Please check the examination details below before entering your candidate information

Candidate surname	Other names

Pearson Edexcel
International Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

Monday 13 January 2020

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)

Candidates must have: Scientific calculator
Data Booklet
Ruler

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

Turn over ▶

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P 6 0 4 7 2 A 0 1 3 2

Pearson

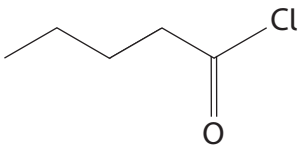
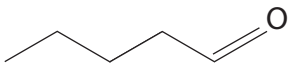
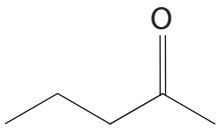
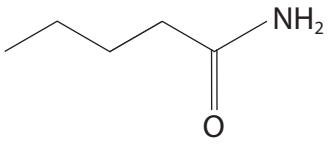
SECTION A

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 This question is about four organic compounds each with five carbon atoms but different functional groups.

Compound	Skeletal formula
1	
2	
3	
4	

(a) Which of these, when mixed with water, produces the solution with the **lowest** pH?

(1)

☒ **A** compound **1**

☒ **B** compound **2**

☒ **C** compound **3**

☒ **D** compound **4**

(b) Which of these reacts with ethylamine, $CH_3CH_2NH_2$, to form an N-substituted amide?

(1)

☒ **A** compound **1**

☒ **B** compound **2**

☒ **C** compound **3**

☒ **D** compound **4**

(c) Which of these reacts with iodine and sodium hydroxide in solution to produce a pale yellow precipitate?

(1)

☒ **A** compound **1**

☒ **B** compound **2**

☒ **C** compound **3**

☒ **D** compound **4**

(Total for Question 1 = 3 marks)

2 Which of these molecules can rotate the plane of plane-polarised light?

☒ **A** H_2NCH_2COOH

☒ **B** $HOCH_2CH_2COOH$

☒ **C** $ClCH_2C(CH_3)(Cl)COOH$

☒ **D** $H_2NC(CH_3)_2COOH$

(Total for Question 2 = 1 mark)

3 A polymer is prepared by the reaction between hexanedioyl dichloride and hexane-1-6-diamine.

What type of polymerisation occurs?

☒ **A** addition

☒ **B** condensation

☒ **C** hydrolysis

☒ **D** substitution

(Total for Question 3 = 1 mark)

4 The compound HOOCCH═CHCOOH reacts with excess sodium hydroxide solution.

What is the organic product formed in the reaction?

☒ **A** NaOOCCH═CHCOONa

☒ **B** HOOCCH═CHCOONa

☒ **C** NaOOCC(OH)HC(OH)HCOONa

☒ **D** NaOOCCH═CHCHO

(Total for Question 4 = 1 mark)

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

5 Which diagram shows the mechanism for the second order reaction between 1-bromoethane and potassium hydroxide in aqueous solution?

Diagram 1

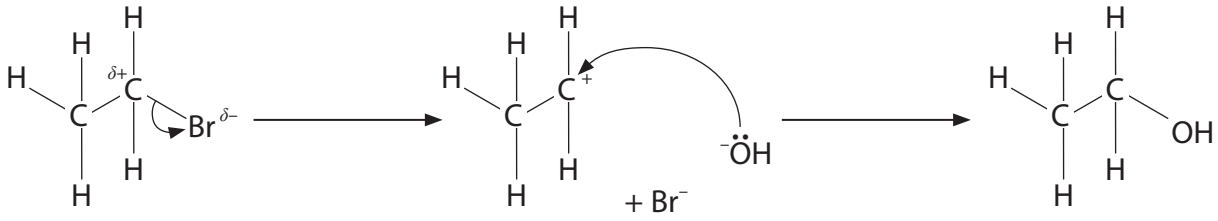


Diagram 2

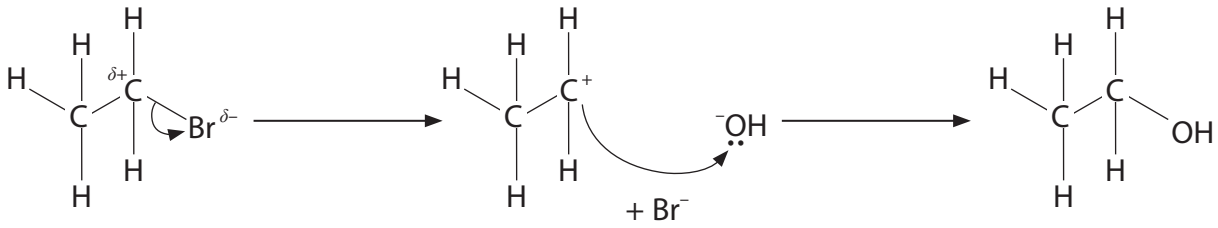


Diagram 3

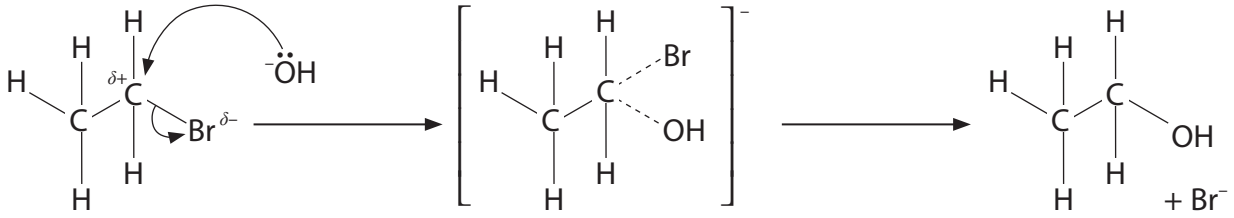
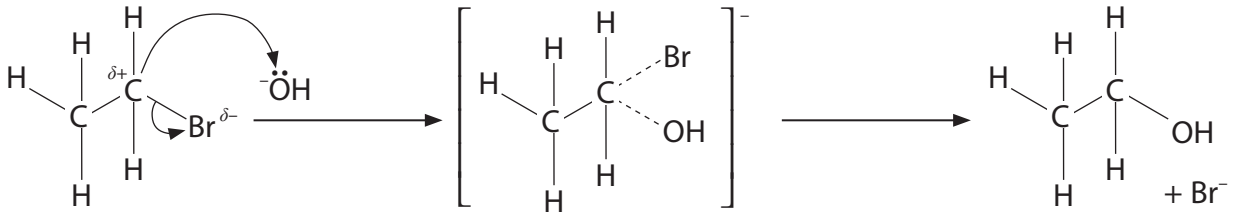


Diagram 4



☒ **A** Diagram 1

☒ **B** Diagram 2

☒ **C** Diagram 3

☒ **D** Diagram 4

(Total for Question 5 = 1 mark)

6 Which of these reacts directly with ethanoic acid to form ethanoyl chloride?

☒ **A** chlorine

☒ **B** chloroethane

☒ **C** hydrogen chloride

☒ **D** phosphorus(V) chloride

(Total for Question 6 = 1 mark)

7 Which of these changes has the largest **increase** in the entropy of the system?

☒ **A** $H_2O(s) \rightarrow H_2O(l)$

☒ **B** $Hg(l) \rightarrow Hg(g)$

☒ **C** $H_2O(l) + HCl(g) \rightarrow H_3O^+(aq) + Cl^-(aq)$

☒ **D** $C(graphite) \rightarrow C(diamond)$

(Total for Question 7 = 1 mark)

8 Equal amounts of W and X are mixed and allowed to reach equilibrium.

$$W + X \rightleftharpoons Y + Z$$

The value of the equilibrium constant is $K_c = 4.85$. At equilibrium, the mixture will contain

☒ **A** almost all Y and Z

☒ **B** almost all W and X

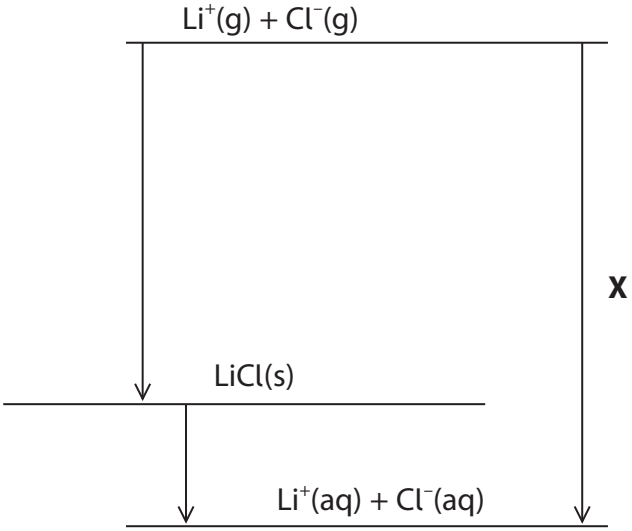
☒ **C** W, X, Y and Z but there is less Y and Z than W and X

☒ **D** W, X, Y and Z but there is more Y and Z than W and X

(Total for Question 8 = 1 mark)

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

9 What does **X** represent on the diagram?



☒ **A** sum of enthalpy changes of hydration of the gaseous ions

☒ **B** enthalpy change of formation of LiCl

☒ **C** enthalpy change of solution of LiCl

☒ **D** lattice energy of LiCl

(Total for Question 9 = 1 mark)

10 How are 20 cm^3 of 0.05 mol dm^{-3} $H_2SO_4(aq)$ and 20 cm^3 of 0.10 mol dm^{-3} $CH_3COOH(aq)$ alike?

Both solutions

☒ **A** have the same pH

☒ **B** have the same total concentration of ions

☒ **C** have the same total concentration of **negative** ions

☒ **D** require 20 cm^3 of 0.10 mol dm^{-3} NaOH(aq) for complete reaction

(Total for Question 10 = 1 mark)

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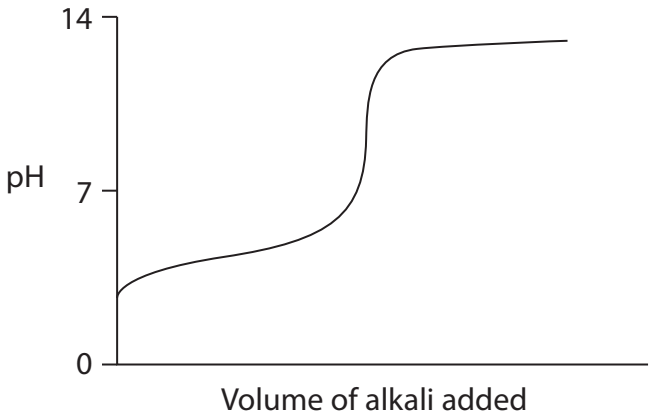
11 Which two solutions, both of concentration 0.10 mol dm^{-3}, have been used to produce this titration curve?



☒ **A** HCl(aq) and KOH(aq)

☒ **B** HCOOH(aq) and KOH(aq)

☒ **C** HCl(aq) and NH_3(aq)

☒ **D** HCOOH(aq) and NH_3(aq)

(Total for Question 11 = 1 mark)

12 A solution of sodium hydroxide of concentration 0.0080 mol dm^{-3} has a pH

☒ **A** between 7 and 9

☒ **B** between 9 and 11

☒ **C** between 11 and 13

☒ **D** above 13

(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 student carried out an experiment to determine the equilibrium constant for the reaction to form ethyl ethanoate from ethanol and ethanoic acid.

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

Different amounts of each substance were added to conical flasks, each containing 2.0 cm^3 of 1.0 mol dm^{-3} hydrochloric acid.

Conical flask	Volume added / cm^3				
	HCl (aq)	H_2O (l)	CH_3COOH (l)	$CH_3COOCH_2CH_3$ (l)	CH_3CH_2OH (l)
1	2.0	1.0	0	2.0	0
2	2.0	0	5.0	0	5.0
3	2.0	0	4.0	0	3.0
4	2.0	0	0	3.0	0

The flasks were then stoppered and left for a week to reach equilibrium.

Each mixture was then titrated with 1.0 mol dm^{-3} sodium hydroxide.

(a) In which flask(s) was the equilibrium approached from the right-hand side of the equation?

(1)

☒ **A** flask 1 only

☒ **B** flask 4 only

☒ **C** flasks 1 and 4 only

☒ **D** flasks 2 and 3 only

(b) Which of these statements explains why it is possible to titrate the reaction mixture directly to find the equilibrium concentrations?

(1)

☒ **A** the equilibrium reaction is slow

☒ **B** the sodium hydroxide quickly hydrolyses the ester

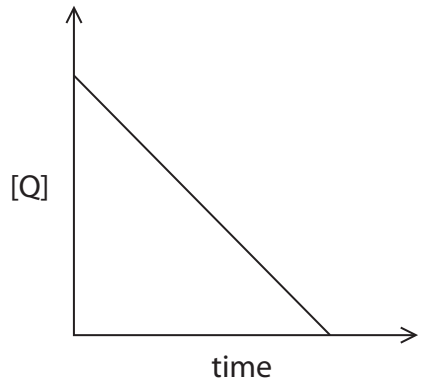
☒ **C** all the reactant concentrations remain constant during the titration

☒ **D** a buffer solution forms in the reaction

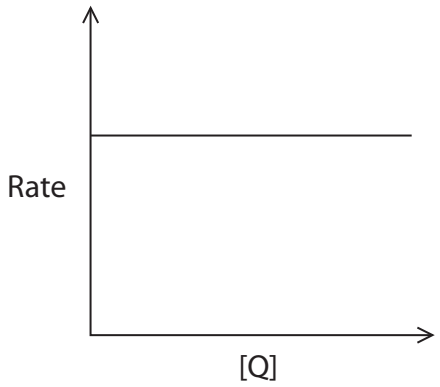
(Total for Question 13 = 2 marks)

14 A reactant Q is converted into two products. Which of these graphs shows that this reaction is first order with respect to Q?

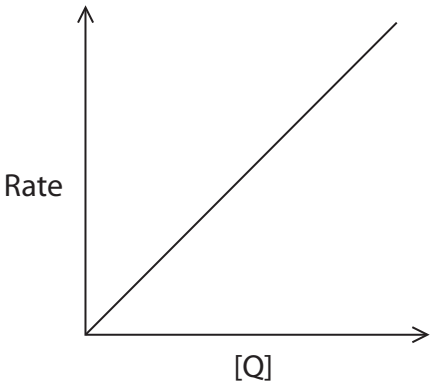
Graph 1



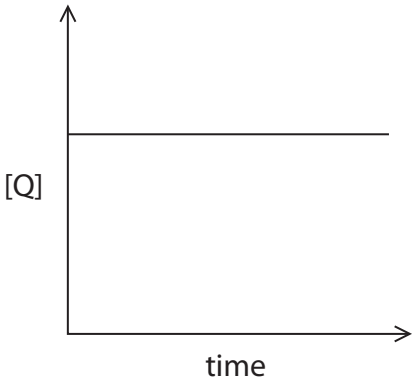
Graph 2



Graph 3



Graph 4



☒ **A** Graph 1

☒ **B** Graph 2

☒ **C** Graph 3

☒ **D** Graph 4

(Total for Question 14 = 1 mark)

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15 This question is about the kinetics of the reaction between nitrogen monoxide and oxygen.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The rate equation for the reaction is rate = $k[NO]^2[O_2]$

(a) Which statement is **not** correct?

(1)

☒ **A** the reaction is third order overall

☒ **B** the units of the rate of the reaction are mol dm^{-3} s^{-1}

☒ **C** the rate of the reaction increases when the pressure is increased

☒ **D** when the concentration of nitrogen monoxide doubles and the concentration of oxygen quadruples, the rate increases by a factor of 8

(b) What are the units of the rate constant, k, for this reaction?

(1)

☒ **A** $dm^9 mol^{-3} s^{-1}$

☒ **B** $mol^3 dm^{-9} s^{-1}$

☒ **C** $mol^2 dm^{-6} s^{-1}$

☒ **D** $dm^6 mol^{-2} s^{-1}$

(c) An experiment was carried out using 1.10×10^{-2} mol dm^{-3} of oxygen and some nitrogen monoxide.
The numerical value of the initial rate and rate constant were:

- initial rate = 3.20×10^{-3}
- rate constant, $k = 1.70 \times 10^3$

What was the initial concentration, in mol dm^{-3}, of the nitrogen monoxide used in the experiment?

(1)

☒ **A** 1.31×10^{-2}

☒ **B** 1.71×10^{-4}

☒ **C** 2.02×10^{-3}

☒ **D** 4.50×10^{-2}

(Total for Question 15 = 3 marks)

TOTAL FOR SECTION A = 20 MARKS

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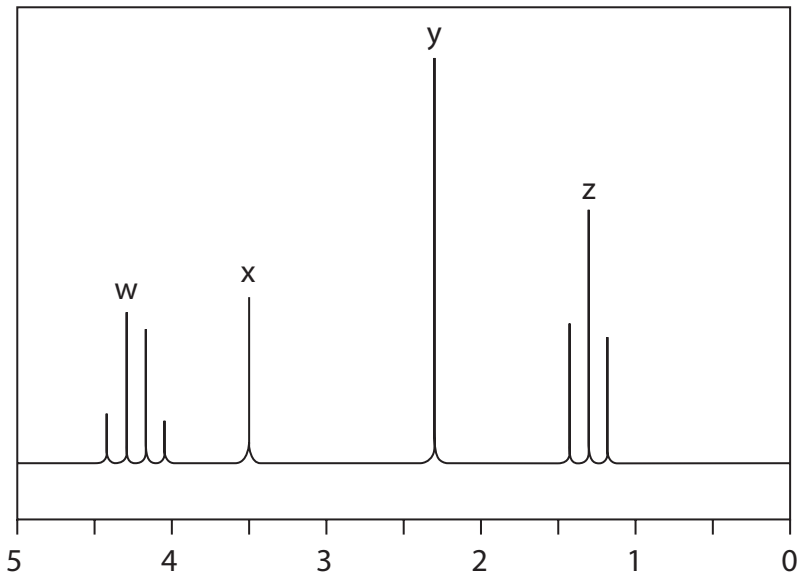
SECTION B

Answer ALL the questions.

Write your answers in the spaces provided.

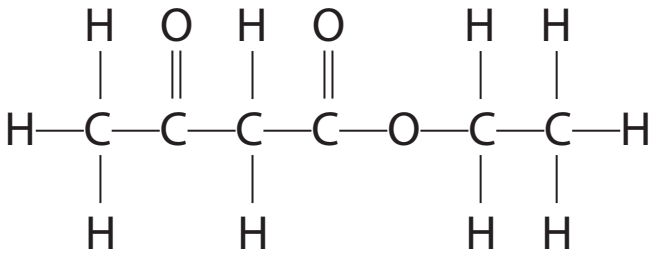
16 The compound ethyl 3-oxobutanoate, which is used in food flavouring, has the formula $CH_3COCH_2COOCH_2CH_3$.

The high resolution proton (^1H) NMR spectrum of this compound is



(a) (i) Identify which groups of hydrogen atoms are responsible for each peak in the spectrum by adding the labels w, x, y and z to the appropriate parts of this displayed formula to match the letters on the spectrum.

(2)



(ii) Explain the splitting patterns of the peaks at 4.2 ppm and 1.3 ppm.

(2)

(iii) The carbon-13 (^{13}C) NMR spectrum of ethyl 3-oxobutanoate has six peaks.

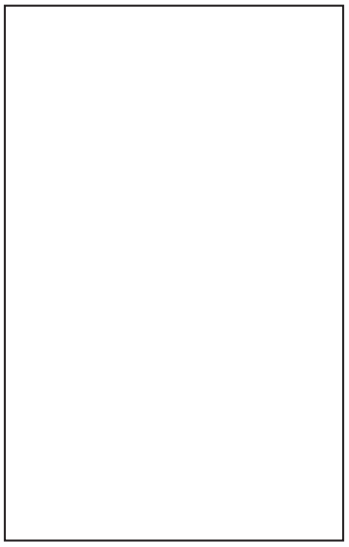
Draw the structure of an **isomer** of ethyl 3-oxobutanoate that contains a carboxylic acid group and a ketone functional group, but only has four peaks in its carbon-13 NMR spectrum.

(1)

(b) A chemist synthesising ethyl 3-oxobutanoate looked for its presence in the reaction mixture using thin-layer chromatography. The solvent used was a mixture of ethoxyethane, $C_2H_5OC_2H_5$, which is polar, and hexane.
Under these conditions, the R_f value for ethyl 3-oxobutanoate was 0.45.

(i) Complete the diagram below, showing a chromatogram for ethyl 3-oxobutanoate, including appropriate labels.

(3)



(ii) Suggest why the R_f value for ethyl 3-oxobutanoate is significantly lower than 0.45 when just hexane is used as the solvent.

(2)

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(Total for Question 16 = 10 marks)

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*17 Compare and contrast the reactions of propanal and propanone with **one** oxidising agent, **one** reducing agent and 2,4-dinitrophenylhydrazine.

In your answer include any relevant observations for the reactions you discuss and equations for any reactions classified as oxidation, using [O] for the oxygen from the oxidising agent.

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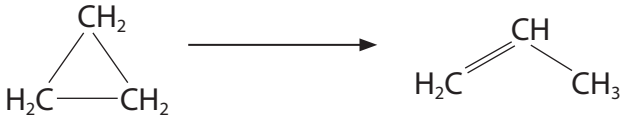
(Total for Question 17 = 6 marks)

18 The rate constant for the reaction to convert cyclopropane to propene was determined at five different temperatures.



The results are shown in the table.

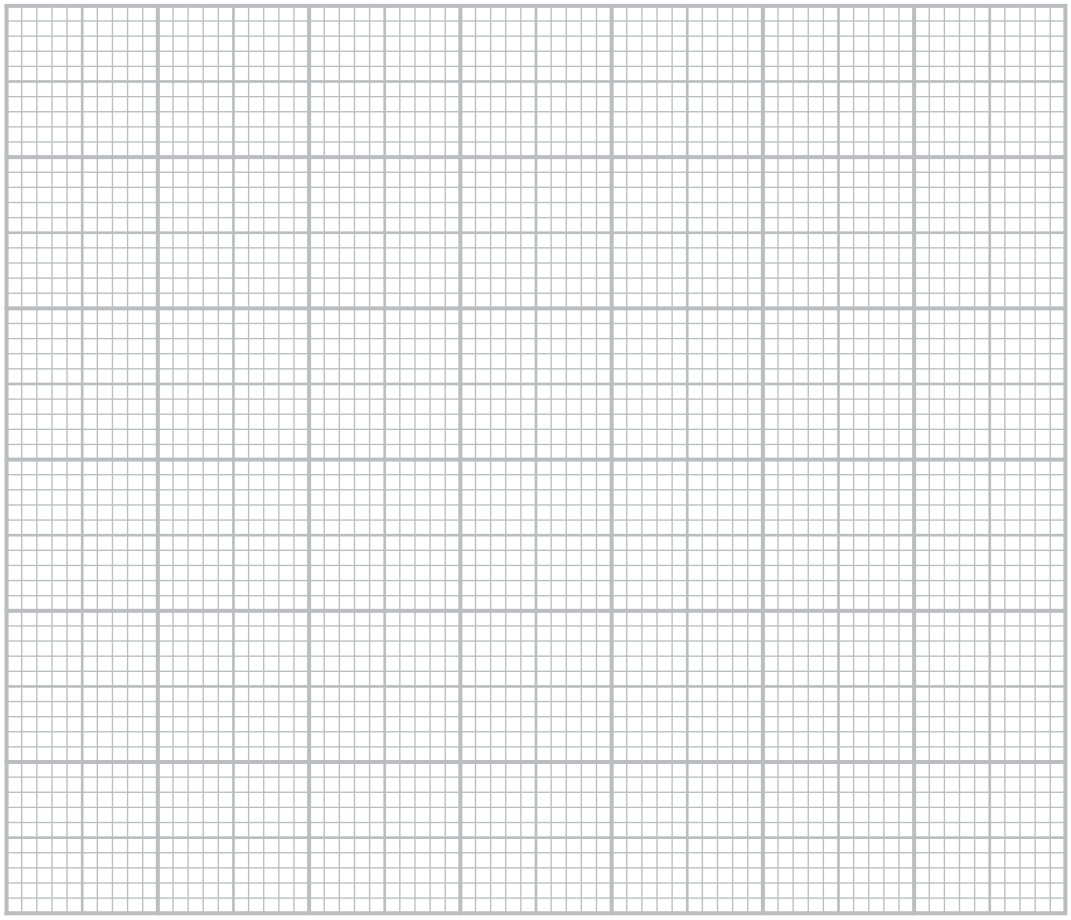
Temperature (T) / K	1 / Temperature ($1/T$) / K^{-1}	Rate constant (k) / s^{-1}	ln k
719	1.39×10^{-3}	2.49×10^{-5}	–10.60
746	1.34×10^{-3}	1.23×10^{-4}	–9.00
791	1.26×10^{-3}	1.66×10^{-3}	
840		1.83×10^{-2}	–4.00
889	1.12×10^{-3}	1.65×10^{-1}	–1.80

(a) (i) Complete the table.

(1)

(ii) Plot a graph of ln k against $1/T$.

(3)



(iii) Use your graph to determine the activation energy, E_a, in kJ mol^{-1}.

You should include the value and units of the gradient of the line.

The Arrhenius equation is

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

(3)

(b) The activation energy for many reactions is around +50 kJ mol^{-1}.

Given this information, comment on your value for E_a.

(2)

(c) Explain the trend in the value of the rate constant k as the temperature increases.

(3)

(Total for Question 18 = 12 marks)

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19 This question is about halides.

(a) Silicon tetrachloride, $SiCl_4$, is used in the manufacture of optical fibres. It can be made by the reaction of silicon carbide, SiC, with hydrogen chloride using a catalyst of nickel(II) chloride.

$$SiC(s) + 4HCl(g) \rightarrow SiCl_4(l) + CH_4(g) \qquad \Delta H = -631.3\,kJ\,mol^{-1}$$

The standard molar entropies $S^{\ominus}$, of the substances are shown in the table.

Substance	SiC(s)	HCl(g)	$SiCl_4(l)$	$CH_4(g)$
$S^{\ominus}$ / $JK^{-1}\,mol^{-1}$	+16.5	+186.8	+239.7	+186.2

(i) Calculate the total entropy change, ΔS_{total}, for this reaction, at 298 K, using the information given.

Include a sign and units in your answer which should be given to an appropriate number of significant figures.

(5)

(ii) In industry, the reaction is carried out at 700 °C.

By considering entropy and other relevant factors, justify the use of this temperature.

(3)

(iii) Use your answer from (a)(i) to calculate the equilibrium constant for the reaction at 298 K.

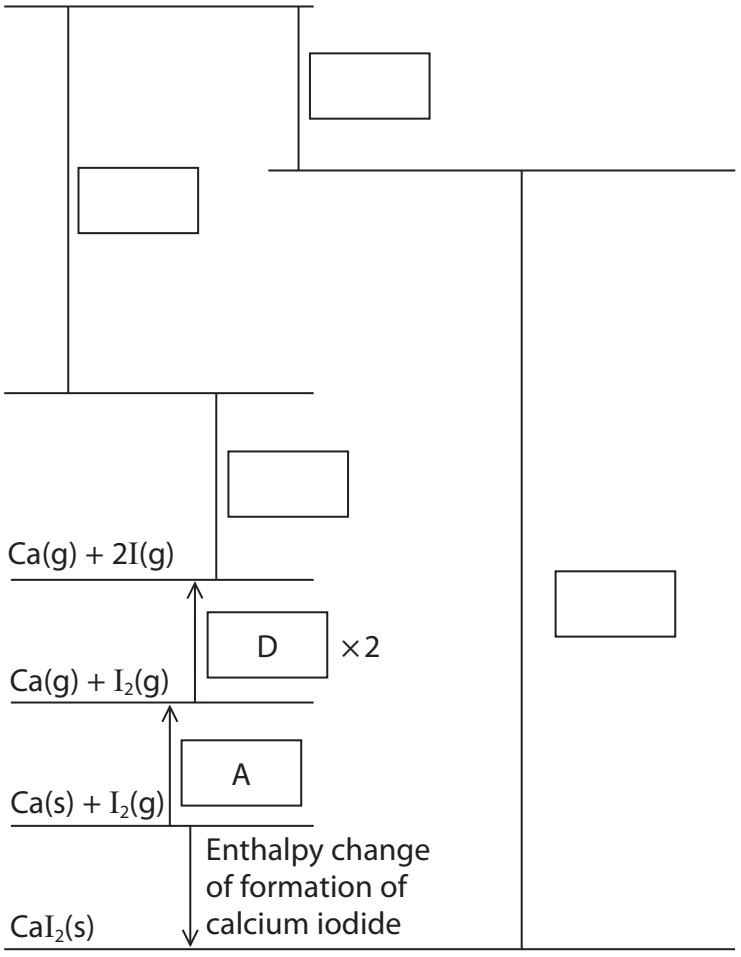
(2)

(b) The following data can be used in a Born-Haber cycle for calcium iodide, CaI_2.

Letter	Energy change	Value / kJ mol^{-1}
A	Enthalpy change of atomisation of calcium	+178.2
B	First ionisation energy of calcium	+590
C	Second ionisation energy of calcium	+1145
D	Enthalpy change of atomisation of iodine ($\frac{1}{2}I_2(s) \rightarrow I(g)$)	+106.8
E	Electron affinity of iodine	–295.4
F	Lattice energy of calcium iodide	–2074

(i) Complete the Born-Haber cycle by adding letters in the boxes for the energy changes, relevant species on the blank lines and arrowheads to show the direction of each energy change.

(3)



(ii) Use the data to calculate the value for the enthalpy change of formation of calcium iodide.

(2)

(iii) The value for the lattice energy of calcium iodide determined experimentally by using the Born-Haber cycle differs significantly from the theoretical calculated value.

Explain why the Born-Haber and the theoretical values for the lattice energies are similar for calcium fluoride but significantly different for calcium iodide.

(4)

(c) The electron affinity of iodine is $-295.4\ kJ\ mol^{-1}$.

Explain how the electron affinity of chlorine differs from that of iodine.

(3)

(Total for Question 19 = 22 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

Answer ALL the questions.

Write your answers in the spaces provided.

20 This question is about ethanoic acid and some of its compounds.

(a) Three students, A, B and C, carried out an investigation to determine the amount of isoamyl acetate, an ester of ethanoic acid, in a banana food flavouring.

They hydrolysed the ester with excess sodium hydroxide solution.

$$CH_3COOCH_2CH_2CH(CH_3)_2 + NaOH \rightarrow CH_3COONa + (CH_3)_2CHCH_2CH_2OH$$

The amount of sodium hydroxide remaining was determined by titrating the reaction mixture with hydrochloric acid.

(i) Give the systematic name for isoamyl acetate.

(1)

.....

(ii) 6.06×10^{-3} mol of sodium hydroxide reacted with the ester present in 1.07 g of the flavouring.

Calculate the percentage by mass of the ester in the food flavouring.

(3)

(iii) The students used 25.0 cm^3 of sodium hydroxide solution with concentration 0.980 mol dm^{-3} for the hydrolysis.

Calculate the pH of the reaction mixture when the hydrolysis is complete.
Assume the total volume is 25.0 cm^3.

[Ionic product of water, $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}]

(3)

(iv) Two indicators, methyl orange and phenolphthalein, were available for this titration.

Student A thought only methyl orange could be used.
Student B thought only phenolphthalein could be used.
Student C suggested either indicator could be used.

Explain which student is correct.

(2)

(v) Describe how the sodium ethanoate in the final reaction mixture could be converted into ethanoic acid.

(1)

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.....

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(b) Ethanoic acid can be used to form buffer solutions.

(i) Calculate the pH of the buffer solution formed when 50.0 cm^3 of ethanoic acid with concentration of 0.150 mol dm^{-3} is mixed with 30.0 cm^3 of sodium hydroxide solution with concentration of 0.142 mol dm^{-3}.

[K_a for ethanoic acid = 1.70×10^{-5} mol dm^{-3}]

(5)

(ii) Small amounts of sodium hydroxide and hydrochloric acid are added to separate samples of the buffer solution in (b)(i).

Explain why these samples resist change in pH.

Illustrate your answer with at least two equations.

(5)

(Total for Question 20 = 20 marks)

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	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