Candidate surname

Other names

Pearson Edexcel
International
Advanced Level

Centre Number

Candidate Number

Tuesday 2 June 2020

Afternoon (Time: 1 hour 45 minutes)

Paper Reference **WCH14/01**

Chemistry

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

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 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 Bromine oxidises methanoic acid to carbon dioxide.

The equation for the reaction is

$$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$
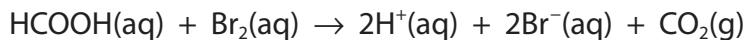
Which of the following methods would **not** be suitable for measuring the progress of this reaction?

⊠ **A** colorimetry

⊠ **B** measuring electrical conductivity

⊠ **C** quenching and titrating with acid

⊠ **D** measuring the volume of gas

(Total for Question 1 = 1 mark)

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

2 The rate of the reaction between two compounds, **Y** and **Z**, was investigated.
The results are shown.

Experiment	Initial concentration of **Y** / mol dm^{-3}	Initial concentration of **Z** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.64	0.24	8.00×10^{-3}
2	0.64	0.48	3.20×10^{-2}
3	0.32	0.48	3.20×10^{-2}

What are the orders of reaction with respect to **Y** and **Z**?

		Order with respect to **Y**	Order with respect to **Z**
⊠	**A**	0	1
⊠	**B**	0	2
⊠	**C**	1	1
⊠	**D**	1	2

(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 inorganic anti-cancer drug *cis*-platin, $Pt(NH_3)_2Cl_2$, is hydrolysed by water to make it active. The reaction is
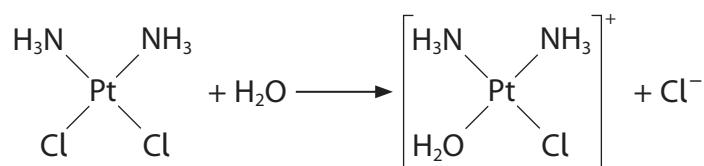
The hydrolysis is first order overall. The half-life can be found from a graph of the concentration of *cis*-platin against time.

Concentration of *cis*-platin $\times 10^{-3}$ / mol dm^{-3}

Time of reaction / min
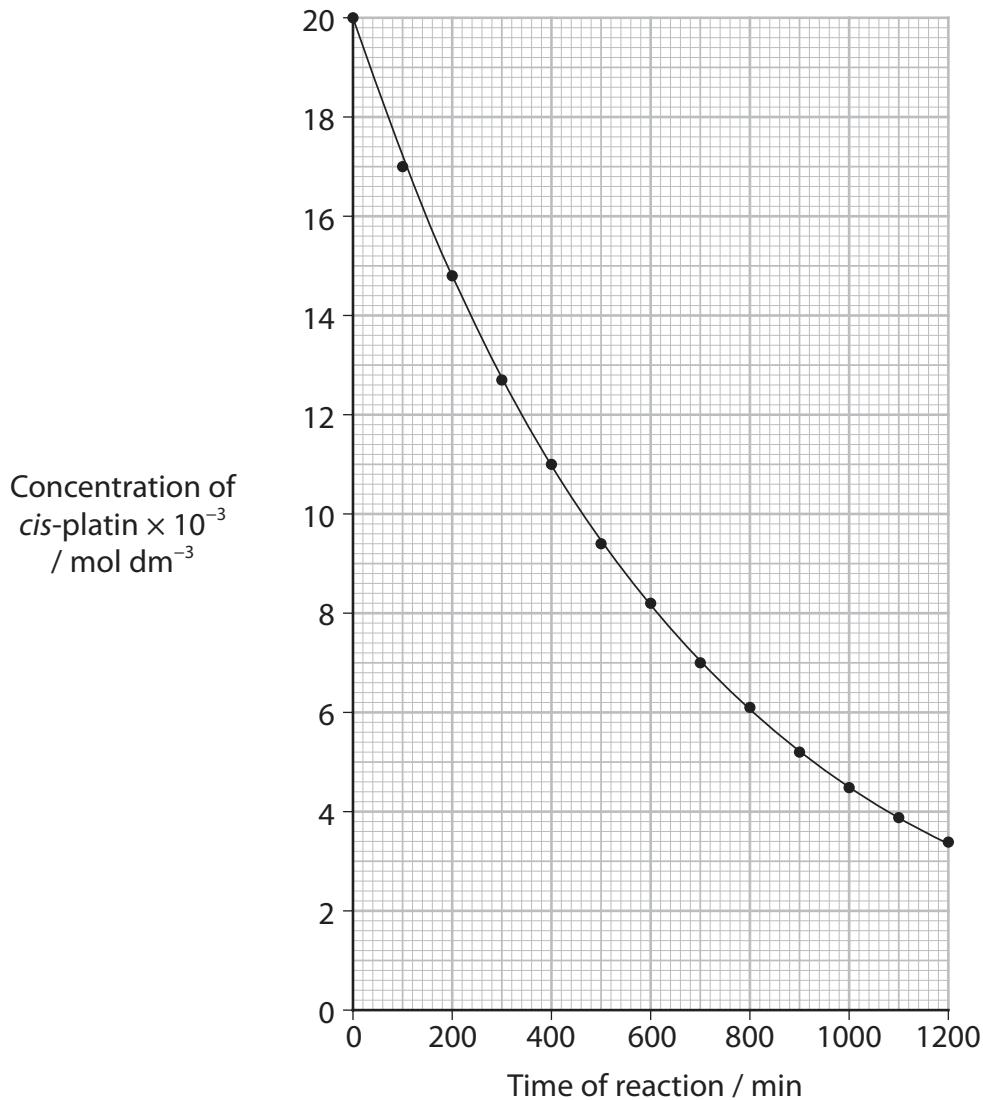
The half-life of the reaction is

- ☒ **A** 430 min
- ☒ **B** 460 min
- ☒ **C** 590 min
- ☒ **D** 600 min

(Total for Question 3 = 1 mark)

4 Propanone reacts with iodine in acidic solution.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$
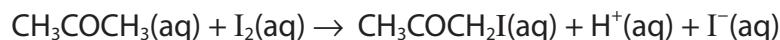
The rate equation for the formation of iodopropanone is found to be

$$rate = k[CH_3COCH_3(aq)][H^+(aq)]$$

(a) Which of the following is true?

(1)

- ☒ **A** the units for the rate constant are $dm^3\ mol^{-1}\ s^{-1}$

- ☒ **B** the reaction is a first order reaction overall

- ☒ **C** the units for the rate are $dm^3\ mol^{-1}\ s^{-1}$

- ☒ **D** doubling the concentrations of propanone and of iodine quadruples the rate

(b) Which of the following is **not** true?

(1)

- ☒ **A** the reaction rate increases if the temperature is raised

- ☒ **B** the rate constant increases if the temperature is raised

- ☒ **C** the addition of a small amount of sodium hydroxide decreases the reaction rate

- ☒ **D** the rate is unchanged when the hydrogen ion concentration is doubled

(Total for Question 4 = 2 marks)

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

5 The equation shows the hydrolysis of a bromoalkane.

$$RBr + OH^- \rightarrow ROH + Br^-$$
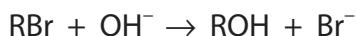
The rate equation is rate = k[RBr]

RBr is most likely to be

☒ **A** bromomethane

☒ **B** 2-bromopropane

☒ **C** 1-bromo-2-methylpropane

☒ **D** 2-bromo-2-methylpropane

(Total for Question 5 = 1 mark)

6 The equation for an exothermic reaction is shown.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Which of these is true?

☒ **A** ΔH is positive

☒ **B** $\Delta S_{surroundings}$ is positive

☒ **C** ΔS_{system} is negative

☒ **D** ΔS_{total} is negative

(Total for Question 6 = 1 mark)

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

7 The equation for the equilibrium decomposition of hydrogen iodide into hydrogen and iodine can be written in two ways.
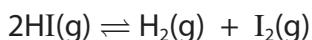
$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ Equilibrium constant $= K_c$

or
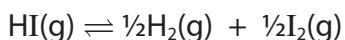
$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$ Equilibrium constant $= K_c'$

What is the expression linking the two equilibrium constants?

- ☒ **A** $K_c = (K_c')^2$
- ☒ **B** $K_c = K_c'$
- ☒ **C** $K_c = 2(K_c')$
- ☒ **D** $K_c = \sqrt{K_c'}$

(Total for Question 7 = 1 mark)

8 A buffer solution contains ethanoic acid, with a concentration of 0.10 mol dm^{-3}, and sodium ethanoate, with a concentration of 0.050 mol dm^{-3}.

K_a for ethanoic acid $= 1.7 \times 10^{-5}$ mol dm^{-3}

The pH of this buffer solution is

- ☒ **A** 2.88
- ☒ **B** 4.47
- ☒ **C** 4.77
- ☒ **D** 5.07

(Total for Question 8 = 1 mark)

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

9 The graphs show the changes in pH during a series of titrations.
Each titration involves two solutions, each of concentration $0.1\,mol\,dm^{-3}$.

Graph **1**

Volume of solution added / cm^3

Graph **2**

Volume of solution added / cm^3

Graph **3**

Volume of solution added / cm^3

Graph **4**

Volume of solution added / cm^3
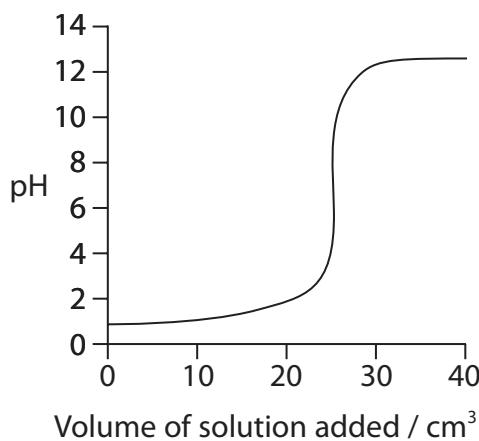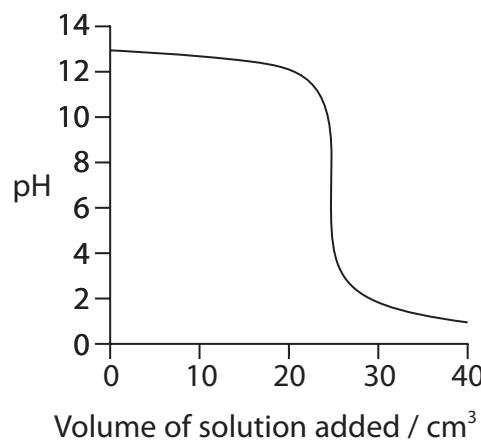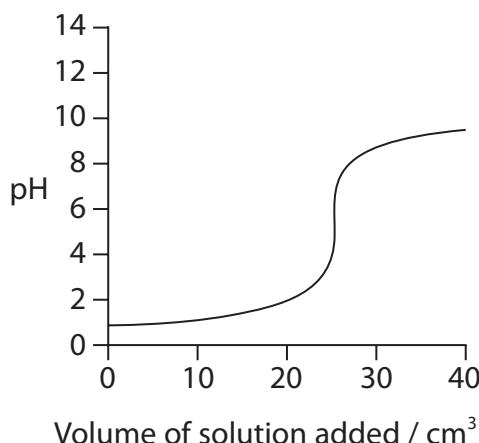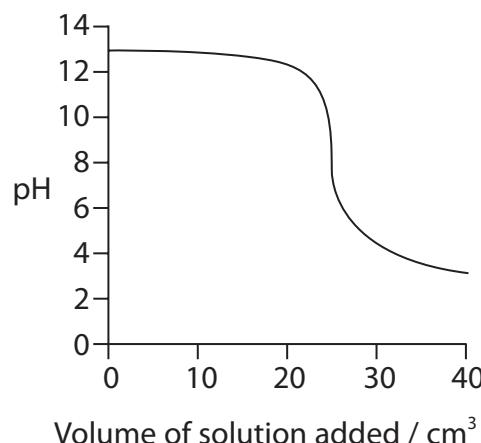
(a) Which graph has ethanoic acid as one of the reactants?

(1)

☒ **A** Graph **1**

☒ **B** Graph **2**

☒ **C** Graph **3**

☒ **D** Graph **4**

(b) Which graph shows a solution that has an acidic pH at the end-point?

(1)

☒ **A** Graph **1**

☒ **B** Graph **2**

☒ **C** Graph **3**

☒ **D** Graph **4**

(c) Which indicator is suitable for the titration shown in Graph **3**?
   Use your Data Booklet.

(1)

☒ **A** bromocresol green

☒ **B** bromothymol blue

☒ **C** phenol red

☒ **D** thymol blue (acid)

(Total for Question 9 = 3 marks)

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

10 Which diagram shows the first step of the mechanism for the nucleophilic addition of hydrogen cyanide to propanone in the presence of potassium cyanide?

☒ **A**

☒ **B**

☒ **C**

☒ **D**
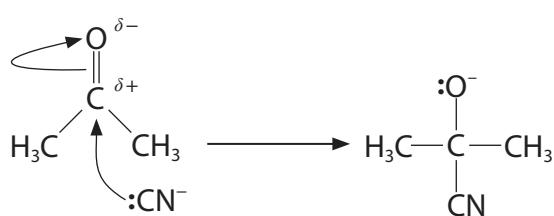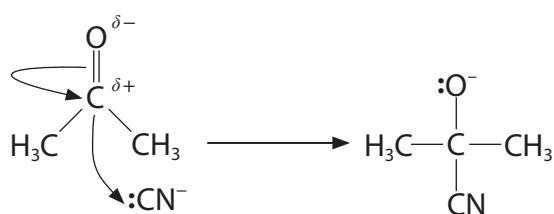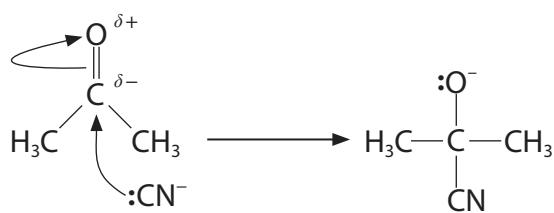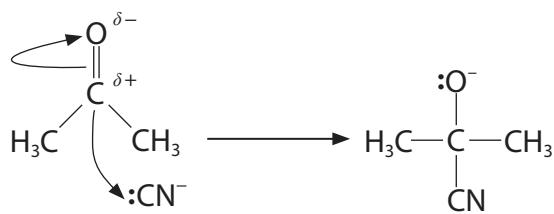
(Total for Question 10 = 1 mark)

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

**11** When propanone reacts with iodine in the presence of sodium hydroxide, the precipitate formed has the formula

☒ **A** CH_3I

☒ **B** CHI_3

☒ **C** CH_3COCH_2I

☒ **D** CH_3COCI_3

(Total for Question 11 = 1 mark)

12 Which of the following could **not** be formed when methylamine is added to ethanoyl chloride?

☒ **A** HCl

☒ **B** $CH_3NH_3^+Cl^-$

☒ **C** CH_3CONH_2

☒ **D** $CH_3CONHCH_3$

(Total for Question 12 = 1 mark)

13 In which of these esters is the percentage by mass of carbon 54.5 %?

☒ **A**   methyl methanoate, $HCOOCH_3$

☒ **B**   methyl ethanoate, CH_3COOCH_3

☒ **C**   ethyl ethanoate, $CH_3COOCH_2CH_3$

☒ **D**   ethyl methanoate, $HCOOCH_2CH_3$

(Total for Question 13 = 1 mark)

14 An organic compound that reacts with **both** lithium tetrahydridoaluminate(III) (lithium aluminium hydride) **and** magnesium could be

☒ **A**   an aldehyde

☒ **B**   a carboxylic acid

☒ **C**   a ketone

☒ **D**   a tertiary alcohol

(Total for Question 14 = 1 mark)

15 The following methods can be used to distinguish between pairs of organic compounds with **no** further tests.

A warm each compound with Fehling's or Benedict's solution

B warm each compound with acidified potassium dichromate(VI) solution

C add 2,4-dinitrophenylhydrazine (Brady's reagent) to each compound

D add a few drops of each compound, drop by drop, to water

(a) Which test would distinguish between 2-methylpropan-2-ol, $(CH_3)_3COH$, and butanone, $CH_3CH_2COCH_3$?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) Which test would distinguish between 2-methylpropan-2-ol, $(CH_3)_3COH$, and butan-1-ol, $CH_3CH_2CH_2CH_2OH$?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) Which test could **not** be used to distinguish between 2-methylpropan-2-ol, $(CH_3)_3COH$, and butanal, $CH_3CH_2CH_2CHO$?

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 15 = 3 marks)

TOTAL FOR SECTION A = 20 MARKS

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

16 This question concerns calcium chloride, $CaCl_2$.

(a) Some energy changes related to calcium chloride are shown.

Energy change	Value / kJ mol^{-1}
Atomisation energy of calcium	+178.2
Atomisation energy of chlorine	+121.7
Electron affinity of chlorine	−348.8
First ionisation energy of calcium	+590.0
Standard enthalpy change of formation of calcium chloride	−795.8
Experimental lattice energy of calcium chloride	−2258
Second ionisation energy of calcium	To be calculated

(i) Complete the Born-Haber cycle by writing appropriate chemical formulae on the horizontal lines. Include state symbols and relevant electrons.

(4)

ΔH_5

ΔH_6

$Ca^{2+}(g) + 2Cl^-(g)$

ΔH_4

ΔH_3

ΔH_7

ΔH_2

$Ca(s) + Cl_2(g)$

ΔH_1
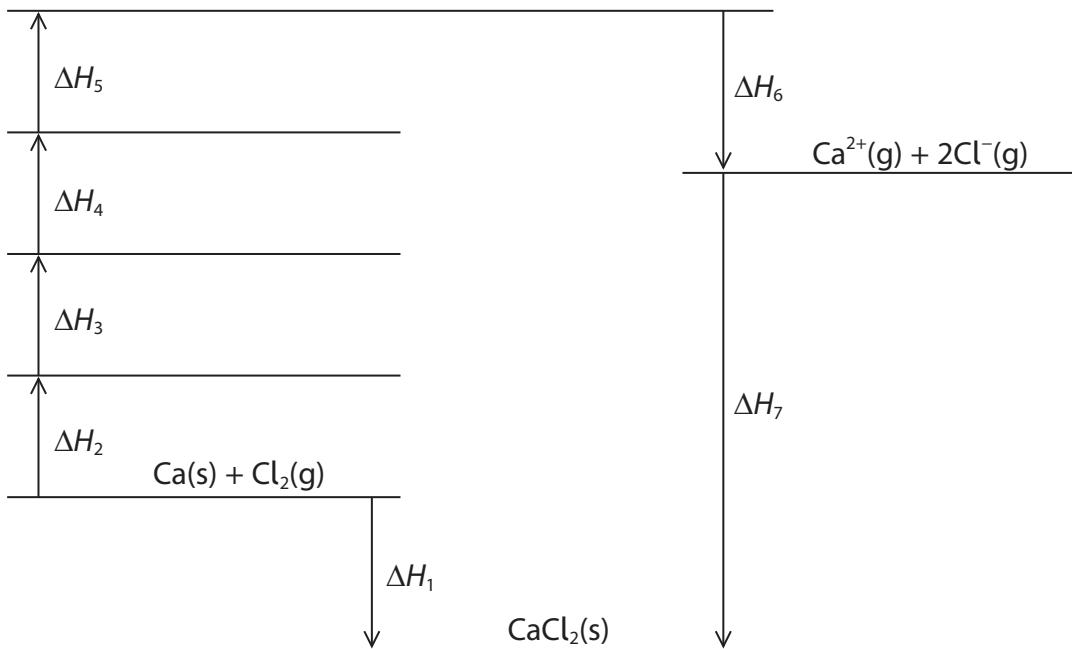
$CaCl_2(s)$

(ii) Calculate the second ionisation energy of calcium using the cycle and the values given in the table. Include a sign and units with your value.

(3)

(b) The theoretical lattice energy of formation of $CaCl_2$ is -2223 kJ mol^{-1}.
Explain why the experimental lattice energy of $CaCl_2$ is more exothermic than the theoretical value.

(3)

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(c) The table shows the theoretical lattice energies of some chlorides of Group 2.

Group 2 metal chloride	magnesium chloride	calcium chloride	strontium chloride	barium chloride
Lattice energy / kJ mol^{-1}	-2326	-2223	-2127	-2033

Explain the trend in **theoretical** lattice energies on descending Group 2.

(3)

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(d) Calculate the enthalpy change of solution of calcium chloride, $CaCl_2$.

Data

$\Delta_{hyd}H^{\ominus}$ (Ca^{2+}) $= -1\,650$ kJ mol^{-1} $\Delta_{hyd}H^{\ominus}$ (Cl^-) $= -364$ kJ mol^{-1}

Experimental lattice energy ($CaCl_2$) $= -2\,258$ kJ mol^{-1}

(2)

(Total for Question 16 = 15 marks)

17 This question concerns six isomers each with the molecular formula $C_5H_{10}O_2$.

(a) Isomers **A**, **B**, **C** and **D** are structural isomers that all react with aqueous sodium carbonate to produce carbon dioxide.

Isomer **A** is a straight-chain compound.

Isomer **B** has only two peaks in its high resolution proton NMR spectrum, both of which are singlets.

Isomer **C** contains a chiral centre but isomer **D** does not.

Give the structures of these **four** isomers.

(4)

A	B

C	D

(b) (i) Isomer **E** contains an ether functional group (R-O-R) and a ketone functional group. The **low** resolution proton NMR spectrum of isomer **E** has four peaks. The displayed formula of isomer **E** is

$$CH_3—O—CH_2—CH_2—\overset{\displaystyle \overset{O}{\|}}{C}—CH_3$$
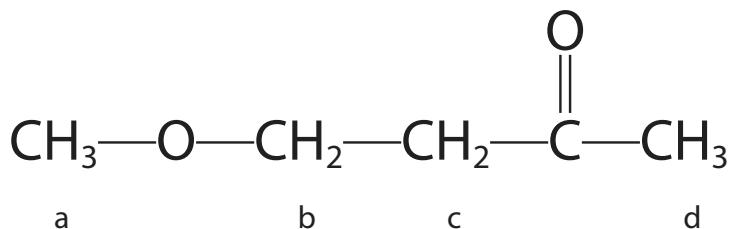
a   b   c   d

The four hydrogen environments responsible for the four peaks are labelled. Complete the table of information regarding these peaks including the splitting pattern in the **high** resolution spectrum.

(3)

Peak	a	b	c	d
Relative peak area	3			
Chemical shift range, δ / ppm	2.9 – 4.2			
Splitting	singlet			

(ii) State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of **E**.

(1)

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(c) Isomer **F** is a neutral compound that smells of pears.

It can be formed by the reaction between compounds **V** and **W** in the presence of concentrated sulfuric acid.

Compound **V** has an absorption in its infrared spectrum at $1720\,\text{cm}^{-1}$ and a broad absorption around $3050\,\text{cm}^{-1}$.

Compound **W** can be formed directly from propanal.

(i) Identify, by name or formula, compounds **V**, **W** and **F**.

Justify your answer by using **all** the available information.

(4)

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(ii) State the conditions required and the reagent needed to form compound **W** from propanal.

(1)

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(iii) State the role of sulfuric acid in the formation of **F**.

(1)

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(d) State which one of the isomers **A**, **E** and **F** has the highest boiling temperature. Justify your answer.

(3)

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(Total for Question 17 = 17 marks)

18 This question concerns acidic solutions.

(a) (i) A solution of hydrochloric acid has a pH of 1.125.

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

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

(2)

(ii) Calculate the volume of water which must be added to 25.0 cm^3 of this solution to increase the pH from 1.125 to 1.500, giving your answer to an appropriate number of significant figures.

(4)

Turn over ▶

(b) Phosphoric(V) acid, H_3PO_4, is a weak acid, which dissolves in water, giving the equilibrium

Equation 1 $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
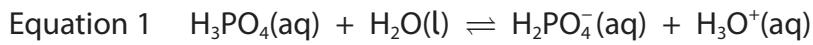
The $H_2PO_4^-$ ion formed when phosphoric(V) acid is added to water can dissociate further into HPO_4^{2-}.

Equation 2 $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

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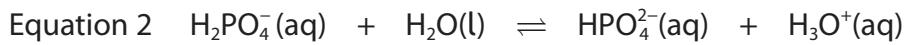
(i) Identify the acids and bases in the spaces below Equation 2, linking the acid-base conjugate pairs.

(2)

(ii) Explain why very little dissociation of the $H_2PO_4^-$ ion occurs in solutions of phosphoric(V) acid.

(2)

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(c) (i) Using Equation 1, write an expression for the acid dissociation constant, K_{a1}, for phosphoric(V) acid, H_3PO_4.

(1)

(ii) A 0.500 mol dm^{-3} solution of phosphoric(V) acid has a pH of 1.20. Calculate the value of K_{a1}, stating its units.

Assume that there is no further dissociation of the $H_2PO_4^-$ ion.

(4)

(d) Phosphate buffer solutions containing hydrogenphosphate ions, HPO_4^{2-}, and dihydrogenphosphate ions, $H_2PO_4^-$, are commonly used in biological research.

Explain, using a relevant ionic equation, how a solution containing these ions can act as a buffer when a small amount of **alkali** is added.

(3)

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(Total for Question 18 = 18 marks)

TOTAL FOR SECTION B = 50 MARKS

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SECTION C

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

19 Ammonia is manufactured in the Haber Process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
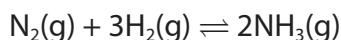
In this process, pressures between 100 atm and 300 atm and temperatures between 675 K and 725 K are usually used.

(a) (i) Calculate $\Delta S^{\ominus}_{system}$ for this reaction at 298 K.
Include a sign and units with your answer.

[Standard molar entropy, $S^{\ominus}$, for 1 mol of each gas, in $J\,K^{-1}\,mol^{-1}$:

$N_2 = 191.6$ $H_2 = 130.6$ $NH_3 = 192.3$]

(2)

(ii) Explain, using ideas about disorder, whether the sign of your answer to (a)(i) is as expected.

(2)

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(iii) At 700 K, the enthalpy change for this reaction is $\Delta H = -110.2$ kJ mol^{-1}.

Calculate the entropy change of the surroundings, $\Delta S_{\text{surroundings}}$, at 700 K.
Include a sign and units in your answer.

(2)

(iv) At 700 K, the total entropy change, $\Delta S_{\text{total}} = -78.7$ J K^{-1} mol^{-1}.

Calculate ΔS_{system} for this reaction at 700 K.
Include a sign and units in your answer.

(1)

*(v) Explain **one** advantage and **one** disadvantage of using a temperature higher than 700 K in the Haber process.

Consider the effect of an increase in temperature on the rate of reaction, on the values of $\Delta S_{surroundings}$ and ΔS_{total} and on the equilibrium constant.

(6)

P 6 4 6 2 0 A 0 2 8 3 2

(b) (i) Write the expression for the equilibrium constant, K_p, for the reaction in the Haber Process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
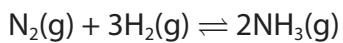
(1)

(ii) A mixture of nitrogen, hydrogen and ammonia is at equilibrium at 255 atm and 700 K. The partial pressure of nitrogen is 25 atm and that of hydrogen is 150 atm.

Calculate the equilibrium constant, K_p, for the formation of ammonia, at 700 K. Include units in your answer.

(3)

(iii) The pressure of the system is doubled at constant temperature.

Explain the effect of this on the yield of ammonia by considering the change in the K_p expression and hence the position of equilibrium.

(3)

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(Total for Question 19 = 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

1.0
H
hydrogen
1

(1)	(2)											(13)	(14)	(15)	(16)	(17)	0 (8) (18)
																	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	(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

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