Pearson Edexcel
International
Advanced Level

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

Thursday 11 January 2018 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH04/01

**Candidates must have: Scientific calculator
Data Booklet**

Total Marks

Instructions

- Use **black** ink or **black** 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.
- Try to answer every question.
- Check your answers if you have time at the end.
- Show all your working in calculations and give units where appropriate.

Turn over ▶

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 half-life of a reaction is

⊠ **A** half the time for the reaction to go to completion.

⊠ **B** the time taken for the rate of reaction to halve.

⊠ **C** **only** the time taken for the concentration of a reactant at $t = 0$ to halve.

⊠ **D** the time taken for **any** concentration of a reactant to halve.

(Total for Question 1 = 1 mark)

2 When dilute aqueous solutions of potassium manganate(VII), ethanedioic acid and sulfuric acid are mixed, the following reaction occurs:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$
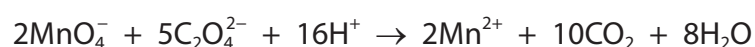
The rate of reaction is slow at first, accelerates rapidly and then gradually slows down. The best explanation for these observations is that the

⊠ **A** reaction is exothermic, so after a small amount of reaction the temperature rises sharply.

⊠ **B** reaction is acid catalysed and the formation of carbon dioxide results in an increased concentration of hydrogen ions.

⊠ **C** reaction is catalysed by the manganese(II) ions which are formed in the reaction.

⊠ **D** high concentration of hydrogen ions from the sulfuric acid inhibits the dissociation of the ethanedioic acid.

(Total for Question 2 = 1 mark)

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

3 In each of the graphs, quantity Y is plotted against quantity X.
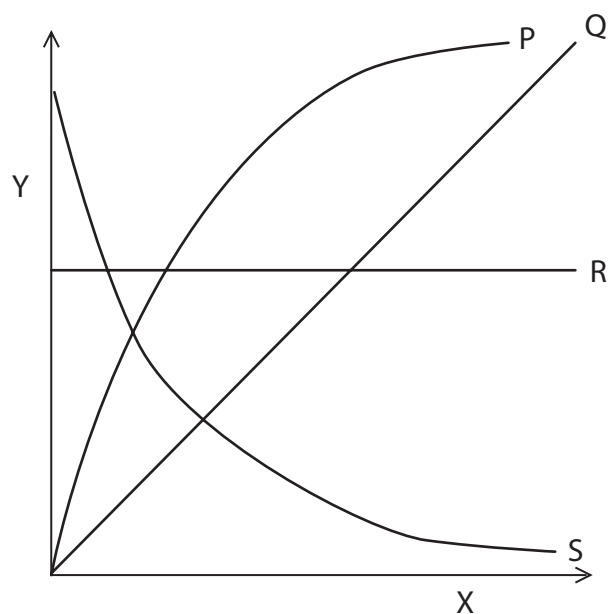
(a) In which graph is Y the concentration of a product and X the time for a **zero** order reaction?

(1)

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

(b) In which graph is Y the rate of reaction and X the concentration of a reactant for a **first** order reaction?

(1)

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

(Total for Question 3 = 2 marks)

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

4 Potassium nitrate is very soluble in water:

$$KNO_3(s) + aq \rightleftharpoons K^+(aq) + NO_3^-(aq) \quad \Delta H^{\ominus} = +34.9 \text{ kJ mol}^{-1}$$

The solubility of potassium nitrate increases rapidly with temperature.
The best explanation for this is

☒ **A** $\Delta S_{surroundings}$ becomes less negative as the temperature increases.

☒ **B** the molar entropy of a substance increases with temperature.

☒ **C** ΔS_{system} increases as the temperature increases.

☒ **D** there are more particles on the right-hand side of the equation.

(Total for Question 4 = 1 mark)

5 Consider the following reactions in the gas phase:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \textbf{F}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \textbf{G}$$

$$C_2H_6(g) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) \qquad \textbf{H}$$
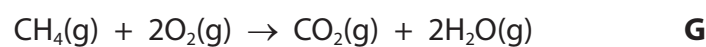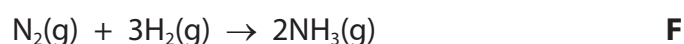
What is the order of **increasing** standard entropy change, $\Delta S^{\ominus}_{system}$, for these reactions, with the most negative first?

☒ **A** F, G, H

☒ **B** F, H, G

☒ **C** G, H, F

☒ **D** H, G, F

(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 standard molar entropy, $S^{\ominus}$, of a substance is zero for all

☒ **A** elements under standard conditions.

☒ **B** monatomic gases under standard conditions.

☒ **C** perfect crystals at absolute zero (0 K).

☒ **D** substances in a system at equilibrium.

(Total for Question 6 = 1 mark)

7 An important reaction in the extraction of iron is

$$Fe_2O_3(s) + 3C(s) \rightleftharpoons 2Fe(s) + 3CO(g)$$
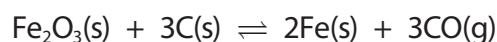
The equilibrium constant, K_c, for this reaction is given by the expression

☒ **A** $K_c = [CO(g)]^3$

☒ **B** $K_c = \dfrac{1}{[CO(g)]^3}$

☒ **C** $K_c = \dfrac{[Fe(s)]^2 \times [CO(g)]^3}{[Fe_2O_3(s)] \times [C(s)]^3}$

☒ **D** $K_c = \dfrac{[Fe_2O_3(s)] \times [C(s)]^3}{[Fe(s)]^2 \times [CO(g)]^3}$

(Total for Question 7 = 1 mark)

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

8 The graph shows the variation with temperature of the percentage yield of product in a gaseous equilibrium at different pressures.
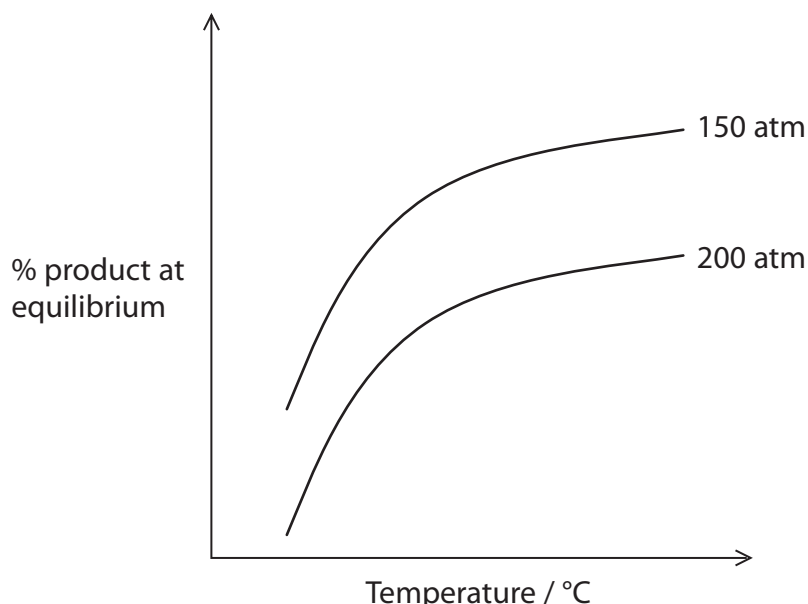
For the forward reaction

	$\Delta H_{reaction}$	Total number of moles
☒ **A**	positive	increases
☒ **B**	positive	decreases
☒ **C**	negative	increases
☒ **D**	negative	decreases

(Total for Question 8 = 1 mark)

9 The reaction between hydrogen and iodine may be represented by two equations:

$$H_2(g) \ + \ I_2(g) \ \rightleftharpoons \ 2HI(g) \qquad\qquad (1)$$

$$\tfrac{1}{2}H_2(g) \ + \ \tfrac{1}{2}I_2(g) \ \rightleftharpoons \ HI(g) \qquad\qquad (2)$$
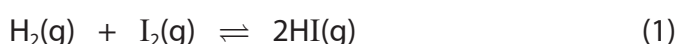
For equation 1, the equilibrium constant is $K_p(1)$ and for equation 2, the equilibrium constant is $K_p(2)$. What is the relationship between $K_p(1)$ and $K_p(2)$?

☒ **A** $K_p(1) = K_p(2)$

☒ **B** $K_p(1) = \sqrt{K_p(2)}$

☒ **C** $K_p(1) = (K_p(2))^2$

☒ **D** $K_p(1) = 2 \times K_p(2)$

(Total for Question 9 = 1 mark)

10 Consider the reaction

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$
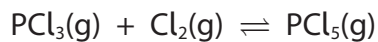
How are K_p and the mole fraction of $PCl_5(g)$ affected when the pressure is increased at constant temperature?

	K_p	Mole fraction of $PCl_5(g)$
☒ **A**	increases	increases
☒ **B**	increases	decreases
☒ **C**	unchanged	increases
☒ **D**	unchanged	decreases

(Total for Question 10 = 1 mark)

11 When concentrated sulfuric acid is added to ethanoic acid, the reaction is

$$H_2SO_4 + CH_3COOH \rightleftharpoons HSO_4^- + CH_3COOH_2^+$$
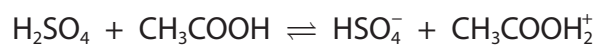
What are the Brønsted-Lowry conjugate acid-base pairs in this equilibrium?

	Acid 1	Conjugate base of acid 1	Acid 2	Conjugate base of acid 2
☒ **A**	H_2SO_4	CH_3COOH	$CH_3COOH_2^+$	HSO_4^-
☒ **B**	H_2SO_4	$CH_3COOH_2^+$	CH_3COOH	HSO_4^-
☒ **C**	H_2SO_4	HSO_4^-	CH_3COOH	$CH_3COOH_2^+$
☒ **D**	H_2SO_4	HSO_4^-	$CH_3COOH_2^+$	CH_3COOH

(Total for Question 11 = 1 mark)

12 When 0.10 mol dm^{-3} sodium hydroxide is titrated with 25 cm^3 of ethanoic acid, of a similar concentration, the best indicator would be

☒ **A** litmus.

☒ **B** methyl orange.

☒ **C** phenolphthalein.

☒ **D** universal indicator.

(Total for Question 12 = 1 mark)

13 For ethanoic acid $pK_a = 4.76$. The pH of a solution of ethanoic acid with a concentration of 1×10^{-10} mol dm^{-3} is approximately

☒ **A** 5.2

☒ **B** 7.0

☒ **C** 7.4

☒ **D** 15

(Total for Question 13 = 1 mark)

14 What type(s) of stereoisomerism will be shown by the compound with the structure given below?
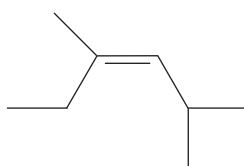
☒ **A** No stereoisomerism.

☒ **B** Geometric isomerism only.

☒ **C** Optical isomerism only.

☒ **D** Both geometric isomerism and optical isomerism.

(Total for Question 14 = 1 mark)

15 Some of the physical properties of aldehydes and ketones can be explained by the fact that they

☒ **A** never form hydrogen bonds.

☒ **B** form hydrogen bonds in the liquid state but not in aqueous solution.

☒ **C** form hydrogen bonds in aqueous solution but not in the liquid state.

☒ **D** form hydrogen bonds in both the liquid state and aqueous solution.

(Total for Question 15 = 1 mark)

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

**16** Which correctly shows the reactions of ethanal and propanone?

	Tollens' reagent	2,4-dinitrophenylhydrazine
☒ **A**	both ethanal and propanone react	both ethanal and propanone react
☒ **B**	only ethanal reacts	only propanone reacts
☒ **C**	only propanone reacts	only ethanal reacts
☒ **D**	only ethanal reacts	both ethanal and propanone react

(Total for Question 16 = 1 mark)

17 Under suitable conditions, butanoic acid

☒ **A** reacts with acidified potassium dichromate(VI) to form butan-1-ol.

☒ **B** reacts with phosphorus(V) chloride to form 1-chlorobutane.

☒ **C** forms when butyl methanoate reacts with sulfuric acid.

☒ **D** forms when butanenitrile reacts with hydrochloric acid.

(Total for Question 17 = 1 mark)

18 This question is about the following compounds:

ethyl ethanoate

methyl propanoate

propyl methanoate

butanoic acid

Which of these compounds are isomers?

☒ **A** Only ethyl ethanoate and methyl propanoate.

☒ **B** Only methyl propanoate and propyl methanoate.

☒ **C** Only ethyl ethanoate, methyl propanoate and propyl methanoate.

☒ **D** All four compounds.

(Total for Question 18 = 1 mark)

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

19 When ethane-1,2-diol, $HOCH_2CH_2OH$, forms a polymer with benzene 1,4-dicarboxylic acid, $HOOCC_6H_4COOH$, the repeat unit of the resulting polymer is

☒ **A** $-OCH_2CH_2OOCC_6H_4CO-$

☒ **B** $-OCH_2CH_2OCC_6H_4CO-$

☒ **C** $-OC_6H_4OOCCH_2CH_2CO-$

☒ **D** $-CH_2CH_2OOCOC_6H_4OCO-$

(Total for Question 19 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

20 Benzenecarboxylic acid (benzoic acid) is a weak acid used as a food preservative.

Data for benzenecarboxylic acid
Formula C_6H_5COOH
Molar mass 122.1 g mol^{-1}
Solubility in water 3.44 g dm^{-3} at $25\,°C$ 56.3 g dm^{-3} at $100\,°C$
pK_a 4.20

(a) (i) Write the equation for the dissociation of benzenecarboxylic acid in water. Include state symbols.

(1)

(ii) Write the expression for K_a for benzenecarboxylic acid.

(1)

(iii) Calculate the pH of a saturated solution of benzenecarboxylic acid at $25\,°C$.

(4)

(iv) State **two** approximations used in the calculation of pH in (a)(iii).

(2)

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(b) An aqueous solution of sodium hydroxide of concentration 0.0025 mol dm^{-3} was added to a flask containing 25.0 cm^3 of a 0.0020 mol dm^{-3} solution of benzenecarboxylic acid. The pH of the solution in the flask was continuously monitored as the sodium hydroxide was added and the results plotted on a graph. The graph is shown below.
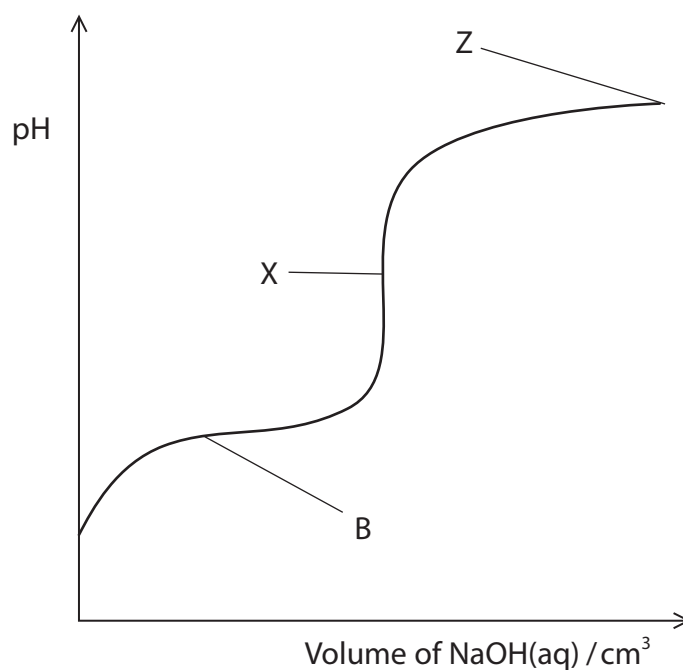
(i) Suggest a value for the pH at X. Justify your answer.

(2)

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12

(ii) Calculate the volume of NaOH(aq) added when X is reached.

(2)

(iii) Calculate the maximum possible pH at Z, when a very large excess of sodium hydroxide solution has been added.

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

(2)

(c) The region labelled B in the graph is referred to as the 'buffer region'.

(i) Define the term 'buffer'.

(2)

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(ii) Explain, by referring **only** to the shape of the graph, why B is a buffer region.

(2)

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*(iii) Identify the species present in the solution at B which are responsible for the buffering action. By referring to these species, explain how the solution acts as a buffer. Equations are **not** required.

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(d) Buffers occur in many biochemical systems, for example blood. Suggest why this is so.

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(Total for Question 20 = 23 marks)

21 This question is about the organic reactions shown in the diagram.
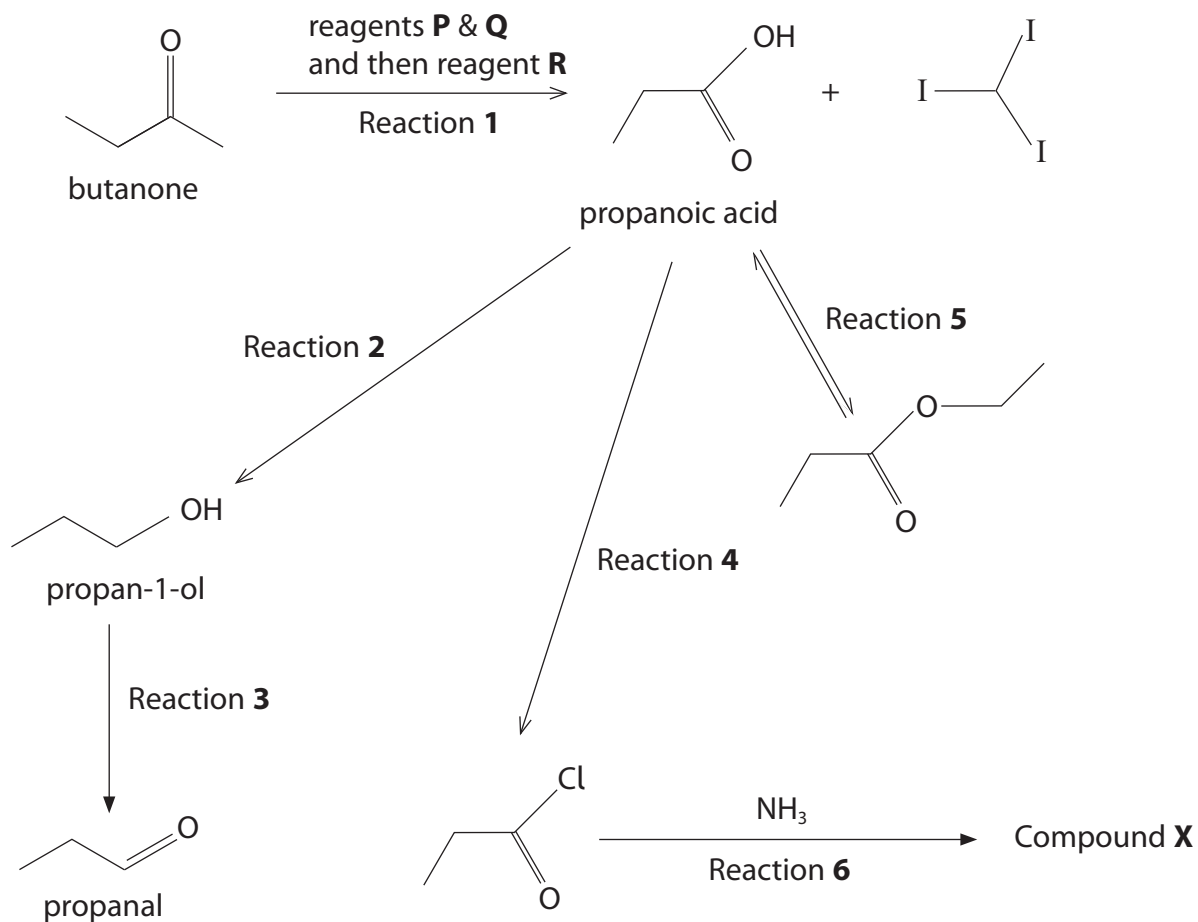
(a) (i) **Name** reagents **P** and **Q** used in Reaction **1**.

(2)

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(ii) Identify reagent **R** used in Reaction **1** and explain why it is needed.

(2)

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P 5 1 9 3 9 A 0 1 5 2 4

(iii) Name the second product formed in Reaction **1**.

(1)

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(iv) Identify the reagent and the solvent required for Reaction **2**, stating the essential condition for the reaction.

(2)

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(v) The reagents used in Reaction **3** are potassium dichromate(VI) and sulfuric acid. State how this reaction must be carried out to ensure that the main product is propanal.

(1)

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(vi) Identify the reagent required for Reaction **4**.

(1)

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(vii) **Name** compound **X** formed in Reaction **6**.

(1)

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(b) Mass spectrometry and infrared spectroscopy were used to analyse samples of butanone and propanal.

(i) The base peak (tallest peak) in the mass spectrum of butanone is at $m / e = 43$ while the base peak in propanal is at $m / e = 29$.
Identify the species responsible for these two peaks.

(2)

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(ii) Explain, by quoting values from your Data Booklet, how infrared spectroscopy could be used to distinguish between butanone and propanal.

(2)

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(c) The full equation for the reaction in Reaction **5** is shown. The molar masses (in g mol^{-1}) of the compounds involved are given below the equation.

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

$$74 \qquad\qquad 46 \qquad\qquad\qquad 102 \qquad\qquad 18$$
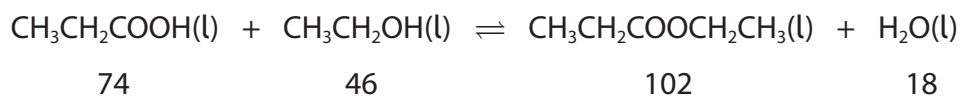
(i) Give the expression for the equilibrium constant, K_c, for this reaction.

(1)

(ii) When this reaction is carried out in the laboratory, a small amount of sulfuric acid is added to the reaction mixture. State the role of the sulfuric acid.

(1)

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*(iii) In an experiment to determine the equilibrium constant, K_c, 18.5 g of propanoic acid, 23.0 g of ethanol and 36.0 g of water were mixed together and a small amount of concentrated sulfuric acid added. After several days, it was found that the equilibrium mixture contained 0.140 mol of propanoic acid. Calculate the equilibrium constant, showing **all** of your working.

(5)

(d) Propanoic acid also reacts with chlorine in the presence of ultraviolet radiation to form 2-chloropropanoic acid.

$$CH_3CH_2COOH \ + \ Cl_2 \xrightarrow{\text{UV radiation}} CH_3CHClCOOH \ + \ HCl$$

(i) What information suggests that the mechanism of this reaction involves free radicals?

(1)

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(ii) Draw the structure of the free radical formed from the propanoic acid.

(1)

(iii) Explain why the product of this reaction has no effect on the plane of plane-polarised light.

(3)

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(Total for Question 21 = 26 marks)

TOTAL FOR SECTION B = 49 MARKS

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

22 Halogenoalkanes react with alkalis to form the corresponding alcohol.

$$RX + OH^- \rightarrow ROH + X^-$$
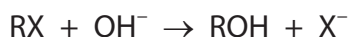
A study of the kinetics of the reaction between a halogenoalkane, C_4H_9Br, and aqueous sodium hydroxide was carried out using various volumes of the solutions, both of which were 0.150 mol dm^{-3}, mixed with ethanol as the solvent.

The results were collected in a table.

Mixture	Volume of C_4H_9Br solution /cm^3	Volume of NaOH(aq) solution /cm^3	Volume of ethanol /cm^3	Total volume / cm^3	Rate / mol dm^{-3} s^{-1}
1	100	250	150	500	2.50×10^{-4}
2	50	250	200	500	1.25×10^{-4}
3	200	250	550	1000	1.25×10^{-4}

(a) One method of monitoring the progress of this reaction in one of these mixtures involves a series of titrations. State the steps involved in this procedure, including how the rate is obtained from the data.

(6)

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(b) Explain why ethanol, rather than water, is used as the solvent.

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(c) (i) Use the results in the table to deduce the rate equation for the reaction of C_4H_9Br with NaOH. Explain, by referring to the data, how you arrived at your answer.

(3)

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(ii) Use the data from Mixture 1 and your answer to (c)(i) to calculate the rate constant for the reaction, stating the units.

(3)

Turn over ▶

(iii) How, if at all, would the rate constant of the reaction change if the bromine atom in C_4H_9Br was replaced by an iodine atom? Fully justify your answer.

(2)

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(iv) State what can be deduced about the mechanism of the reaction of C_4H_9Br with NaOH by considering **only** the rate equation for the reaction.

(1)

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(v) Draw the most likely **displayed** formula of C_4H_9Br. Justify your answer.

(2)

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(d) Bromoethane, C_2H_5Br, reacts with alkali in an S_N2 mechanism. Draw the **first** step of this mechanism.
Show the relevant curly arrows and lone pair, and the species formed.

(3)

(Total for Question 22 = 21 marks)

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

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

(1)	(2)											(13)	(14)	(15)	(16)	(17)	(18)
1	2							1.0 **H** hydrogen 1				3	4	5	6	7	0 (8) 4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	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

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