Please check the examination details below before entering your candidate information

Candidate surname	Other names

Pearson Edexcel
International Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

Friday 8 January 2021

Afternoon (Time: 1 hour 45 minutes) | Paper Reference **WCH14/01**

Chemistry

International Advanced Level
Unit 4: Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

You must have:
Data Booklet, scientific calculator, ruler

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.*
- Show all your working in calculations and include units where appropriate.

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.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

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P 6 7 7 4 6 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 Which of these has the **highest** standard molar entropy at 298 K and 1 atm pressure?

☒ **A** carbon dioxide, CO_2

☒ **B** copper, Cu

☒ **C** ethanol, C_2H_5OH

☒ **D** hydrogen, H_2

(Total for Question 1 = 1 mark)

2 The entropy change of the surroundings, $\Delta S_{surroundings}$, and the entropy change of the system, ΔS_{system}, for four different reactions are given.

Reaction	$\Delta S_{surroundings}$ / J K^{-1} mol^{-1}	ΔS_{system} / J K^{-1} mol^{-1}
P	+245	+34
Q	+350	−276
R	−482	+65
S	−563	−128

Which of these is thermodynamically feasible?

☒ **A** reaction **P** only

☒ **B** reactions **P** and **Q** only

☒ **C** reaction **R** only

☒ **D** reactions **R** and **S** only

(Total for Question 2 = 1 mark)

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

3 Which equation represents the standard enthalpy change of atomisation, $\Delta_{at}H$, of bromine?

☒ **A** $\frac{1}{2}Br_2(l) \rightarrow Br(g)$

☒ **B** $Br_2(l) \rightarrow 2Br(g)$

☒ **C** $\frac{1}{2}Br_2(g) \rightarrow Br(g)$

☒ **D** $Br_2(g) \rightarrow 2Br(g)$

(Total for Question 3 = 1 mark)

4 This question is about four ionic compounds.

(a) Which of these compounds would be expected to have the **least** exothermic lattice energy?

(1)

☒ **A** calcium chloride

☒ **B** magnesium chloride

☒ **C** potassium bromide

☒ **D** sodium bromide

(b) Which of these compounds would be expected to have the **largest** difference between their experimental (Born–Haber) and theoretical lattice energies?

(1)

☒ **A** calcium chloride

☒ **B** magnesium chloride

☒ **C** potassium bromide

☒ **D** sodium bromide

(Total for Question 4 = 2 marks)

5 The standard enthalpy change of solution of potassium chloride, KCl, is +17 kJ mol^{-1}.

The solubility of potassium chloride in water at 298 K is 359 g dm^{-3}.

Which of these explains the solubility of potassium chloride in water?

☒ **A** the hydration enthalpy of K^+ and the lattice energy of KCl are exothermic

☒ **B** the hydration enthalpy of K^+ and the lattice energy of KCl are endothermic

☒ **C** the total entropy change when KCl dissolves is positive

☒ **D** the total entropy change when KCl dissolves is negative

(Total for Question 5 = 1 mark)

6 The total entropy change, ΔS_{total}, of a reaction at 298 K is $-85.0\,J\,K^{-1}\,mol^{-1}$.

What is the value of the equilibrium constant for this reaction at 298 K?

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

☒ **A** 3.61×10^{-5}

☒ **B** 9.07×10^{-1}

☒ **C** 9.66×10^{-1}

☒ **D** 2.77×10^{4}

(Total for Question 6 = 1 mark)

7 Propanone reacts with iodine in the presence of a catalyst of dilute hydrochloric acid. The reaction occurs in aqueous solution.

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

The rate equation for this reaction is

$$\text{rate} = k[CH_3COCH_3][H^+]$$

Which is a possible mechanism for the reaction?

☒ **A**

$CH_3COCH_3 + H^+$	$\rightleftharpoons CH_3C(\overset{+}{O}H)CH_3$	fast
$CH_3C(\overset{+}{O}H)CH_3$	$\rightarrow CH_3C(OH){=}CH_2 + H^+$	slow
$CH_3C(OH){=}CH_2 + I_2$	$\rightarrow CH_3COCH_2I + HI$	fast

☒ **B**

$CH_3COCH_3 + H^+$	$\rightleftharpoons CH_3C(\overset{+}{O}H)CH_3$	fast
$CH_3C(\overset{+}{O}H)CH_3$	$\rightarrow CH_3C(OH){=}CH_2 + H^+$	fast
$CH_3C(OH){=}CH_2 + I_2$	$\rightarrow CH_3COCH_2I + HI$	slow

☒ **C**

CH_3COCH_3	$\rightarrow CH_3COCH_2^- + H^+$	slow
I_2	$\rightarrow I^+ + I^-$	slow
$CH_3COCH_2^- + I^+$	$\rightarrow CH_3COCH_2I$	fast

☒ **D**

I_2	$\rightarrow I^+ + I^-$	slow
$CH_3COCH_3 + I^-$	$\rightarrow CH_3COCH_2^- + HI$	slow
$CH_3COCH_2^- + I^+$	$\rightarrow CH_3COCH_2I$	fast

(Total for Question 7 = 1 mark)

8 The rate equation for a reaction is

$$\text{rate} = k[A]^2[B]^0$$

The initial rate of reaction is 9.0×10^{-5} mol dm^{-3} s^{-1} when [A] = 0.30 mol dm^{-3} and [B] = 0.20 mol dm^{-3}.

What is the value of the rate constant in dm^3 mol^{-1} s^{-1}?

☒ **A** 8.1×10^{-6}

☒ **B** 3.0×10^{-4}

☒ **C** 1.0×10^{-3}

☒ **D** 5.0×10^{-3}

(Total for Question 8 = 1 mark)

9 This question is about weak acids.

pK_a of ethanoic acid, CH_3COOH = 4.8

pK_a of chloroethanoic acid, $CH_2ClCOOH$ = 2.9

(a) What is the pH of a 0.100 mol dm^{-3} solution of chloroethanoic acid?

(1)

☒ **A** 0.27

☒ **B** 1.95

☒ **C** 2.90

☒ **D** 3.90

(b) Which is the acid-conjugate base pair in the reaction between ethanoic acid and chloroethanoic acid?

(1)

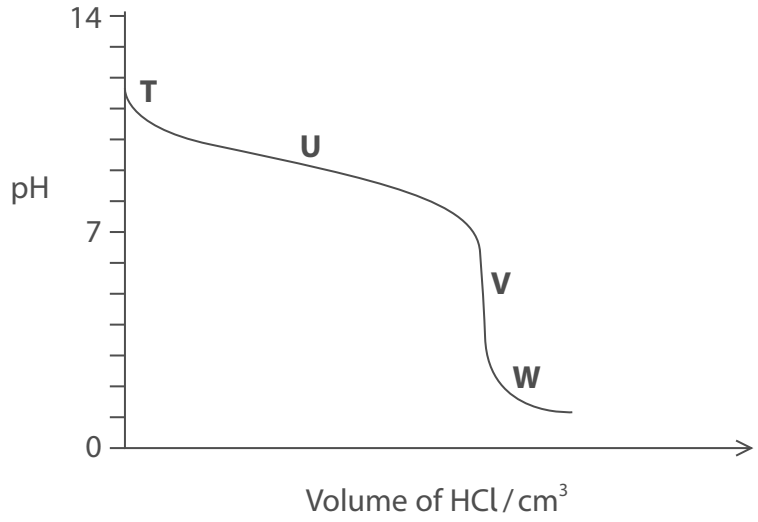
	Acid	Conjugate base
☒ **A**	CH_3COOH	CH_3COO^-
☒ **B**	CH_3COOH	$CH_3COOH_2^+$
☒ **C**	$CH_2ClCOOH$	CH_2ClCOO^-
☒ **D**	$CH_2ClCOOH$	$CH_2ClCOOH_2^+$

(Total for Question 9 = 2 marks)

10 A titration was carried out by adding 0.1 mol dm^{-3} hydrochloric acid to 0.1 mol dm^{-3} aqueous ammonia.

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

The titration curve is shown.



(a) Which region of the graph represents the most effective buffer solution?

(1)

☒ **A** region **T**

☒ **B** region **U**

☒ **C** region **V**

☒ **D** region **W**

(b) Which of these is the best indicator to use in this titration?

[Refer to the Data Booklet]

(1)

☒ **A** methyl red

☒ **B** phenol red

☒ **C** phenolphthalein

☒ **D** thymol blue

(c) What is the approximate pH of an ammonium chloride solution?

(1)

☒ **A** 2.0

☒ **B** 5.8

☒ **C** 9.7

☒ **D** 11.3

(Total for Question 10 = 3 marks)

11 A diprotic acid, H_2A, was titrated with sodium hydroxide solution.

$$H_2A(aq) + 2NaOH(aq) \rightarrow Na_2A(aq) + 2H_2O(l)$$

A 25.0 cm^3 portion of 0.100 mol dm^{-3} sodium hydroxide solution required 12.80 cm^3 of the solution of the diprotic acid for complete neutralisation.

What is the concentration of H_2A in mol dm^{-3}?

☒ **A** 2.56×10^{-2}

☒ **B** 9.77×10^{-2}

☒ **C** 1.95×10^{-1}

☒ **D** 3.91×10^{-1}

(Total for Question 11 = 1 mark)

12 A sample of a bromoalkane, RBr, containing a single optical isomer reacts with hydroxide ions in an S_N1 mechanism.

$$RBr + OH^- \rightarrow ROH + Br^-$$

The alcohol formed is a racemic mixture.

From this information, it can be deduced that RBr is most likely to be

☒ **A** primary only

☒ **B** secondary only

☒ **C** tertiary only

☒ **D** primary, secondary or tertiary

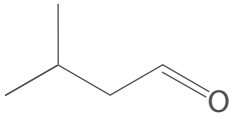
(Total for Question 12 = 1 mark)

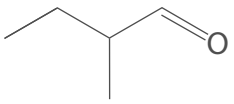
Use this space for any rough working. Anything you write in this space will gain no credit.

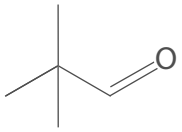
13 A compound **X**, with molecular formula $C_5H_{10}O$, gave an orange precipitate with 2,4-dinitrophenylhydrazine.

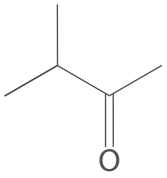
X gave a silver mirror with Tollens' reagent.

Which of these could **not** be **X**?

☒ **A** 

☒ **B** 

☒ **C** 

☒ **D** 

(Total for Question 13 = 1 mark)

14 Propyl ethanoate, $CH_3COOCH_2CH_2CH_3$, is hydrolysed with aqueous sodium hydroxide.

Which products are formed?

☒ **A** CH_3COOH and $CH_3CH_2CH_2OH$

☒ **B** CH_3COOH and $CH_3CH_2CH_2ONa$

☒ **C** CH_3COONa and $CH_3CH_2CH_2OH$

☒ **D** CH_3COONa and $CH_3CH_2CH_2ONa$

(Total for Question 14 = 1 mark)

15 2.95 g of ethanoic acid is produced from 2.50 g of ethanol.

What is the percentage yield of ethanoic acid?

[Molar masses in g mol^{-1}: ethanoic acid = 60 ethanol = 46]

☒ **A** 65.0 %

☒ **B** 84.7 %

☒ **C** 90.5 %

☒ **D** 118 %

(Total for Question 15 = 1 mark)

16 A mixture of organic compounds was analysed using thin-layer chromatography.

The R_f value was 0.92 for one of the components in the mixture.

What can be deduced about the attractions between that component and the stationary and mobile phases?

	Attraction between component and stationary phase	Attraction between component and mobile phase
☒ **A**	strong	strong
☒ **B**	strong	weak
☒ **C**	weak	weak
☒ **D**	weak	strong

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

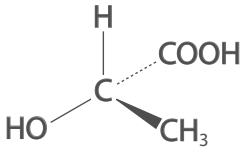
Answer ALL the questions.

Write your answers in the spaces provided.

17 This question is about carboxylic acids and their derivatives.

(a) Lactic acid, $CH_3CH(OH)COOH$, is produced in muscles as a result of anaerobic respiration.

(i) The structure of lactic acid is



Give a reason why lactic acid shows optical isomerism.

(1)

(ii) A laboratory sample of lactic acid does **not** rotate the plane of plane-polarised monochromatic light.

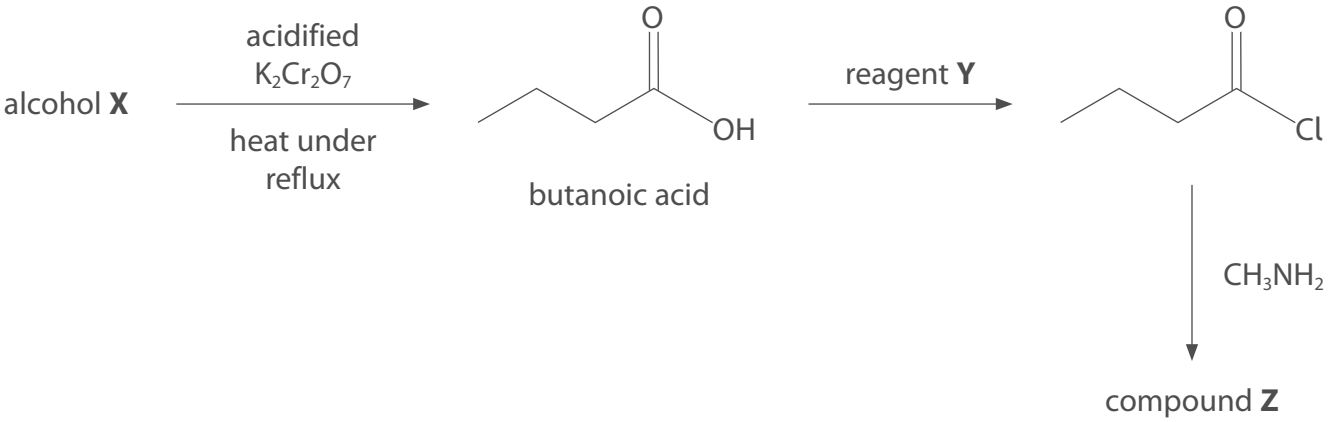
Give a reason for this observation.

(1)

(iii) Give the structure of the organic product formed when lactic acid reacts with concentrated phosphoric(V) acid, H_3PO_4.

(1)

(b) A reaction scheme involving butanoic acid is shown.

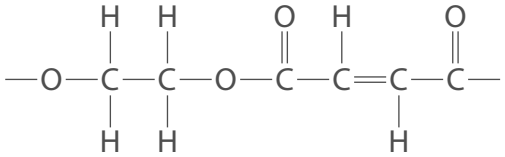


Identify **X**, **Y** and **Z** by name or formula.

(3)

Alcohol **X**
Reagent **Y**
Compound **Z**

(c) The repeat unit of a polyester is shown.



Give the structures of the two monomers that could form this polyester.

(2)

Monomer 1	Monomer 2

(d) An organic compound **E** contains carbon, hydrogen and oxygen only.

(i) The accurate relative atomic masses, A_r, of the three elements in **E** are shown in the table.

Element	A_r
hydrogen	1.0078
carbon	12.0000
oxygen	15.9949

E contains five carbon atoms and gives a molecular ion peak at $m/z = 102.0678$ in its mass spectrum.

Deduce the molecular formula of **E**.

(1)

(ii) Aqueous sodium hydrogencarbonate is added to a sample of **E**.
No effervescence occurs.

State what can be deduced by this observation.

(1)

.....

.....

(iii) The infrared spectrum of **E** has an absorption in the range 1750 – 1735 cm^{-1}.

Name the functional group in **E**.

(1)

.....

(iv) Data from the high resolution proton NMR spectrum of **E** is shown.

Peak	Chemical shift, δ / ppm for TMS	Splitting pattern	Relative peak area
A	4.02	triplet	2
B	2.05	singlet	3
C	1.65	sextet	2
D	0.95	triplet	3

Deduce the structure of **E**.
Justify your answer by labelling the protons responsible for each peak.

(3)

(Total for Question 17 = 14 marks)

18 This question is about sulfuric acid and its salts.

(a) The manufacture of sulfuric acid involves the equilibrium

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta_r H = -197\,kJ\,mol^{-1}$$

(i) A catalyst of vanadium(V) oxide is used in this reaction.

State the effect, if any, of the catalyst on the value of the equilibrium constant, K_p.

(1)

.....

.....

(ii) The temperature used for this reaction in industry is 700 K.

Explain, in terms of the equilibrium constant and the equilibrium position, the effect of an increase in temperature on the equilibrium yield of sulfur trioxide.

(2)

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.....

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.....

(iii) Write the expression for the equilibrium constant, K_p, for this equilibrium. State symbols are not required.

(1)

(iv) A mixture of 2.00 mol of sulfur dioxide and 1.00 mol of oxygen is allowed to reach equilibrium at 5.00 atm pressure.
1.60 mol of sulfur trioxide is formed.

Calculate the value of K_p.
Include units and give your answer to an appropriate number of significant figures.

(4)

(b) Sulfur trioxide is used to produce sulfuric acid.

(i) Commercial concentrated sulfuric acid contains 98.5 % H_2SO_4 and 1.5 % water by mass.
The density of concentrated sulfuric acid is 1800 g dm^{-3}.

Calculate the concentration of this sulfuric acid in mol dm^{-3}.

(2)

(ii) The pH of a 0.10 mol dm^{-3} solution of sulfuric acid at 25 °C is 0.97.

Calculate the concentration of hydrogen ions, in mol dm^{-3}, in this solution.

(1)

(iii) In an aqueous solution of sulfuric acid, the following equilibria exist.

$H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq)$ K_a very large

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$ $K_a = 0.012$ mol dm^{-3}

Explain, in terms of these equilibria, why the concentration of hydrogen ions in a 0.10 mol dm^{-3} solution of sulfuric acid is **not** 0.20 mol dm^{-3}.
No calculation is required.

(2)

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(c) A buffer solution is made from HSO_4^- and SO_4^{2-} ions.

(i) Write two ionic equations involving HSO_4^- and SO_4^{2-} ions to show how this solution acts as a buffer.
State symbols are not required.

(2)

(ii) A buffer solution is formed by mixing

$25.0\,cm^3$ of a solution that is $0.150\,mol\,dm^{-3}$ with respect to SO_4^{2-} ions with $75.0\,cm^3$ of a solution that is $0.100\,mol\,dm^{-3}$ with respect to HSO_4^- ions.

Calculate the pH of this buffer solution.

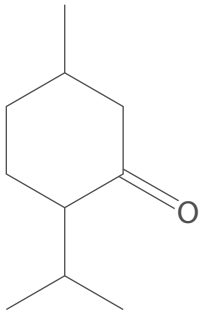
[K_a for HSO_4^- ions = $0.012\,mol\,dm^{-3}$]

(5)

(Total for Question 18 = 20 marks)

19 This question is about carbonyl compounds.

(a) The skeletal formula of menthone is shown.



Give the molecular formula of menthone.

(1)

(b) Ethanal, CH_3CHO, reacts with hydrogen cyanide in the presence of cyanide ions to form 2-hydroxypropanenitrile.

Draw the mechanism for this reaction.
Include curly arrows, and any relevant lone pairs and dipoles.

(4)

(c) A carbonyl compound, **F**, has the molecular formula $C_6H_{12}O$.

(i) **F** reacts with iodine in an alkaline solution to give a pale yellow precipitate.

Give the name or formula of the group in **F** identified by this test.

(1)

.....

(ii) Draw the **skeletal** formulae of the four possible structures of carbonyl compound **F**.

(2)

(iii) The carbon-13 (^{13}C) NMR spectrum of **F** has four peaks.

Identify **F** by drawing its **displayed** formula.
Justify your answer by labelling the carbon atoms or groups of carbon atoms responsible for the four peaks in the spectrum.

(2)

*(d) Explain, in terms of all the intermolecular forces involved, why butanal has a higher boiling temperature than pentane but a lower boiling temperature than propanoic acid.

Substance	Boiling temperature / °C
butanal	76
pentane	36
propanoic acid	141

(6)

(Total for Question 19 = 16 marks)

TOTAL FOR SECTION B = 50 MARKS

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SECTION C

Answer ALL the questions.

Write your answers in the spaces provided.

20 This question is about some compounds of bromine.

(a) Potassium bromate(V) decomposes to form potassium bromide and oxygen.

$$2KBrO_3(s) \rightarrow 2KBr(s) + 3O_2(g) \qquad \Delta_r H^{\ominus} = -67.2\,kJ\,mol^{-1}$$

The standard molar entropies of these substances are given in the table.

Substance	$KBrO_3(s)$	$KBr(s)$	$O_2(g)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	149.2	95.9	205.0

Calculate the total entropy change, ΔS_{total}, for this reaction at 298 K.

(5)

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(b) Bromide ions react with bromate(V) ions in acidic solution.

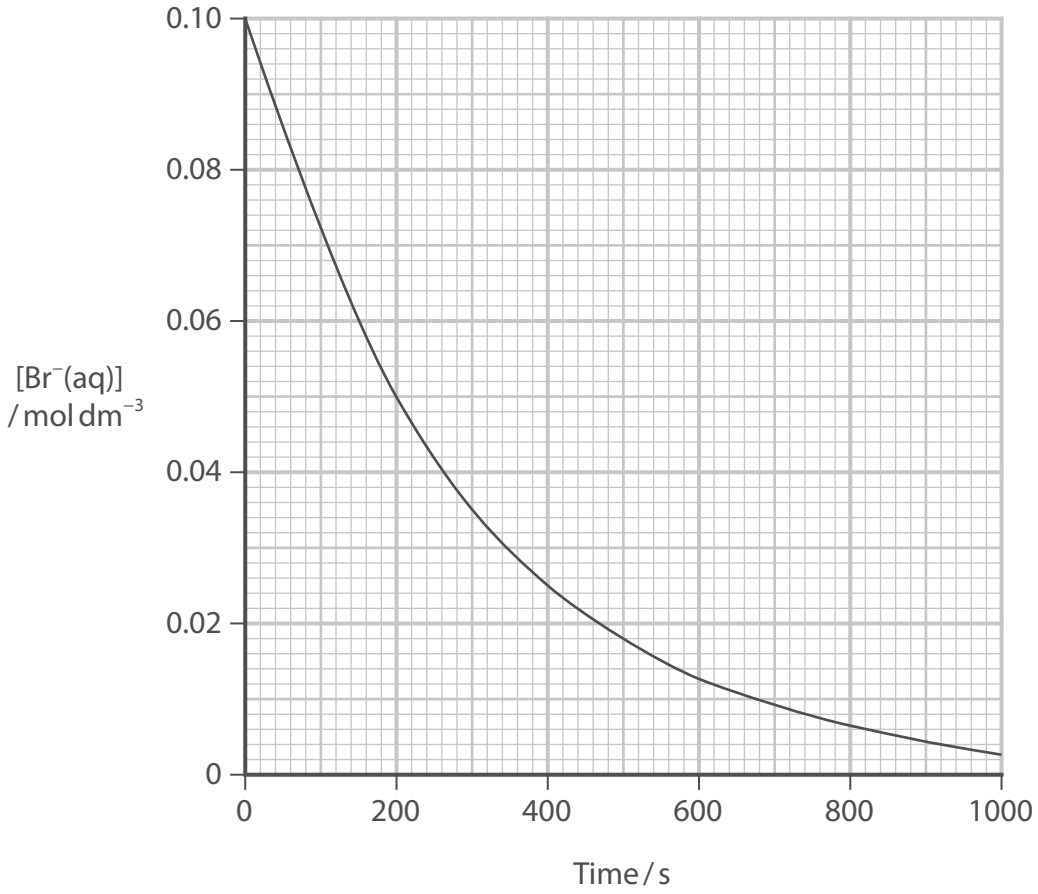
$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Two experiments are carried out.

(i) **Experiment 1**

The concentration of Br^- ions is determined at different times.
The concentrations of BrO_3^- ions and H^+ ions are in large excess and effectively constant.

The graph of concentration of Br^- ions against time is shown.



Determine the order of the reaction with respect to bromide ions.
Show your working on the graph.

(3)

(ii) **Experiment 2**

The initial concentrations of BrO_3^- ions and H^+ ions are changed and the initial rate of reaction is determined.
The initial concentration of Br^- ions is constant and in large excess.

Run	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.1	0.1	3.6×10^{-3}
2	0.2	0.1	7.2×10^{-3}
3	0.3	0.2	4.3×10^{-2}

Determine the order of reaction with respect to BrO_3^- ions and to H^+ ions.

You must explain your working.

(3)

(iii) Give the overall rate equation for this reaction.
Include the units for the rate constant.

(2)

(c) The rate constant for the reaction between bromoalkane and cyanide ions is determined at five different temperatures.

The results are given in the table.

Temperature (T) / K	1/Temperature ($1/T$) / K^{-1}	Rate constant (k) / s^{-1}	$\ln k$
300	3.33×10^{-3}	3.72×10^{-5}	−10.20
310	3.23×10^{-3}	1.34×10^{-4}	−8.92
320	3.13×10^{-3}	5.48×10^{-4}	−7.51
330	3.03×10^{-3}	2.01×10^{-3}	−6.21
340	2.93×10^{-3}	7.23×10^{-3}	−4.93

Plot a graph of $\ln k$ against $1/T$ and use it to determine the activation energy, E_a.

Include the sign and units of the gradient and the activation energy.

(7)

The Arrhenius equation can be expressed as

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

[$R = 8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$]

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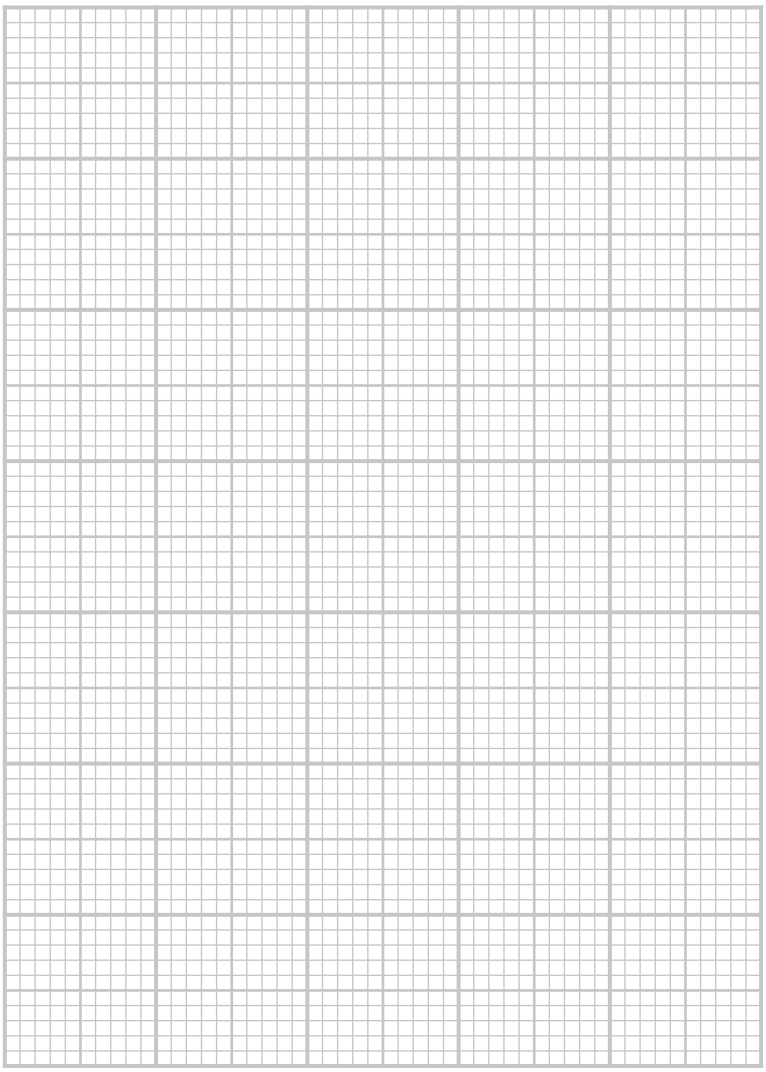

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

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									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									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

* Actinide 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
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