Please check the examination details below before entering your candidate information

Candidate surname	Other names

Centre Number

Candidate Number

Pearson Edexcel International Advanced Level

Monday 8 January 2024

Morning (Time: 1 hour 45 minutes)

Paper reference **WCH14/01**

Chemistry

International Advanced Level
UNIT 4: Rates, Equilibria and Further Organic Chemistry

You must have:
Scientific calculator, Data Booklet, ruler

Total Marks

Instructions

- Use **black** ink or ball-point pen.
- If pencil is used for diagrams/sketches/graphs it must be dark (HB or B).
- **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.*
- In the question marked with an **asterisk (*)**, marks will be awarded for your ability to structure your answer logically, showing how the points that you make are related or follow on from each other where appropriate.
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Show all your working in calculations and include units where appropriate.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

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 The equation for a reaction is shown.

$$A(g) + 2B(g) \rightleftharpoons 3C(s) + 4D(g)$$

(a) Some collisions between reactant molecules do not lead to the formation of products.

What is the best explanation for this?

(1)

☒ **A** the reactant concentrations are too low

☒ **B** the collisions do not have sufficient energy

☒ **C** the reaction is at equilibrium

☒ **D** the molecules do not collide in the correct ratio

(b) What are the units of the equilibrium constant, K_p, for this reaction?

(1)

☒ **A** atm

☒ **B** atm^{-1}

☒ **C** atm^{4}

☒ **D** atm^{-4}

(Total for Question 1 = 2 marks)

2 Nitrogen(V) oxide, N_2O_5, decomposes in a first order reaction.
At 45 °C, the half-life for this reaction is 1400 s.
In an experiment, the initial concentration of nitrogen(V) oxide is 1.0 mol dm^{-3}.

What is the concentration, in mol dm^{-3}, of nitrogen(V) oxide after 4200 s?

☒ **A** 0.875

☒ **B** 0.500

☒ **C** 0.250

☒ **D** 0.125

(Total for Question 2 = 1 mark)

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3 Ammonia is produced by the reaction of nitrogen with hydrogen in the presence of an iron catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

(a) Which of the following statements about the catalyst is **not** correct?

(1)

☒ **A** it lowers the activation energy of the reaction

☒ **B** it has no effect on the equilibrium constant for the reaction

☒ **C** it alters the enthalpy change of the reaction

☒ **D** it reduces the energy cost of the reaction

(b) Which conditions favour the highest percentage of ammonia in an equilibrium mixture from identical amounts of nitrogen and hydrogen?

(1)

☒ **A** a temperature of 400 K and a pressure of 200 kPa

☒ **B** a temperature of 400 K and a pressure of 200 atm

☒ **C** a temperature of 400 °C and a pressure of 200 kPa

☒ **D** a temperature of 400 °C and a pressure of 200 atm

(Total for Question 3 = 2 marks)

4 The equations for three reactions involving hydrogen are shown.

J $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

K $N_2(g) + 2H_2(g) \rightarrow N_2H_4(l)$

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

What is the order of **increasing** standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for these reactions?

☒ **A** J, K, L

☒ **B** K, L, J

☒ **C** K, J, L

☒ **D** L, K, J

(Total for Question 4 = 1 mark)

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

5 Methane reacts with steam to produce carbon dioxide and hydrogen.

$$CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$$

The standard molar entropies of the reactants and products are given in the table.

Substance	$S^{\ominus}$ / J K^{-1} mol^{-1}
$CH_4(g)$	186
$H_2O(g)$	189
$CO_2(g)$	214
$H_2(g)$	131

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

☒ **A** –174

☒ **B** –30

☒ **C** +30

☒ **D** +174

(Total for Question 5 = 1 mark)

6 What are the signs of the entropy changes at 373 K when water vapour condenses?

$$H_2O(g) \rightarrow H_2O(l)$$

		ΔS_{system}	$\Delta S_{surroundings}$
☒	**A**	positive	positive
☒	**B**	positive	negative
☒	**C**	negative	positive
☒	**D**	negative	negative

(Total for Question 6 = 1 mark)

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

7 At 50 °C, the ionic product of water, K_w, is 5.5×10^{-14} $mol^2\,dm^{-6}$.

At this temperature, water is

☒ **A** neutral with a pH of 7.0

☒ **B** neutral with a pH of 6.6

☒ **C** acidic with a pH of 6.6

☒ **D** alkaline with a pH of 7.4

(Total for Question 7 = 1 mark)

8 Equimolar solutions of four acids are prepared. Which solution has the **lowest** pH?

Use electronegativity values from the Data Booklet.

☒ **A** CH_3COOH

☒ **B** $CH_2ClCOOH$

☒ **C** $CH_2BrCOOH$

☒ **D** CH_2ICOOH

(Total for Question 8 = 1 mark)

9 Some equations for acid-base equilibria are shown.

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$$

What is the conjugate acid of HPO_4^{2-}?

☒ **A** H_3PO_4

☒ **B** H_3O^+

☒ **C** $H_2PO_4^-$

☒ **D** PO_4^{3-}

(Total for Question 9 = 1 mark)

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

10 What is the pH of a 0.200 mol dm^{-3} solution of strontium hydroxide, $Sr(OH)_2$?

$$K_w = 1.00 \times 10^{-14}\ \text{mol}^2\,\text{dm}^{-6}$$

☒ **A** 14.0

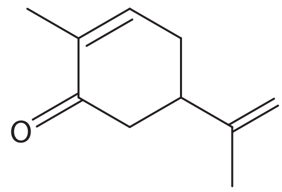
☒ **B** 13.6

☒ **C** 13.3

☒ **D** 12.6

(Total for Question 10 = 1 mark)

11 Carvone is an oil used in aromatherapy.



(a) Carvone shows

(1)

☒ **A** geometric and optical isomerism

☒ **B** geometric isomerism only

☒ **C** optical isomerism only

☒ **D** neither geometric nor optical isomerism

(b) Which reagent gives a positive result when added to carvone?

(1)

☒ **A** ammoniacal silver nitrate (Tollens' reagent)

☒ **B** aqueous sodium carbonate

☒ **C** iodine in the presence of an alkali

☒ **D** 2,4-dinitrophenylhydrazine

(c) How many peaks would be expected to appear in a carbon-13 (^{13}C) NMR spectrum of carvone?

(1)

☒ **A** 10

☒ **B** 9

☒ **C** 8

☒ **D** 7

(Total for Question 11 = 3 marks)

12 From which two reactants could $CH_3(CH_2)_2COO(CH_2)_4CH_3$ be made?

- ☒ **A** butanoic acid and pentan-1-ol
- ☒ **B** butanoyl chloride and butan-1-ol
- ☒ **C** butanal and pentan-1-ol
- ☒ **D** pentanoic acid and butan-1-ol

(Total for Question 12 = 1 mark)

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13 The reaction between ethanoic acid and lithium tetrahydridoaluminate(III) is best described as

- ☒ **A** elimination
- ☒ **B** oxidation
- ☒ **C** reduction
- ☒ **D** substitution

(Total for Question 13 = 1 mark)

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14 Which substance is the least soluble in water?

- ☒ **A** propanal
- ☒ **B** propan-1-ol
- ☒ **C** propanoic acid
- ☒ **D** sodium propanoate

(Total for Question 14 = 1 mark)

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

15 (a) The mass spectrum of compound **X** shows a large peak at m/z = 59.

This peak is due to the fragmentation of the molecular ion.

Which compound is most likely to be **X**?

(1)

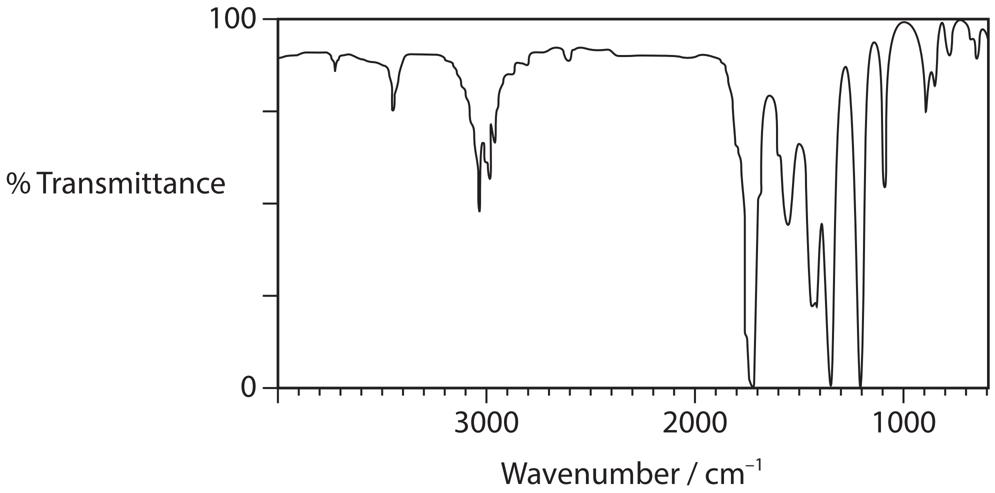
☒ **A** 2-methylpropan-2-ol

☒ **B** pentane

☒ **C** propanal

☒ **D** propanone

(b) Compound **Y** does not react with acidified aqueous sodium dichromate. The infrared spectrum of **Y** is shown.



Which compound is most likely to be **Y**? Refer to the Data Booklet.

(1)

☒ **A** 2-methylpropan-2-ol

☒ **B** pentane

☒ **C** propanal

☒ **D** propanone

(Total for Question 15 = 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.

16 A group of students investigated the kinetics of a 'clock' reaction.

The reaction investigated was that between hydrogen peroxide and iodide ions in the presence of acid.

Reaction 1 $H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$

In this 'clock' reaction, a fixed volume of aqueous sodium thiosulfate, $Na_2S_2O_3$, and a small amount of starch were added to the reaction mixture.

The added thiosulfate ions react with the iodine produced in **Reaction 1**.

Reaction 2 $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

When all the thiosulfate ions have reacted, the presence of iodine is detected by the formation of a starch-iodine complex. The students recorded the time taken for this complex to form.

(a) (i) State the final colour of the mixture containing the starch-iodine complex.

(1)

....

(ii) Under appropriate conditions, the reciprocal of time can be used as an approximate measure of the initial rate of the reaction.

Explain why the concentration of the sodium thiosulfate must be low compared with the initial concentrations of the other reagents.

(2)

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(b) Four reaction mixtures, with different initial concentrations of hydrogen peroxide, hydrogen ions and iodide ions, were prepared.

Each mixture had the same volume and contained the same amount of sodium thiosulfate and starch.

Mixture	$[H_2O_2]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	Time / s	1 ÷ time / s^{-1}
1	5.4×10^{-2}	1.7×10^{-5}	8.2×10^{-3}	195	5.13×10^{-3}
2	2.7×10^{-2}	1.7×10^{-5}	8.2×10^{-3}	391	2.56×10^{-3}
3	5.4×10^{-2}	1.7×10^{-5}	1.6×10^{-2}	97	1.03×10^{-2}
4	5.4×10^{-2}	1.7×10^{-4}	8.2×10^{-3}	204	4.90×10^{-3}

(i) Use the results in the table to deduce the order of **Reaction 1** with respect to hydrogen peroxide, hydrogen ions and iodide ions.
Justify each answer by referring to relevant data from the table.

(3)

Hydrogen peroxide ....

....

Hydrogen ions ....

....

Iodide ions ....

....

(ii) Write the overall rate equation for **Reaction 1** using your answers to (b)(i).

(1)

(iii) All four mixtures contained 8.50×10^{-5} mol of sodium thiosulfate.
Calculate the amount of iodine that had reacted with the sodium thiosulfate when the colour changed in **Reaction 2**.

(1)

(iv) Calculate the rate of reaction, in mol dm^{-3} s^{-1}, with respect to **hydrogen peroxide** using the answer from (b)(iii), the stoichiometry of **Reaction 1** and data from Mixture 1.
The total volume of **each** Mixture was 0.050 dm^3.

(2)

(v) Calculate a value for the rate constant of **Reaction 1** using data from Mixture 1 and your answers to (b)(ii) and (b)(iv).
Include the units of the rate constant.

(2)

(c) The activation energy for **Reaction 1** may be found by repeating the experiment at different temperatures.
Each student carried out an experiment at a different temperature.
One of the students misread the thermometer in their experiment.

ln rate	T / K	$1 \div T$ / K^{-1}
–1.8	333	0.00300
–2.5	323	0.00310
–3.6	308	0.00325
–4.0	307	0.00326
–4.7	291.5	0.00343
–6.0	278	0.00360

The activation energy, E_a, for a reaction may be found by plotting a graph of ln rate against $1/T$.
The gradient of the resulting line of best fit can be used in the Arrhenius equation to determine a value for E_a, in $kJ\,mol^{-1}$.

(i) Determine the value for E_a for **Reaction 1** by plotting a graph using the axes provided.
You should take into account the error made by one of the students.

$$\ln \text{rate} = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31\,J\,K^{-1}\,mol^{-1}$$

(5)

E_a .... kJ mol^{-1}

(ii) The students all used thermometers capable of reading to the same precision. Use your graph to deduce the temperature that the student who made the error should have read on their thermometer.

(2)

(Total for Question 16 = 19 marks)

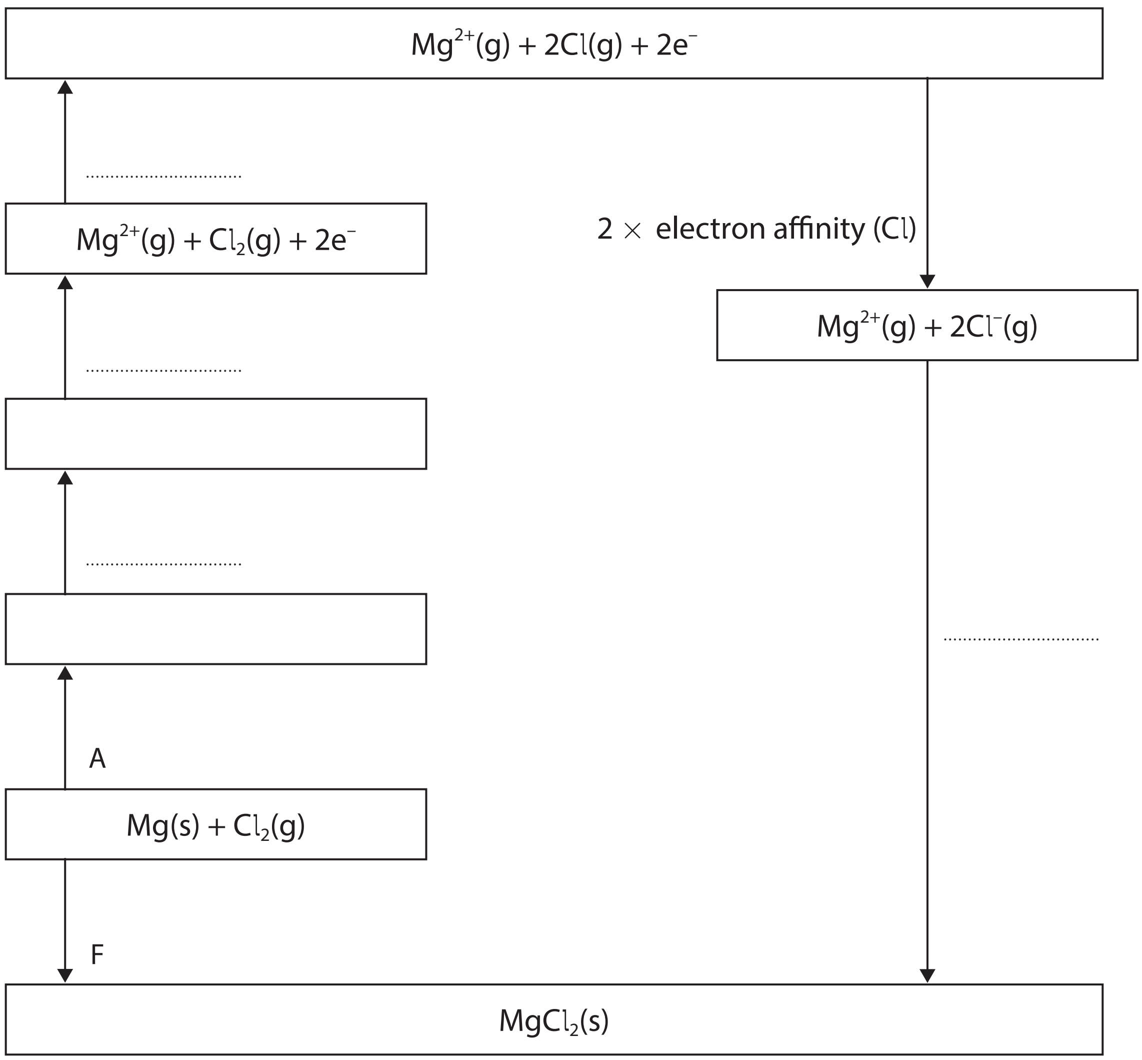
17 The question is about lattice energies.

The table shows energy values used in a Born–Haber cycle for magnesium chloride, $MgCl_2$.

Energy change	Label	Value / $kJ\,mol^{-1}$
Enthalpy change of atomisation of magnesium	A	+148
First ionisation energy of magnesium	B	+738
Second ionisation energy of magnesium	C	+1451
Enthalpy change of atomisation of chlorine	D	+122
Lattice energy of magnesium chloride	E	–2526
Enthalpy change of formation of magnesium chloride	F	–641

(a) (i) Complete the Born–Haber cycle for magnesium chloride by adding labels for each of the four energy changes and writing formulae in the two empty boxes.

(3)



(ii) Calculate a value for the electron affinity of chlorine, in $kJ\,mol^{-1}$, using the data in the table and the completed Born–Haber cycle.

(2)

(iii) Explain why, when magnesium reacts with chlorine, $MgCl_2$ is formed rather than $MgCl_3$.

(2)

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(iv) Calculate the standard molar enthalpy change of solution of magnesium chloride, in $kJ\,mol^{-1}$, using the data shown and the value for the lattice energy, LE[$MgCl_2$], given in the table.

Data $\Delta_{hyd}H^{\ominus}[Mg^{2+}(g)] = -1920\,kJ\,mol^{-1}$ $\Delta_{hyd}H^{\ominus}[Cl^{-}(g)] = -364\,kJ\,mol^{-1}$

(2)

*(b) Lattice energies from the Born–Haber cycle are based on experimental values. Theoretical lattice energies can also be calculated. Experimental and theoretical values for three different crystal lattices are shown.

Compound	Experimental lattice energy / kJ mol^{-1}	Theoretical lattice energy / kJ mol^{-1}
sodium fluoride NaF	–918	–912
magnesium fluoride MgF_2	–2957	–2913
magnesium chloride $MgCl_2$	–2526	–2326

Discuss the reasons for the differences in these six values of lattice energy in terms of the structure and bonding in these three substances.

(6)

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(Total for Question 17 = 15 marks)

P 7 3 4 5 6 A 0 1 7 2 8

18 Methyl 2-hydroxypropanoate is used as an industrial solvent.
It may be prepared in three steps using ethanal as the starting material.

$$CH_3CHO \xrightarrow{\text{Step } \mathbf{1}} CH_3CH(OH)CN \xrightarrow{\text{Step } \mathbf{2}} CH_3CH(OH)COOH \xrightarrow{\text{Step } \mathbf{3}} CH_3CH(OH)COOCH_3$$

(a) Name the reagent(s) in Step **1** and Step **2**.

(2)

Step 1

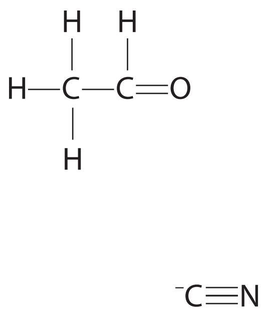
Reagent(s) ....

Step 2

Reagent(s) ....

(b) (i) Complete the mechanism for Step **1**, using curly arrows and relevant lone pairs, charges and dipoles.

(4)



(ii) Explain why the 2-hydroxypropanoic acid, $CH_3CH(OH)COOH$, produced is **not** optically active.

(3)

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(c) (i) State the type of reaction in Step **3**.

(1)

....

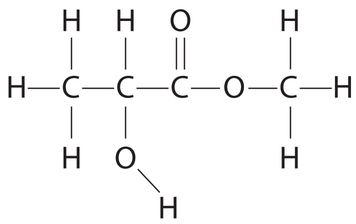
(ii) A small amount of a polymeric compound is formed during Step **3**. Deduce the structure for the repeat unit of the polymer formed.

(1)

(d) The high-resolution proton nuclear magnetic resonance (NMR) spectrum of methyl 2-hydroxypropanoate gives four peaks, **J**, **K**, **L** and **M**.
Peaks **L** and **M** are **singlets** with relative intensities of **one** and **three** respectively.

(i) Label the displayed formula to show the protons responsible for these two peaks.

(2)



(ii) Complete the table to show the expected number of hydrogen atoms and expected splitting pattern for peaks **J** and **K**.

(2)

Peak	δ / ppm	Number of hydrogen atoms	Splitting pattern
J	1.3		
K	4.1		
L	3.6	1	singlet
M	3.7	3	singlet

(Total for Question 18 = 15 marks)

TOTAL FOR SECTION B = 49 MARKS

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SECTION C

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

19 (a) Ethyl propanoate, $CH_3CH_2COOCH_2CH_3$, smells of pineapple and is used as a flavouring. It may be hydrolysed using hydrochloric acid as a catalyst to produce propanoic acid and ethanol.

$$CH_3CH_2COOCH_2CH_3(l) + H_2O(l) \rightleftharpoons CH_3CH_2COOH(l) + CH_3CH_2OH(l)$$

A mixture was prepared using 0.100 mol of ethyl propanoate and 0.200 mol of water containing the catalyst.
The mixture was left to reach equilibrium at 25 °C.
The equilibrium mixture contained 0.0440 mol of propanoic acid.

(i) Calculate the value for K_c for this equilibrium at 25 °C.
Give your answer to an appropriate number of significant figures.

(4)

(ii) The standard enthalpy change, $\Delta_r H^{\ominus}$, for this reaction is close to, but not exactly zero. Explain this statement by considering the type and number of bonds being broken and made. No calculations are required.

(2)

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(iii) Deduce the effect of increasing the temperature on the total entropy change of this reaction, ΔS_{total}, and on the value of the equilibrium constant, K_c.
Assume that ΔS_{system} does not change with temperature.

(3)

(b) Propanoic acid is a weak acid.

(i) State the difference between a weak acid and a strong acid such as hydrochloric acid.

(1)

(ii) Calculate the pH of 0.500 mol dm^{-3} hydrochloric acid at 25 °C.

(1)

(iii) Calculate the pH of 0.500 mol dm^{-3} propanoic acid at 25 °C.

K_a (propanoic acid) = 1.30×10^{-5} mol dm^{-3} at 25 °C.

(3)

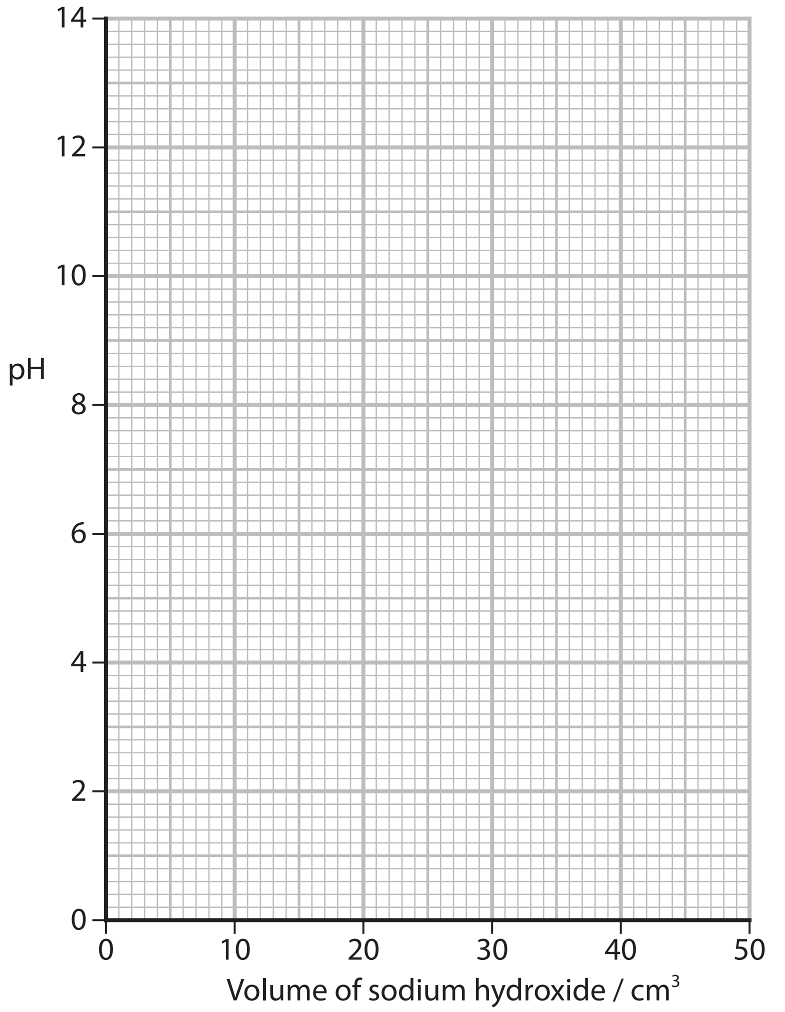
(c) The number of moles of propanoic acid in a solution may be determined by titration with aqueous sodium hydroxide.

(i) Calculate the pH at the point in the titration where half the acid has been neutralised. You must show your working.

(2)

(ii) Sketch the titration curve showing the change in pH when $50\,cm^3$ of $0.500\,mol\,dm^{-3}$ sodium hydroxide is added to $25.0\,cm^3$ of propanoic acid of the same concentration, using your answers to (b)(iii) and (c)(i).

(3)



(iii) Suggest a suitable indicator for this titration. Justify your choice by referring to your titration curve in (c)(ii).
Use the Data Booklet.

(2)

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(Total for Question 19 = 21 marks)

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

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The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1.0 **H** hydrogen 1

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)
																	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