Please check the examination deta	ails below	before enter	ering your candidate information						
Candidate surname			Other names						
Pearson Edexcel International Advanced Level	Centre	Number	Candidate Number						
Tuesday 4 Jui	ne 2	2019	9						
Afternoon (Time: 1 hour 40 minu	Paper Re	eference WCH04/01							
Chemistry Advanced Unit 4: General Principles Equilibria and Furt (including synoptic	her O	rganic [*] C	Chemistry						
Candidates must have: Scienti Data B		ulator	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 ▶





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.
- ☑ 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.

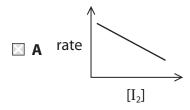
(Total for Question 2 = 1 mark)

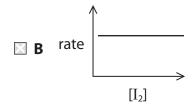
3 The chemical equation and the rate equation for the reaction of iodine with excess propanone in the presence of an acid catalyst are shown.

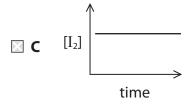
$$I_2 + CH_3COCH_3 \rightarrow CH_3COCH_2I + HI$$

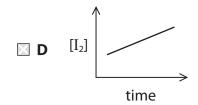
rate = $k[CH_3COCH_3][H^+]$

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







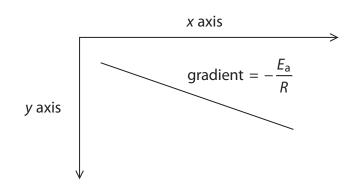


(Total for Question 3 = 1 mark)

4 The Arrhenius equation is

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

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



The axes on the graph are

		x axis	y axis
X	A	ln k	$\frac{1}{T}$
X	В	ln k	$-\frac{1}{T}$
X	C	$\frac{1}{T}$	In <i>k</i>
×	D	$-\frac{1}{T}$	In <i>k</i>

(Total for Question 4 = 1 mark)

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

$$H_2O(I) \rightarrow H_2O(s)$$

		ΔS_{system}	$\Delta S_{ m surroundings}$
X	A	negative	positive
X	В	positive	negative
X	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 CH₃COOH and C₂H₅COOH
- ☑ B CH₃COOH and C₂H₅COOH₂
- ☑ D CH₃COO⁻ and C₂H₅COOH₂¹

(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)
- 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)



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

Compound 1 CH₃COOH

Compound 2 CH₃COCl

Compound 3 CH₃COONa

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

- A CH₃COOH < CH₃COCl < CH₃COONa
- B CH₃COCl < CH₃COOH < CH₃COONa
- ☑ C CH₃COONa < CH₃COOH < CH₃COCI
 </p>
- ☑ D CH₃COCl < CH₃COONa < CH₃COOH
 </p>

(Total for Question 9 = 1 mark)

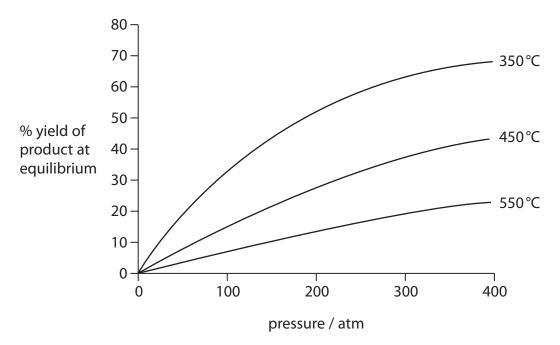
10 What are the units of K_c for the following equilibrium?

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

- A moldm⁻³
- \square **B** dm³ mol⁻¹
- \square C mol² dm⁻⁶
- **D** no units

(Total for Question 10 = 1 mark)

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 $R \ln K$?
 - \square **A** $R \ln K = \Delta S_{\text{system}} \Delta H/T$
 - \blacksquare **B** $R \ln K = \Delta S_{\text{system}} + \Delta H/T$
 - \square **C** $R \ln K = \Delta S_{\text{system}} T \Delta H$
 - \square **D** $R \ln K = \Delta S_{\text{system}} + T \Delta H$

(Total for Question 12 = 1 mark)

- **13** Which compound is **most** soluble in water?
 - \triangle A C_4H_9Cl
 - \square **B** C_4H_9Br

 - ☑ D CH₃COOC₂H₅

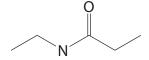
(Total for Question 13 = 1 mark)

- 14 Which compound reacts with phosphorus(V) chloride to form ethanoyl chloride?
 - A CH₃CHO
 - B CH₃CH₂OH

 - □ CH₃COOH

(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)

16 The repeat unit of a polymer is shown.

Which monomers react to make this polymer?

- A HOOC(CH₂)₂COOH and Cl(CH₂)₂Cl
- B Cloc(CH₂)₂COCl and HO(CH₂)₂OH
- D HOOC(CH₂)₂COOCH₃ and ClOC(CH₂)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
- **D** pentan-1-ol

(Total for Question 17 = 1 mark)

18 A compound has the structure

$$CH_3(CH_2)_4CH_2$$
 $CH_2(CH_2)_6CH_2OH$ $C=C$

The systematic name of the compound is

- B Z-hexadec-7-en-1-ol
- C E-hexadec-9-en-1-ol
- □ 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.

Which compound is used as a fuel, following the transesterification of this fat with methanol?

- A C₁₇H₃₃COOCH₃
- CHOOCCH₃ CHOOCCH₃ CH₂OOCCH₃
- D CH₂OH CHOH CH₂OH

(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 concentra	Initial rate / mol dm ⁻³ s ⁻¹	
	[NO(g)]	initial rate / morum s	
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.

/	7	٦
	-5	1

Order with respect to NO
Order with respect to H ₂
Justification

(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. $2NO(g) \to N_2O_2(g)$ 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 = 1	10 marks)



- **22** Propanoic acid is a weak acid with $K_a = 1.30 \times 10^{-5} \, \text{mol dm}^{-3}$.
 - (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 $0.120\,\mathrm{mol\,dm^{-3}}$.

(3)

(b) 25.00 cm³ 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.

$$CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COONa + H_2O$$

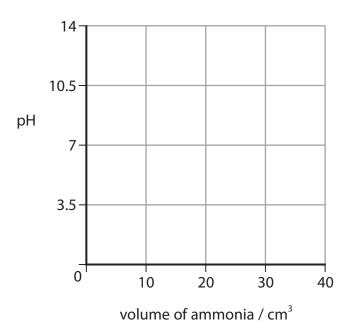
(i) Use the value of K_a to calculate the pH of the mixture in the flask when enough sodium hydroxide has been added to react with **half** of the acid.

(2)

Explain the reason for this	s gradual change in pH.	/=1
		(3)
/**\		. 91
all of the propanoic acid.	olume of sodium hydroxide required to	
		(2)
(iv) Calculate the pH when 40	cm ³ of sodium hydroxide (an excess) v	
		(3)

- (c) In another titration, a solution of aqueous ammonia with a concentration of $0.120\,\mathrm{mol\,dm}^{-3}$ was added to $25.00\,\mathrm{cm}^3$ propanoic acid with a concentration of $0.120\,\mathrm{mol\,dm}^{-3}$.
 - (i) Sketch the shape of the titration curve on the grid.

(2)



(ii) Explain why an indicator **cannot** be used to determine the end-point of this reaction.

(1)

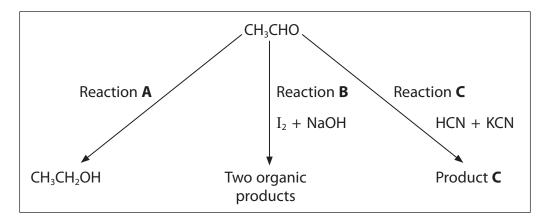
(Total for Question 22 = 17 marks)

16

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23 This question is about some reactions involving ethanal, CH₃CHO.



(a) Ethanal is a carbonyl compound.

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

(2)

(1)

- (b) Identify, by name or formula, the reagent needed to carry out Reaction **A**.
- (c) (i) Identify the **two** organic products of Reaction **B**. (2)
 - (ii) State what you would **see** when Reaction **B** is carried out.

(1)



, (,	Name the reaction type and mechanism that occurs in Reaction ${\bf C}$.	(1)
(ii)	Draw the mechanism for Reaction C .	
	Include curly arrows, and all the relevant dipoles and lone pairs.	(4)
/::: :	The even mis product of Decetion C is a resonais maintains	
(III)	The organic product of Reaction \mathbf{C} is a racemic mixture. State the meaning of 'racemic mixture'.	(1)
		(" /
*(iv	By referring to the mechanism of Reaction C , explain why a racemic mixture	
*(iv)	By referring to the mechanism of Reaction \mathbf{C} , explain why a racemic mixture forms in this reaction.	(2)
*(iv)		



- **24** This question is about compounds of iodine.
 - (a) Potassium iodate(V) can be decomposed by heating.

$$KIO_3(s) \rightarrow KI(s) + 1\frac{1}{2}O_2(g)$$

(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, $\Delta S_{\text{system}}^{\Theta}.$

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

(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)



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

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

lon	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)

(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)



	Use this information to deduce the sign of $\Delta S_{\text{surroundings}}$ for the forward reaction.	
	Give your reasoning. $ An organic compound, \textbf{P}, has the molecular formula $C_5H_8O_3$. $	(2)
o) Ar	organic compound, ${\bf P}$, has the molecular formula $C_5H_8O_3$.	
Α	·	
tw	o different functional groups.	
	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	
	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	
	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	(2)

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

Suggest the structural formula of the fragment causing this peak.

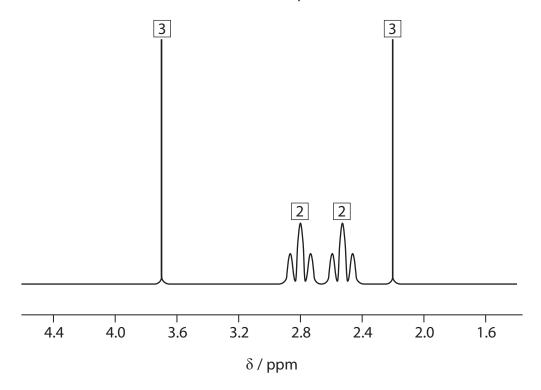
(1)



*(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.



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

(4)



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

(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

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^{*} Lanthanide series

9

[257]

102

^{*} Actinide series

Md No Lr mendelevium nobelium lawrencium Tm Yb thulium ytterbium [256] Cf Es Fm caltifornium einsteinium fermium 167 **Er** erbium 165 **Ho** holmium [254] 67 163 **Dy** dysprosium [251] 99 [245]
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97 159 **Tb** terbium 65 157 **Gd** gadolinium Carium 8 [247] 4 n neptunium plutonium americium 93 94 os
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 Nd
 Pm
 Sm
 Eu

 neodymium promethium samarium
 samarium europium
 [243] 63 [242] **Pu** 62 uranium 92 238 9 Pr Praseodymium protactinium 59 58 232 **Th** thorium Ce cerium 8