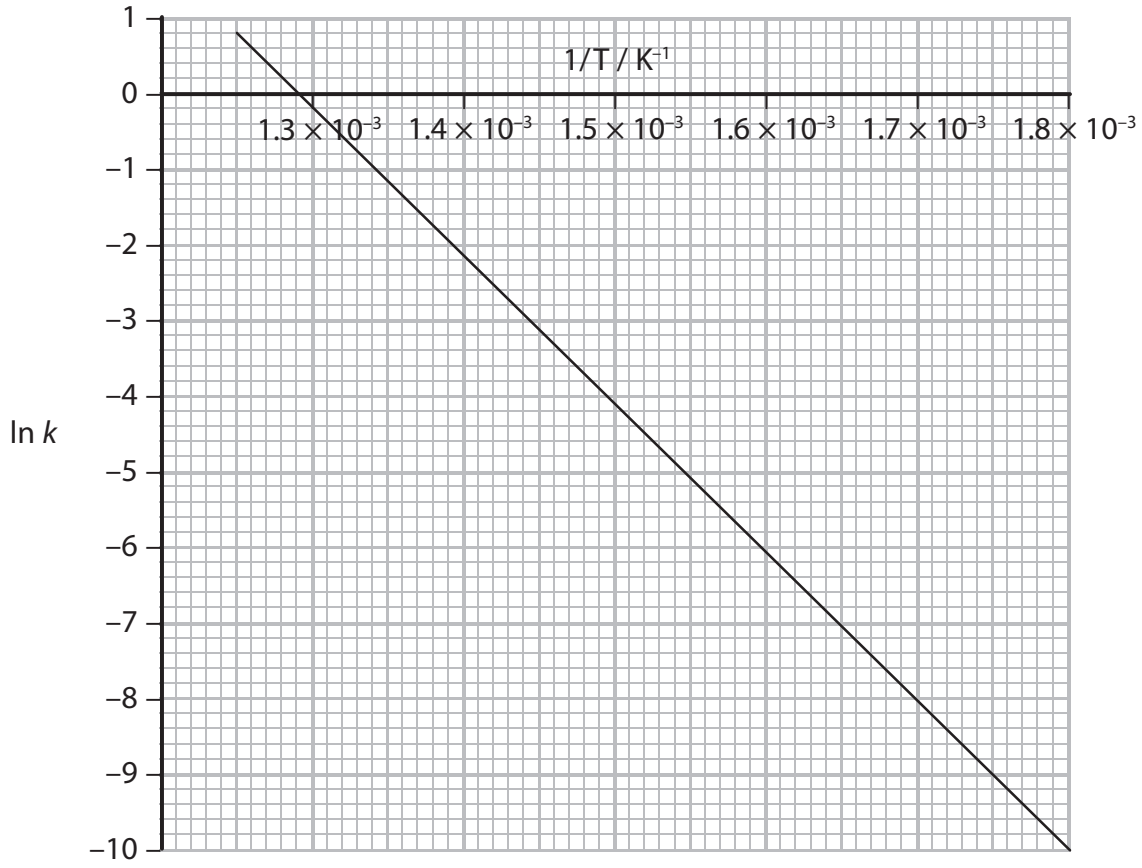
Explain your reasoning.

(2)

(b) Iodine also forms hydrogen iodide by direct reaction with hydrogen.

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

A graph of ln *k* against 1/T for this reaction is shown below.



(i) Calculate the gradient of the graph. Include a sign and units in your answer.

(2)

(ii) Use your value for the gradient of the graph to calculate the activation energy, E_a. Include units and give your answer to **three** significant figures.

The Arrhenius equation is

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

[Gas constant, $R = 8.31$ J mol^{-1} K^{-1}]

(2)

(Total for Question 21 = 15 marks)

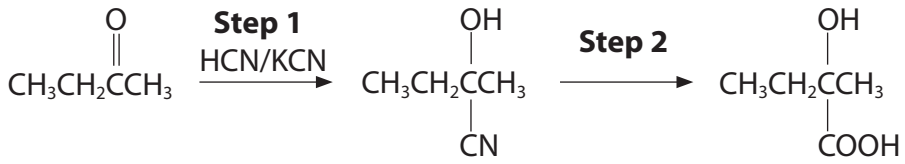
22 Butanone, $CH_3CH_2COCH_3$, is used as an industrial solvent.

(a) State each stage in the procedure in which 2,4-dinitrophenylhydrazine is used to confirm the identity of a carbonyl compound thought to be butanone.

Detailed practical descriptions are not required.

(3)

(b) Butanone can be converted into 2-hydroxy-2-methylbutanoic acid, $CH_3CH_2C(OH)(CH_3)COOH$, in two steps:



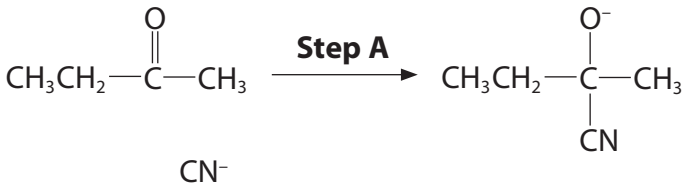
(i) Classify the type and mechanism of the reaction taking place in **Step 1**.

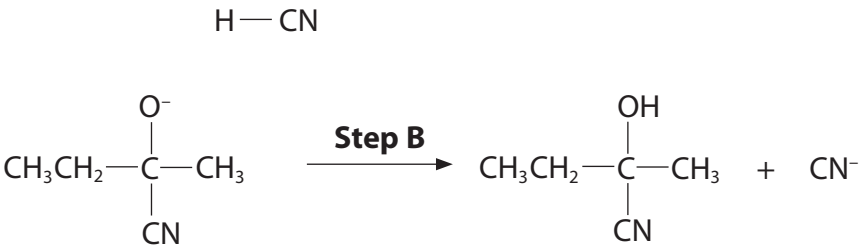
(2)

(ii) Identify the reagent(s) and conditions for the reaction taking place in **Step 2**.

(2)

(iii) The incomplete mechanism for **Step 1** is shown below.





On the incomplete mechanism above, draw the curly arrows **and** the relevant lone pairs of electrons to complete the mechanism.

(3)

(iv) Explain why the 2-hydroxy-2-methylbutanoic acid produced in this reaction is **not** optically active.

(3)

(c) Draw **two** repeat units of the polymer that could be formed from 2-hydroxy-2-methylbutanoic acid.

(2)

(Total for Question 22 = 15 marks)

23 Ethanoic acid, CH_3COOH, is a weak acid found in vinegar. Successive replacement of the methyl hydrogen atoms by chlorine atoms gives

chloroethanoic acid, $CH_2ClCOOH$

dichloroethanoic acid, $CHCl_2COOH$

trichloroethanoic acid, CCl_3COOH

(a) (i) Explain the term **weak acid**.

(2)

Weak .....

.....

Acid .....

.....

(ii) Write the expression for the acid dissociation constant, K_a, of dichloroethanoic acid, $CHCl_2COOH$.

(1)

(iii) Use the K_a data from page 18 in the Data Booklet to place the four acids, named in the introduction to the question, in order of increasing strength. State how the order that you have given can be deduced from the K_a data.

(2)

weakest acid .....

.....

.....

strongest acid .....

Reason

.....

.....

.....

(b) (i) Calculate the pH of a solution of 0.10 mol dm^{-3} ethanoic acid.

State clearly any assumptions you have made.

(4)

Assumptions

.....

.....

.....

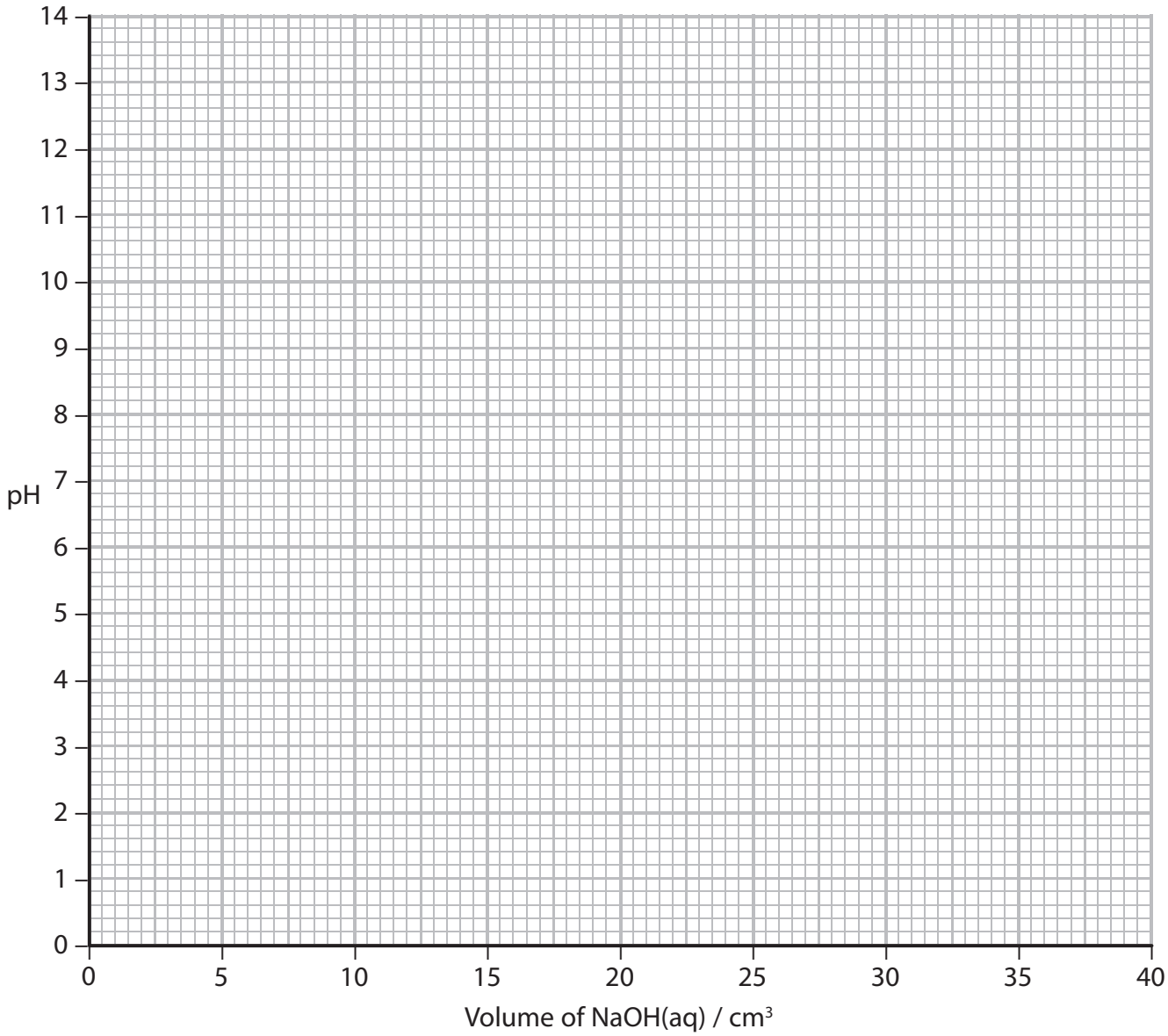
.....

.....

.....

(ii) Draw the titration curve, showing the change in pH when 0.10 mol dm^{-3} sodium hydroxide solution is added to 25 cm^3 of 0.10 mol dm^{-3} ethanoic acid, until 40 cm^3 of sodium hydroxide has been added.

(4)



*(iii) Select a suitable indicator for this titration.

Justify your selection.

(2)

.....

.....

.....

.....

.....

.....

(c) Ethanoic acid and trichloroethanoic acid react together in an acid-base reaction.

Complete the equation by writing the formulae of the acid and base produced in this reaction.

Identify the conjugate acid-base pairs in the spaces under the formulae.

(2)

$CH_3COOH + CCl_3COOH \rightarrow$ ..... + ...

....

(Total for Question 23 = 17 marks)

TOTAL FOR SECTION B = 47 MARKS

SECTION C

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

24 (a) Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, $CH_3COOC_2H_5$, and water.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l) \quad \Delta H = -3.5 \text{ kJ mol}^{-1}$$

(i) Give the expression for the equilibrium constant, K_c, for this reaction.

(1)

(ii) By considering the effect of temperature on the entropy change of the surroundings, suggest why changing the temperature has little effect on this equilibrium.

(3)

*(iii) An experiment was carried out to determine the value of K_c for this reaction.

- 0.120 mol of ethanoic acid was added to 0.220 mol of ethanol.
- 5.00 cm^3 of 1.00 mol dm^{-3} hydrochloric acid was added as a catalyst. This contains 0.278 mol of water.
- The mixture was left to reach equilibrium.
- The mixture was titrated with 1.00 mol dm^{-3} sodium hydroxide, which reacted with **both** of the acids.
- The titre was 45.0 cm^3.

Use these data to determine the value for K_c.

(6)

(b) Ethanoic acid reacts with another alcohol, **Y**, to produce an ester **Z**.

(i) Alcohol **Y** has molar mass 74 g mol^{-1} and the following composition by mass:

carbon, C = 64.9%

hydrogen, H = 13.5%

oxygen, O = 21.6%.

Use all these data to confirm that the molecular formula for **Y** is $C_4H_{10}O$.
Show your working.

(2)

(ii) Draw the displayed formulae of the **four** possible structures of alcohol **Y**.

(2)

Alcohol 1	Alcohol 2
Alcohol 3	Alcohol 4

(iii) The mass spectrum of alcohol **Y** has a major peak at $m/e = 45$.
Suggest the structures of two species that could give this peak.

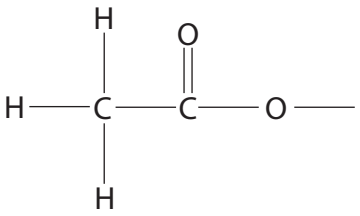
(2)

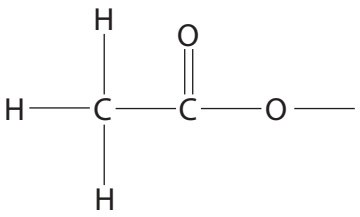
(iv) Use your answers to (b)(ii) and (b)(iii) to identify which two of the alcohols you have drawn in (b)(ii) could be alcohol **Y**.

(1)

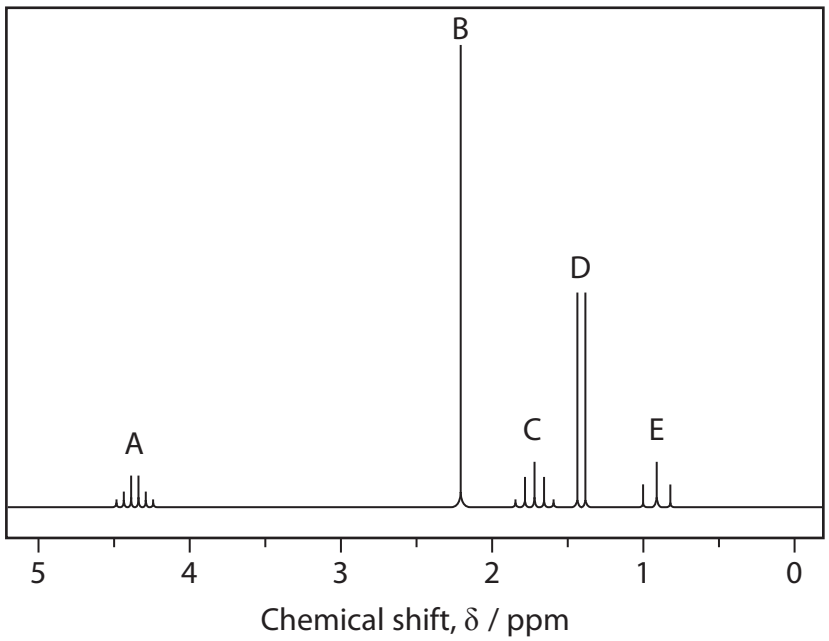
(v) Complete the displayed formulae for the two possible esters that could be **Z**.

(1)





*(vi) The high resolution proton nmr spectrum of ester **Z** is shown below.



The relative number of protons causing the peaks shown are:
A = 1, B = 3, C = 2, D = 3 and E = 3.

Use the nmr spectrum to determine the structural formula for ester **Z** that is consistent with this data.

Draw your formula below and on it label the protons responsible for the peaks A to E.

Explain the splitting patterns of the spectrum.

(5)

Structure

Explanation of splitting patterns

(Total for Question 24 = 23 marks)

TOTAL FOR SECTION C = 23 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key: relative atomic mass / atomic symbol / name / atomic (proton) number									(13)	(14)	(15)	(16)	(17)	
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	(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