Please check the examination details below before entering your candidate information

Candidate surname		Other names

Pearson Edexcel
International
Advanced Level

Centre Number

Candidate Number

Tuesday 4 June 2019

Afternoon (Time: 1 hour 40 minutes)	Paper Reference **WCH04/01**

Chemistry
Advanced
**Unit 4: General Principles of Chemistry I – Rates,
         Equilibria and Further Organic Chemistry
         (including synoptic assessment)**

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

Turn over ▶

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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   The rate equation for the reaction of a bromoalkane, RBr, with hydroxide ions is

rate = k[RBr]

The bromoalkane that is hydrolysed according to this rate equation is **most** likely to be

⊠ **A** 1-bromohexane.

⊠ **B** 1-bromo-2-methylpentane.

⊠ **C** 2-bromo-2-methylpentane.

⊠ **D** 2-bromo-3-methylpentane.

(Total for Question 1 = 1 mark)

2   Which method is most suitable for comparing the rate of hydrolysis of a primary iodoalkane and a tertiary iodoalkane in aqueous silver nitrate?

⊠ **A** Measuring the increase in pH.

⊠ **B** Measuring the change in mass.

⊠ **C** Measuring the time to form a precipitate.

⊠ **D** Taking samples followed by titrating with sodium thiosulfate.

(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 chemical equation and the rate equation for the reaction of iodine with excess propanone in the presence of an acid catalyst are shown.

$$I_2 + CH_3COCH_3 \rightarrow CH_3COCH_2I + HI$$
$$rate = k[CH_3COCH_3][H^+]$$

Which of the following sketch graphs is correct for this reaction?

☒ **A**   rate

[I$_2$]

☒ **B**   rate

[I$_2$]

☒ **C**   [I$_2$]

time

☒ **D**   [I$_2$]

time
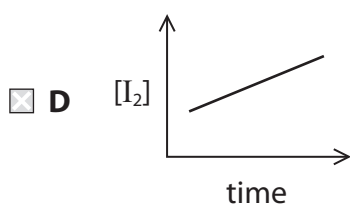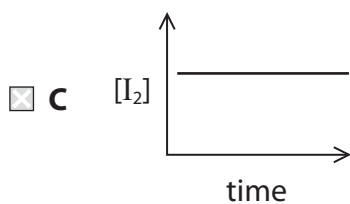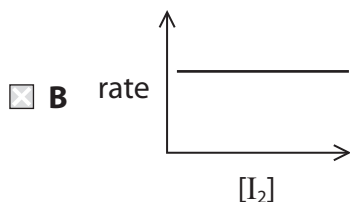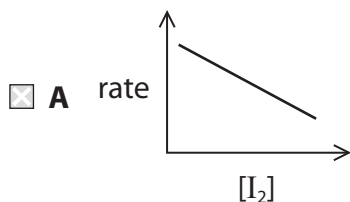
(Total for Question 3 = 1 mark)

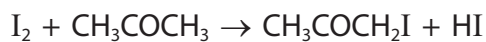**Use this space for any rough working. Anything you write in this space will gain no credit.**

4 The Arrhenius equation is

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

The activation energy, E_a, is determined from the gradient of the graph shown.
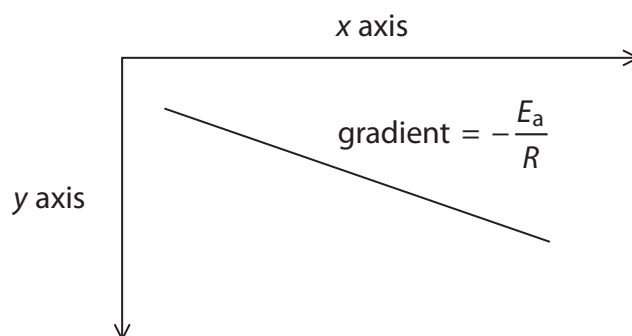
The axes on the graph are

	x axis	*y* axis
☒ **A**	$\ln k$	$\frac{1}{T}$
☒ **B**	$\ln k$	$-\frac{1}{T}$
☒ **C**	$\frac{1}{T}$	$\ln k$
☒ **D**	$-\frac{1}{T}$	$\ln k$

(Total for Question 4 = 1 mark)

5 What are the signs of the entropy changes at 273 K when water freezes?

$$H_2O(l) \rightarrow H_2O(s)$$
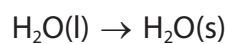
	ΔS_{system}	$\Delta S_{surroundings}$
☒ **A**	negative	positive
☒ **B**	positive	negative
☒ **C**	negative	negative
☒ **D**	positive	positive

(Total for Question 5 = 1 mark)

6 Which are the Brønsted-Lowry acids in the following equilibrium?

$$CH_3COOH + C_2H_5COOH \rightleftharpoons CH_3COO^- + C_2H_5COOH_2^+$$
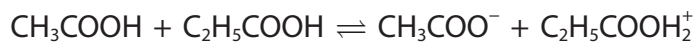
* ☒ **A** CH_3COOH and C_2H_5COOH

* ☒ **B** CH_3COOH and $C_2H_5COOH_2^+$

* ☒ **C** C_2H_5COOH and CH_3COO^-

* ☒ **D** CH_3COO^- and $C_2H_5COOH_2^+$

(Total for Question 6 = 1 mark)

7 In a titration of hydrochloric acid with aqueous ammonia, which indicator would be **most** suitable to detect the end-point?

Refer to your Data Booklet.

* ☒ **A** Azolitmin (litmus)

* ☒ **B** Bromocresol purple

* ☒ **C** Phenolphthalein

* ☒ **D** Alizarin yellow R

(Total for Question 7 = 1 mark)

8 A solution of hydrochloric acid has pH = 2.

The solution is diluted to one tenth of its original concentration.

What is the pH of the diluted solution?

* ☒ **A** 0.70

* ☒ **B** 1.0

* ☒ **C** 2.7

* ☒ **D** 3.0

(Total for Question 8 = 1 mark)

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

9 Equal amounts of three compounds were placed in separate beakers and the same volume of water was added to each.

Compound 1 CH_3COOH

Compound 2 CH_3COCl

Compound 3 CH_3COONa

Which shows the order of **increasing** pH in the mixtures?

☒ **A** $CH_3COOH < CH_3COCl < CH_3COONa$

☒ **B** $CH_3COCl < CH_3COOH < CH_3COONa$

☒ **C** $CH_3COONa < CH_3COOH < CH_3COCl$

☒ **D** $CH_3COCl < CH_3COONa < CH_3COOH$

(Total for Question 9 = 1 mark)

10 What are the units of K_c for the following equilibrium?

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$$
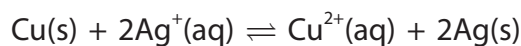
☒ **A** $mol\,dm^{-3}$

☒ **B** $dm^3\,mol^{-1}$

☒ **C** $mol^2\,dm^{-6}$

☒ **D** no units

(Total for Question 10 = 1 mark)

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

11 The graph shows the percentage yield of a product in a gaseous equilibrium under different conditions.
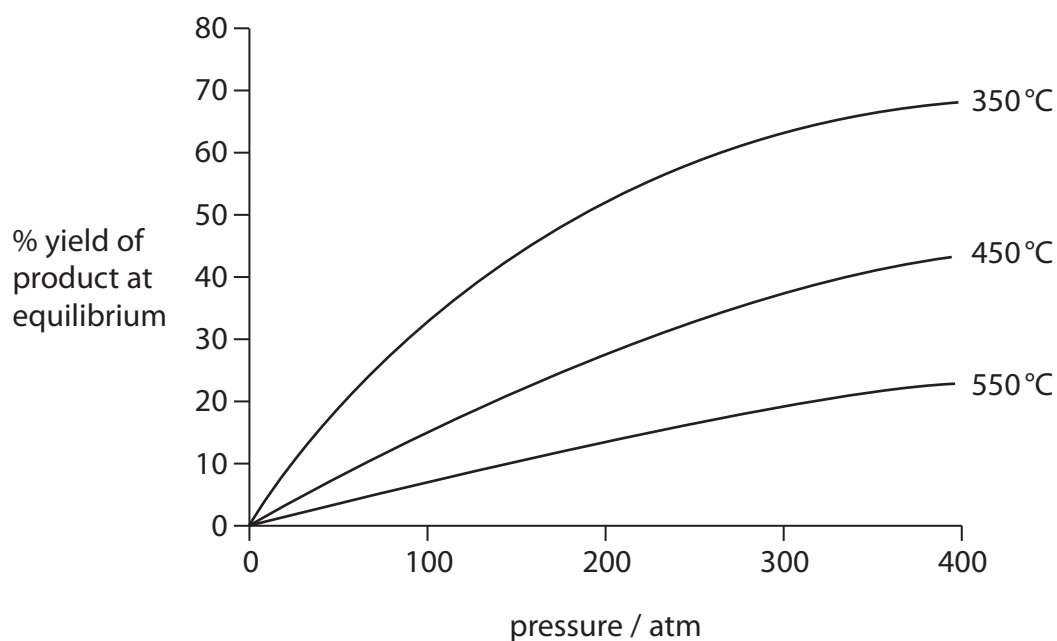
The forward reaction in the equilibrium is

- ☒ **A** exothermic with the number of moles of gas decreasing.

- ☒ **B** exothermic with the number of moles of gas increasing.

- ☒ **C** endothermic with the number of moles of gas decreasing.

- ☒ **D** endothermic with the number of moles of gas increasing.

(Total for Question 11 = 1 mark)

12 Which is the correct expression for $R \ln K$?

- ☒ **A** $R \ln K = \Delta S_{system} - \Delta H/T$

- ☒ **B** $R \ln K = \Delta S_{system} + \Delta H/T$

- ☒ **C** $R \ln K = \Delta S_{system} - T\Delta H$

- ☒ **D** $R \ln K = \Delta S_{system} + T\Delta H$

(Total for Question 12 = 1 mark)

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

13 Which compound is **most** soluble in water?

- ☒ **A** C_4H_9Cl
- ☒ **B** C_4H_9Br
- ☒ **C** C_3H_7COOH
- ☒ **D** $CH_3COOC_2H_5$

(Total for Question 13 = 1 mark)

14 Which compound reacts with phosphorus(V) chloride to form ethanoyl chloride?

- ☒ **A** CH_3CHO
- ☒ **B** CH_3CH_2OH
- ☒ **C** CH_3COCH_3
- ☒ **D** CH_3COOH

(Total for Question 14 = 1 mark)

15 Which two compounds react together to make the compound shown?
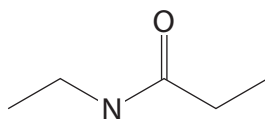
- ☒ **A** Ethanoyl chloride and ethylamine
- ☒ **B** Ethanoyl chloride and propylamine
- ☒ **C** Propanoyl chloride and ethylamine
- ☒ **D** Propanoyl chloride and propylamine

(Total for Question 15 = 1 mark)

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

16 The repeat unit of a polymer is shown.
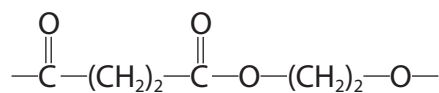
$$-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_2-\overset{\displaystyle O}{\overset{\|}{C}}-O-(CH_2)_2-O-$$

Which monomers react to make this polymer?

☒ **A** $HOOC(CH_2)_2COOH$ and $Cl(CH_2)_2Cl$

☒ **B** $ClOC(CH_2)_2COCl$ and $HO(CH_2)_2OH$

☒ **C** $ClOC(CH_2)_2COCl$ and $HOOC(CH_2)_2COOH$

☒ **D** $HOOC(CH_2)_2COOCH_3$ and $ClOC(CH_2)_2COCl$

(Total for Question 16 = 1 mark)

17 The retention time in gas chromatography is the time it takes for a compound to pass through the chromatography column.

A column is packed with a stationary phase that is polar.

Which of the following will have the **longest** retention time in the column?

☒ **A** hexane

☒ **B** hex-1-ene

☒ **C** pentane

☒ **D** pentan-1-ol

(Total for Question 17 = 1 mark)

18 A compound has the structure

$$CH_3(CH_2)_4CH_2 \qquad CH_2(CH_2)_6CH_2OH$$
$$\overset{\displaystyle |}{C}=\overset{\displaystyle |}{C}$$
$$\overset{\displaystyle |}{H} \qquad \overset{\displaystyle |}{H}$$
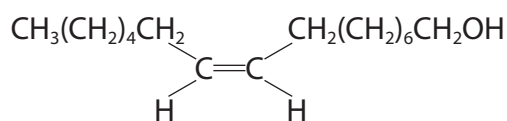
The systematic name of the compound is

☒ **A** *E*-hexadec-7-en-1-ol

☒ **B** *Z*-hexadec-7-en-1-ol

☒ **C** *E*-hexadec-9-en-1-ol

☒ **D** *Z*-hexadec-9-en-1-ol

(Total for Question 18 = 1 mark)

19 Fats, such as the one shown, can be converted into fuels for biodiesel by transesterification.

$$CH_2OOCC_{17}H_{33}$$
$$CHOOCC_{17}H_{33}$$
$$CH_2OOCC_{17}H_{33}$$
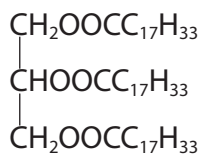
Which compound is used as a fuel, following the transesterification of this fat with methanol?

☒ **A** $C_{17}H_{33}COOCH_3$

☒ **B** $C_{17}H_{33}COOH$

☒ **C** CH_2OOCCH_3
  $CHOOCCH_3$
  CH_2OOCCH_3

☒ **D** CH_2OH
  $CHOH$
  CH_2OH

(Total for Question 19 = 1 mark)

20 The type of radiation used in nmr spectroscopy is

☒ **A** infrared.

☒ **B** microwave.

☒ **C** radio waves.

☒ **D** ultraviolet.

(Total for Question 20 = 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.

21 When nitrogen(II) oxide, NO, reacts with hydrogen at high temperatures, the products are nitrogen and water.

(a) Write an equation for this reaction. State symbols are not required.

(1)

(b) The table shows the results of a series of experiments to measure the rate of this reaction.

Experiment number	Initial concentration / mol dm^{-3}		Initial rate / mol dm^{-3} s^{-1}
	[NO(g)]	[H$_2$(g)]	
1	0.0020	0.020	5.5×10^{-3}
2	0.0040	0.040	4.4×10^{-2}
3	0.0080	0.020	8.8×10^{-2}

(i) Deduce the order of reaction with respect to nitrogen(II) oxide and to hydrogen.

Justify your answers by referring to data from the table.

(3)

Order with respect to NO ....

Order with respect to H$_2$ ....

Justification ....

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(ii) Write the rate equation for the reaction.

(1)

(iii) Calculate the value of the rate constant and give its units.

(2)

(c) There is more than one step in the reaction mechanism.

(i) Suggest why the reaction is unlikely to take place in a single step.

(1)

(ii) The first step of a three-step reaction mechanism is shown.

$$2NO(g) \rightarrow N_2O_2(g)$$
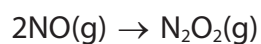
The second step of the mechanism is the rate determining step.

Suggest an equation for the rate determining step.

Justify your suggestion.

(2)

(Total for Question 21 = 10 marks)

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

22 Propanoic acid is a weak acid with $K_a = 1.30 \times 10^{-5} \, mol \, dm^{-3}$.

(a) (i) Write the expression for the acid dissociation constant, K_a, of propanoic acid.

(1)

(ii) Calculate the pH of a solution of propanoic acid with a concentration of $0.120 \, mol \, dm^{-3}$.

(3)

(b) $25.00 \, cm^3$ of propanoic acid, with a concentration of $0.120 \, mol \, dm^{-3}$, was pipetted into a conical flask.

This solution was titrated with sodium hydroxide of concentration $0.150 \, mol \, dm^{-3}$.

$$CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COONa + H_2O$$
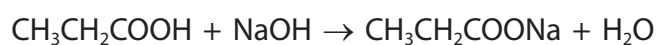
(i) Use the value of K_a to calculate the pH of the mixture in the flask when enough sodium hydroxide has been added to react with **half** of the acid.

(2)

*(ii) In the region where the acid is half neutralised, the pH of the titration mixture changes more gradually than it does when the end-point is approached.

Explain the reason for this gradual change in pH.

(3)

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(iii) Calculate the minimum volume of sodium hydroxide required to react with **all** of the propanoic acid.

(2)

(iv) Calculate the pH when $40\,cm^3$ of sodium hydroxide (an excess) was added.

(3)

(c) In another titration, a solution of aqueous ammonia with a concentration of 0.120 mol dm^{-3} was added to 25.00 cm^3 propanoic acid with a concentration of 0.120 mol dm^{-3}.

(i) Sketch the shape of the titration curve on the grid.

(2)

volume of ammonia / cm^3
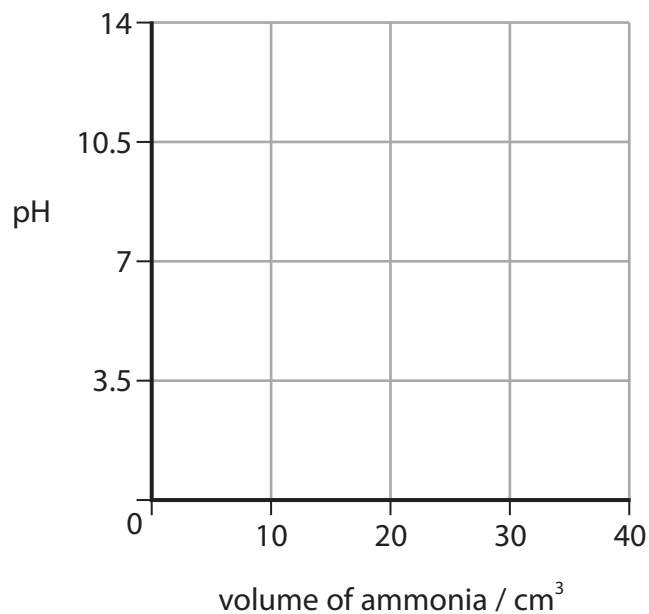
(ii) Explain why an indicator **cannot** be used to determine the end-point of this reaction.

(1)

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(Total for Question 22 = 17 marks)

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23 This question is about some reactions involving ethanal, CH_3CHO.

CH_3CHO

Reaction **A**   Reaction **B**   Reaction **C**

I_2 + NaOH   HCN + KCN

CH_3CH_2OH Two organic   Product **C**
                          products
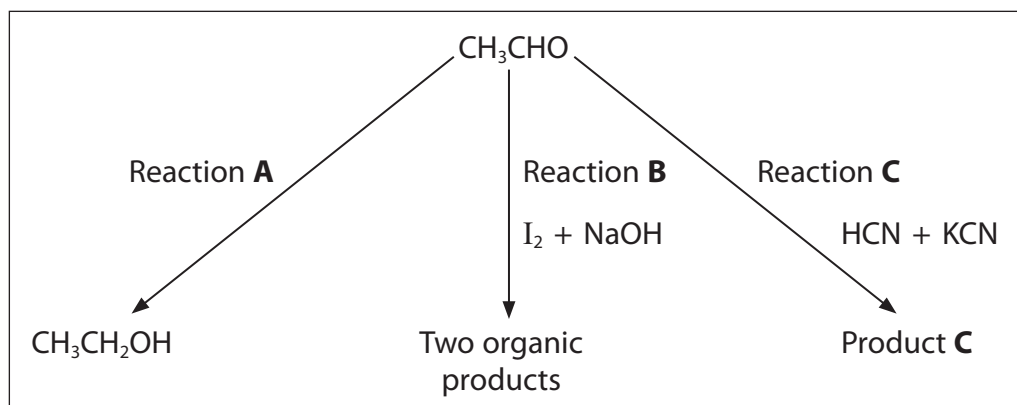
(a) Ethanal is a carbonyl compound.

Describe the test for a **carbonyl** compound and give the result.

(2)

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(b) Identify, by name or formula, the reagent needed to carry out Reaction **A**.

(1)

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....

(c) (i)   Identify the **two** organic products of Reaction **B**.

(2)

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....

(ii) State what you would **see** when Reaction **B** is carried out.

(1)

....

(d) (i) Name the reaction type and mechanism that occurs in Reaction **C**.

(1)

....

(ii) Draw the mechanism for Reaction **C**.

Include curly arrows, and all the relevant dipoles and lone pairs.

(4)

(iii) The organic product of Reaction **C** is a racemic mixture.
State the meaning of 'racemic mixture'.

(1)

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*(iv) By referring to the mechanism of Reaction **C**, explain why a racemic mixture forms in this reaction.

(2)

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(Total for Question 23 = 14 marks)

24 This question is about compounds of iodine.

(a) Potassium iodate(V) can be decomposed by heating.

$$KIO_3(s) \rightarrow KI(s) + 1\tfrac{1}{2}O_2(g)$$
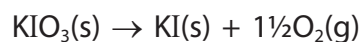
(i) Use data from your Data Booklet to calculate the enthalpy change for this reaction.

(2)

(ii) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$.

[The standard molar entropy of $\tfrac{1}{2}O_2(g)$ is $102.5\,J\,mol^{-1}\,K^{-1}$]

(2)

(iii) Use your answers to (a)(i) and (a)(ii) to calculate the minimum temperature for this reaction to be spontaneous.

Show your working clearly.

(2)

(iv) Explain why some reactions which are thermodynamically favourable do not occur spontaneously.

(1)

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(b) Some data about potassium iodide and its ions are shown.

Enthalpy change of solution of KI $= +20.3\,\text{kJ mol}^{-1}$

Ion	Enthalpy change of hydration / kJ mol^{-1}
K$^+$(g)	−320
I$^-$(g)	−308

(i) Use these data to calculate the lattice energy of potassium iodide.

(2)

*(ii) Explain why the lattice energy of sodium iodide is more exothermic than that of potassium iodide.

(2)

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(Total for Question 24 = 11 marks)
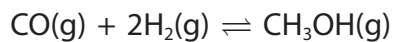
TOTAL FOR SECTION B = 52 MARKS

SECTION C

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

25 This question is about the chemistry of methanol.

(a) Methanol can be synthesised by the reaction of carbon monoxide with hydrogen.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

A mixture of 18.5 mol of carbon monoxide and 13.5 mol of hydrogen was allowed to reach equilibrium at 550 K and 60 atm pressure.

At equilibrium the mixture contained 5.5 mol of methanol.

(i) Write the expression for the equilibrium constant in terms of pressure, K_p, for this reaction.

(1)

(ii) Calculate the number of mol of carbon monoxide and hydrogen remaining at equilibrium.

Hence calculate the value of K_p at 550 K.

Give your answer to **three** significant figures and include the units.

(5)

(iii) The value of K_p is greater when the reaction is carried out at a **lower** temperature.

Use this information to deduce the sign of $\Delta S_{surroundings}$ for the forward reaction.

Give your reasoning.

(2)

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(b) An organic compound, **P**, has the molecular formula $C_5H_8O_3$.

A molecule of **P** has a carbon chain that is **not** branched, and contains **two** different functional groups.

(i) **P** reacts with sodium carbonate solution, forming bubbles of a colourless gas. There is no colour change when **P** is warmed with a mixture of potassium dichromate(VI) and sulfuric acid.

Use all the information provided to identify, by name or formulae, the **two** functional groups present in **P**.

(2)

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(ii) The mass spectrum of **P** has a strong peak at $m / e = 43$.

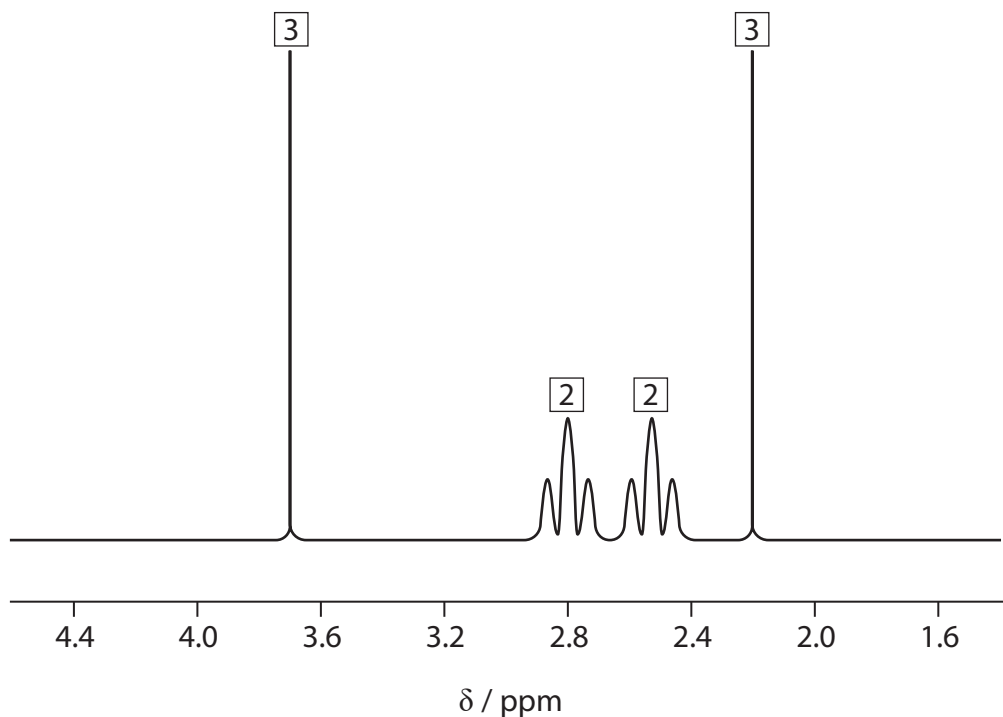Suggest the structural formula of the fragment causing this peak.

(1)

*(iii) When **P** is heated with methanol, in the presence of dilute sulfuric acid, a pleasant smelling compound, **Q**, is formed.

The **high resolution** proton nmr spectrum of **Q** is shown.

The numbers show the relative areas of the peaks.

δ / ppm

Draw the structure of **Q**. Justify your answer by considering the relative areas of the four peaks, and their splitting patterns.

(4)

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(iv) Write an equation using structural formulae to show the reaction of **P** with methanol in the presence of dilute sulfuric acid to form **Q**.

(2)

(v) The reaction of **P** with methanol does not give a 100% yield of **Q** because of the equilibrium position which is reached.

Suggest the formula of a compound which would react with methanol to form **Q** in a reaction which is **not** reversible.

(1)

(Total for Question 25 = 18 marks)

TOTAL FOR SECTION C = 18 MARKS
TOTAL FOR PAPER = 90 MARKS

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The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

(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

1.0 **H** hydrogen 1

* 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

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