Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
8	
TOTAL	

General Certificate of Education
Advanced Level Examination
January 2013

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Monday 14 January 2013 1.30 pm to 3.15 pm

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

Time allowed
- 1 hour 45 minutes

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 75 minutes on **Section A** and about 30 minutes on **Section B**.

Section A

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

1 (a) The data in the following table were obtained in two experiments about the rate of the reaction between substances **B** and **C** at a constant temperature.

Experiment	Initial concentration of **B** / mol dm^{-3}	Initial concentration of **C** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	4.2×10^{-2}	2.6×10^{-2}	8.4×10^{-5}
2	6.3×10^{-2}	7.8×10^{-2}	To be calculated

The rate equation for this reaction is known to be

$$\text{rate} = k[\mathbf{B}]^2[\mathbf{C}]$$

1 (a) (i) Use the data from Experiment **1** to calculate a value for the rate constant k at this temperature and deduce its units.

Calculation .....

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Units .....

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(3 marks)

(Extra space) .....

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1 (a) (ii) Calculate a value for the initial rate in Experiment **2**.

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(1 mark)

1 (b) The data in the following table were obtained in a series of experiments about the rate of the reaction between substances **D** and **E** at a constant temperature.

Experiment	Initial concentration of **D** / mol dm^{-3}	Initial concentration of **E** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
3	0.13	0.23	0.26×10^{-3}
4	0.39	0.23	2.34×10^{-3}
5	0.78	0.46	9.36×10^{-3}

1 (b) (i) Deduce the order of reaction with respect to **D**.

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(1 mark)

1 (b) (ii) Deduce the order of reaction with respect to **E**.

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(1 mark)

Question 1 continues on the next page

1 (c) The compound $(CH_3)_3CBr$ reacts with aqueous sodium hydroxide as shown in the following equation.

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$

This reaction was found to be first order with respect to $(CH_3)_3CBr$ but zero order with respect to hydroxide ions.

The following two-step process was suggested.

Step **1** $(CH_3)_3CBr \longrightarrow (CH_3)_3C^+ + Br^-$

Step **2** $(CH_3)_3C^+ + OH^- \longrightarrow (CH_3)_3COH$

1 (c) (i) Deduce the rate-determining step in this two-step process.

.....

(1 mark)

1 (c) (ii) Outline a mechanism for this step using a curly arrow.

(1 mark)

8

2 In this question, give all values of pH to 2 decimal places.

2 (a) The ionic product of water has the symbol K_w

2 (a) (i) Write an expression for the ionic product of water.

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(1 mark)

2 (a) (ii) At 42 °C, the value of K_w is 3.46×10^{-14} mol^2 dm^{-6}.

Calculate the pH of pure water at this temperature.

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(2 marks)

2 (a) (iii) At 75 °C, a 0.0470 mol dm^{-3} solution of sodium hydroxide has a pH of 11.36

Calculate a value for K_w at this temperature.

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(2 marks)

Question 2 continues on the next page

2 (b) Methanoic acid (HCOOH) dissociates slightly in aqueous solution.

2 (b) (i) Write an equation for this dissociation.

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(1 mark)

2 (b) (ii) Write an expression for the acid dissociation constant K_a for methanoic acid.

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(1 mark)

2 (b) (iii) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25 °C.

Calculate the pH of a 0.0560 mol dm^{-3} solution of methanoic acid.

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(3 marks)

2 (b) (iv) The dissociation of methanoic acid in aqueous solution is endothermic.

Deduce whether the pH of a solution of methanoic acid will increase, decrease or stay the same if the solution is heated. Explain your answer.

Effect on pH .....

Explanation .....

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(3 marks)

(Extra space) .....

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Do not write outside the box

2 (c) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25 °C.
A buffer solution is prepared containing 2.35×10^{-2} mol of methanoic acid and 1.84×10^{-2} mol of sodium methanoate in 1.00 dm^3 of solution.

2 (c) (i) Calculate the pH of this buffer solution at 25 °C.

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(3 marks)

(Extra space) .....

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2 (c) (ii) A 5.00 cm^3 sample of 0.100 mol dm^{-3} hydrochloric acid is added to the buffer solution in part **(c) (i)**.

Calculate the pH of the buffer solution after this addition.

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(4 marks)

(Extra space) .....

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20

Turn over ▶

3 Esters are produced by the reaction of alcohols with other esters and by the reaction of alcohols with carboxylic acids.

3 (a) The esters which make up biodiesel are produced industrially from the esters in vegetable oils.

3 (a) (i) Complete the equation for this formation of biodiesel.

$$\begin{array}{l} CH_2OOCC_{17}H_{35} \\ | \\ CHOOCC_{17}H_{31} \\ | \\ CH_2OOCC_{17}H_{29} \end{array} + \text{.....} \rightleftharpoons \begin{array}{l} C_{17}H_{35}COOCH_3 \\ C_{17}H_{31}COOCH_3 \\ C_{17}H_{29}COOCH_3 \end{array} + \text{.....}$$

(2 marks)

3 (a) (ii) Write an equation for the complete combustion of $C_{17}H_{35}COOCH_3$

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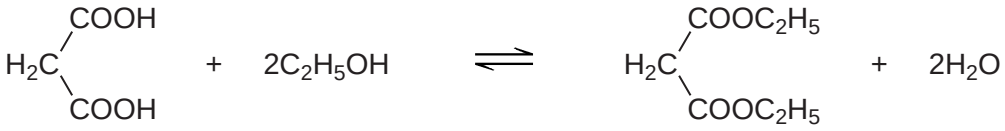
(2 marks)

3 (b) The ester commonly known as diethyl malonate (**DEM**) occurs in strawberries and grapes. It can be prepared from acid **A** according to the following equilibrium.



A **DEM**

3 (b) (i) A mixture of 2.50 mol of **A** and 10.0 mol of ethanol was left to reach equilibrium in an inert solvent in the presence of a small amount of concentrated sulfuric acid. The equilibrium mixture formed contained 1.80 mol of **DEM** in a total volume, V dm^3, of solution.

Calculate the amount (in moles) of **A**, of ethanol and of water in this equilibrium mixture.

Moles of **A** .....

Moles of ethanol .....

Moles of water.....

(3 marks)

Do not write outside the box

3 (b) (ii) The total volume of the mixture in part **(b) (i)** was doubled by the addition of more of the inert solvent.

State and explain the effect of this addition on the equilibrium yield of **DEM**.

Effect .....

Explanation .....

.....

(2 marks)

3 (b) (iii) Using **A** to represent the acid and **DEM** to represent the ester, write an expression for the equilibrium constant K_c for the reaction.

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(1 mark)

3 (b) (iv) In a second experiment, the equilibrium mixture was found to contain 0.85 mol of **A**, 7.2 mol of ethanol, 2.1 mol of **DEM** and 3.4 mol of water.

Calculate a value of K_c for the reaction and deduce its units.

Calculation.....

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Units.....

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(3 marks)

13

Turn over ▶

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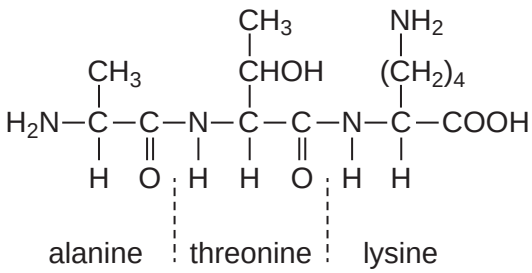
4 (a) The tripeptide shown is formed from the amino acids alanine, threonine and lysine.



4 (a) (i) Draw a separate circle around **each** of the asymmetric carbon atoms in the tripeptide.

(1 mark)

4 (a) (ii) Draw the zwitterion of alanine.

(1 mark)

4 (a) (iii) Give the IUPAC name of threonine.

.....

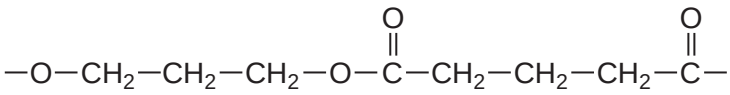
(1 mark)

4 (a) (iv) Draw the species formed by lysine at low pH.

(1 mark)

Question 4 continues on the next page

4 (b) The repeating unit shown represents a polyester.



4 (b) (i) Name this type of polymer.

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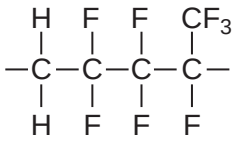
(1 mark)

4 (b) (ii) Give the IUPAC name for the alcohol used to prepare this polyester.

.....

(1 mark)

4 (c) The repeating unit shown represents a polyalkene co-polymer. This co-polymer is made from two different alkene monomers.



4 (c) (i) Name the type of polymerisation occurring in the formation of this co-polymer.

.....

(1 mark)

4 (c) (ii) Draw the structure of each alkene monomer.

Alkene monomer 1 Alkene monomer 2

(2 marks)

Do not write outside the box

4 (d) One of the three compounds shown in parts **(a)**, **(b)** and **(c)** **cannot** be broken down by hydrolysis.

Write the letter **(a)**, **(b)** or **(c)** to identify this compound and explain why hydrolysis of this compound does **not** occur.

Compound .....

Explanation .....

.....

.....

(2 marks)

11

Turn over for the next question

5 This question concerns isomers of $C_6H_{12}O_2$ and how they can be distinguished using n.m.r. spectroscopy.

5 (a) The non-toxic, inert substance TMS is used as a standard in recording both ^1H and ^{13}C n.m.r. spectra.

5 (a) (i) Give **two** other reasons why TMS is used as a standard in recording n.m.r. spectra.

Reason 1 .....

.....

Reason 2 .....

.....

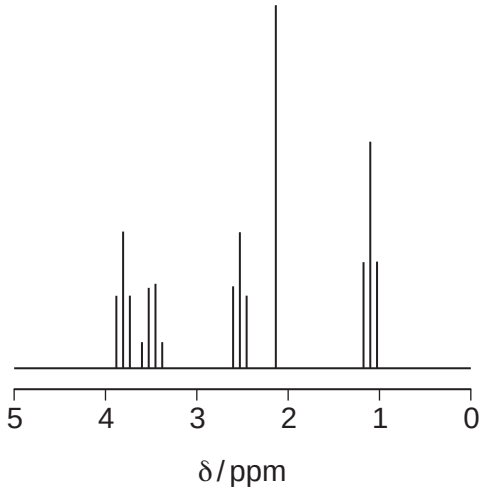
(2 marks)

5 (a) (ii) Give the structural formula of TMS.

(1 mark)

5 (b) The proton n.m.r. spectrum of compound **P** ($C_6H_{12}O_2$) is represented in **Figure 1**.

Figure 1



The integration trace gave information about the five peaks as shown in **Figure 2**.

Figure 2

δ / ppm	3.8	3.5	2.6	2.2	1.2
Integration ratio	2	2	2	3	3

Do not write outside the box

5 (b) (i) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peak at δ 2.2

(1 mark)

5 (b) (ii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.5 and 1.2

(1 mark)

5 (b) (iii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.8 and 2.6

(1 mark)

5 (b) (iv) Deduce the structure of **P**.

(1 mark)

Question 5 continues on the next page

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5 (c) These questions are about different isomers of **P** ($C_6H_{12}O_2$).

5 (c) (i) Draw the structures of the two esters that both have only two peaks in their proton n.m.r. spectra. These peaks both have an integration ratio of 3:1

Ester 1

Ester 2

(2 marks)

5 (c) (ii) Draw the structure of an optically active carboxylic acid with five peaks in its ^{13}C n.m.r. spectrum.

(1 mark)

5 (c) (iii) Draw the structure of a cyclic compound that has only two peaks in its ^{13}C n.m.r. spectrum and has no absorption for C = O in its infrared spectrum.

(1 mark)

11

Turn over for the next question

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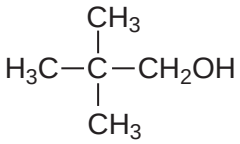
ANSWER IN THE SPACES PROVIDED

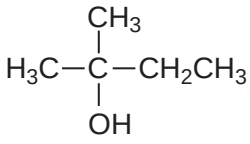
6 Describe how you could distinguish between the compounds in the following pairs using **one** simple test-tube reaction in each case.

For each pair, identify a reagent and state what you would observe when both compounds are tested separately with this reagent.

6 (a)



R



S

Reagent .....

Observation with **R** .....

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Observation with **S** .....

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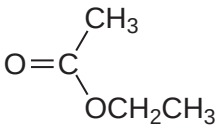
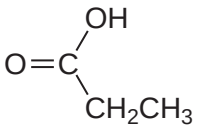
(3 marks)

6 (b)



T



U

Reagent .....

Observation with **T** .....

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Observation with **U** .....

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(3 marks)

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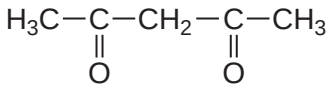
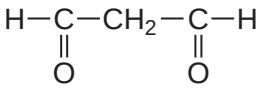
6 (c)



V



W

Reagent .....

Observation with **V** .....

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Observation with **W** .....

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(3 marks)

9

Turn over for the next question

Section B

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

7 Each of the following conversions involves reduction of the starting material.

7 (a) Consider the following conversion.

Identify a reducing agent for this conversion.

Write a balanced equation for the reaction using molecular formulae for the nitrogen-containing compounds and [H] for the reducing agent.

Draw the repeating unit of the polymer formed by the product of this reaction with benzene-1,4-dicarboxylic acid.

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(5 marks)

(Extra space) .....

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7 (b) Consider the following conversion.

Identify a reducing agent for this conversion.

State the empirical formula of the product.

State the bond angle between the carbon atoms in the starting material and the bond angle between the carbon atoms in the product.

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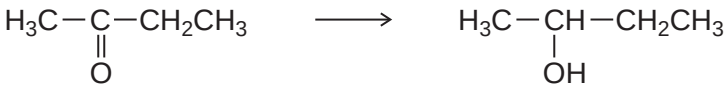
(4 marks)

Question 7 continues on the next page

Do not write outside the box

7 (c) The reducing agent in the following conversion is $NaBH_4$



7 (c) (i) Name and outline a mechanism for the reaction.

Name of mechanism .....

Mechanism

(5 marks)

7 (c) (ii) By considering the mechanism of this reaction, explain why the product formed is optically inactive.

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(3 marks)

17

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8 Acyl chlorides such as CH_3COCl are useful compounds in synthesis.

8 (a) The acyl chloride CH_3COCl reacts with benzene.

8 (a) (i) Write an equation for this reaction and name the organic product.

Identify a catalyst for the reaction.

Write an equation to show how this catalyst reacts with CH_3COCl to produce a reactive intermediate.

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(4 marks)

8 (a) (ii) Name and outline a mechanism for the reaction of benzene with the reactive intermediate in part **(a) (i)**.

Name of mechanism .....

Mechanism

(4 marks)

Question 8 continues on the next page

Turn over ▶

Do not write outside the box

8 (b) Nucleophiles such as alcohols can react with CH_3COCl
The ion CH_3COO^- can act as a nucleophile in a similar way.

State the meaning of the term *nucleophile*.

Draw the structure of the organic product formed by the reaction of CH_3COO^- with CH_3COCl

Name the functional group produced in this reaction.

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(3 marks)

11

END OF QUESTIONS