Please check the examination details below before entering your candidate information

Candidate surname	Other names

Pearson Edexcel
International Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

Time 1 hour 45 minutes

Paper reference **WCH14/01**

Chemistry

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

You must have:
Scientific calculator, Data Booklet, ruler

Total Marks

Instructions

- Use **black** ink or ball-point pen.
- **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.
- Good luck with your examination.

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 Which of these gases would have the greatest standard molar entropy?

☒ **A** NH_3

☒ **B** H_2

☒ **C** N_2

☒ **D** SO_2

(Total for Question 1 = 1 mark)

2 What is the standard entropy change of the system, in J K^{-1} mol^{-1}, for the reaction between nitrogen and hydrogen to form ammonia?

$$N_2 + 3H_2 \rightarrow 2NH_3$$

	Standard molar entropy / J K^{-1} mol^{-1}
H_2	130.6
N_2	191.6
NH_3	192.3

☒ **A** −198.8

☒ **B** −129.9

☒ **C** +129.9

☒ **D** +198.8

(Total for Question 2 = 1 mark)

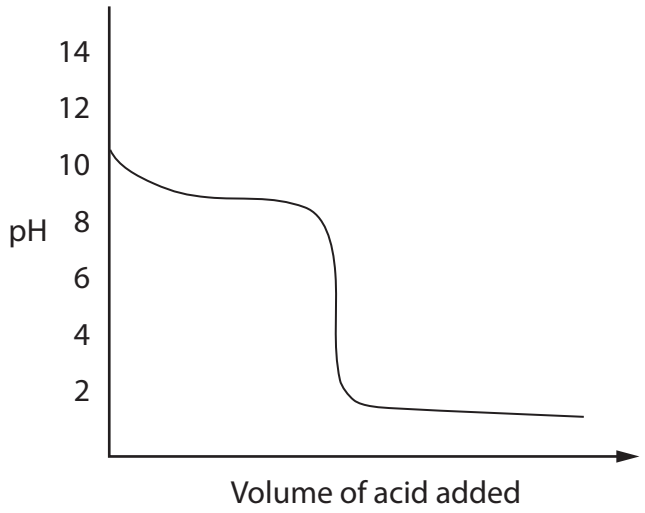
3 The enthalpy change of solution of sodium sulfate, Na_2SO_4, may be calculated using three pieces of data. Which of these pieces of data is **not** required?

- ☒ **A** lattice energy of Na_2SO_4
- ☒ **B** enthalpy change of hydration of Na^+
- ☒ **C** enthalpy change of formation of Na_2SO_4
- ☒ **D** enthalpy change of hydration of SO_4^{2-}

(Total for Question 3 = 1 mark)

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

4 A graph of pH against volume of acid added for an acid-base titration is shown.



(a) Which acidic solution was used in the titration?

(1)

- ☒ **A** 0.1 mol dm^{-3} CH_3COOH
- ☒ **B** 1.0 mol dm^{-3} CH_3COOH
- ☒ **C** 0.1 mol dm^{-3} HCl
- ☒ **D** 1.0 mol dm^{-3} HCl

(b) Which basic solution was used in the titration?

(1)

- ☒ **A** NH_3
- ☒ **B** LiOH
- ☒ **C** $Ba(OH)_2$
- ☒ **D** NaOH

(c) A student suggested five indicators that might be used in this titration:

thymol blue
methyl orange
bromophenol blue
bromocresol green
phenolphthalein

How many of these indicators would be suitable? Use your Data Booklet.

(1)

☒ **A** 5

☒ **B** 4

☒ **C** 3

☒ **D** 2

(Total for Question 4 = 3 marks)

5 The halogenoalkane 2-bromo-2-methylbutane was hydrolysed with sodium hydroxide solution, NaOH(aq).
Which suggestion about the mechanism of this reaction is correct?

	Type of mechanism	Number of steps in mechanism
☒ **A**	S_N2	one
☒ **B**	S_N2	two
☒ **C**	S_N1	one
☒ **D**	S_N1	two

(Total for Question 5 = 1 mark)

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

6 Nitrogen monoxide and hydrogen react together to form nitrogen and water.

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

The steps in the mechanism of the reaction are

Step 1 $2NO \rightleftharpoons N_2O_2$ fast

Step 2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ slow

Step 3 $N_2O + H_2 \rightarrow N_2 + H_2O$ fast

Which statement about the reaction is correct?

☒ **A** Step 3 is the rate determining step and the overall order is 2

☒ **B** Step 3 is the rate determining step and the overall order is 4

☒ **C** Step 2 is the rate determining step and the overall order is 2

☒ **D** Step 2 is the rate determining step and the overall order is 3

(Total for Question 6 = 1 mark)

7 The Arrhenius equation can be shown as

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

A graph is plotted of ln k against $1/T$ for a reaction.
The activation energy, E_a, of this reaction equals

☒ **A** – gradient ÷ R

☒ **B** + gradient ÷ R

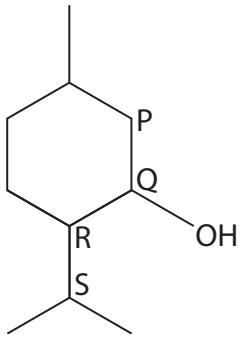
☒ **C** – gradient × R

☒ **D** + gradient × R

(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 compound menthol has the structure shown.
Some of the carbon atoms are labelled P, Q, R and S.



menthol

(a) What is the number of chiral centres in a molecule of menthol?

(1)

☒ **A** 1

☒ **B** 2

☒ **C** 3

☒ **D** 4

(b) Which of the carbon atoms is responsible for a peak at 72 ppm in the ^{13}C NMR spectrum of menthol?

(1)

☒ **A** P

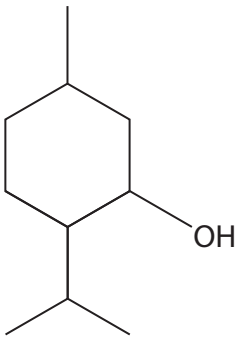
☒ **B** Q

☒ **C** R

☒ **D** S

(c) Four groups of students warmed samples of menthol with sodium dichromate(VI) in acid. They purified the reaction mixture and carried out a series of qualitative tests on the organic product.

The findings of each group in the class are shown in the table.



menthol

Group	Qualitative test		
	Add 2,4-dinitrophenylhydrazine	Warm with Fehling's solution	Add PCl_5
One	✓	×	✓
Two	✓	×	×
Three	✓	✓	×
Four	×	×	✓

A tick (✓) shows a positive result, a cross (×) shows a negative result.
Which group recorded the results you would expect?

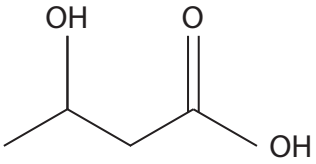
(1)

- ☒ **A** One
- ☒ **B** Two
- ☒ **C** Three
- ☒ **D** Four

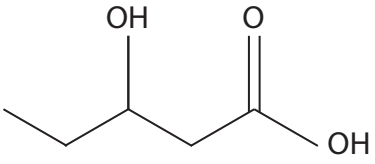
(Total for Question 8 = 3 marks)

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

9 The substance known as PHBV is a biodegradable polymer formed from 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



3-hydroxybutanoic acid

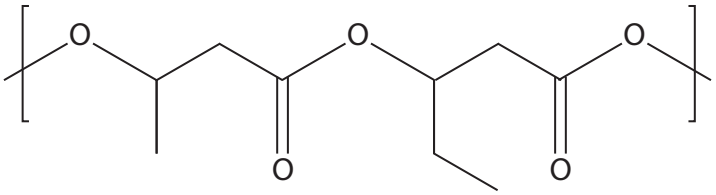


3-hydroxypentanoic acid

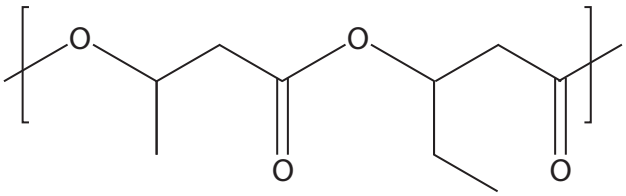
(a) Which of these is the repeat unit of the polymer?

(1)

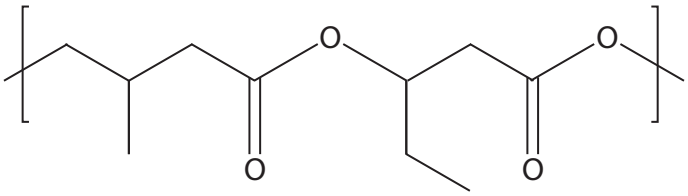
☒ **A**



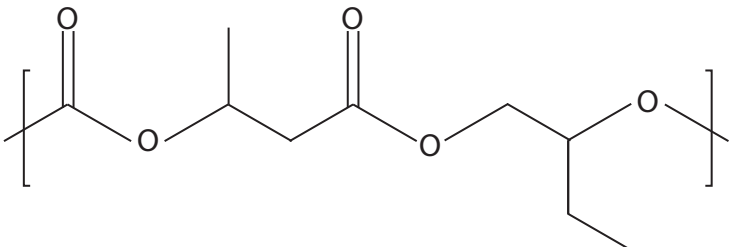
☒ **B**



☒ **C**



☒ **D**



(b) What reaction occurs when PHBV biodegrades to its monomers?

(1)

☒ **A** condensation

☒ **B** hydrolysis

☒ **C** hydration

☒ **D** hydrogenation

10 Which reagent reacts at room temperature with methylamine, CH_3NH_2, to form the compound N-methylethanamide?

- ☒ **A** CH_3COCH_3
- ☒ **B** CH_3COOH
- ☒ **C** CH_3COOCH_3
- ☒ **D** CH_3COCl

(Total for Question 10 = 1 mark)

11 This question is about chromatography.

(a) A spot caused by an amino acid has moved 42 mm from the baseline of a paper chromatogram.
The R_f value for the amino acid under these conditions is 0.62.

What is the distance moved by the solvent?

(1)

- ☒ **A** 680 mm
- ☒ **B** 68 mm
- ☒ **C** 42 mm
- ☒ **D** 26 mm

(b) In gas chromatography, GC, which of these would be the most suitable carrier gas?

(1)

- ☒ **A** argon
- ☒ **B** hydrogen
- ☒ **C** methane
- ☒ **D** oxygen

(Total for Question 11 = 2 marks)

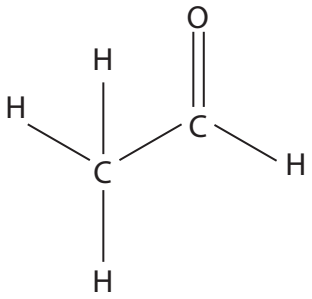
Use this space for any rough working. Anything you write in this space will gain no credit.

12 The high resolution mass spectrum of a compound X has a molecular ion peak at $m/z = 44.0632$. Accurate relative atomic masses are given in the table.

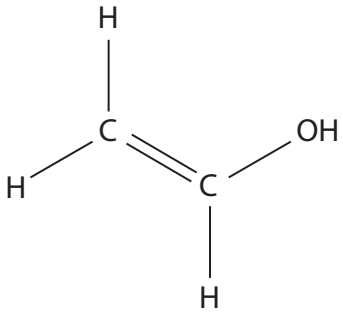
Element	Relative atomic mass
Hydrogen	1.0079
Carbon	12.0000
Oxygen	15.9949

Which of these compounds, with a relative molecular mass of 44, gives rise to this peak?

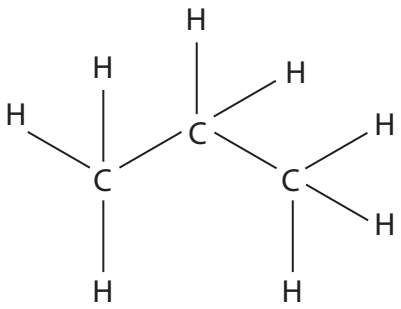
☒ **A**

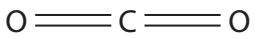


☒ **B**



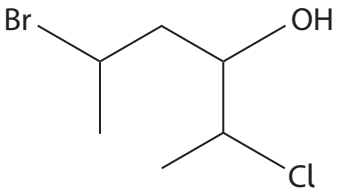
☒ **C**



☒ **D** 

(Total for Question 12 = 1 mark)

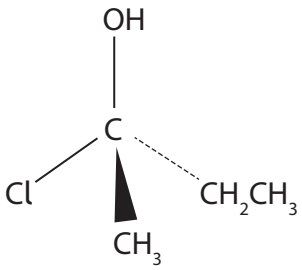
13 How many optical isomers does this molecule have?



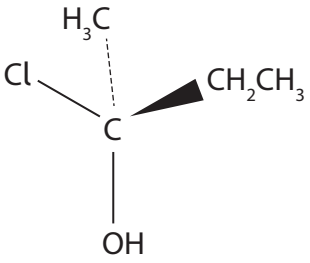
- ☒ **A** 2
- ☒ **B** 3
- ☒ **C** 6
- ☒ **D** 8

(Total for Question 13 = 1 mark)

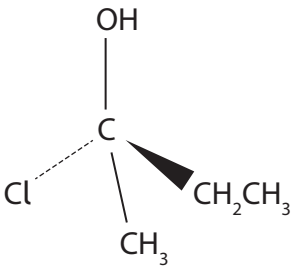
14 Which of these structures is **not** identical to the others?



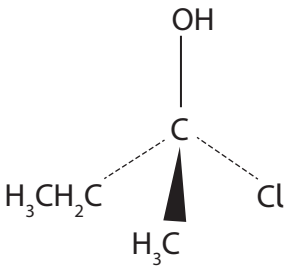
Structure A



Structure B



Structure C



Structure D

- ☒ **A** Structure A
- ☒ **B** Structure B
- ☒ **C** Structure C
- ☒ **D** Structure D

(Total for Question 14 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

15 The standard enthalpy change of solution for ammonium nitrate, NH_4NO_3, is +25.7 kJ mol^{-1}.

(a) Calculate the value for the standard entropy change in the surroundings, $\Delta S^{\ominus}_{surroundings}$, when ammonium nitrate dissolves in water at 298 K. Include a sign and units with your answer.

(2)

(b) Explain what can be deduced from your answer in (a) about the sign and the value of the standard entropy change in the system, $\Delta S^{\ominus}_{system}$, when NH_4NO_3 dissolves.

(3)

(Total for Question 15 = 5 marks)

16 A student investigated the kinetics of the reaction between bromate(V) ions and bromide ions in acidic conditions.

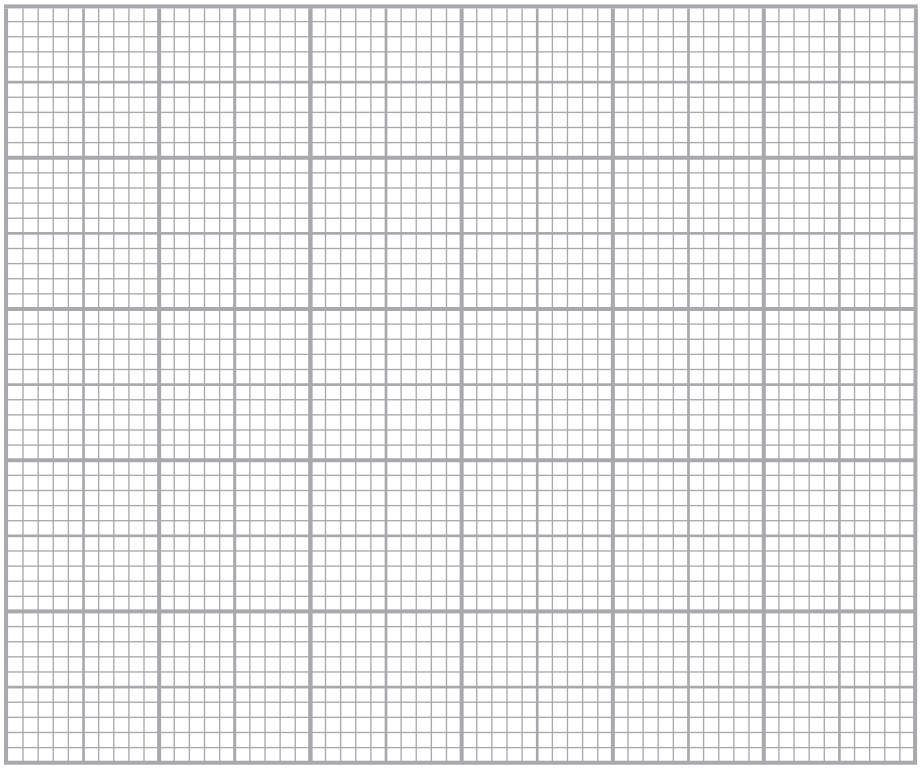
$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

(a) In the first experiment, the student measured the initial rate of the reaction at five different concentrations of bromate(V) ions, BrO_3^-. In each case, the initial concentrations of bromide ions and hydrogen ions were constant and in large excess. The results obtained are shown.

Initial concentration of bromate(V) ions / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
0.030	4.17×10^{-7}
0.060	8.34×10^{-7}
0.090	1.25×10^{-6}
0.120	1.67×10^{-6}
0.150	2.09×10^{-6}

(i) Use the results to plot a suitable graph that can be used to show that the reaction is first order with respect to bromate(V) ions.

(3)



(ii) State how your graph shows that the reaction is first order with respect to bromate(V) ions.

(1)

.....

.....

(b) In the second experiment, the student determined the initial rates of the same reaction starting with different concentrations of the reactants.

Run	$[BrO_3^-]$ / mol dm^{-3}	$[Br^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.062	0.21	0.40	1.52×10^{-5}
2	0.31	0.21	0.20	1.90×10^{-5}
3	0.062	0.63	0.40	4.56×10^{-5}

(i) Use these results and your answer to (a) to deduce the orders with respect to Br^- ions and H^+ ions.

(2)

Br^- ions .....

H^+ ions .....

(ii) Write the rate equation for the reaction.

(1)

(iii) Use the results for Run 1 and your rate equation from (b)(ii) to calculate the value for the rate constant, *k*. Include units in your answer.

(3)

(c) The presence of bromate(V) ions in drinking water is harmful to humans. Bromate(V) ions can be converted to less harmful bromide ions by passing the water through palladium with a reducing agent.

Describe how a heterogeneous catalyst, such as palladium, increases the rate of a reaction.

(3)

.....

.....

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.....

.....

(Total for Question 16 = 13 marks)

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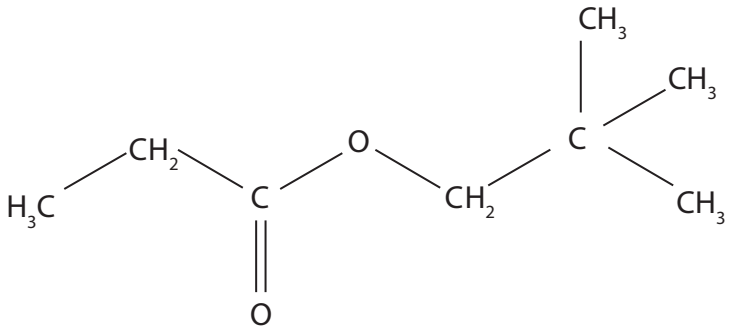
17 This question is about an ester, **Y**, with the molecular formula $C_8H_{16}O_2$.

(a) **Y** contains 66.7% carbon, 11.1% hydrogen and 22.2% oxygen by mass. Show that these data are consistent with its molecular formula.

(2)

(b) The structure of compound **Y** is



(i) Give the IUPAC name of **Y**.

(2)

.....

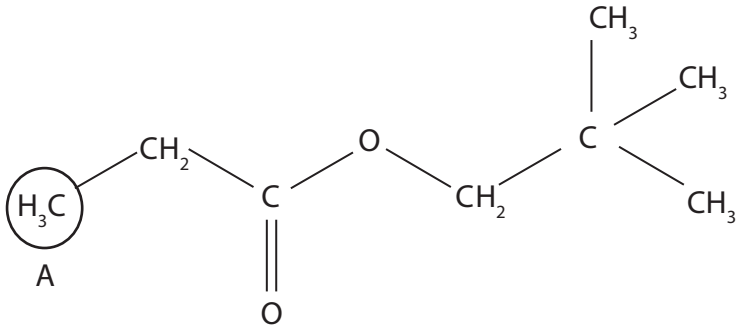
(ii) Draw the structures of two organic compounds that would react together to form **Y**.

(1)

(c) The high resolution proton NMR spectrum of compound **Y** was obtained.

(i) Label the three remaining hydrogen environments B, C and D on the structure.

(1)



(ii) Complete the table.

(3)

Hydrogen environment	Splitting pattern of peak	Relative peak area
A	triplet	3
B		
C		
D		

(Total for Question 17 = 9 marks)

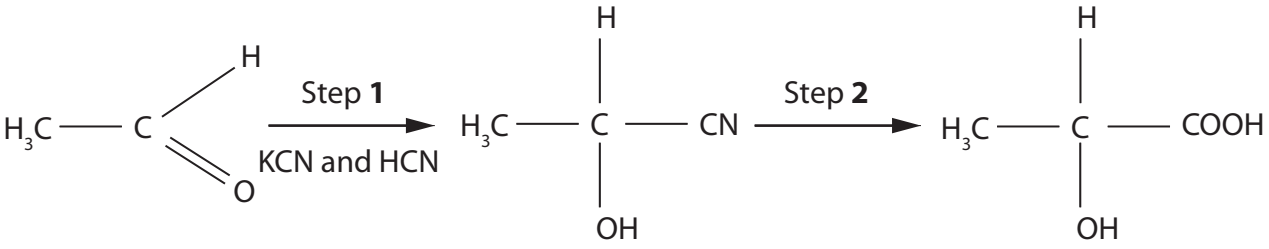
***18** The table shows the theoretical and experimental (Born-Haber) lattice energy data for two metal halide compounds, sodium chloride and magnesium iodide.

	Lattice energy / kJ mol^{-1}	
Metal halide	Theoretical	Experimental (Born-Haber)
Sodium chloride	−770	−780
Magnesium iodide	−1944	−2327

Using the data, compare and contrast the type and strength of bonding in these compounds.
Give reasons for your answers.

(6)

19 The compound lactic acid can be synthesised from ethanal in two steps.



ethanal

lactic acid

(a) (i) Give the mechanism for Step **1**. Include curly arrows, and any relevant lone pairs and dipoles.

(4)

(ii) A student predicted that the product of Step **1** would rotate the plane of plane-polarised light.

Comment on this prediction.

(3)

(iii) Complete the table that summarises information about Step **2**.
State symbols are not required for the equation.

(4)

Conversion of $CH_3CH(OH)CN$ to lactic acid	
Reaction type	
Reagent	
Conditions	
Equation	

(b) Sodium hydrogencarbonate, $NaHCO_3$, has been used by some athletes to help prevent lactic acid causing muscle pain during exercise.

Write an equation for the reaction between sodium hydrogencarbonate and lactic acid.

(1)

(c) Sodium hydrogencarbonate is part of a buffer in the body that controls the pH of blood. Two of the equilibria involved in this process are shown.

Equilibrium 1 $HCO_3^- + H_3O^+ \rightleftharpoons H_2CO_3 + H_2O$

Equilibrium 2 $H_2CO_3 \rightleftharpoons CO_2 + H_2O$

(i) Use the equilibria to explain how the buffer keeps the pH of blood nearly constant when a small increase in the concentration of hydrogen ions occurs.

(3)

(ii) The pH of a blood sample was found to be 7.41.
Calculate the ratio of the concentration of HCO_3^- to H_2CO_3 in the blood sample.

$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$

$K_a = 4.50 \times 10^{-7}$ mol dm^{-3}

(3)

(Total for Question 19 = 18 marks)

SECTION C

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

20 The reversible reaction between hydrogen chloride and oxygen produces water **vapour** and chlorine.

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g) \qquad \Delta H = -114 \text{ kJ mol}^{-1}$$

(a) Explain what effect, if any, each of the following changes has on the yield of chlorine at equilibrium **and** on the equilibrium constant, K_p.

(i) An increase in the total pressure

(3)

(ii) An increase in the temperature

(2)

(iii) The use of a catalyst

(2)

(b) 0.850 mol of hydrogen chloride was mixed with 0.600 mol of oxygen and allowed to reach equilibrium in a closed flask.
At equilibrium the total pressure was 1.50 atm and there was 0.250 mol of chlorine in the flask.

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$$

(i) Complete the table.

(3)

Substance	Initial amount / mol	Equilibrium amount / mol	Mole fraction at equilibrium
HCl	0.850		
O_2	0.600		
H_2O	0		
Cl_2	0	0.250	0.189
Total moles at equilibrium =			

(ii) Write the expression for the equilibrium constant, K_p.

(1)

(iii) Use your answers to (b)(i) and (b)(ii) to calculate the value for K_p. Give your answer to an appropriate number of significant figures, and include units.

(3)

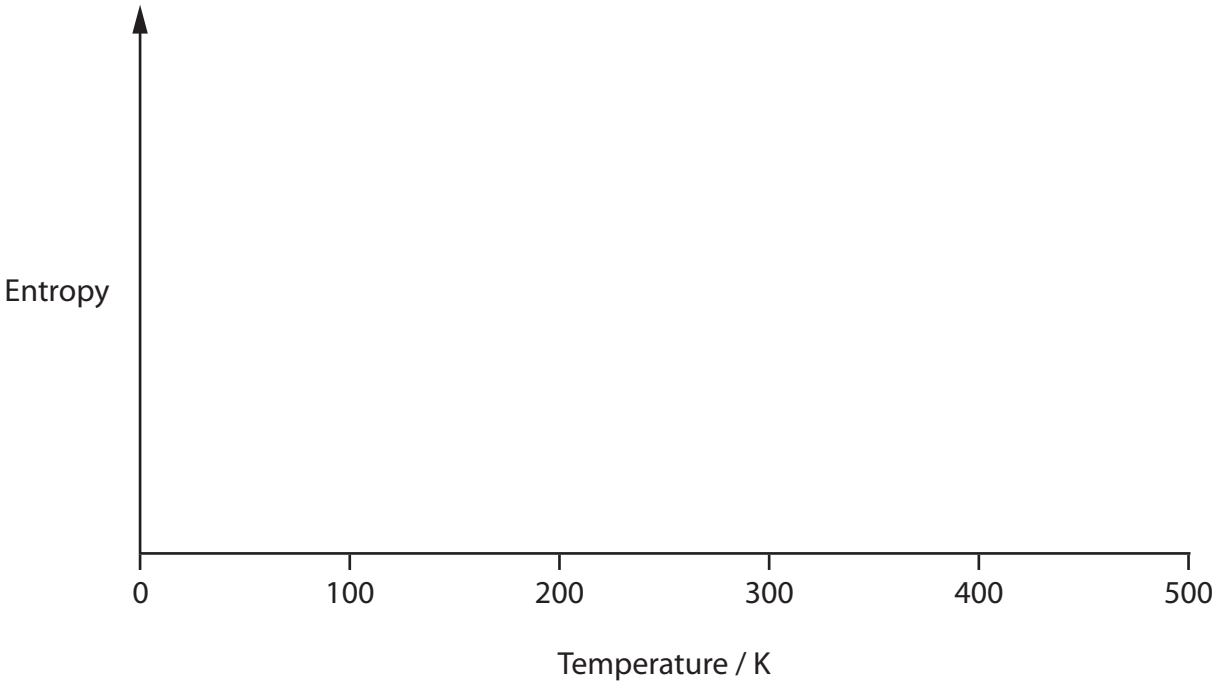
(iv) Use your answer to (b)(iii) to calculate a value for the total entropy change of the reaction, ΔS_{total}.

(2)

(c) Draw a sketch of entropy against temperature for water to illustrate the entropy changes as temperature increases, including when water changes state.

A scale is not required for the vertical axis

(3)



(Total for Question 20 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS
TOTAL FOR PAPER = 90 MARKS

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The Periodic Table of Elements

2											3	4	5	6	7	0 (8)
																(18)
																4.0 **He** helium 2
(2)			Key				1.0 **H** hydrogen 1				(13)	(14)	(15)	(16)	(17)	
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
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
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
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
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
[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

anthanide 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
ctinide 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