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<h1 style="margin: 0;">Chemistry</h1> <h2 style="margin: 0;">Advanced</h2> <h3 style="margin: 0;">Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)</h3>	
Thursday 11 January 2018 – Afternoon <b>Time: 1 hour 40 minutes</b>	Paper Reference <b>WCH04/01</b>
Candidates must have: Scientific calculator Data Booklet	Total Marks <input style="width: 50px; height: 30px;" type="text"/>

### 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 ►

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## SECTION A

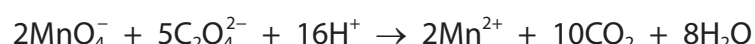
Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box . If you change your mind, put a line through the box  and then mark your new answer with a cross .

1 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:



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)

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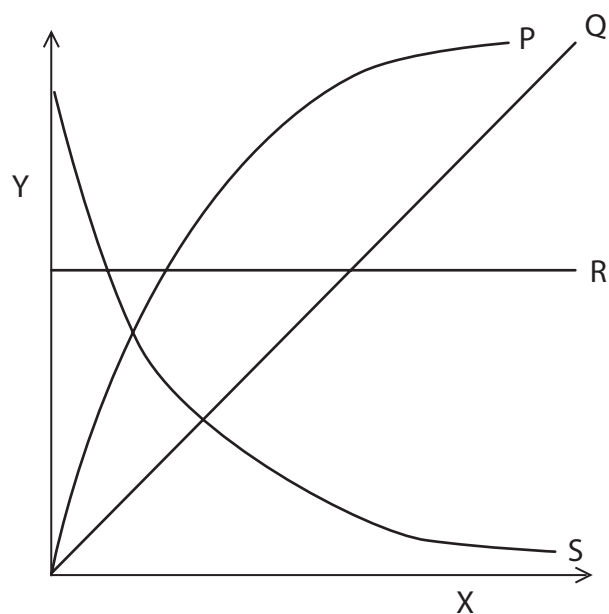
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3 In each of the graphs, quantity Y is plotted against quantity X.



(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)

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P 5 1 9 3 9 A 0 3 2 4

4 Potassium nitrate is very soluble in water:

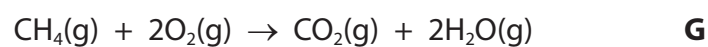
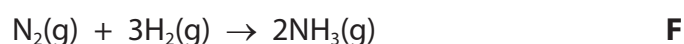


The solubility of potassium nitrate increases rapidly with temperature.  
The best explanation for this is

- A  $\Delta S_{\text{surroundings}}$  becomes less negative as the temperature increases.
- B the molar entropy of a substance increases with temperature.
- C  $\Delta S_{\text{system}}$  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:



What is the order of **increasing** standard entropy change,  $\Delta S_{\text{system}}^\ominus$ , 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)

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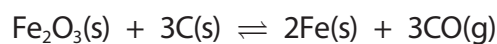


6 The standard molar entropy,  $S^\ominus$ , of a substance is zero for all

- 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



The equilibrium constant,  $K_c$ , for this reaction is given by the expression

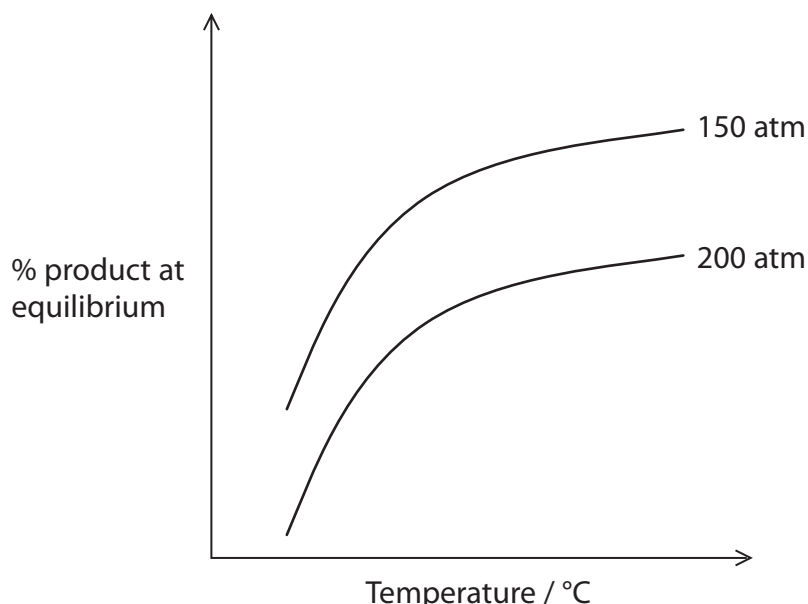
- A  $K_c = [\text{CO}(\text{g})]^3$
- B  $K_c = \frac{1}{[\text{CO}(\text{g})]^3}$
- C  $K_c = \frac{[\text{Fe}(\text{s})]^2 \times [\text{CO}(\text{g})]^3}{[\text{Fe}_2\text{O}_3(\text{s})] \times [\text{C}(\text{s})]^3}$
- D  $K_c = \frac{[\text{Fe}_2\text{O}_3(\text{s})] \times [\text{C}(\text{s})]^3}{[\text{Fe}(\text{s})]^2 \times [\text{CO}(\text{g})]^3}$

(Total for Question 7 = 1 mark)

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

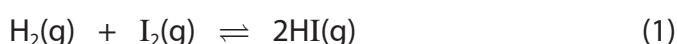


For the forward reaction

	$\Delta H_{\text{reaction}}$	Total number of moles
<input type="checkbox"/> A	positive	increases
<input type="checkbox"/> B	positive	decreases
<input type="checkbox"/> C	negative	increases
<input type="checkbox"/> D	negative	decreases

(Total for Question 8 = 1 mark)

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



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  $K_p(2)$ ?

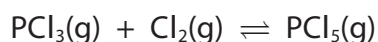
- A  $K_p(1) = K_p(2)$
- B  $K_p(1) = \sqrt{K_p(2)}$
- C  $K_p(1) = (K_p(2))^2$
- D  $K_p(1) = 2 \times K_p(2)$

(Total for Question 9 = 1 mark)





10 Consider the reaction

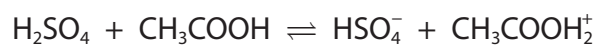


How are  $K_p$  and the mole fraction of  $\text{PCl}_5(\text{g})$  affected when the pressure is increased at constant temperature?

	$K_p$	Mole fraction of $\text{PCl}_5(\text{g})$
<input type="checkbox"/> A	increases	increases
<input type="checkbox"/> B	increases	decreases
<input type="checkbox"/> C	unchanged	increases
<input type="checkbox"/> D	unchanged	decreases

(Total for Question 10 = 1 mark)

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



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
<input type="checkbox"/> A	$\text{H}_2\text{SO}_4$	$\text{CH}_3\text{COOH}$	$\text{CH}_3\text{COOH}_2^+$	$\text{HSO}_4^-$
<input type="checkbox"/> B	$\text{H}_2\text{SO}_4$	$\text{CH}_3\text{COOH}_2^+$	$\text{CH}_3\text{COOH}$	$\text{HSO}_4^-$
<input type="checkbox"/> C	$\text{H}_2\text{SO}_4$	$\text{HSO}_4^-$	$\text{CH}_3\text{COOH}$	$\text{CH}_3\text{COOH}_2^+$
<input type="checkbox"/> D	$\text{H}_2\text{SO}_4$	$\text{HSO}_4^-$	$\text{CH}_3\text{COOH}_2^+$	$\text{CH}_3\text{COOH}$

(Total for Question 11 = 1 mark)

12 When  $0.10 \text{ mol dm}^{-3}$  sodium hydroxide is titrated with  $25 \text{ cm}^3$  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)

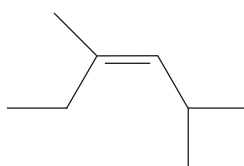


13 For ethanoic acid  $pK_a = 4.76$ . The pH of a solution of ethanoic acid with a concentration of  $1 \times 10^{-10} \text{ mol dm}^{-3}$  is approximately

- 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)

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16 Which correctly shows the reactions of ethanal and propanone?

	Tollens' reagent	2,4-dinitrophenylhydrazine
<input type="checkbox"/> A	both ethanal and propanone react	both ethanal and propanone react
<input type="checkbox"/> B	only ethanal reacts	only propanone reacts
<input type="checkbox"/> C	only propanone reacts	only ethanal reacts
<input type="checkbox"/> 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)

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19 When ethane-1,2-diol, HOCH<sub>2</sub>CH<sub>2</sub>OH, forms a polymer with benzene 1,4-dicarboxylic acid, HOOC<sub>6</sub>H<sub>4</sub>COOH, the repeat unit of the resulting polymer is

- A  $\text{-OCH}_2\text{CH}_2\text{OOC}_6\text{H}_4\text{CO-}$
- B  $\text{-OCH}_2\text{CH}_2\text{OCC}_6\text{H}_4\text{CO-}$
- C  $\text{-OC}_6\text{H}_4\text{OOCCH}_2\text{CH}_2\text{CO-}$
- D  $\text{-CH}_2\text{CH}_2\text{OOCOC}_6\text{H}_4\text{OCO-}$

(Total for Question 19 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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## 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	$\text{C}_6\text{H}_5\text{COOH}$
Molar mass	$122.1 \text{ g mol}^{-1}$
Solubility in water	$3.44 \text{ g dm}^{-3}$ at $25^\circ\text{C}$ $56.3 \text{ g dm}^{-3}$ at $100^\circ\text{C}$
$\text{p}K_a$	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  $25^\circ\text{C}$ .

(4)



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

(2)

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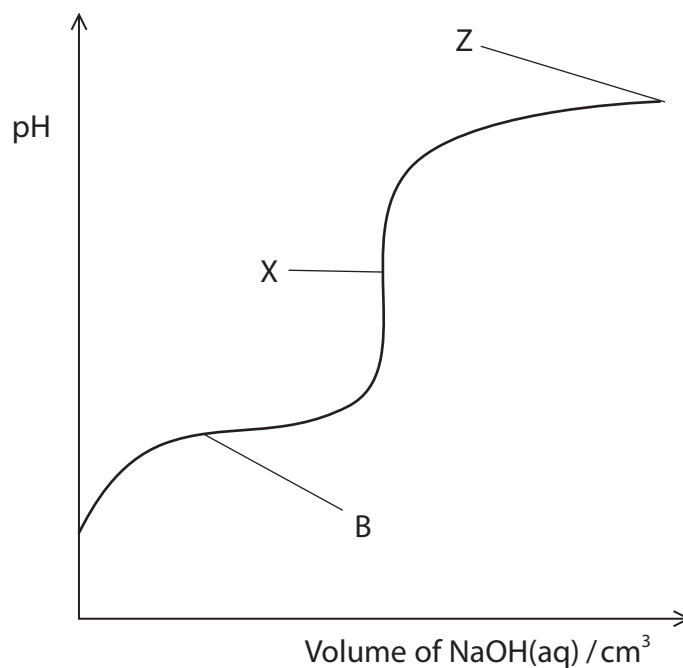
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(b) An aqueous solution of sodium hydroxide of concentration  $0.0025 \text{ mol dm}^{-3}$  was added to a flask containing  $25.0 \text{ cm}^3$  of a  $0.0020 \text{ mol dm}^{-3}$  solution of benzenecarboxylic acid. The pH of the solution in the 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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(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.

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

(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.

(4)

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(d) Buffers occur in many biochemical systems, for example blood. Suggest why this is so. (1)

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**(Total for Question 20 = 23 marks)**

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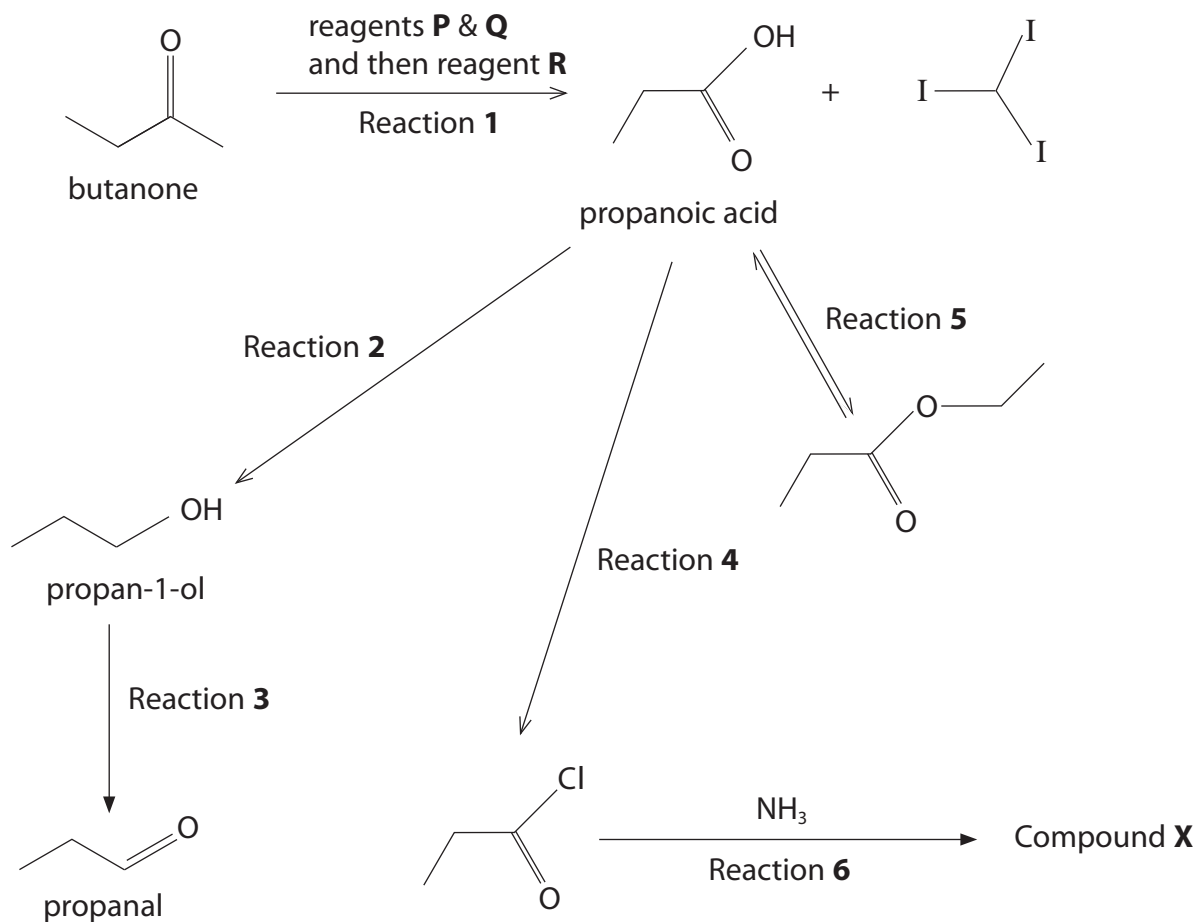
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21 This question is about the organic reactions shown in the diagram.



(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)

(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)

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

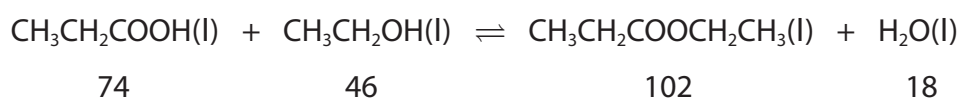
- (i) The base peak (tallest peak) in the mass spectrum of butanone is at  $m/e = 43$  while the base peak in propanal is at  $m/e = 29$ . Identify the species responsible for these two peaks.

(2)

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

(2)

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



- (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)

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



(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)

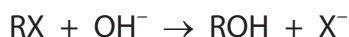
**TOTAL FOR SECTION B = 49 MARKS**



### SECTION C

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

22 Halogenoalkanes react with alkalis to form the corresponding alcohol.



A study of the kinetics of the reaction between a halogenoalkane,  $\text{C}_4\text{H}_9\text{Br}$ , and aqueous sodium hydroxide was carried out using various volumes of the solutions, both of which were  $0.150 \text{ mol dm}^{-3}$ , mixed with ethanol as the solvent.

The results were collected in a table.

Mixture	Volume of $\text{C}_4\text{H}_9\text{Br}$ solution / $\text{cm}^3$	Volume of $\text{NaOH(aq)}$ solution / $\text{cm}^3$	Volume of ethanol / $\text{cm}^3$	Total volume / $\text{cm}^3$	Rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	100	250	150	500	$2.50 \times 10^{-4}$
2	50	250	200	500	$1.25 \times 10^{-4}$
3	200	250	550	1000	$1.25 \times 10^{-4}$

(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.

(1)

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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)

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(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



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

# The Periodic Table of Elements

	1	2	Key										18																						
	(1)	(2)	(3)		(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)																
	relative atomic mass		atomic symbol		name		atomic (proton) number																												
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	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	4.0	He helium 2						
23.0	Na sodium 11	24.3	Mg magnesium 12	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	79.9	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	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	[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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