AQA

Please write clearly in block capitals.

Centre number | | | | | | Candidate number | | | | |

Surname Model Answer

Forename(s)

Candidate signature

# A-level CHEMISTRY

## Unit 4 Kinetics, Equilibria and Organic Chemistry

Tuesday 14 June 2016 Afternoon Time allowed: 1 hour 45 minutes

**Materials**

For this paper you must have:
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- a ruler with millimetre measurements
- a calculator.

**Instructions**
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

**Information**
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  - use good English
  - organise information clearly
  - use scientific terminology accurately.

**Advice**
- You are advised to spend about 80 minutes on **Section A** and about 25 minutes on **Section B**.

## Section A

Answer **all** questions in the spaces provided.

**1** Nitric acid ($HNO_3$) is a strong acid. Ethanoic acid ($CH_3COOH$) is a weak acid.

**1 (a)** Write an equation to show how ethanoic acid behaves as a weak acid in its reaction with water.

**[1 mark]**

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

**1 (b)** When pure ethanoic acid reacts with pure nitric acid, ethanoic acid acts as a base.

Write an equation for this reaction.

An odd question but one where you just need to understand a base is a proton acceptor.

**[1 mark]**

$CH_3COOH + HNO_3 \rightleftharpoons CH_3COOH_2^+ + NO_3^-$

**1 (c)** Two beakers, **A** and **B**, each contain 100.0 $cm^3$ of 0.0125 mol $dm^{-3}$ nitric acid.

**1 (c) (i)** Calculate the pH of the solution formed after 50.0 $cm^3$ of distilled water are added to beaker **A**.
Give your answer to 2 decimal places.

**[2 marks]**

$C = \frac{n}{V}$ $0.0125 \times \left(\frac{100}{1000}\right) = 1.25 \times 10^{-3}$ moles $\frac{1.25 \times 10^{-3}}{(150/1000)} = 0.0083^{\bullet}$ mol$dm^{-3}$

$pH = -\log[H^+]$ $pH = -\log(0.0083^{\bullet})$ $pH = 2.08$

**1 (c) (ii)** Calculate the pH of the solution formed after 50.0 $cm^3$ of 0.0108 mol $dm^{-3}$ aqueous sodium hydroxide are added to beaker **B**.
Give your answer to 2 decimal places.

**[4 marks]**

$HNO_3 + NaOH \rightleftharpoons NaNO_3 + H_2O$

$C = \frac{n}{V}$ $0.0108 \times \left(\frac{50}{1000}\right) = 5.4 \times 10^{-4}$ moles of NaOH

$1.25 \times 10^{-3}$ moles of $HNO_3$ $-$ $5.4 \times 10^{-4}$ moles of NaOH $= 7.1 \times 10^{-4}$ moles of excess $HNO_3$.

(new volume!)

$\frac{7.1 \times 10^{-4}}{(150/1000)} = 0.00473^{\bullet}$ mol$dm^{-3}$ of $HNO_3$ $pH = -\log[H^+]$ $pH = -\log(0.00473^{\bullet})$ $pH = 2.32$

**1 (d)** A third beaker, **C**, contains 100.0 $cm^3$ of 0.0125 mol $dm^{-3}$ ethanoic acid.
The acid dissociation constant $K_a$ for ethanoic acid has the value $1.74 \times 10^{-5}$ mol $dm^{-3}$ at 25 °C.

**1 (d) (i)** Write an expression for $K_a$ for ethanoic acid and use it to calculate the pH of the ethanoic acid solution in beaker **C**.
Show your working. Give your answer to 2 decimal places.

**[4 marks]**

$K_a$ $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

Calculation $1.74 \times 10^{-5} = \frac{[H^+]^2}{0.0125}$ $\sqrt{1.74 \times 10^{-5} \times 0.0125} = [H^+]$

$[H^+] = 4.66 \times 10^{-4}$ $pH = -\log[H^+]$ $pH = 3.33$

**1 (d) (ii)** Aqueous sodium hydroxide is added to beaker **C** until the pH of the solution becomes 4.84

Name the salt formed in the reaction of ethanoic acid with sodium hydroxide.

**[1 mark]**

Sodium Ethanoate

**1 (d) (iii)** Calculate the value of $\frac{[\text{salt}]}{[\text{ethanoic acid}]}$ in the solution with the pH of 4.84

**[3 marks]**

$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ $10^{-4.84} = 1.445 \times 10^{-5} = [H^+]$

$\frac{1.74 \times 10^{-5}}{1.445 \times 10^{-5}} = \frac{[CH_3COO^-]}{[CH_3COOH]}$ $= 1.20$

**1 (e)** Explain why chloroethanoic acid is a stronger acid than ethanoic acid.

**[2 marks]**

Chloroethanoic acid is stronger as the electronegative Chlorine withdraws electrons which in turn weakens the O-H bond allowing it to be released more easily.

**1 (f)** Explain why data books do not usually contain values of $K_a$ for strong acids.

**[2 marks]**

strong acids totally dissociate so equilibrium lies almost totally to the right therefore Ka values would be very large.

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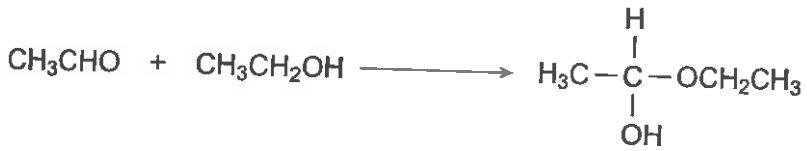
**2** Hemiacetals and acetals are compounds formed by the reaction of aldehydes with alcohols, such as the reaction of ethanal with ethanol.



a hemiacetal

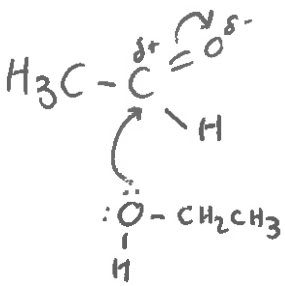
**2 (a) (i)** Use your knowledge of carbonyl mechanisms to suggest the name of the mechanism of this reaction.

**[1 mark]**

Nucleophilic Addition

**2 (a) (ii)** Outline how an ethanol molecule reacts with an ethanal molecule in the first step of this mechanism. Include two curly arrows to show the movement of electron pairs.

**[2 marks]**



Be careful they only want the first step here. (In real life this isn't actually quite right but it is what they want!)

**2 (b)** The reaction produces a racemic mixture of chiral molecules.

**2 (b) (i)** Explain the meaning of the term racemic mixture.

**[1 mark]**

Equal mixture of enantiomers.

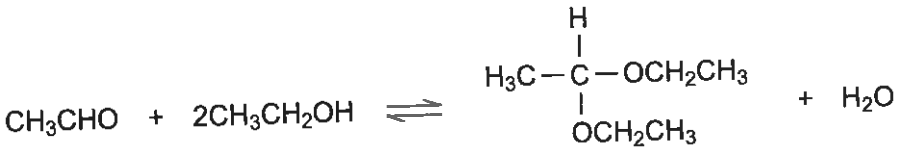
**2 (b) (ii)** State the relationship between two chiral molecules with the same structural formula.

**[1 mark]**

They are non-superimposable mirror images of each other.

**2 (c)** In the presence of an acid catalyst such as dry hydrogen chloride, ethanal reacts with an excess of ethanol to form an acetal.

The overall reaction of ethanal with an excess of ethanol forms an equilibrium mixture as shown. All reactants and products are liquids.



an acetal

A mixture of 0.75 mol of ethanal and 5.00 mol of ethanol was left to reach equilibrium in the presence of dry hydrogen chloride at a given temperature. The equilibrium mixture contained 0.42 mol of the acetal.

**2 (c) (i)** Calculate the amount, in moles, of ethanal and of ethanol in this equilibrium mixture. **[2 marks]**

Amount of ethanal 0·33 mol

Amount of ethanol 4·16 mol

Space for working

| | $CH_3CHO$ | + $2CH_3CH_2OH$ ⇌ | Acetal | + water | |
|---|---|---|---|---|---|
| I | 0·75 | 5·00 | | | |
| Eq | 0·75 − 0·42 = 0·33 | 5 − (0·42 × 2) = 4·16 | 0·42 | 0·42 | |

Do not write outside the box

**2 (c) (ii)** In a different experiment using the same reaction as in part **(c)**, an equilibrium mixture was established at a given temperature.
This mixture contained 0.58 mol of ethanal, 3.76 mol of ethanol, 0.37 mol of the acetal and 0.65 mol of water in a total volume of 310 $cm^3$.

Write an expression for the equilibrium constant $K_c$ for this reaction.
Calculate a value for $K_c$ at this temperature. Give units with your answer.

**[4 marks]**

$K_c$ $K_c = \frac{[\text{acetal}][H_2O]}{[CH_3CHO][CH_3CH_2OH]^2}$ $\frac{310}{1000} = 0.310\,dm^3$

Calculation

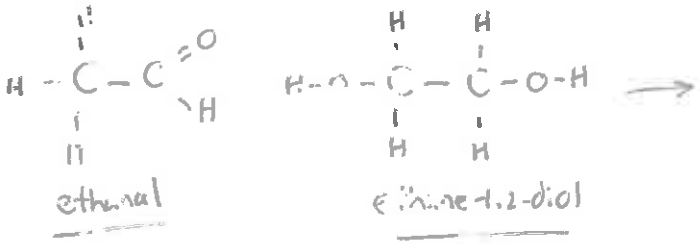
$K_c = \frac{(0.37)}{(0.310)} \times \frac{(0.65)}{(0.310)}$ $\frac{mol\,dm^{-3} \times mol\,dm^{-3}}{mol\,dm^{-3} \times mol\,dm^{-3} \times mol\,dm^{-3}}$

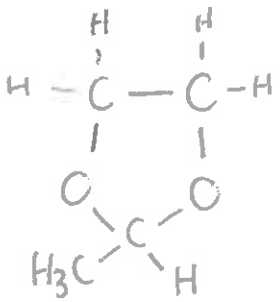
$\frac{(0.58)}{(0.310)} \times \frac{(3.76)^2}{(0.310)}$

$K_c = 9.09 \times 10^{-3}\ mol^{-1}\,dm^3$

**2 (d)** Draw the structure of the acetal ($C_4H_8O_2$) formed by the reaction of ethanal with ethane-1,2-diol.

**[1 mark]**



tough question but the trick here is to use the given molecular formula to come up with an answer!

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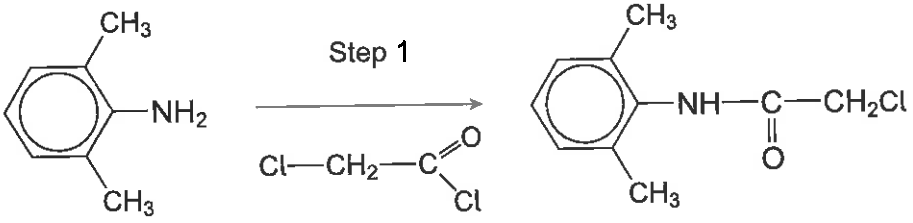
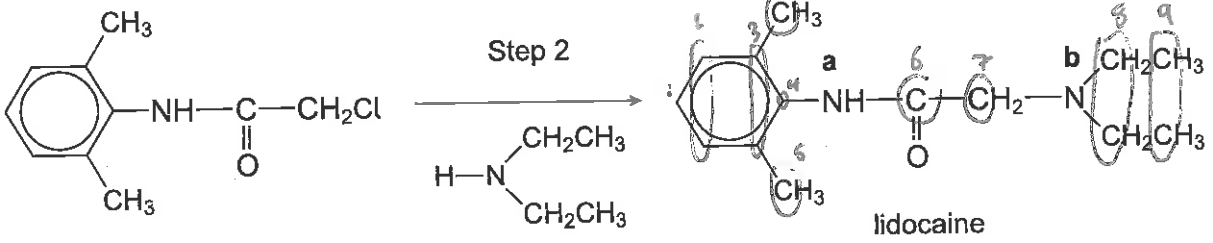
**3** Lidocaine is a local anaesthetic used in dentistry and in minor surgical operations. The synthesis of lidocaine in 2 steps from 2,6-dimethylphenylamine is shown.




**X**




lidocaine

**Y**

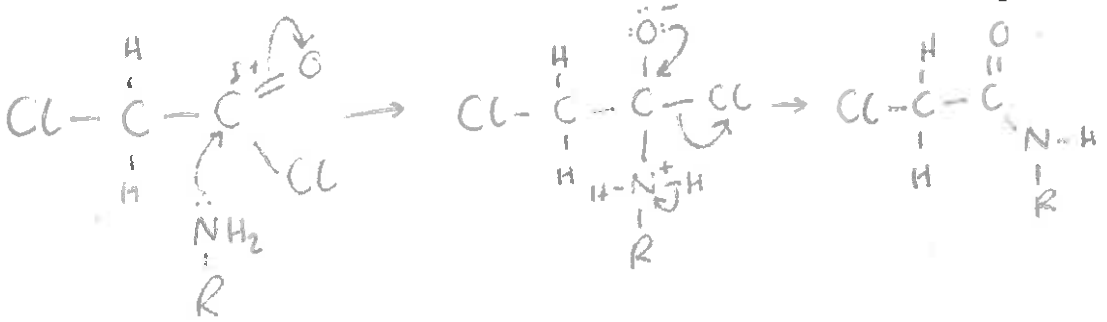
**3 (a) (i)** Give the IUPAC name of reagent **X** in Step 1.

**[1 mark]**

2-chloroethanoyl chloride

**3 (a) (ii)** Outline a mechanism for Step 1.
In your answer, use $RNH_2$ to represent 2,6-dimethylphenylamine.

**[4 marks]**



**3 (b)** Name the mechanism for Step 2.

**[1 mark]**

Nucleophilic Substitution.

**3 (c)** Which of these is the total number of peaks in the $^{13}C$ n.m.r spectrum of lidocaine?

Tick (✓) one box.

[see other page for diagram with labelled carbons.]

**[1 mark]**

| 8 | | 9 | ✓ | 11 | | 12 | |
|---|---|---|---|---|---|---|---|

**3 (d)** Calculate the percentage by mass of hydrogen in a molecule of lidocaine.

**[2 marks]**

lidocaine = $C_{14}H_{22}N_2O$ $M_r = 234$

$\frac{22}{234} \times 100 = 9.4\%$

**3 (e)** Give the name, including the classification, of the functional group that contains the nitrogen atom labelled **b**.

(N atom with three R groups)

**[1 mark]**

Tertiary amine

**3 (f)** Lidocaine is used medically as the salt lidocaine hydrochloride.

**3 (f) (i)** Suggest which one of the nitrogen atoms labelled **a** or **b** is protonated in lidocaine hydrochloride. Explain your answer.

This is an example of the positive inductive effect.

**[3 marks]**

Nitrogen atom protonated b

Explanation alkyl groups release electrons to Nitrogen meaning lone pair on b is more readily available

**3 (f) (ii)** Suggest why lidocaine hydrochloride is used medically in preference to lidocaine. Explain your answer.

**[2 marks]**

lidocaine hydrochloride is an ionic salt a therefore more soluble.

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**4** Compound **X** ($ClCH_2COCl$) is used as a reagent in organic synthesis.

**4 (a)** The mass spectrum of **X** contains several molecular ion peaks.

**4 (a) (i)** Chlorine exists as the isotopes $^{35}Cl$ and $^{37}Cl$ in a 3:1 ratio.

Calculate the *m/z* value of the most abundant molecular ion peak in the mass spectrum of **X**.

Both chlorine atoms = 35

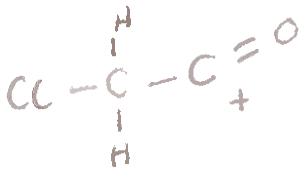
**[1 mark]**

35 + 12 + 2 + 12 + 16 + 35 = 112

**4 (a) (ii)** The most abundant fragment ion in the mass spectrum of **X** has *m/z* = 77.

Draw the **displayed** formula of this fragment ion.

**[1 mark]**



112 - 35 = 77! the chlorine would be lost from the acyl chloride easily.

**4 (a) (iii)** A molecular ion of **X** that contains one $^{35}Cl$ atom and one $^{37}Cl$ atom undergoes fragmentation to form an ion with *m/z* = 65 and one other species.

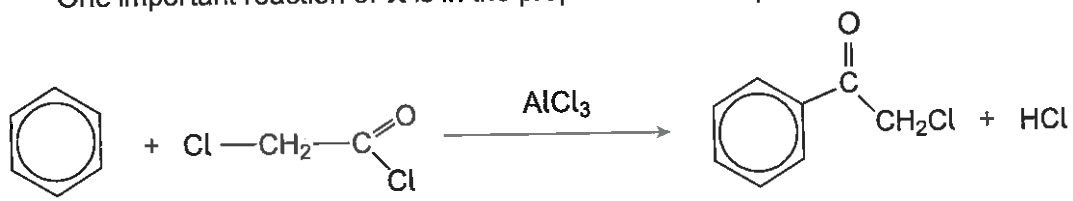
Write an equation for this fragmentation. Show which isotope of chlorine is present in each product species.

Don't forget its a positive ion and the free radical is lost.

**[2 marks]**

$[ClCH_2COCl]^+ \longrightarrow [^{35}ClCH_2]^\bullet + [CO^{37}Cl]^+$

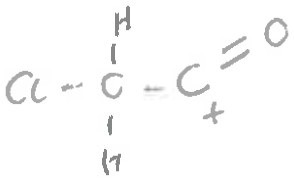
**4 (b)** One important reaction of **X** is in the preparation of compound **P** as shown.




**X** **P**

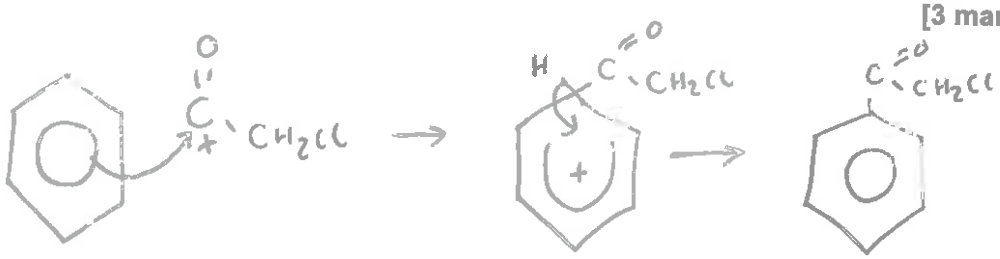
**4 (b) (i)** Draw the structure of the electrophile formed by the reaction of **X** with $AlCl_3$

**[1 mark]**

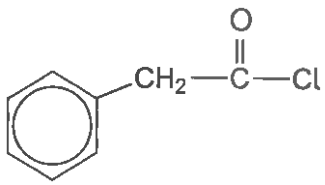


**4 (b) (ii)** Outline the mechanism for the reaction of the electrophile from part **(b)(i)** with benzene in the preparation of **P**.

**[3 marks]**



**4 (c)** Compound **Q** is an alternative product that could be formed when **X** reacts with benzene.



**Q**

Describe how you could distinguish between **P** and **Q** by a test-tube reaction. Give the reagent used and the observation with each compound.

**[3 marks]**

Reagent water

Observation with **P** No reaction

Observation with **Q** Steamy white fumes

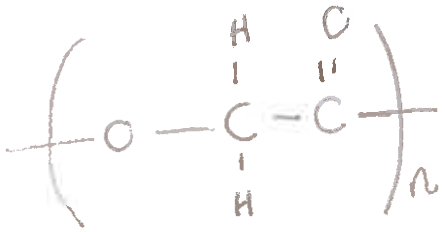
acyl chlorides react with water to give fumes of HCl.

**Turn over ▶**

**4 (d)** **X** is also used to make the compound $HOCH_2COOH$. This compound is polymerised to form the polymer known as PGA. PGA is used in surgical sutures (stitches).

**4 (d) (i)** Draw the repeating unit of PGA.

**[1 mark]**

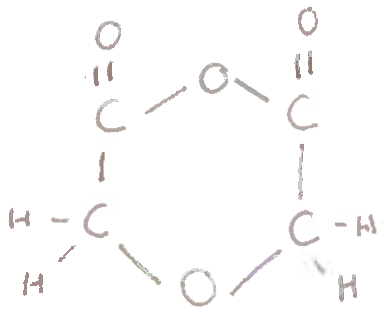


You should only draw one repeat unit here!! you could have the oxygen on the Carbonyl side if you choose.

**4 (d) (ii)** Production of PGA occurs via a cyclic compound. Two $HOCH_2COOH$ molecules react together to form the cyclic compound and two molecules of water.

Draw the structure of this cyclic compound.

**[1 mark]**

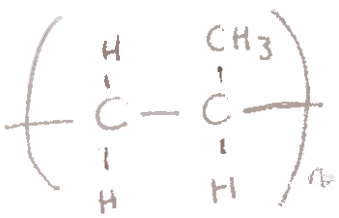


this is the same as polymerisation except your arrows bonding each end to each other!

**4 (e)** Poly(propene) is also used in surgical sutures.

**4 (e) (i)** Draw the repeating unit of poly(propene).

**[1 mark]**



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**4 (e) (ii)** Suggest an advantage of surgical sutures made from PGA rather than from poly(propene).
Explain your answer.

**[2 marks]**

As PGA has polar bonds then it is able to be broken down and hence is biodegradable.

polypropene - being non polar is not biodegradable

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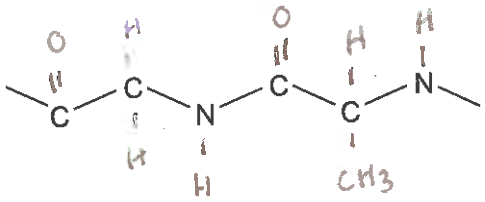
**Turn over for the next question**

**5** Proteins contain sequences of amino acids joined by peptide links.
Amino acid chains (polypeptides) are attracted to each other by hydrogen bonding.

**5 (a) (i)** A section of a protein is formed from one molecule of each of the amino acids glycine ($H_2NCH_2COOH$) and alanine ($H_2NCH(CH_3)COOH$).

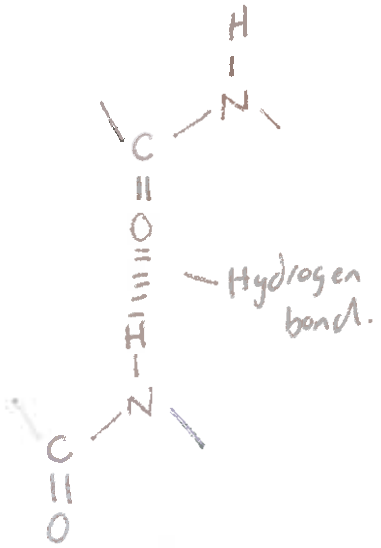
Add bonds and atoms to the diagram to complete a structural formula for this section of the protein.

**[2 marks]**



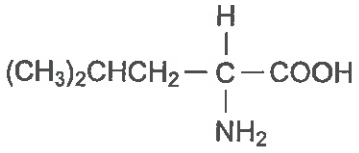

**5 (a) (ii)** Draw a diagram to show how an amino acid chain can form a hydrogen bond with another amino acid chain.
Your diagram need only show the relevant atoms from one amino acid in each chain.

**[1 mark]**

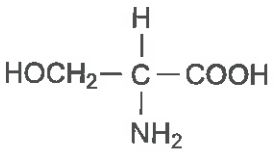



You only really need to show the peptide bond hydrogen bonding with another peptide bond.

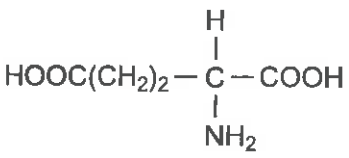
**5 (b)** Leucine, serine and glutamic acid are naturally-occurring amino acids.



leucine



serine



glutamic acid

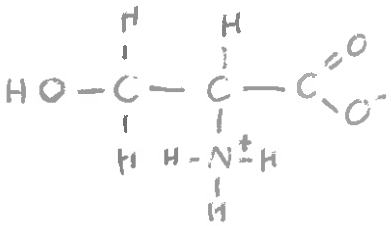
**5 (b) (i)** Give the IUPAC name of leucine.

**[1 mark]**

2-amino-4methylpentanoic acid.

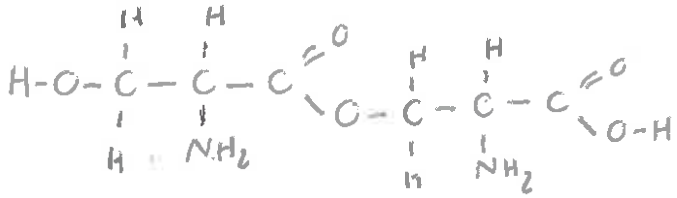
**5 (b) (ii)** Draw the structure of the zwitterion of serine.

**[1 mark]**



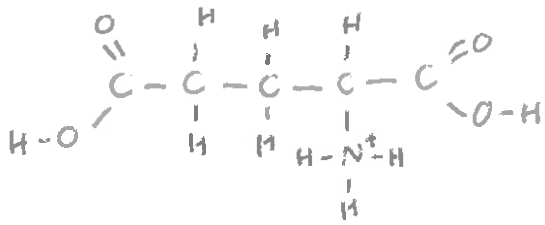
**5 (b) (iii)** Draw the structure of the ester formed by two molecules of serine.

**[1 mark]**



**5 (b) (iv)** Draw the structure of the species formed by glutamic acid at low pH.

**[1 mark]**



↑ this is acidic! $NH_2$ group will accept a proton to form $^+NH_3$.

7

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ANSWER IN THE SPACES PROVIDED

**6** The initial rate of the reaction between gases **D** and **E** was measured in a series of experiments at a constant temperature. The results are shown in **Table 1**.

**Table 1**

| Expt | Initial [D] / mol dm$^{-3}$ | Initial [E] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | $1.25 \times 10^{-2}$ | $5.81 \times 10^{-1}$ | $1.16 \times 10^{-2}$ |
| 2 | $1.88 \times 10^{-2}$ | $8.73 \times 10^{-1}$ | $3.92 \times 10^{-2}$ |
| 3 | $1.88 \times 10^{-2}$ | 1.75 | $1.57 \times 10^{-1}$ |

×1.5 ×1.5 ×3 ×2 ×4

**6 (a)** Deduce the order of reaction with respect to **D** and the order with respect to **E**.

**[2 marks]**

Order with respect to **D** 1st order

Order with respect to **E** 2nd order

Space for working for (D): $1.16 \times 10^{-2} \times 3^2 = 1.044 \times 10^{-1}$

$1.57 \times 10^{-1} / 1.044 \times 10^{-1} = 1.5\times$

$\therefore$ D = 1st.

I annotated the table above to help you work this out.

**6 (b)** Suggest why initial rates of reaction are used to determine these orders rather than rates of reaction at other times during the experiments.

**[1 mark]**

At a time of zero concentrations are known.

**6 (c)** State how the initial rate is obtained from a graph of the concentration of the product against time.

**[2 marks]**

Calculate the gradient of the slope when time = zero seconds.

5

Turn over ▶

**7** The reaction between propanone and iodine in the presence of hydrochloric acid was studied at a constant temperature.

$$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$$

The following rate equation was deduced.

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

**7 (a)** Suggest why the order with respect to iodine is zero.

**[1 mark]**

As iodine is not involved in the rate determining step.

**7 (b)** In an experiment the initial concentrations of propanone, iodine and hydrochloric acid were as shown in **Table 2**. The initial rate of reaction in this experiment was $8.64 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$.

**Table 2**

| | Initial concentration / mol dm$^{-3}$ |
|---|---|
| $CH_3COCH_3$ | $5.82 \times 10^{-2}$ |
| $I_2$ | $1.78 \times 10^{-3}$ |
| $H^+$ | $4.76 \times 10^{-1}$ |

Use the data in **Table 2** and the rate equation to calculate a value for the rate constant at this temperature.
Give units with your answer.

**[2 marks]**

$k = \dfrac{\text{rate}}{[CH_3COCH_3][H^+]}$ $\quad k = \dfrac{8.64\times10^{-7}}{(5.82\times10^{-2} \times 4.76\times10^{-1})}$

$k = 3.12\times10^{-5}$ mol$^{-1}$ dm$^3$ s$^{-1}$ $\quad \dfrac{\text{mol dm}^{-3}\,(s^{-1})}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}$

**7 (c)** A series of experiments was carried out using concentrations of propanone approximately 100 times the concentrations of iodine and hydrochloric acid.

Suggest the rate equation under these conditions.
Explain your answer.

**[2 marks]**

As propanone is so large it is effectively constant therefore

rate = k[H+]

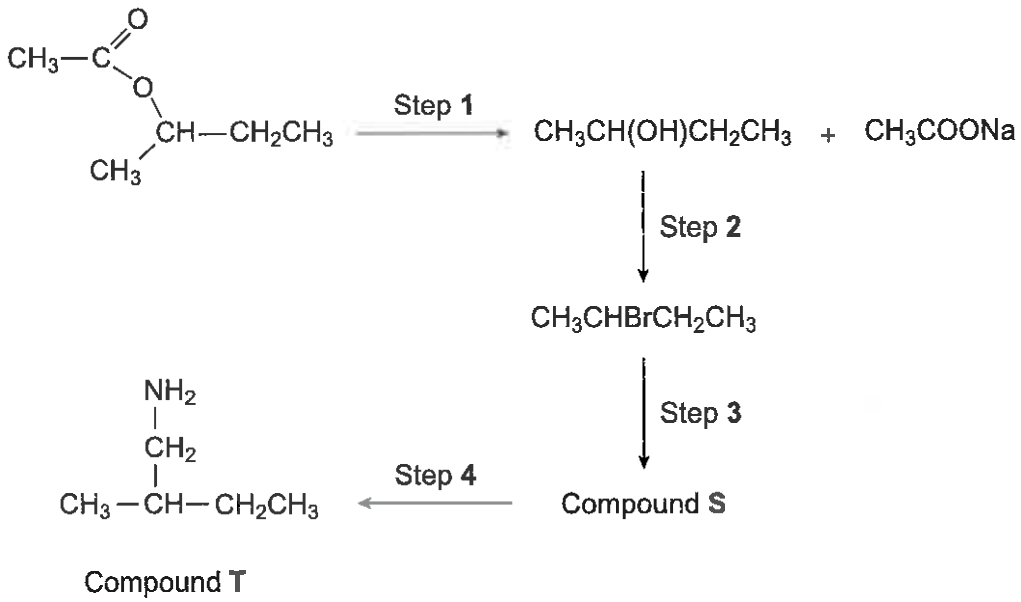
5

**Turn over for the next question**

## Section B

Answer **all** questions in the spaces provided.

**8** A four-step synthesis of compound **T** is shown.



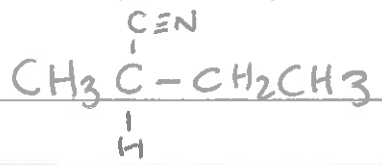

**8 (a)** Give the reagent and conditions for Step **1**.
State how you could obtain a sample of the alcohol from the reaction mixture formed in Step **1**.

**[3 marks]**

NaOH in aqueous conditions and alcohol to be distilled off.

This is alkaline hydrolysis of esters. Alcohol distilled off due to lower b.p

**8 (b)** Draw the structure of compound **S**.
For each of Steps **3** and **4**, give a reagent and one condition, other than heat.
**[5 marks]**



to form this from the halloalkane then add KCN in ethanolic conditions.

to change nitrile into amine then add $LiAlH_4$ in ether.

This is reasonably straight forward if you know your conditions.

8

**9** Compound **R** contains 61.0% carbon and 11.9% hydrogen by mass. The remainder is oxygen.
The mass spectrum of **R** contains a molecular ion peak at $m/z = 118$

**9 (a)** Use these data to show that the molecular formula of **R** is $C_6H_{14}O_2$ **[3 marks]**

C H O

$\frac{61.0}{12} = \frac{11.9}{1} = \frac{27.1}{16} =$

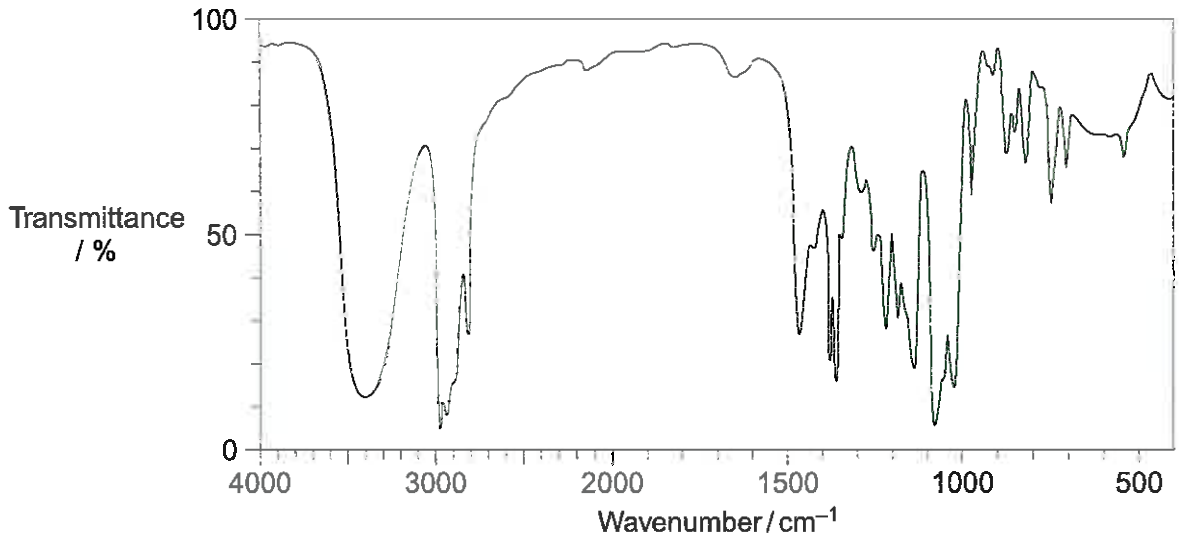
$\frac{5.083}{1.694} \quad \frac{11.9}{1.694} \quad \frac{1.694}{1.694}$

$= 3 \quad = 7 \quad = 1$

$C_3H_7O = 59 \times 2 = 118 \therefore C_6H_{14}O_2$

**9 (b)** The infrared spectrum of **R** ($C_6H_{14}O_2$) is shown in **Figure 1**.

**Figure 1**




The proton n.m.r. spectrum of **R** contains five peaks. The chemical shift values, integration ratios and splitting patterns of these peaks are given in **Table 3**.

**Table 3**

| **Chemical shift/ppm** | 3.8 | 3.2 | 3.1 | 1.4 | 1.1 |
|---|---|---|---|---|---|
| **Integration ratio** | 2 | 3 | 1 | 2 | 6 |
| **Splitting patterns** | triplet | singlet | singlet | triplet | singlet |

Do not write outside the box

When **R** is warmed with acidified potassium dichromate(VI) a green solution is formed.

Use **Table A** and **Table B** on the data sheet and all of the data provided in the question to deduce the structure of **R**.
In your answer, explain how you have used the data provided in the question.

**[9 marks]**

$C_6H_{14}O_2$

I.R Spec

- O–H alcohol (a) 3400cm$^{-1}$
- No C=O peak at 1750cm$^{-1}$
- C–O peak at 1300cm$^{-1}$

R turns acidified dichromate green ∴ 1° or 2° alcohol!

NmR: peak (a) 3.1 is singlet and integration of 2 – (O–H)

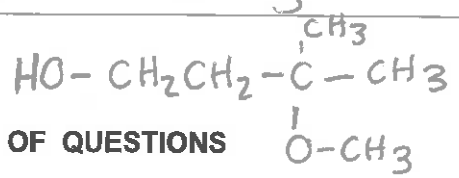
peaks (a) 3.8 is triplet and so is 1.4

so $-CH_2-CH_2-$

peak (a) 1.1 has 6 in the environment so equivalence.

also singlet so ~~not~~ attached to a (H).

peak (a) 3.2 $-OCH_3$



This was a real toughie. I would advise you to write all NMR ideas and do your best with structures for interpretations. Lots of marks

**END OF QUESTIONS**

12

There are no questions printed on this page

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ANSWER IN THE SPACES PROVIDED