Please check the examination details below before entering your candidate information

Candidate surname	Other names

Centre Number ☐☐☐☐☐ Candidate Number ☐☐☐☐

Pearson Edexcel International Advanced Level

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 **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 ▶

Pearson

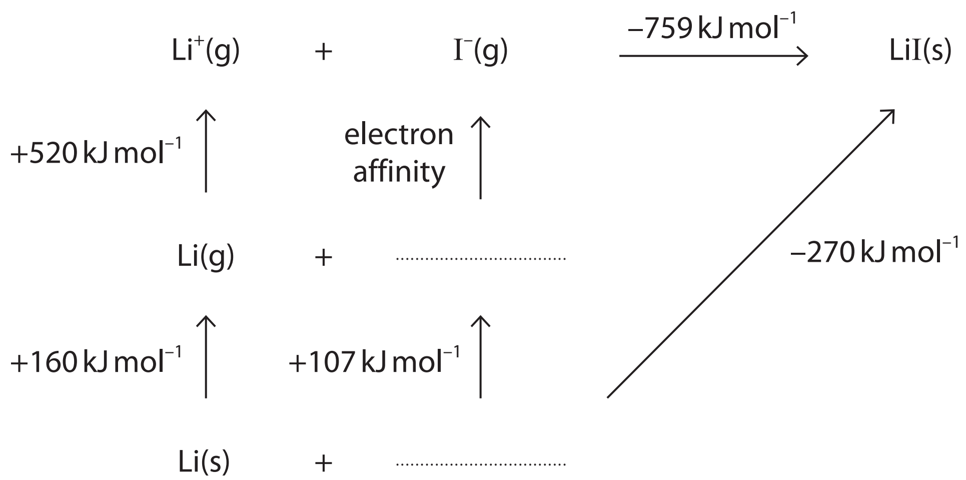
SECTION A

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 A simplified Born-Haber cycle for the formation of lithium iodide is shown.



(a) The enthalpy change of atomisation of iodine ($+107\ kJ\ mol^{-1}$) is given by the equation

(1)

- ☒ **A** $\frac{1}{2}I_2(g) \rightarrow I(g)$
- ☒ **B** $\frac{1}{2}I_2(s) \rightarrow I(g)$
- ☒ **C** $I_2(g) \rightarrow 2I(g)$
- ☒ **D** $I_2(s) \rightarrow 2I(g)$

(b) Use the information in the cycle to calculate the electron affinity of iodine.

(1)

- ☒ **A** $-298\ kJ\ mol^{-1}$
- ☒ **B** $-242\ kJ\ mol^{-1}$
- ☒ **C** $+242\ kJ\ mol^{-1}$
- ☒ **D** $+298\ kJ\ mol^{-1}$

(Total for Question 1 = 2 marks)

2 Some energy changes are given in the table.

Energy change	Value / kJ mol^{-1}
Lattice energy for $CaCl_2$(s)	–2258
Enthalpy change of solution of $CaCl_2$(s)	–120
Enthalpy change of hydration of Cl^-(g)	–364

Use these data to calculate the enthalpy change of hydration of Ca^{2+}(g).

☒ **A** –1410 kJ mol^{-1}

☒ **B** –1650 kJ mol^{-1}

☒ **C** –2014 kJ mol^{-1}

☒ **D** –3106 kJ mol^{-1}

(Total for Question 2 = 1 mark)

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

3 The reaction shown is at equilibrium. The forward reaction is endothermic.

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

(a) Which will **increase** when the temperature is lowered?

(1)

☒ **A** the mole fraction of carbon dioxide

☒ **B** the partial pressure of carbon monoxide

☒ **C** the rate of the backward reaction

☒ **D** the value of K_p for the forward reaction

(b) At 680 °C and 1 atm, 52.6 % of the molecules in the gas mixture are carbon monoxide. What is the partial pressure of carbon dioxide, in atmospheres?

(1)

☒ **A** 0.237

☒ **B** 0.263

☒ **C** 0.474

☒ **D** 0.526

(Total for Question 3 = 2 marks)

4 The equation for the precipitation of lead(II) chloride is shown.

$$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightleftharpoons PbCl_2(s)$$

What are the units of the equilibrium constant, K_c?

☒ **A** $dm^9\,mol^{-3}$

☒ **B** $dm^6\,mol^{-2}$

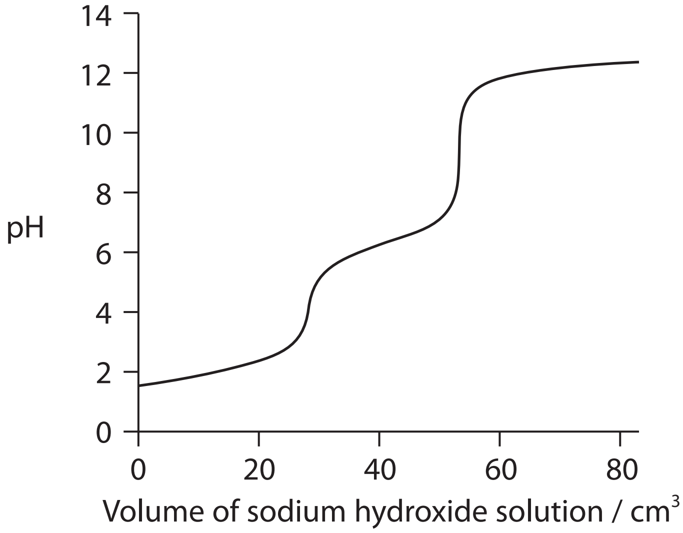
☒ **C** $mol^2\,dm^{-6}$

☒ **D** $mol^3\,dm^{-9}$

(Total for Question 4 = 1 mark)

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

5 An example of a diprotic acid is *cis*-butenedioic acid. Titration of this acid using sodium hydroxide solution gave the titration curve shown.



Which indicator would be most suitable for measuring the end-point of the neutralisation of the proton in *cis*-butenedioic acid which has a pK_a = 6.33?

Use your Data Booklet.

☒ **A** bromocresol green

☒ **B** bromothymol blue

☒ **C** litmus

☒ **D** phenolphthalein

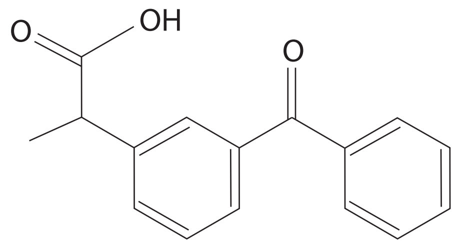
(Total for Question 5 = 1 mark)

6 At 25 °C, the pH of pure water is 7.00 and at 100 °C, the pH of pure water is 6.14.
What can be deduced from this information?

	Enthalpy change of dissociation of water	Concentration of hydrogen ions
☒ **A**	endothermic	higher at 100 °C than at 25 °C
☒ **B**	endothermic	lower at 100 °C than at 25 °C
☒ **C**	exothermic	higher at 100 °C than at 25 °C
☒ **D**	exothermic	lower at 100 °C than at 25 °C

(Total for Question 6 = 1 mark)

7 The anti-inflammatory drug ketoprofen has the structure shown.

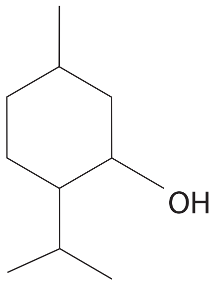


What is the molecular formula of ketoprofen?

- ☒ **A** $C_{15}H_{12}O_3$
- ☒ **B** $C_{16}H_{13}O_3$
- ☒ **C** $C_{16}H_{14}O_3$
- ☒ **D** $C_{16}H_{17}O_3$

(Total for Question 7 = 1 mark)

8 Menthol has a number of medicinal uses. It can be extracted from the peppermint plant.
The structure of menthol is



How many chiral centres are there in one molecule of menthol?

- ☒ **A** 1
- ☒ **B** 2
- ☒ **C** 3
- ☒ **D** 4

(Total for Question 8 = 1 mark)

DO NOT WRITE IN THIS AREA

9 Which of these reactions does **not** result in the formation of a racemic mixture?

☒ **A** but-2-ene with HCl

☒ **B** but-1-ene with HCl

☒ **C** propanal with HCN

☒ **D** propanone with HCN

(Total for Question 9 = 1 mark)

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10 When a single enantiomer of 2-iodobutane reacts with sodium hydroxide, the product is a mixture of enantiomers. This is because

☒ **A** the reaction is a nucleophilic substitution

☒ **B** the reaction proceeds via a negatively charged transition state

☒ **C** the reaction proceeds via a carbocation intermediate

☒ **D** the reaction rate depends on the concentration of 2-iodobutane

(Total for Question 10 = 1 mark)

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11 How many structural isomers with the molecular formula $C_5H_{10}O$ react with Tollens' reagent?

☒ **A** 2

☒ **B** 3

☒ **C** 4

☒ **D** 5

(Total for Question 11 = 1 mark)

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

12 Propanone reacts with iodine in both acidic and alkaline conditions.

(a) The products of the reactions under the stated conditions include

(1)

		Acidic conditions	Alkaline conditions
☒	**A**	CH_3I	CH_3COO^-
☒	**B**	CH_3COCI_3	CH_3COO^-
☒	**C**	CH_3COCH_2I	CH_3I
☒	**D**	CH_3COCH_2I	CHI_3

(b) The rate equation for the reaction between propanone and iodine in acidic conditions is

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

The reaction was carried out at two different pH values, all other conditions remaining unchanged.

In the first reaction pH = 2.0

In the second reaction the rate was found to be ⅓ of the original value.

What was the pH of the second reaction, to 1 decimal place?

(1)

☒ **A** 0.7

☒ **B** 1.5

☒ **C** 2.5

☒ **D** 2.7

(Total for Question 12 = 2 marks)

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13 But-2-ene-1,4-diol may be converted into 2-oxobutanedioic acid in a two-step synthesis through an intermediate compound **W**.

$$HOCH_2CH{=}CHCH_2OH \xrightarrow[\text{Step 1}]{\text{steam and } H_2SO_4} \mathbf{W} \xrightarrow[\text{Step 2}]{} HO_2CCOCH_2CO_2H$$

but-2-ene-1,4-diol → 2-oxobutanedioic acid

Identify the intermediate compound **W** and the reagent for Step **2**.

	Compound **W**	Reagent for Step **2**
☒ **A**	$HOCH_2CH(OH)CH_2CH_2OH$	$LiAlH_4$ in dry ether
☒ **B**	$HOOCH_2CH{=}CHCOOH$	$LiAlH_4$ in dry ether
☒ **C**	$OHCCH(OH)CH_2CHO$	hot acidified $K_2Cr_2O_7$
☒ **D**	$HOCH_2CH(OH)CH_2CH_2OH$	hot acidified $K_2Cr_2O_7$

(Total for Question 13 = 1 mark)

14 Compound **X**, $C_4H_{10}O$, is oxidised to form compound **Y**.

Compound **Y** reacts with ethanol in the presence of concentrated sulfuric acid to give an ester, **Z**.

Which of these could be the formula of **Z**?

☒ **A** $CH_3COOC(CH_3)_3$

☒ **B** $CH_3CH_2COO(CH_2)_3CH_3$

☒ **C** $(CH_3)_2CHCOOCH_2CH_3$

☒ **D** $CH_3CH_2COOCH_2CH(CH_3)_2$

(Total for Question 14 = 1 mark)

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

15 Which of these compounds is a product of the hydrolysis of $CH_3COOC_3H_7$ by refluxing with aqueous sodium hydroxide?

- ☒ **A** CH_3OH
- ☒ **B** C_3H_7OH
- ☒ **C** C_3H_7COOH
- ☒ **D** $C_3H_7COO^-Na^+$

(Total for Question 15 = 1 mark)

16 In gas chromatography, a gas containing a mixture is passed over a liquid stationary phase. The main reason a mixture is separated into its components is because they have different

- ☒ **A** boiling temperatures
- ☒ **B** forces of attraction to the liquid
- ☒ **C** relative molecular masses
- ☒ **D** volatilities

(Total for Question 16 = 1 mark)

17 In HPLC, the mobile and stationary phases are

	Mobile phase	Stationary phase
☒ **A**	gas	liquid
☒ **B**	gas	solid
☒ **C**	liquid	gas
☒ **D**	liquid	solid

(Total for Question 17 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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SECTION B

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

18 Bromate(V) ions, BrO_3^-, oxidise bromide ions, Br^-, in dilute acid.

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

Experiments to determine initial reaction rates were carried out using different initial concentrations of the three reactants.

The results are shown in the table.

Experiment number	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.10	0.25	0.30	3.36×10^{-5}
2	0.10	0.25	0.60	1.34×10^{-4}
3	0.15	0.50	0.30	1.01×10^{-4}
4	0.15	0.25	0.60	2.01×10^{-4}

(a) The reaction is first order with respect to bromate(V) ions.

(i) Deduce the rate equation for the reaction.
Justify your answer using the data.

(4)

(ii) Use the data from Experiment 4 and your answer to (a)(i) to calculate the rate constant for the reaction. Include units in your answer.

(3)

(b) Give **one** possible reason why the rate equation shows that the reaction cannot proceed in one step.

(1)

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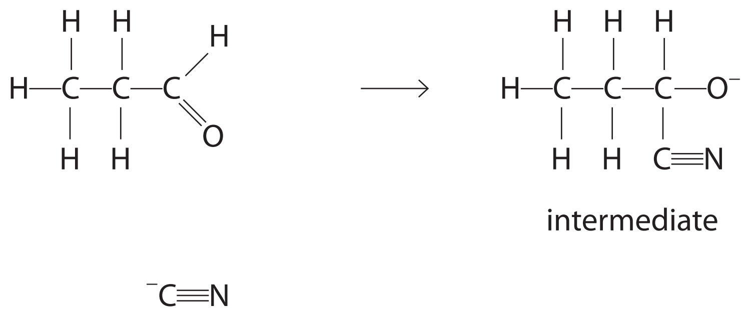
(Total for Question 18 = 8 marks)

19 Propanal reacts very slowly with HCN at 298 K. To increase the rate of reaction potassium cyanide, KCN, is added.

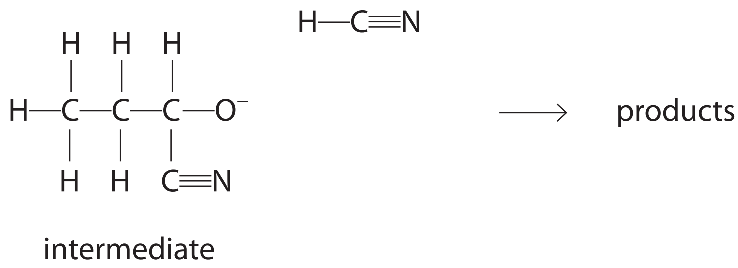
(a) (i) Complete the mechanism for this reaction by adding curly arrows, and relevant lone pairs and dipoles to Step **1** and Step **2**.

(4)

Step **1**



Step **2**



(ii) Explain why the reaction between propanal and HCN in the absence of KCN is very slow, referring to the value of K_a. No calculation is required.

[For HCN, $K_a = 4.9 \times 10^{-10}\ \text{mol dm}^{-3}$]

(2)

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(iii) KCN is a **homogeneous catalyst** in this reaction.
Justify this description by referring to the mechanism.

(2)

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(b) The organic products of this reaction are enantiomers.

Draw the three-dimensional structures of these enantiomers.

(2)

(Total for Question 19 = 10 marks)

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20 This question is about compounds with the molecular formula $C_6H_{12}O_2$.

(a) Hexanoic acid, $C_5H_{11}COOH$, is a weak acid.

(i) Write the equation for the acid dissociation constant, K_a, of hexanoic acid.

(1)

(ii) Calculate the pH of a 0.100 mol dm^{-3} solution of hexanoic acid.

[pK_a of hexanoic acid = 4.88]

(4)

(iii) The solubility of hexanoic acid in water is 1.08 g per 100 g of water. The isomer of hexanoic acid, butyl ethanoate, $CH_3CO_2C_4H_9$, has a solubility of 0.68 g per 100 g of water.

Explain the differences in these data in terms of the hydrogen bonding between hexanoic acid and water, and between butyl ethanoate and water.

(3)

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(b) (i) Compound **A** is thought to be another isomer of hexanoic acid.

10 g of compound **A** is found to contain 6.21 g of carbon and 1.03 g of hydrogen, with the remainder being oxygen.

Use the data to calculate the empirical formula of compound **A**.

You must show **all** your working.

(3)

(ii) State how you might use your answer to (b)(i) and a mass spectrum of compound **A** to prove that compound **A** is an isomer of hexanoic acid.

(1)

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*(iii) A series of tests was performed on compound **A**.

	Test	Observation
1	addition of phosphorus(V) chloride	misty fumes
2	addition of 2,4-dinitrophenylhydrazine	orange precipitate
3	addition of Benedict's or Fehling's reagent	solution remains blue with no precipitate
4	addition of acidified potassium dichromate(VI)	solution remains orange
5	test using polarimetry	plane of plane polarised light is rotated

Deduce the structure for compound **A**.
Justify your answer by using all the test results.

(6)

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(c) Compound **B**, another isomer with the molecular formula $C_6H_{12}O_2$, contains a ring of six carbon atoms.

The carbon-13 NMR spectrum has only two peaks, one of which is at 69 ppm.

Draw the structure of compound **B**.

(2)

(Total for Question 20 = 20 marks)

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21 Esters are used in flavourings and perfumes.
They can be made by reactions involving alcohols.

(a) A flask containing a mixture of 0.200 mol of ethanoic acid and 0.150 mol of ethanol was left at 25 °C, in the presence of a catalyst, until equilibrium had been established.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

The ethanoic acid present in the equilibrium mixture required 34.8 cm^3 of a 2.50 mol dm^{-3} solution of sodium hydroxide for complete neutralisation.

(i) Calculate the value of the equilibrium constant, K_c, for this reaction at 25 °C.

(4)

(ii) The enthalpy change for this reaction is small.

Explain, by reference to the type and number of bonds being broken and made, how this might have been predicted.

(2)

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(b) An ester which smells of raspberries can be formed by either of two different reactions.

Reaction **1**

$$HCOOH + (CH_3)_2CHCH_2OH \overset{\text{catalyst}}{\rightleftharpoons} HCOOCH_2CH(CH_3)_2 + H_2O$$

Reaction **2**

$$HCOCl + (CH_3)_2CHCH_2OH \rightarrow HCOOCH_2CH(CH_3)_2 + HCl$$

(i) **Name** the carboxylic acid, alcohol and catalyst used in Reaction **1**.

(2)

$HCOOH$ ....

catalyst ....

$(CH_3)_2CHCH_2OH$ ....

(ii) Explain **one** advantage and **one** disadvantage of using Reaction **2** rather than Reaction **1**.

(4)

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(Total for Question 21 = 12 marks)

TOTAL FOR SECTION B = 50 MARKS

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SECTION C

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

22 The equation for the formation of ammonia in the Haber Process is shown

$$\tfrac{1}{2}N_2(g) \quad + \quad 1\tfrac{1}{2}H_2(g) \quad \rightleftharpoons \quad NH_3(g)$$

(a) At 298 K the standard entropy change of the system, $\Delta S^{\ominus}_{system} = -98\ J\ K^{-1}\ mol^{-1}$.

Calculate the standard entropy of one mole of ammonia.

Use the value of $\Delta S^{\ominus}_{system}$ and the data in the table.

Substance	Standard molar entropy, $S^{\ominus}$ / $J\ K^{-1}\ mol^{-1}$
N_2	192
H_2	131

(2)

(b) The value of the total entropy change, ΔS_{total}, varies with temperature.
Data for the value of ΔS_{total} at different temperatures but at standard pressure of 100 kPa are given for this reaction.

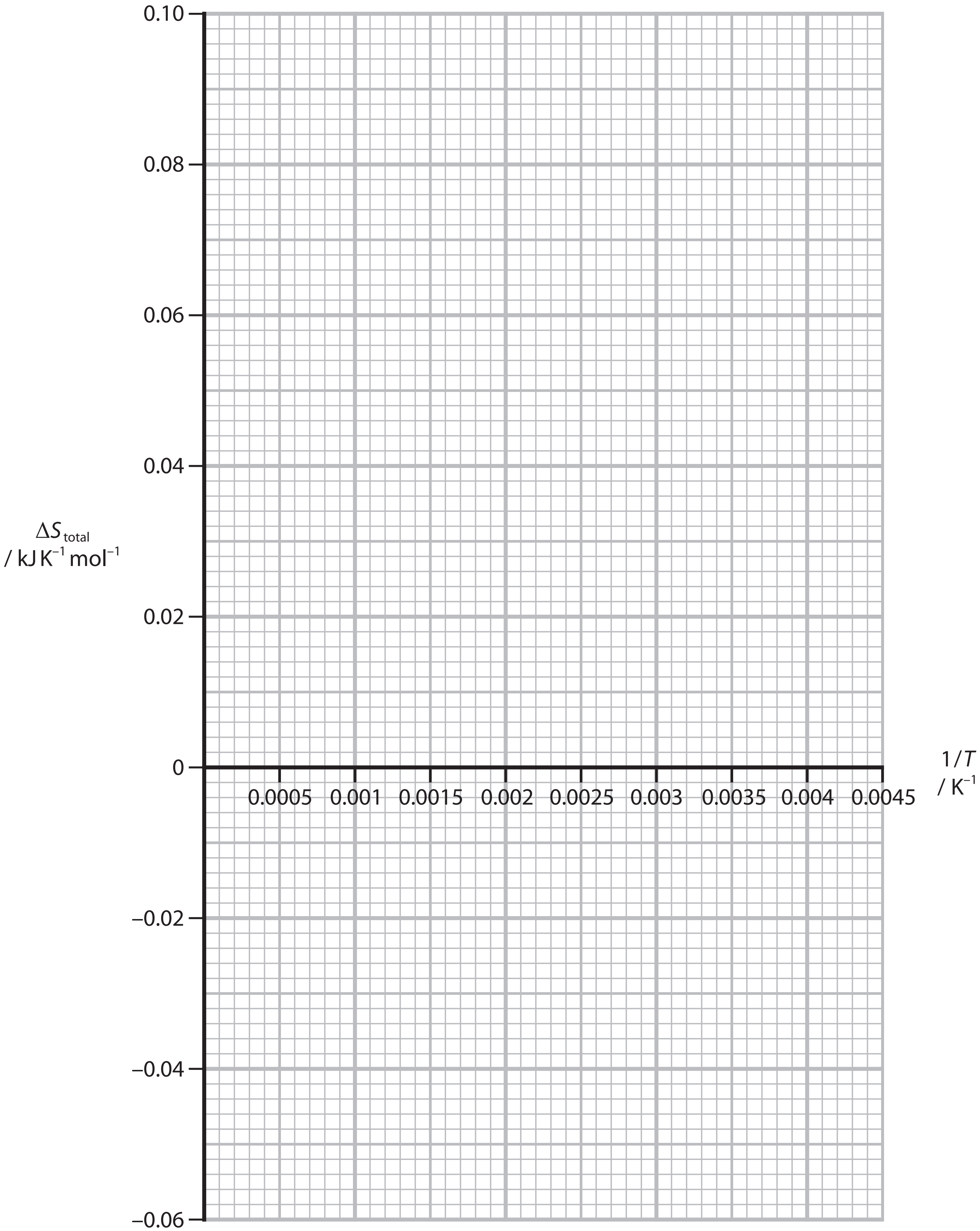
Temperature / K	$1/T$ / K^{-1}	ΔS_{total} / $kJ\ K^{-1}\ mol^{-1}$
250	4.00×10^{-3}	8.27×10^{-2}
375	2.67×10^{-3}	2.25×10^{-2}
500	2.00×10^{-3}	-0.764×10^{-2}
625	1.60×10^{-3}	-2.57×10^{-2}
750	1.33×10^{-3}	-3.77×10^{-2}

P 6 9 5 0 7 A 0 2 6 3 2

Plot a graph of ΔS_{total} against $1/T$ on the grid.

Include a line of best fit.

(2)



(c) The relationship between ΔS_{total} and $1/T$ can be found by combining the two equations:

$$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system}$$

and $\Delta S_{surroundings} = -\Delta H/T$

to give

$$\Delta S_{total} = -\Delta H/T + \Delta S_{system}$$

(i) Determine the gradient of the line plotted in (b), including units in your answer.

(1)

(ii) Identify the thermodynamic quantity that can be obtained from this gradient.

(1)

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(iii) Determine the temperature at which the reaction ceases to be thermodynamically feasible at a pressure of 100 kPa.

(1)

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(d) The industrial synthesis of ammonia

$$\tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}H_2(g) \rightleftharpoons NH_3(g)$$

is carried out at pressures of about 20 000 kPa and temperatures between 700 K and 750 K. These temperatures are higher than the answer to (c)(iii).

(i) State the relationship between the total entropy, ΔS_{total}, and the equilibrium constant, *K*.

(1)

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(ii) Calculate the value of the equilibrium constant *K* at 750 K.

[ΔS_{total} at 750 K = –37.7 J K^{-1} mol^{-1}]

(2)

(iii) Explain why ΔS_{total} decreases with an increase in temperature.

(3)

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(iv) State how the Haber Process is made economically feasible at 750 K even though the total entropy change is negative.

(1)

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(e) Ammonia from the Haber Process reacts with acids.
With phosphoric acid, H_3PO_4, a number of products are formed in solution.
One of these is the fertiliser diammonium hydrogenphosphate.

(i) Write an equation for the production of this fertiliser.
State symbols are not required.

(2)

(ii) Write an **ionic** equation to show that ammonium ions are acidic in aqueous solution.
State symbols are not required.

(1)

(iii) A solution containing both ammonia and ammonium ions acts as a buffer. Explain, using a relevant ionic equation, the effect of adding a small amount of acid to this buffer.

(3)

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(Total for Question 22 = 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