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)

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 ▶

P51939A

6/5/5/5/4/1/

P 5 1 9 3 9 A 0 1 2 4

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 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.

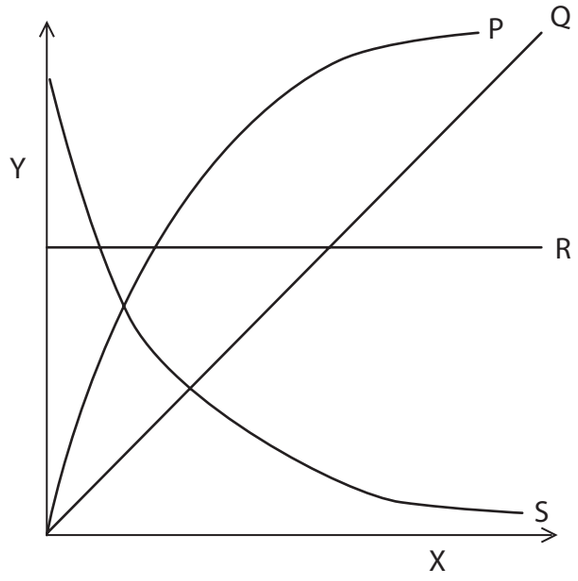
☒ **C** reaction is catalysed by the manganese(II) ions which are formed in the reaction.

☒ **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:

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

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

$$C_2H_6(g) + 3½O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) \qquad \textbf{H}$$

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** $K_c = \dfrac{1}{[CO(g)]^3}$

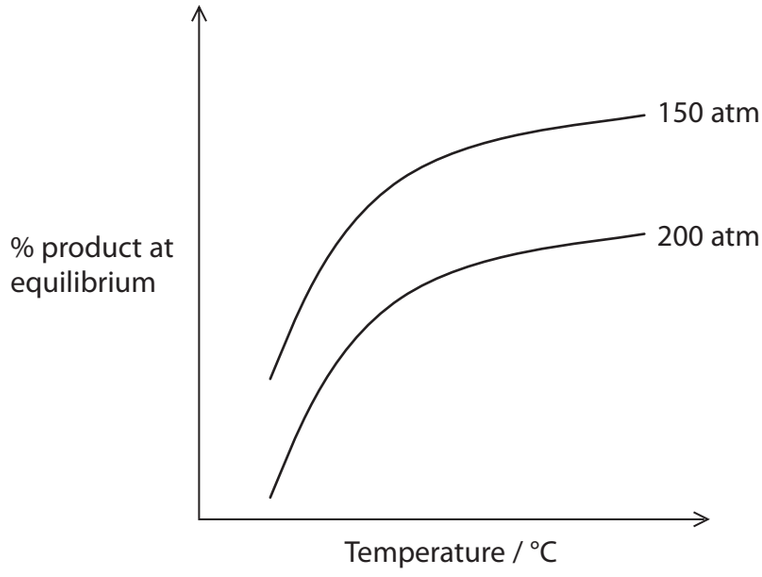
☒ **C** $K_c = \dfrac{[Fe(s)]^2 \times [CO(g)]^3}{[Fe_2O_3(s)] \times [C(s)]^3}$

☒ **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:

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

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons HI(g) \quad (2)$$

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

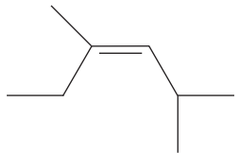
☒ **B** 7.0

☒ **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)

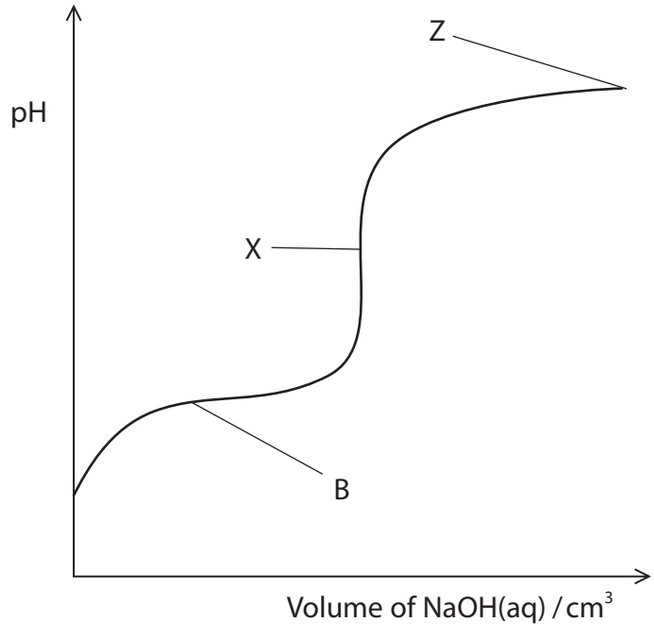
(iii) Calculate the pH of a saturated solution of benzenecarboxylic acid at 25 °C.

(4)

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

(2)

(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)

(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)

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

(2)

*(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.

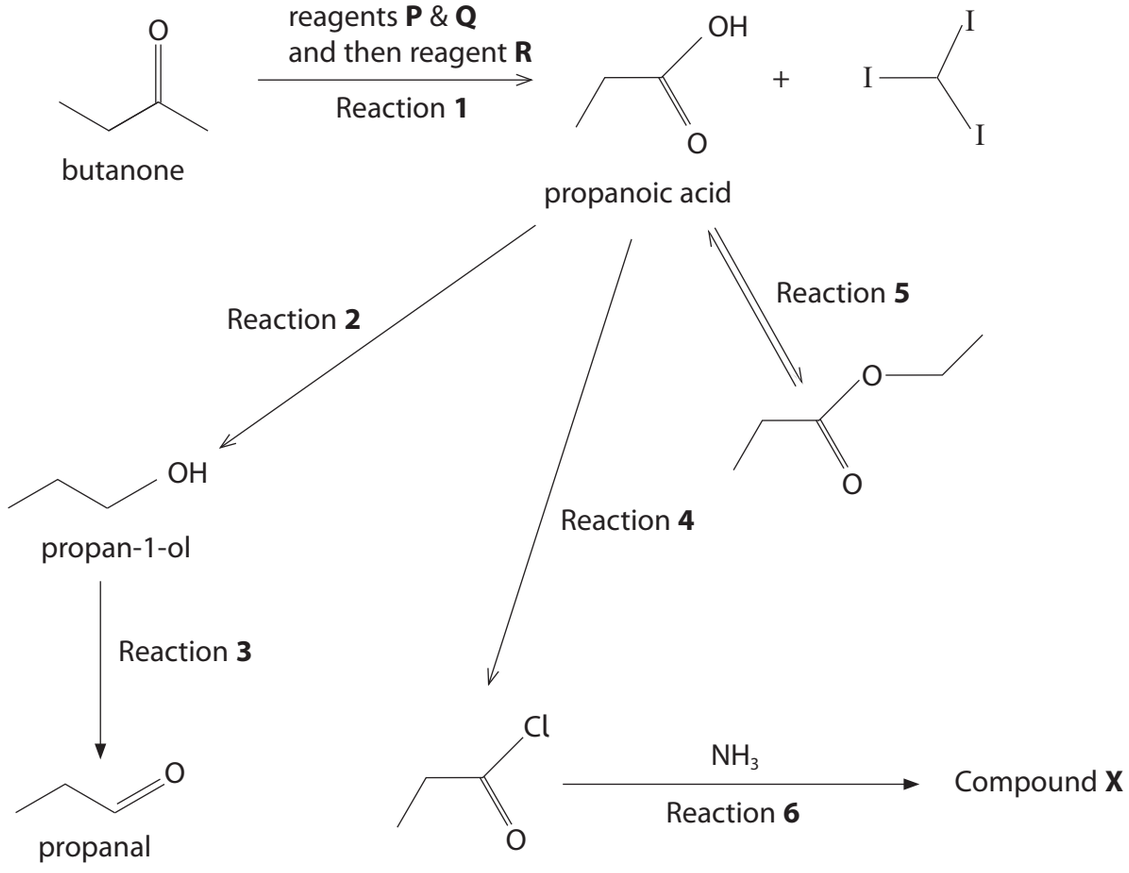
(4)

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

(1)

(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)

.....

.....

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

(2)

.....

.....

.....

.....

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

(1)

.....

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

(2)

.....

.....

.....

(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)

.....

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

(1)

.....

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

(1)

.....

(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)

.....

.....

(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.

$$\underset{74}{CH_3CH_2COOH(l)} + \underset{46}{CH_3CH_2OH(l)} \rightleftharpoons \underset{102}{CH_3CH_2COOCH_2CH_3(l)} + \underset{18}{H_2O(l)}$$

(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)

.....

*(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)

.....

.....

(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

SECTION C

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)

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

(1)

(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)

(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)

(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)

(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)

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

(2)

(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

1	2											3	4	5	6	7	0 (8)
							1.0 H hydrogen 1										(18) 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

140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103

* Lanthanide series

* Actinide series