Write your name here

Surname	Other names

Pearson Edexcel GCE

Centre Number | | | | | |

Candidate Number | | | | |

Chemistry

Advanced

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

Tuesday 14 June 2016 – Afternoon

Time: 1 hour 40 minutes

Paper Reference **6CH04/01**

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or 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.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

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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 Consider the reaction

$$CH_3COOC_2H_5 + CH_3OH \rightleftharpoons CH_3COOCH_3 + C_2H_5OH$$

This is an example of

☒ **A** acylation.

☒ **B** hydrolysis.

☒ **C** substitution.

☒ **D** transesterification.

(Total for Question 1 = 1 mark)

2 When a vegetable oil such as palm oil is hydrolysed, the alcohol produced is

☒ **A** propan-1-ol

☒ **B** propane-1,2-diol

☒ **C** propane-1,3-diol

☒ **D** propane-1,2,3-triol

(Total for Question 2 = 1 mark)

3 Which of the following types of radiation can directly result in bond breaking?

☒ **A** Infrared

☒ **B** Microwave

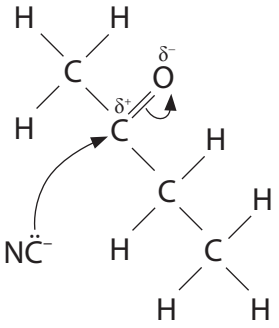
☒ **C** Radio wave

☒ **D** Ultraviolet

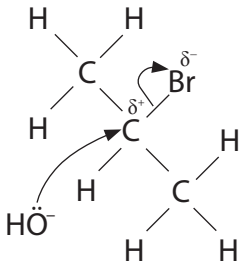
(Total for Question 3 = 1 mark)

4 The first steps of two **different** reaction mechanisms are shown.

First
Reaction Mechanism



Second
Reaction Mechanism



(a) What do **both** reaction mechanism steps have in common?

(1)

☒ **A** They involve addition.

☒ **B** They involve substitution.

☒ **C** As one bond is made, one bond is broken.

☒ **D** The attack is on a planar group.

(b) Only **one** of the first steps above

(1)

☒ **A** leads to the formation of a racemic mixture.

☒ **B** involves initial attack by a nucleophile.

☒ **C** involves initial attack by an electrophile.

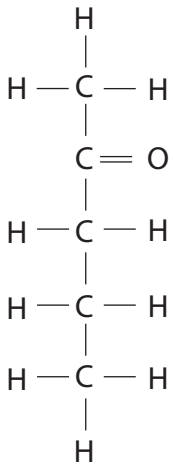
☒ **D** leads to an elimination.

(Total for Question 4 = 2 marks)

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

5 The following molecules are structural isomers with molecular formula $C_5H_{10}O$.

W



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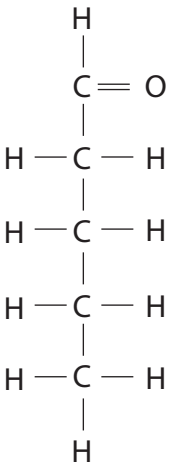
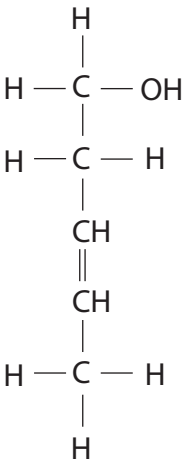
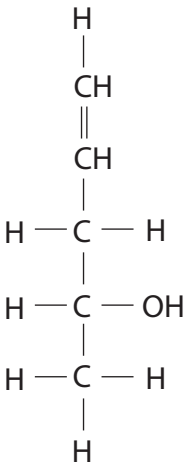


Y



Z



(a) Which of the molecules would exhibit optical isomerism?

(1)

☒ **A** W

☒ **B** X

☒ **C** Y

☒ **D** Z

(b) Which of the molecules would exhibit geometric isomerism?

(1)

☒ **A** W

☒ **B** X

☒ **C** Y

☒ **D** Z

(c) Which of the molecules would produce iodoform when reacting with iodine in alkaline solution?

(1)

☒ **A** W only

☒ **B** W and X

☒ **C** W and Y

☒ **D** W and Z

(d) Which of the molecules would be oxidized to a carboxylic acid using acidified sodium dichromate(VI)?

(1)

☒ **A** X only

☒ **B** Z only

☒ **C** X and Y

☒ **D** X, Y and Z

(e) Which of the molecules would form a crystalline product with 2,4-dinitrophenylhydrazine?

(1)

☒ **A** W only

☒ **B** W and X

☒ **C** W, X and Z

☒ **D** X only

(Total for Question 5 = 5 marks)

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

6 Chromatography is used to separate the components of a mixture and can be carried out in a range of different ways.

(a) A suitable example of a 'carrier gas' in gas chromatography is

(1)

☒ **A** chlorine.

☒ **B** nitrogen.

☒ **C** steam.

☒ **D** not possible to state, as there should be a vacuum.

(b) Separation is achieved in gas chromatography due to the components in the mixture having different

(1)

☒ **A** interactions with the stationary phase.

☒ **B** interactions with the mobile phase.

☒ **C** colours.

☒ **D** solubility in the moving solvent.

(Total for Question 6 = 2 marks)

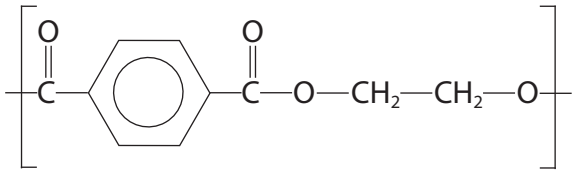
Use this space for rough working. Anything you write in this space will gain no credit.

7 Polyesters are condensation polymers.

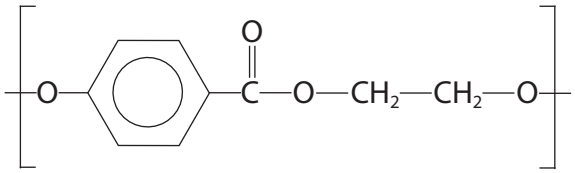
(a) PET, polyethylene terephthalate, can be produced from the condensation of ethane-1,2-diol and benzene-1,4-dicarboxylic acid.

Which of the following is the repeat unit of this polymer?

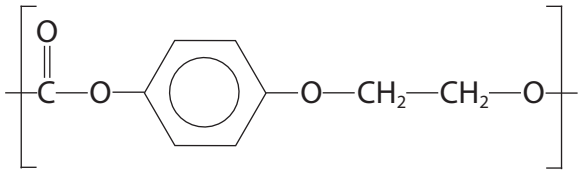
(1)



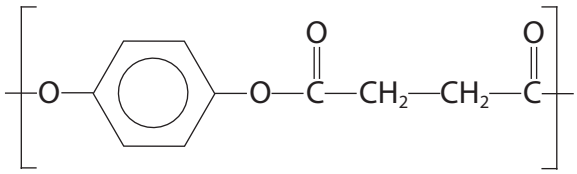
☒ **A**



☒ **B**

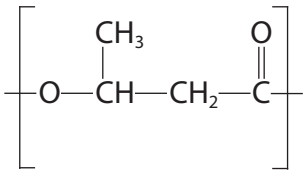


☒ **C**



☒ **D**

(b) The repeat unit of the biodegradable polymer PHB, is shown below.



This is made from a single monomer which could be

(1)

☒ **A** 2-hydroxybutanoic acid.

☒ **B** 3-hydroxybutanoic acid.

☒ **C** 2-hydroxy-2-methylpropanoic acid.

☒ **D** 3-hydroxy-3-methylpropanoic acid.

(Total for Question 7 = 2 marks)

8 The reaction of ammonia with propanoyl chloride, C_2H_5COCl, forms

- ☒ **A** $C_2H_5NH_2$
- ☒ **B** $C_2H_5CONH_2$
- ☒ **C** $C_2H_5CH(OH)NH_2$
- ☒ **D** $C_2H_5CONHC_2H_5$

(Total for Question 8 = 1 mark)

9 The dihydrogenphosphate-hydrogenphosphate ion system is an important buffer in the human body.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$

(a) In this system, there are two acid-base conjugate pairs. These are

(1)

	acid with its conjugate base	base with its conjugate acid
☒ **A**	$H_2PO_4^- / HPO_4^{2-}$	H_2O / H_3O^+
☒ **B**	H_2O / H_3O^+	$HPO_4^{2-} / H_2PO_4^-$
☒ **C**	H_3O^+ / H_2O	$H_2PO_4^- / HPO_4^{2-}$
☒ **D**	$H_2PO_4^- / HPO_4^{2-}$	H_3O^+ / H_2O

(b) A formula that can be used for the calculation of the pH of this buffer solution is

$$pH = pK_a + \log\left(\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}\right)$$

Calculate the pH of this buffer using

$pK_a = 7.20$ $[HPO_4^{2-}] = 3.98 \times 10^{-8}$ mol dm^{-3} $[H_2PO_4^-] = 3.89 \times 10^{-7}$ mol dm^{-3}

(1)

- ☒ **A** 6.19
- ☒ **B** 6.21
- ☒ **C** 7.20
- ☒ **D** 8.19

(Total for Question 9 = 2 marks)

10 The Ostwald Process is a method for making nitric acid. The equation for the first stage of this process is

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H = -905 \text{ kJ mol}^{-1}$$

(a) The equilibrium yield of nitrogen monoxide, NO, is **increased** by

(1)

☒ **A** increasing both the pressure and the temperature.

☒ **B** decreasing both the pressure and the temperature.

☒ **C** decreasing the pressure and increasing the temperature.

☒ **D** increasing the pressure and decreasing the temperature.

(b) For this stage of the process, the catalyst is an alloy of platinum and rhodium. A pressure of between 4 and 10 atm and a temperature of 1150 K are used. Unreacted reactants are recycled.

Which one of the following changes will affect the value of the equilibrium constant, K_p?

(1)

☒ **A** Changing the composition of the platinum-rhodium catalyst.

☒ **B** Increasing the pressure above 10 atm.

☒ **C** Decreasing the temperature below 1150 K.

☒ **D** Not recycling unreacted reactants.

(Total for Question 10 = 2 marks)

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

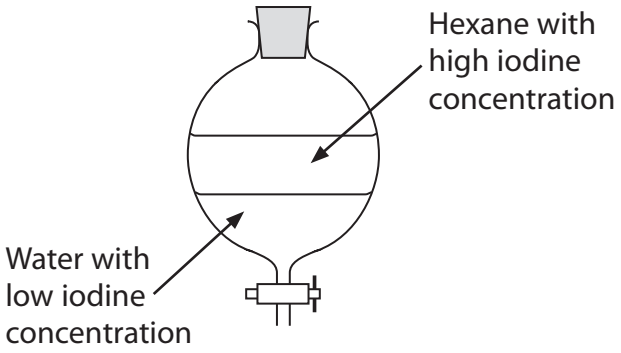
11 Iodine is soluble in both water and hexane. If iodine is added to a mixture of the two solvents, then the following equilibrium is set up.

$$I_2(aq) \rightleftharpoons I_2(hexane)$$

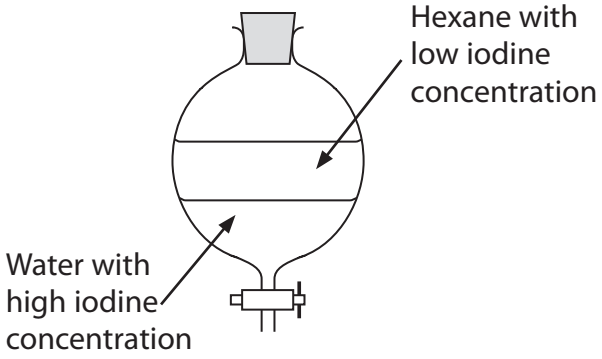
The equilibrium constant, known as the partition coefficient, is 85.

The density of hexane is 0.66 g cm^{-3}. The density of water is 1.00 g cm^{-3}.

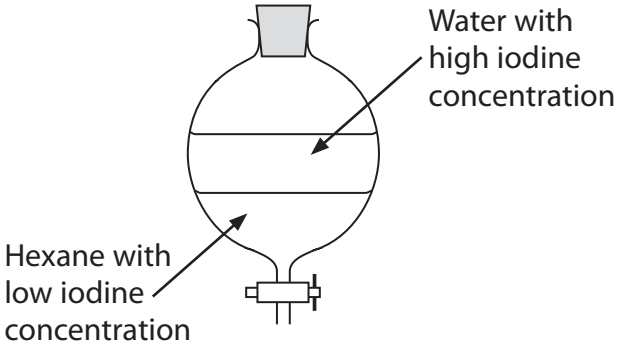
Which of the following diagrams is correct for this system at equilibrium?



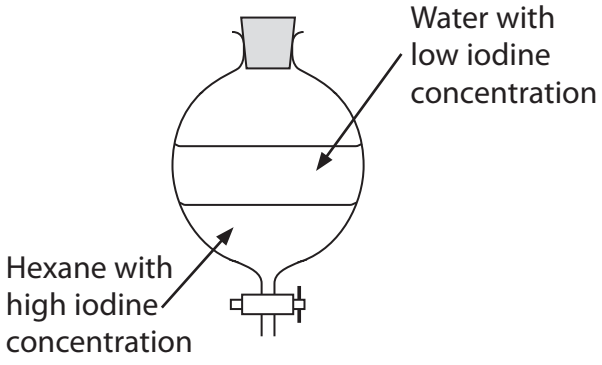
☒ **A**



☒ **B**



☒ **C**



☒ **D**

(Total for Question 11 = 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.

12 Sulfuric acid, H_2SO_4, is a well known acid containing sulfur. However, two other sulfur-containing acids are hydrogen sulfide, H_2S, and sulfurous acid, H_2SO_3.

(a) Hydrogen sulfide is a weak acid and dissociates in two stages as shown.

Stage 1 $H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$ $K_{a1} = 8.91 \times 10^{-8}$ mol dm^{-3}

Stage 2 $HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)$ $K_{a2} = 1.20 \times 10^{-13}$ mol dm^{-3}

Write the K_a expressions for

(2)

Stage 1 $K_{a1} =$

Stage 2 $K_{a2} =$

(b) A solution of hydrogen sulfide has an initial concentration of 0.100 mol dm^{-3}.

$$K_{a1} = 8.91 \times 10^{-8} \text{ mol dm}^{-3}$$

(i) Use K_{a1} to calculate the equilibrium concentration, in mol dm^{-3}, of the hydrogensulfide ion, HS^-. Give your answer to **three** significant figures.

(2)

(ii) Use your answer to (b)(i) to calculate the pH of this solution.

(1)

*(iii) State the **three** assumptions you have made in your calculations in (b)(i) and (b)(ii).

(3)

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(c) Sulfurous acid, H_2SO_3, is also a diprotic acid. The values of K_{a1} and K_{a2} can be determined from the results of an acid-base titration. Diprotic acids require two OH^- ions per molecule for complete neutralization.

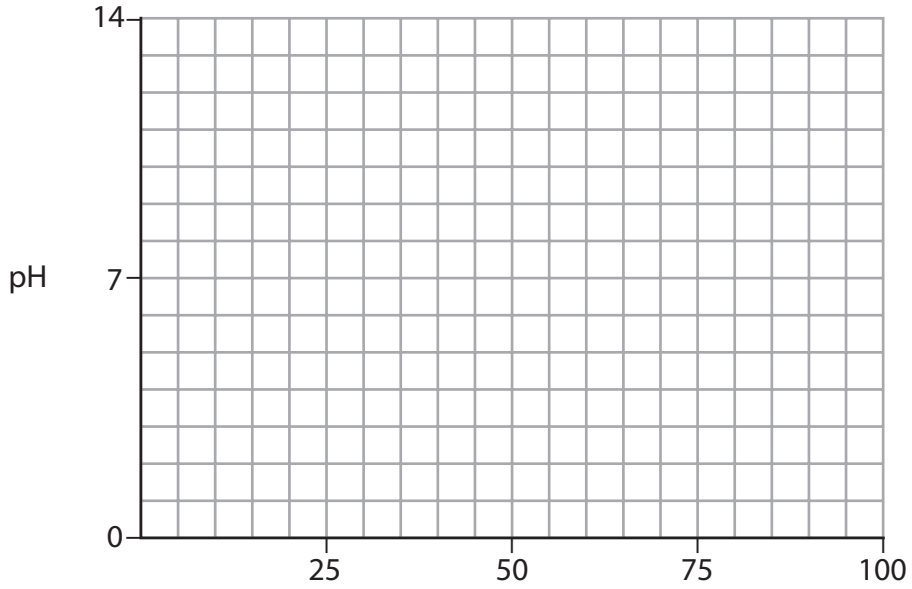
Sulfurous acid, H_2SO_3, is a stronger acid than H_2S and a 0.100 mol dm^{-3} solution has a pH of 1.5.

(i) On the grid below, sketch the likely shape of the titration curve for sulfurous acid, H_2SO_3, during the neutralization process.

- 25 cm^3 of sulfurous acid solution with a concentration of 0.100 mol dm^{-3} is used
- 100 cm^3 of the sodium hydroxide solution with a concentration of 0.100 mol dm^{-3} is added
- $pK_{a1} = 1.9$ and $pK_{a2} = 7.2$

Clearly label any equivalence points in the sketch.

(5)



(ii) Describe how you would use this graph to confirm the value of pK_{a1}.

(1)

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(Total for Question 12 = 14 marks)

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13 This is a question about entropy changes.

Consider the reaction between the two solids, hydrated barium hydroxide and ammonium chloride. When these substances are mixed together, a white paste is formed and the temperature decreases. An equation for this process is given below.

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + 10H_2O(l) + BaCl_2(s)$$

(a) (i) Identify **one** hazard associated with a named substance in this reaction.

(1)

.....

.....

(ii) Use the standard molar entropies below to calculate the standard entropy change of the system ($\Delta S^{\ominus}_{system}$) for this reaction at 298 K. Give a sign and units with your answer.

Compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Ba(OH)_2.8H_2O(s)$	427
$NH_4Cl(s)$	95
$NH_3(g)$	192
$H_2O(l)$	70
$BaCl_2(s)$	124

(3)

*(iii) Give **two** reasons why the sign of your answer to (a)(ii) is as you would expect.

(2)

(b) The standard enthalpy change for this reaction is $\Delta H_r^{\ominus} = +162$ kJ mol^{-1}.

Use this value to calculate the standard entropy change of the surroundings ($\Delta S^{\ominus}_{\text{surroundings}}$) for this reaction at 298 K. Include a sign and units in your answer.

(2)

(c) Use your answers to (a)(ii) and (b) to calculate the total entropy change ($\Delta S^{\ominus}_{\text{total}}$) for this reaction. Include a sign and units in your answer.

(1)

(d) What would be the effect, if any, on the value of $\Delta S^{\ominus}_{\text{total}}$ from (c) of a small increase in temperature? Justify your answer and state any assumptions that you have made.

(3)

(e) The values of total entropy change and equilibrium constant of a reaction are related by the following equation.

$$\Delta S_{total} = R \ln K$$

The equation for the dissolving of barium hydroxide is

$$Ba(OH)_2(s) + aq \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq) \quad \Delta S^{\ominus}_{total} = -44 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Calculate the value of the equilibrium constant, K, for this equation at 298 K.

$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

(1)

(ii) What does the value of the equilibrium constant suggest about the solubility of barium hydroxide?

Justify your answer.

(1)

.....

.....

(iii) For the dissolving of calcium hydroxide, the value of the total entropy change is $-106 \text{ J mol}^{-1} \text{ K}^{-1}$

Compare the values of the total entropy changes for these two hydroxides and show that they are consistent with the trend in the solubility of Group 2 hydroxides.

(2)

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(Total for Question 13 = 16 marks)

14 This is a question about how 'clock reactions' are used to study reaction kinetics.

The 'bromine clock' involves a reaction between bromide ions and bromate(V) ions in acid solution:

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

In order to monitor this reaction, phenol and methyl orange are added to the reaction mixture.

- A small fixed amount of phenol is present which reacts immediately with the bromine as it is produced, thus removing it from solution.
- Once the bromine produced has reacted with all of the phenol present, then any further bromine produced will bleach the methyl orange solution providing a means to monitor the reaction rate.

(a) It is assumed that the **initial** rate of reaction is proportional to 1/time taken for the methyl orange to be bleached.

Explain why it is essential for the amount of phenol to be small compared to the amounts of the reactants for this assumption to be valid.

(1)

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.....

(b) A series of experiments was carried out where only the concentration of bromide ions present was varied and the solution contained a large excess of BrO_3^- and H^+ ions. The total volume of the mixture was kept constant.

(i) Why was it important that the solution contained a large excess of BrO_3^- and H^+ ions?

(1)

.....

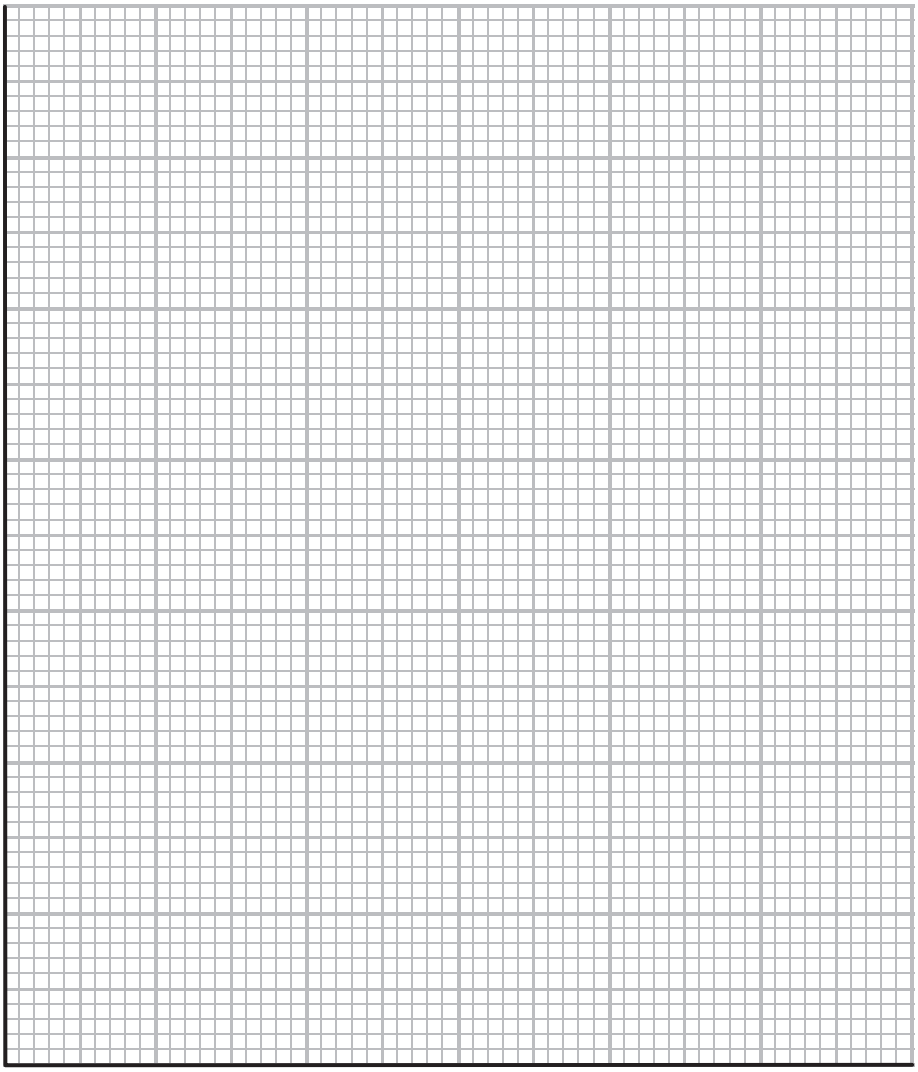
.....

(ii) The following results were obtained.

Complete the table and use the results to plot a graph of 1/time on the vertical axis against the volume of bromide ions.

(4)

Volume of $Br^-(aq)$ / cm^3	10.0	8.0	6.0	5.0	4.0	2.0
Time / s	180	226	300	364	444	900
(1/time) / 10^{-3} s^{-1}	5.56	4.42	3.33		2.25	1.11



(iii) Deduce the order of the reaction with respect to bromide ions.

Justify your answer.

(2)

(iv) The reaction is first order with respect to bromate(V) ions and second order with respect to hydrogen ions. Write the overall rate equation for the 'bromine clock' reaction and deduce the units of the rate constant.

(2)

Rate equation:

Units of rate constant .....

(c) Another 'clock reaction' is the 'iodine clock' reaction, where hydrogen peroxide solution is mixed with a solution containing sodium thiosulfate, potassium iodide and starch.

The main reaction is

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

- The thiosulfate ions present react immediately with the iodine as it is produced, thus removing it from solution.
- Once all of the thiosulfate ions are used up, further iodine produced reacts with the starch present.

(i) Why are the potassium ions omitted from the above equation?

(1)

(ii) State the observation made after all of the thiosulfate ions are used up and more iodine is produced.

(1)

(d) 'Iodine clock' reactions can be used to determine the activation energy of a reaction using the equation:

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

(i) State the experimental measurements you would make to provide the numerical data for the calculation of the activation energy.

(1)

(ii) Describe how you would use your experimental measurements to obtain a value for the activation energy.

You should include

- how the data is processed
- the graph you would plot and its expected shape
- how the activation energy of the reaction can be determined from the graph produced.

(6)

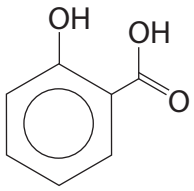
(Total for Question 14 = 19 marks)

TOTAL FOR SECTION B = 49 MARKS

SECTION C

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

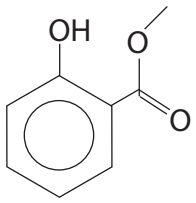
15 Salicylic acid is the active ingredient in one method of treatment of verrucas, warts and acne. The structure of salicylic acid is shown below.



A laboratory method of preparing salicylic acid is the hydrolysis of the ester, methyl salicylate, which is present in Oil of Wintergreen. A sample of the ester is initially refluxed with sodium hydroxide and salicylic acid is then precipitated by adding a strong acid.

(a) (i) Complete the equation for the alkaline hydrolysis of the ester group in methyl salicylate, using sodium hydroxide.

(1)



+ NaOH → ..... + ...

(ii) The salicylic acid is precipitated out of solution by the addition of dilute sulfuric acid until it is in excess.

How could you tell that the sulfuric acid is in excess?

(1)

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(b) Salicylic acid is sparingly soluble in water. Explain this observation in terms of intermolecular forces.

(2)

.....

.....

.....

.....

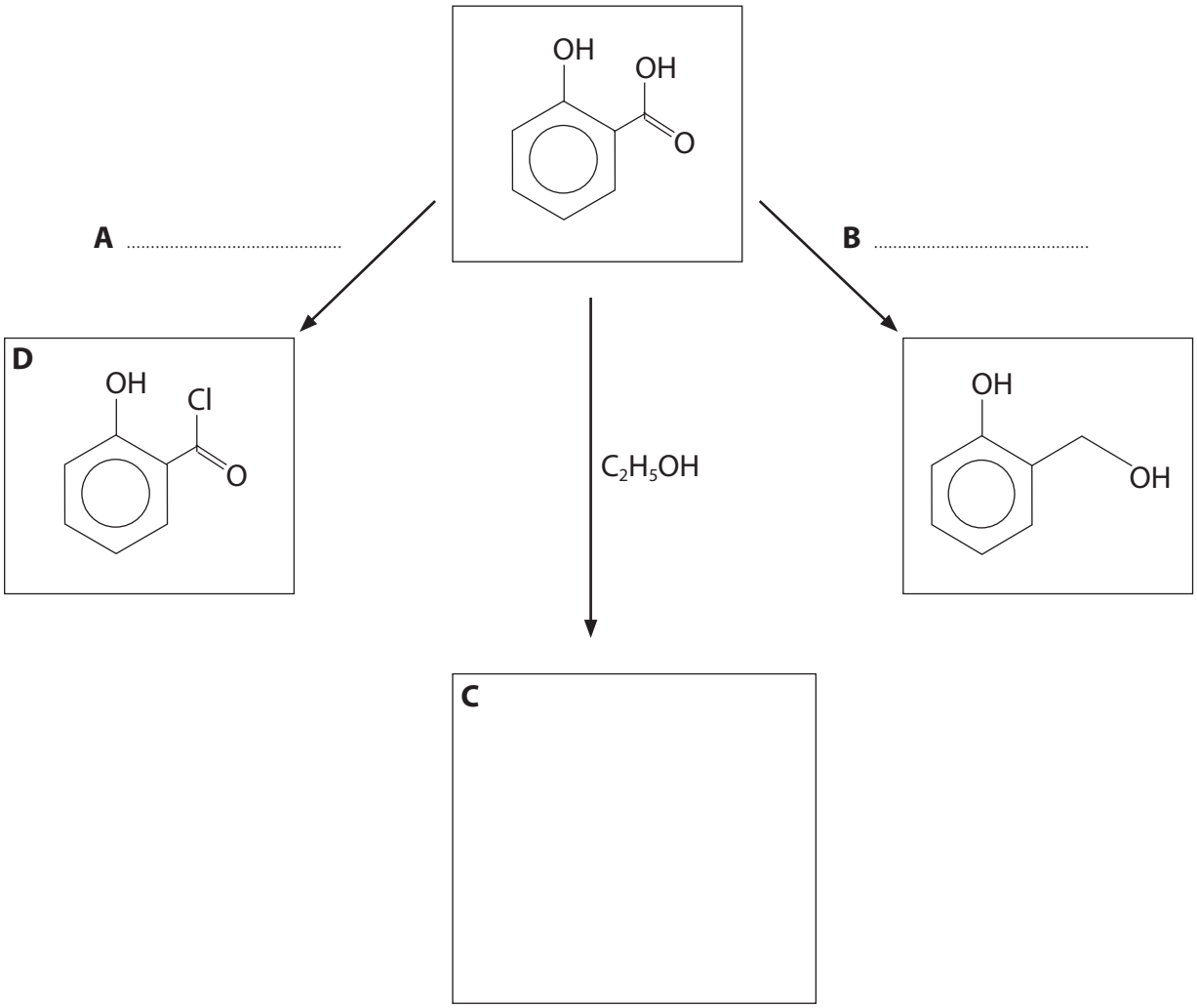
(c) State **three** ways in which the acid hydrolysis of an ester differs from the alkaline hydrolysis of an ester.

(3)

(d) Salicylic acid can undergo various reactions as outlined below.

(i) Give the **formula** of the reagents **A** and **B** and the **skeletal** formula of the product **C**.

(3)



(ii) Both compound **D** and salicylic acid react with ethanol. State **two** differences between these reactions.

(2)

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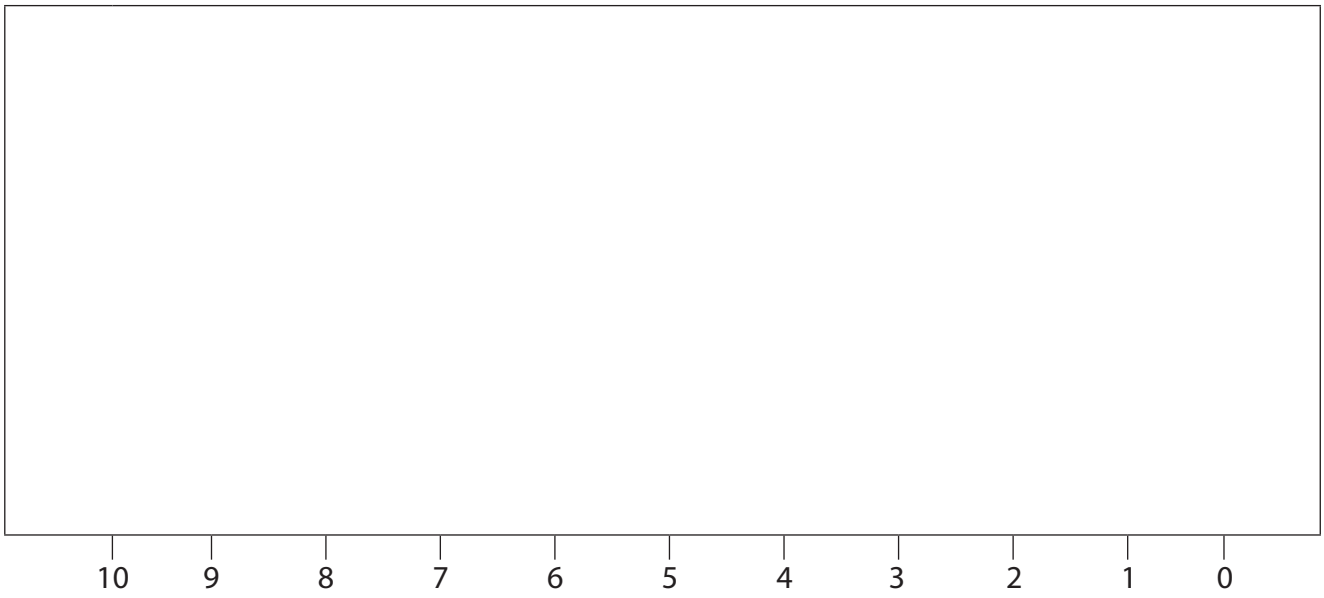
*(e) Use chemical shift data from the Data Booklet to sketch the **high** resolution proton nmr spectrum for ethanol. The peaks do not overlap.

Explain the number of peaks, their splitting pattern and the ratio of the areas under each set of peaks.

(5)



(f) Tetramethylsilane, $Si(CH_3)_4$, is used as a reference standard in nmr spectra.

Suggest why it gives a very strong signal in the spectrum.

(1)

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(g) State the type of radiation that is used to create the nmr spectrum.

(1)

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(h) Use the Data Booklet to state **two** differences between the infrared spectra of salicylic acid and compound **D**. Include the wave numbers of the relevant groups or bonds.

(2)

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(Total for Question 15 = 21 marks)

TOTAL FOR SECTION C = 21 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: relative atomic mass / atomic symbol / name / atomic (proton) number									(13)	(14)	(15)	(16)	(17)	
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