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)

Tuesday 5 June 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.
- Check your answers if you have time at the end.
- Show all your working in calculations and include units where appropriate.

Turn over ▶

5/4/1/5/5/2/2/
P 5 1 9 3 6 A 0 1 2 8

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 In gas chromatography, the time taken for a substance to travel through the column is called the

☐ **A** reference time.

☐ **B** retention time.

☐ **C** separation time.

☐ **D** travelling time.

(Total for Question 1 = 1 mark)

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2 Propanoyl chloride, C_2H_5COCl, is formed when propanoic acid reacts with

☐ **A** Cl_2

☐ **B** HCl

☐ **C** NH_4Cl

☐ **D** PCl_5

(Total for Question 2 = 1 mark)

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

3 Different types of radiation are used for a range of purposes in chemistry.

(a) Which types of radiation could be used to heat chemical reactions?

(1)

☒ **A** Infrared and microwave

☒ **B** Microwave and ultraviolet

☒ **C** Radio wave and infrared

☒ **D** Ultraviolet and radio wave

(b) Which type of radiation is used in the initiation step of some chemical reactions?

(1)

☒ **A** Infrared

☒ **B** Microwave

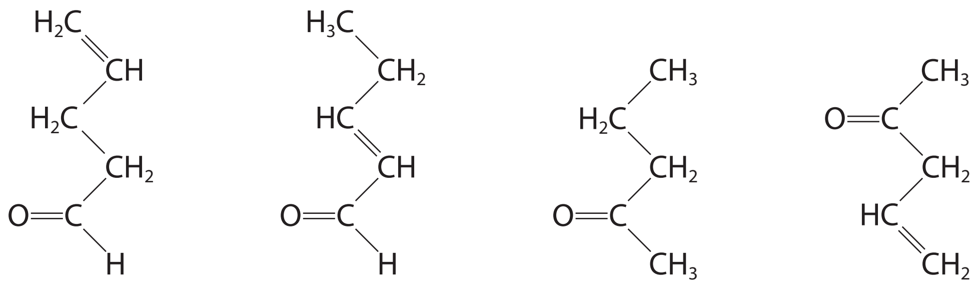
☒ **C** Radio wave

☒ **D** Ultraviolet

(Total for Question 3 = 2 marks)

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

4 This question refers to the following molecules, all of which have a carbonyl group.



W X Y Z

(a) A pale yellow precipitate is formed when iodine in alkali reacts with

(1)

☒ **A** **W** and **X** only.

☒ **B** **Y** only.

☒ **C** **Y** and **Z** only.

☒ **D** **Z** only.

(b) Geometric isomerism is shown by

(1)

☒ **A** **W** only.

☒ **B** **X** only.

☒ **C** **Y** and **Z** only.

☒ **D** none of **W**, **X**, **Y** or **Z**.

(c) A brick red precipitate is formed on warming blue Benedict's or Fehling's solutions with

(1)

☒ **A** **W** only.

☒ **B** **X** only.

☒ **C** **W** and **X** only.

☒ **D** **Y** and **Z** only.

(d) Pentan-2-ol is formed when lithium tetrahydridoaluminate(III) in dry ether reduces

(1)

☒ **A** **W** and **X** only.

☒ **B** **Y** only.

☒ **C** **Y** and **Z** only.

☒ **D** **Z** only.

(e) A molecule with a branched carbon chain is formed by nucleophilic addition of hydrogen cyanide, in the presence of potassium cyanide, with

(1)

☒ **A** **W** only.

☒ **B** **W** and **X** only.

☒ **C** **Y** only.

☒ **D** **Y** and **Z** only.

(f) A mass spectrum fragment with an *m* / *e* value of 29 would be expected for

(1)

☒ **A** **W** and **X** only.

☒ **B** **X** and **Y** only.

☒ **C** **Y** and **Z** only.

☒ **D** **W**, **X** and **Y** only.

(Total for Question 4 = 6 marks)

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

5 The equilibrium between dichromate(VI) ions and chromate(VI) ions can be represented by

$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$

orange yellow

(a) At equilibrium, the expression for the equilibrium constant, K_c, is

(1)

☒ **A** $K_c = \dfrac{[CrO_4^{2-}]^2 \times [H^+]^2}{[Cr_2O_7^{2-}]}$

☒ **B** $K_c = \dfrac{2[CrO_4^{2-}] \times 2[H^+]}{[Cr_2O_7^{2-}]}$

☒ **C** $K_c = \dfrac{[CrO_4^{2-}]^2 + [H^+]^2}{[Cr_2O_7^{2-}]}$

☒ **D** $K_c = \dfrac{2[CrO_4^{2-}] + 2[H^+]}{[Cr_2O_7^{2-}]}$

(b) The addition of a small quantity of sodium hydroxide to an orange equilibrium mixture

(1)

☒ **A** turns the solution from orange to green.

☒ **B** turns the solution from orange to colourless.

☒ **C** shifts the equilibrium position to the left.

☒ **D** shifts the equilibrium position to the right.

(Total for Question 5 = 2 marks)

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

6 The reaction between solid copper and aqueous silver nitrate is

$$Cu(s) + 2Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$

What are the units for the equilibrium constant for this reaction?

(1)

☒ **A** $dm^3\,mol^{-1}$

☒ **B** $mol\,dm^{-3}$

☒ **C** $mol^{-1}\,dm^{-3}$

☒ **D** None, because there are equal moles on each side of the equation.

(Total for Question 6 = 1 mark)

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7 The equilibrium involving phosphorus(V) chloride, phosphorus(III) chloride and chlorine gas is

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The numerical value of K_p is 1.8 at 250 °C.

(a) The expression for the partial pressure of chlorine gas is

(1)

☒ **A** total pressure × (moles of chlorine gas ÷ total moles of gas)

☒ **B** total pressure × moles of chlorine gas

☒ **C** total pressure ÷ (moles of chlorine gas ÷ total moles of gas)

☒ **D** total pressure ÷ moles of chlorine gas

(b) The equilibrium partial pressures of phosphorus(III) chloride and chlorine gas are 0.614 atm and 0.946 atm respectively at 250 °C.
What is the equilibrium partial pressure, in atm, of phosphorus(V) chloride?

(1)

☒ **A** 0.24

☒ **B** 0.32

☒ **C** 1.05

☒ **D** 3.10

(Total for Question 7 = 2 marks)

8 Methanol is produced by the catalysed reaction between carbon monoxide and hydrogen:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90\,kJ\,mol^{-1}$$

(a) The equilibrium yield of methanol is favoured by **both**

(1)

☒ **A** a low temperature and a low pressure.

☒ **B** a low temperature and a high pressure.

☒ **C** a high temperature and a low pressure.

☒ **D** a high temperature and a high pressure.

(b) The equilibrium constant, K_c, for this reaction has a numerical value of 3.64 at a certain temperature.

This value of K_c means that at this temperature

(1)

☒ **A** 3.64 mol of methanol is made.

☒ **B** 3.64 mol of methanol is formed from 1 mol of carbon monoxide.

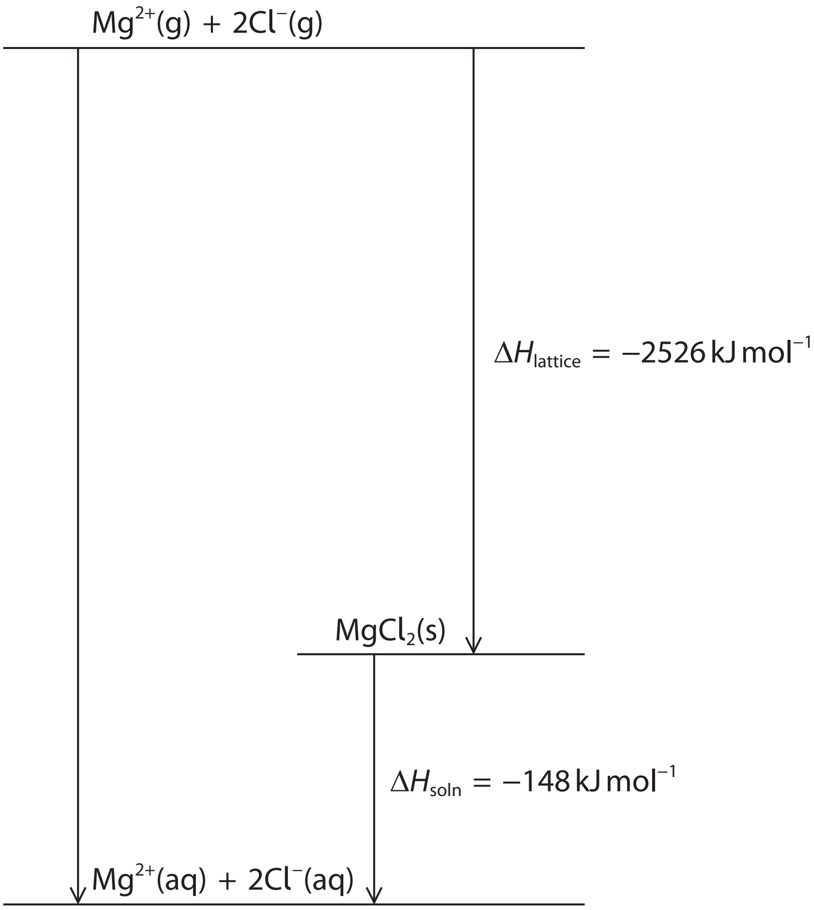
☒ **C** the numerator in the K_c expression is 3.64 times larger than the denominator.

☒ **D** the equilibrium concentration of methanol is 3.64 times that of hydrogen.

(Total for Question 8 = 2 marks)

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

9 The energy cycle for the dissolving of magnesium chloride in water is



(a) The enthalpy of hydration of the magnesium ion is $-1920\ kJ\ mol^{-1}$.

What is the enthalpy of hydration, in $kJ\ mol^{-1}$, of the chloride ion?

(1)

☒ **A** −303

☒ **B** −377

☒ **C** −606

☒ **D** −754

(b) The enthalpy of hydration of potassium ions is less exothermic than the value for magnesium ions because

(1)

☒ **A** potassium ions form weaker bonds in the ionic lattice.

☒ **B** potassium has a lower ionisation energy.

☒ **C** potassium ions are smaller.

☒ **D** potassium ions have a smaller charge density.

(Total for Question 9 = 2 marks)

10 Chloric(I) acid, HClO, and nitric(III) acid, HNO_2, form the equilibrium

$$HClO + HNO_2 \rightleftharpoons H_2ClO^+ + NO_2^-$$

A Brønsted-Lowry acid and its conjugate base are

	Acid	Conjugate base
☒ **A**	HClO	H_2ClO^+
☒ **B**	HClO	HNO_2
☒ **C**	HNO_2	NO_2^-
☒ **D**	H_2ClO^+	NO_2^-

(Total for Question 10 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

11 This is a question about weak acids.

(a) Calculate the pH of a 0.0500 mol dm^{-3} solution of propanoic acid given that $K_a = 1.34 \times 10^{-5}$ mol dm^{-3} at 25 °C.

Give your answer to **two** decimal places.

$$CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$$

(2)

(b) A 0.0400 mol dm^{-3} solution of pentanoic acid with pH = 3.13 was used in a titration experiment at 25 °C.

A 25.0 cm^3 sample of the pentanoic acid solution was placed in a conical flask and the burette filled with a 0.0400 mol dm^{-3} solution of potassium hydroxide.

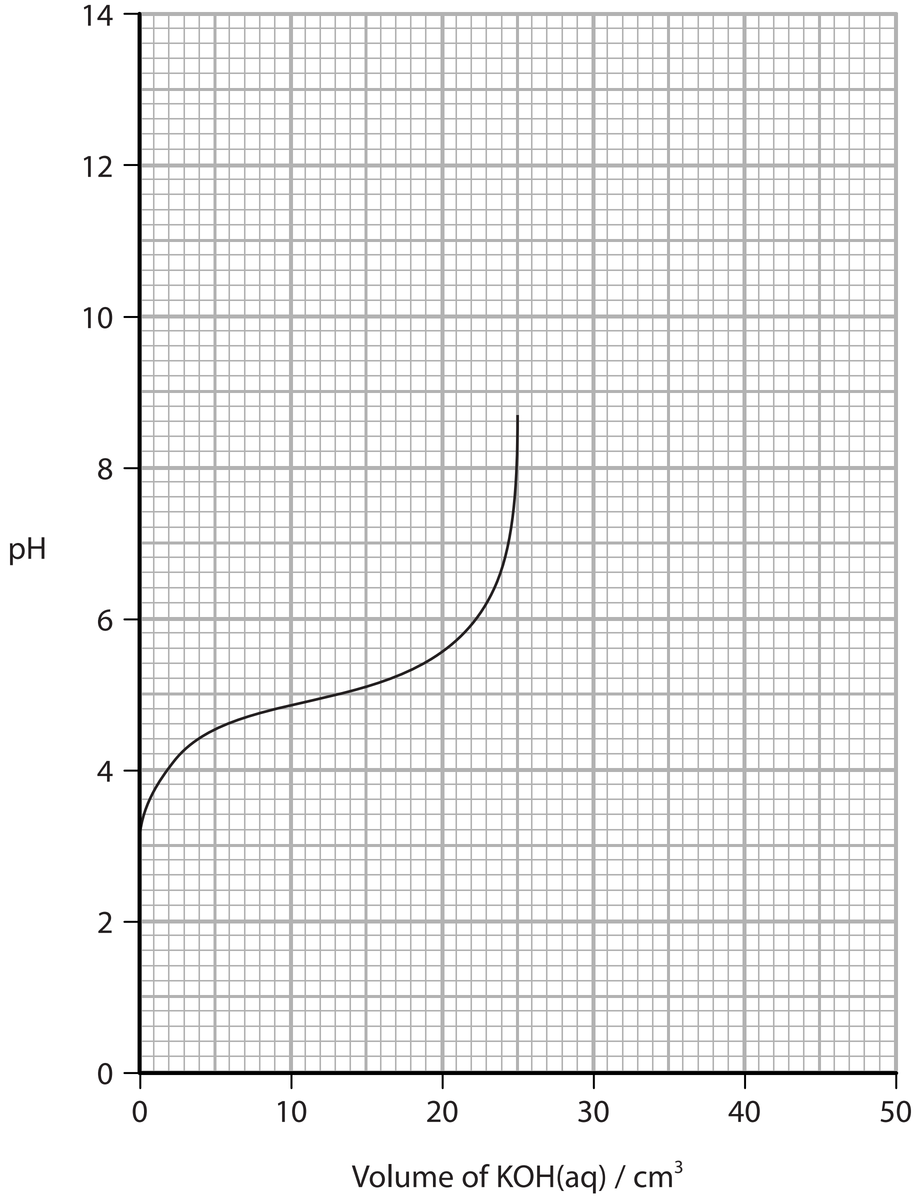
(i) Calculate the pH of the potassium hydroxide solution.

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

(1)

(ii) A total of 50 cm^3 of the potassium hydroxide solution was added. Complete the sketch to show how the pH changed as the potassium hydroxide solution was added.

(1)



(iii) From the sketch in part (b)(ii), read off the value of pK_a of pentanoic acid and hence calculate its K_a value at 25 °C.

Give your answer to **two** significant figures.

(2)

P 5 1 9 3 6 A 0 1 2 2 8

(iv) Some indicators are

Indicator	pH range
Bromophenol blue	2.8 – 4.6
Methyl red	4.2 – 6.3
Thymolphthalein	8.3 – 10.6
Alizarin yellow R	10.1 – 13.0

From these indicators, choose the best indicator for a titration of potassium hydroxide with pentanoic acid. Justify your choice.

(2)

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(c) To 25.0 cm^3 of a 0.0600 $mol\,dm^{-3}$ solution of butanoic acid, 15.0 cm^3 of 0.0800 $mol\,dm^{-3}$ potassium hydroxide solution was added to make a buffer solution.

Calculate the pH of this buffer solution.

[$K_a = 1.50 \times 10^{-5}\ mol\,dm^{-3}$ for butanoic acid at 25 °C]

(4)

*(d) A buffer solution was made from ethanoic acid and sodium ethanoate.

Explain why there is no significant change in the pH of the buffer solution when a small quantity of sodium hydroxide is added.

(3)

(Total for Question 11 = 15 marks)

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12 This is a question about esters.

(a) The esters ethyl ethanoate, $CH_3COOC_2H_5$, and methyl propanoate, $C_2H_5COOCH_3$, are structural isomers, with the molecular formula $C_4H_8O_2$.

(i) Draw the **skeletal** formulae for the two other ester isomers with this molecular formula.

(2)

(ii) Calculate the percentage by mass of carbon in these isomers.

(1)

(b) Give the name of the reagent that could be used to react with propanoic acid to produce methyl propanoate, and complete the balanced equation. State symbols are not required.

(2)

Name of reagent ....

C_2H_5COOH + ... $\rightleftharpoons$ $C_2H_5COOCH_3$ + ...

(c) Ethyl ethanoate can be hydrolysed using alkali.

(i) Write the equation for the hydrolysis of ethyl ethanoate using sodium hydroxide and name the organic products.
State symbols are not required.

(2)

Names of organic products ....

(ii) One student says that the hydrolysis reaction is catalysed by the alkali.

Another student says that the alkali is not a catalyst.

Suggest one piece of evidence in each case that supports the students' statements.

(2)

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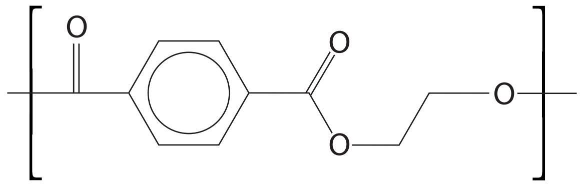
*(d) Compare the **high** resolution proton nmr spectrum of ethyl ethanoate, $CH_3COOC_2H_5$, with that of methyl propanoate, $C_2H_5COOCH_3$. You should include

- **two** similarities and **two** differences
- information from the Data Booklet, quoting chemical shift ranges for all the peaks
- an explanation for **one** splitting pattern of your choice.

(5)

(e) Polyesters are condensation polymers.

(i) The polyester, polyethylene terephthalate, PET, has the following repeat unit.



PET is made from the condensation of two monomers. From the repeat unit shown, draw the structures of these monomers.

(2)

Monomer 1	Monomer 2

(ii) A biodegradable polymer can be made using 3-hydroxypentanoic acid as the only monomer. Draw two repeat units of this polymer.

(2)

(Total for Question 12 = 18 marks)

13 Kinetic data obtained from the hydrolysis of halogenoalkanes gives insight into the mechanisms of the reactions.

(a) Draw the **structural** formulae of a primary, a secondary and a tertiary iodoalkane, each with **four** carbon atoms and one iodine atom.

(2)

Classification	Example
Primary iodoalkane	
Secondary iodoalkane	
Tertiary iodoalkane	

(b) The halogenoalkane, 1-bromopropane, was hydrolysed at 20 °C with aqueous sodium hydroxide. The results were:

Experiment number	$[C_3H_7Br]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Rate of reaction / mol dm^{-3} s^{-1}
1	0.010	0.005	0.16
2	0.010	0.020	0.66
3	0.020	0.020	1.34

(i) Deduce the order with respect to 1-bromopropane and the order with respect to hydroxide ions in this reaction.
Fully justify your answers.

(4)

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(ii) The replacement of sodium hydroxide with potassium hydroxide has no effect on the results obtained.
What does this indicate about the sodium and potassium ions in the steps of the reaction mechanism?

(1)

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(c) The halogenoalkane, 2-bromopentane, was hydrolysed at 20 °C with sodium hydroxide of similar concentration and the results gave the rate equation

$$\text{rate} = k[CH_3CH_2CH_2CHBrCH_3]$$

(i) Write the mechanism for the hydrolysis of 2-bromopentane. Include curly arrows, and any relevant dipoles and lone pairs of electrons.

You may use R to represent the $CH_3CH_2CH_2$ group.

(3)

(ii) State how your mechanism is consistent with the rate equation.

(1)

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(iii) A single optical isomer of 2-bromopentane is hydrolysed by this mechanism. Explain fully whether or not the product of this hydrolysis is optically active.

(3)

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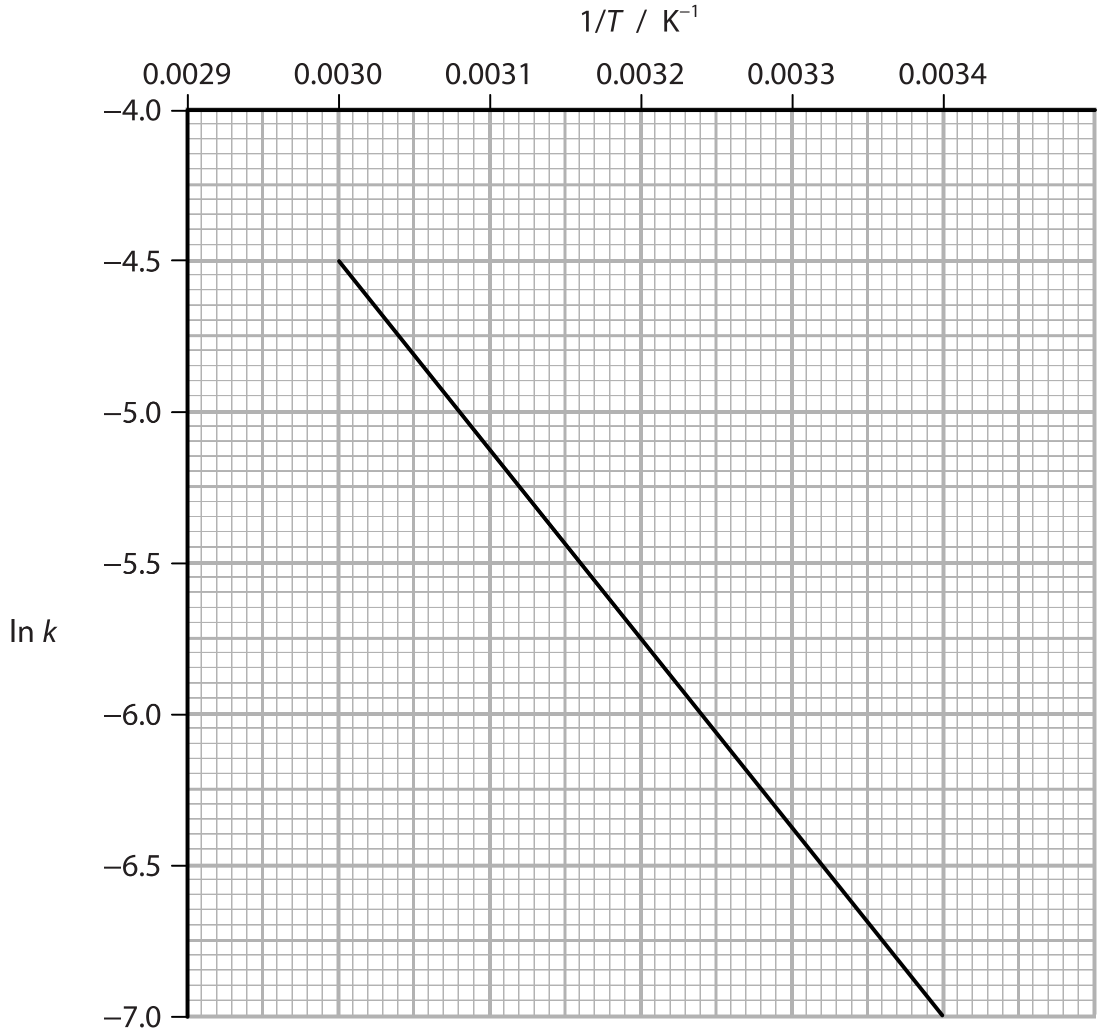
(d) The rate constant for the hydrolysis of a halogenoalkane with sodium hydroxide was measured at several different temperatures and the results plotted in the graph shown.



From the graph, determine the gradient of the line and hence calculate the activation energy for this reaction. Include signs and units in your answers.

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31 \text{ J K}^{-1}\text{ mol}^{-1}$$

(3)

(Total for Question 13 = 17 marks)

TOTAL FOR SECTION B = 50 MARKS

P 5 1 9 3 6 A 0 2 2 2 8

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SECTION C

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

14 Endothermic changes can be thermodynamically feasible.

(a) One example of an endothermic reaction is between the solids hydrated barium hydroxide and ammonium chloride. An equation for the reaction is

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(s) + 10H_2O(l) + 2NH_3(g)$$

(i) Suggest **two** experimental observations that you would expect to make when carrying out this reaction without additional chemical tests.

(2)

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(ii) Predict the sign of the standard entropy change of the system ($\Delta S^{\ominus}_{system}$) for this reaction and give **two** reasons to justify your prediction.

(2)

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(b) Another example of a reaction between two solids involves anhydrous barium hydroxide and ammonium nitrate. An equation for this reaction is

$$Ba(OH)_2(s) + 2NH_4NO_3(s) \rightarrow Ba(NO_3)_2(s) + 2H_2O(l) + 2NH_3(g)$$

(i) Use the standard molar entropies from your Data Booklet to calculate the standard entropy change of the system ($\Delta S^{\ominus}_{system}$) for this reaction at 298 K. Give a sign and units with your answer.

(3)

(ii) Use the standard enthalpy changes of formation given in Table 1 to calculate the standard enthalpy change of this reaction at 298 K. Include a sign and units in your answer.

(2)

Table 1

Compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$Ba(OH)_2(s)$	−944.7
$NH_4NO_3(s)$	−365.6
$Ba(NO_3)_2(s)$	−992.1
$H_2O(l)$	−285.8
$NH_3(g)$	−46.1

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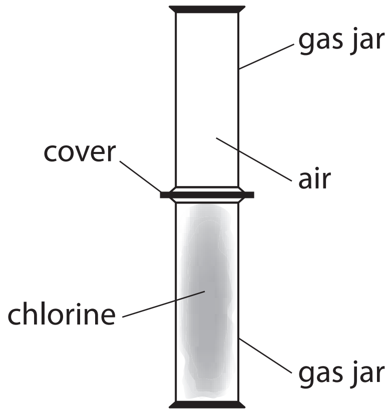
(iii) Using your answer to (b)(ii), calculate the standard entropy change of the surroundings ($\Delta S^{\ominus}_{surroundings}$) for this reaction at 298 K. Include a sign and units in your answer.

(2)

(iv) Using your answers to (b)(i) and (b)(iii), calculate the total entropy change ($\Delta S^{\ominus}_{total}$). Include a sign and units in your answer.

(1)

(c) The feasibility of chemical changes can be related to entropy in terms of the dispersal of molecules and of energy quanta between molecules.



(i) Describe what happens to the chlorine gas when the cover between the gas jars is removed. Explain the change in terms of entropy.

(2)

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(ii) Complete the table to show the five different ways that **four** energy quanta can be shared between two molecules, compared with just a single way for one molecule.

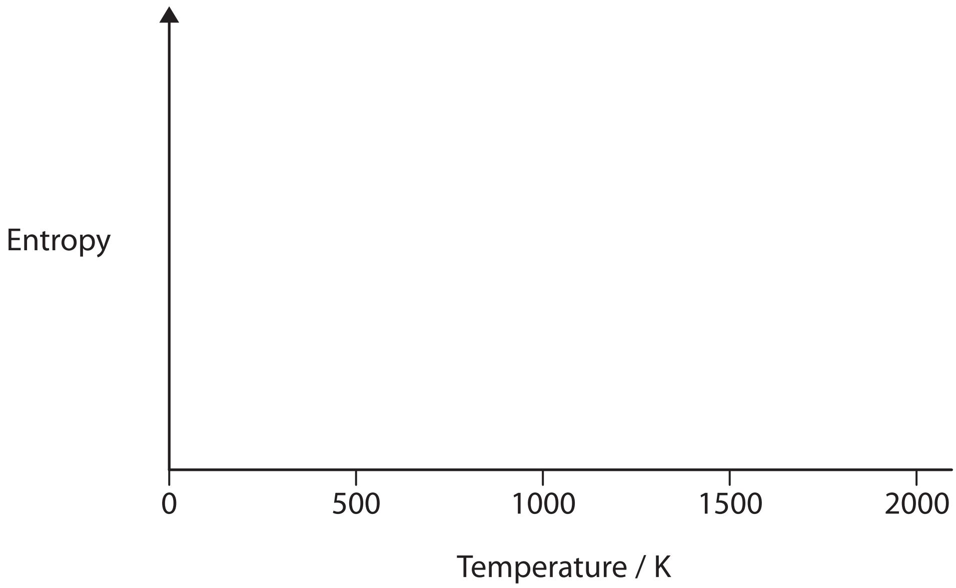
(1)

Molecule A	Molecule B
2	2
3	1

(d) Complete the sketch of entropy against temperature for sodium chloride to illustrate the entropy changes as temperature increases, and the sodium chloride changes state.

Use your Data Booklet to find any temperatures where significant entropy changes occur. Label these changes. The vertical axis does not have to be to scale.

(3)



*(e) Explain why the entropy of the system increases when sodium chloride dissolves in water.

(2)

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(Total for Question 14 = 20 marks)

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

The Periodic Table of Elements

Key

relative atomic mass **atomic symbol** name atomic (proton) number

1 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (8) (18)
							1.0 **H** hydrogen 1										4.0 **He** helium 2
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											27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac*** actinium 89	[261] **Rf** rutherfordium 104	[262] **Db** dubnium 105	[266] **Sg** seaborgium 106	[264] **Bh** bohrium 107	[277] **Hs** hassium 108	[268] **Mt** meitnerium 109	[271] **Ds** darmstadtium 110	[272] **Rg** roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

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