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	

AQA

General Certificate of Education
Advanced Level Examination
June 2014

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Monday 9 June 2014 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a ruler with millimetre measurements
- 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 70 minutes on **Section A** and about 35 minutes on **Section B**.

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Section A

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

1 This question is about the gaseous equilibrium between compounds **E**, **F** and **G** as shown in the equation.

$$\mathbf{E}(g) + 2\mathbf{F}(g) \rightleftharpoons 2\mathbf{G}(g) \qquad \Delta H = -50 \text{ kJ mol}^{-1}$$

1 (a) A 2.0 mol sample of **E** was heated in a sealed container with a 1.0 mol sample of **F**. Equilibrium was established at a given temperature and the equilibrium mixture formed contained 0.80 mol of **G**.

Calculate the amount, in moles, of **E** and of **F** in this equilibrium mixture.

[2 marks]

Moles of **E** .....

Moles of **F** .....

1 (b) Write an expression for the equilibrium constant K_c for this equilibrium.
State the units of K_c

[2 marks]

Expression .....

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Units .....

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Do not write outside the box

1 (c) A different mixture of **E** and **F** reached equilibrium at temperature T_1 in a container of volume 1.50 dm^3. This equilibrium mixture contained 2.50 mol of **E**, 1.20 mol of **F** and 0.85 mol of **G**.

Calculate a value of K_c for the equilibrium at temperature T_1

[2 marks]

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1 (d) The mixture in Question **1 (c)** was allowed to reach equilibrium at temperature T_1 in a different container of volume 3.00 dm^3.

State whether the amount of **G** in the equilibrium mixture will increase, decrease or stay the same. Explain your answer.

[3 marks]

Effect on the amount of **G** .....

Explanation .....

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1 (e) The mixture in Question **1 (c)** was allowed to reach equilibrium at temperature T_2 in the original container of volume 1.50 dm^3.

The value of K_c for the equilibrium was found to have increased.

State and explain which of T_1 or T_2 is the higher temperature.

[3 marks]

Higher temperature .....

Explanation .....

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2 This question is about alkalis and carboxylic acids.

In this question, all data are quoted at 25 ºC.

2 (a) Carboxylic acids are weak acids.

State the meaning of the term **weak** as applied to carboxylic acids.

[1 mark]

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2 (b) Write an equation for the reaction of propanoic acid with sodium carbonate.

[1 mark]

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2 (c) Calculate the pH of a 0.0120 mol dm^{-3} solution of calcium hydroxide.
The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}.
Give your answer to 2 decimal places.

[3 marks]

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[Extra space].....

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2 (d) The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

2 (d) (i) Write an expression for the acid dissociation constant K_a for benzenecarboxylic acid.

[1 mark]

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2 (d) (ii) Calculate the pH of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid. Give your answer to 2 decimal places.

[3 marks]

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[Extra space] .....

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Question 2 continues on the next page

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2 (d) (iii) A buffer solution with a pH of 4.00 is made using benzenecarboxylic acid and sodium benzenecarboxylate.

Calculate the mass of sodium benzenecarboxylate (M_r = 144.0) that should be dissolved in 1.00 dm^3 of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid to produce a buffer solution with a pH of 4.00

The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

[5 marks]

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[Extra space] .....

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2 (e) Two solutions, one with a pH of 4.00 and the other with a pH of 9.00, were left open to the air.

The pH of the pH 9.00 solution changed more than that of the other solution.

Suggest what substance might be present in the air to cause the pH to change.
Explain how and why the pH of the pH 9.00 solution changes.

[3 marks]

Substance present in air .....

Explanation .....

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17

Turn over for the next question

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3 (a) **Table 1** shows the results of three experiments to investigate the rate of reaction between compounds **A** and **B** dissolved in a given solvent.
All three experiments were carried out at the same temperature.

Table 1

	Experiment 1	**Experiment 2**	**Experiment 3**
Initial concentration of A / mol dm^{-3}	1.60×10^{-2}	2.40×10^{-2}	3.60×10^{-2}
Initial concentration of B / mol dm^{-3}	4.20×10^{-2}	6.30×10^{-2}	6.30×10^{-2}
Initial rate / mol dm^{-3} s^{-1}	8.00×10^{-5}	1.80×10^{-4}	4.05×10^{-4}

3 (a) (i) Deduce the order of reaction with respect to **A**.
Tick (✓) **one** box.

[1 mark]

Order of reaction with respect to A	**Tick (✓)**
0	
1	
2	

3 (a) (ii) Deduce the order of reaction with respect to **B**.
Tick (✓) **one** box.

[1 mark]

Order of reaction with respect to B	**Tick (✓)**
0	
1	
2	

Do not write outside the box

3 (b) The reaction between two different compounds, **C** and **D**, is studied at a given temperature.
The rate equation for the reaction is found to be

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

3 (b) (i) When the initial concentration of **C** is 4.55×10^{-2} mol dm^{-3} and the initial concentration of **D** is 1.70×10^{-2} mol dm^{-3}, the initial rate of reaction is 6.64×10^{-5} mol dm^{-3} s^{-1}.

Calculate the value of the rate constant at this temperature and deduce its units.

[3 marks]

Calculation .....

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Units of rate constant .....

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3 (b) (ii) The experiment in Question **3 (b) (i)** is repeated at the same temperature but after the addition of extra solvent so that the total volume of the mixture is doubled.

Deduce the new initial rate of reaction.

[1 mark]

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Turn over for the next question

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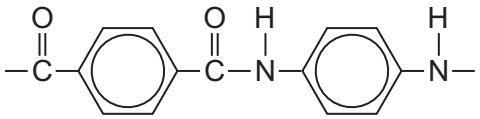
4 Kevlar is a polymer used in protective clothing.
The repeating unit within the polymer chains of Kevlar is shown.



4 (a) Name the strongest type of interaction between polymer chains of Kevlar.

[1 mark]

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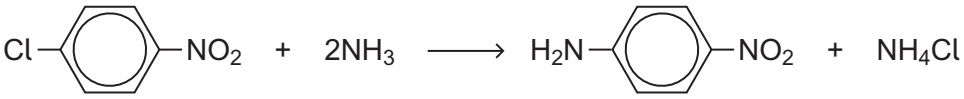
4 (b) One of the monomers used in the synthesis of Kevlar is

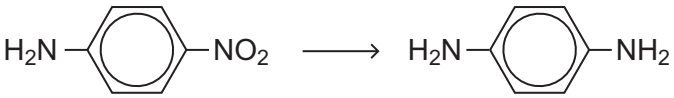
An industrial synthesis of this monomer uses the following two-stage process starting from compound **X**.

Stage **1**



X

Stage **2**



4 (b) (i) Suggest why the reaction of ammonia with **X** in Stage **1** might be considered unexpected.

[2 marks]

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4 (b) (ii) Suggest a combination of reagents for the reaction in Stage **2**.

[1 mark]

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4 (b) (iii) Compound **X** can be produced by nitration of chlorobenzene.

Give the combination of reagents for this nitration of chlorobenzene.
Write an equation or equations to show the formation of a reactive intermediate from these reagents.

[3 marks]

Reagents .....

.....

Equation(s) .....

.....

4 (b) (iv) Name and outline a mechanism for the formation of **X** from chlorobenzene and the reactive intermediate in Question **4 (b) (iii)**.

[4 marks]

Name of mechanism .....

Mechanism

Turn over for the next question

11

Do not write outside the box

5 The carbonyl compound CH_3CH_2CHO reacts very slowly with HCN

5 (a) Name and outline a mechanism for the reaction of CH_3CH_2CHO with HCN

[5 marks]

Name of mechanism .....

Mechanism

5 (b) The reaction in Question **5 (a)** produces a pair of enantiomers.

5 (b) (i) Draw the structure of each enantiomer to show how they are related to each other.

[2 marks]

Do not write outside the box

5 (b) (ii) State and explain how you could distinguish between the two enantiomers.

[2 marks]

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5 (c) Give the IUPAC name of the product of the reaction in Question **5 (a)**.

[1 mark]

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5 (d) In practice, KCN rather than HCN is added to the carbonyl compound.

Given that K_a for HCN = 4.0×10^{-10} mol dm^{-3}, suggest why the reaction with HCN is very slow.

[2 marks]

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Question 5 continues on the next page

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5 (e) Acrylic fibres are used as a substitute for wool. Acrylics are copolymers of acrylonitrile with other compounds.

Acrylonitrile is the common name for the following compound.

$$H_2C = CH - C \equiv N$$

5 (e) (i) Acrylonitrile can be formed from propene.

Write an equation for the reaction of propene with ammonia and oxygen to form acrylonitrile and one other product.

[1 mark]

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5 (e) (ii) The term copolymer is used to describe the product obtained when two or more different monomers form a polymer.

Draw the repeating unit of the acrylic copolymer that contains 75% acrylonitrile monomer and 25% chloroethene monomer.

[1 mark]

5 (e) (iii) Name the type of polymerisation involved in Question **5 (e) (ii)**.

[1 mark]

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Turn over for the next question

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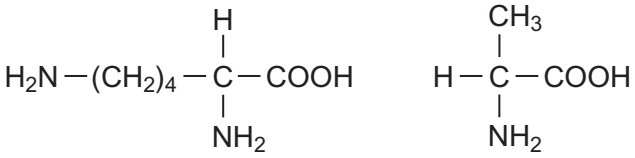
6 Lysine and alanine are two amino acids.



lysine alanine

6 (a) Give the IUPAC name of lysine.

[1 mark]

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6 (b) Draw structures to show the product formed in each case when lysine reacts with

6 (b) (i) an excess of aqueous HCl

[1 mark]

6 (b) (ii) an excess of aqueous NaOH

[1 mark]

6 (b) (iii) methanol in the presence of a small amount of concentrated H_2SO_4

[1 mark]

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6 (c) The mass spectrum of alanine gives a major peak at $m/z = 44$

Write an equation for the fragmentation of the molecular ion of alanine to give an ion that produces this peak.
In your answer, draw the displayed formula for this fragment ion.

[2 marks]

6 (d) Draw a dipeptide formed from one molecule of lysine and one molecule of alanine.

[1 mark]

6 (e) The dipeptide in Question **6 (d)** is hydrolysed in acid conditions and the mixture produced is analysed by column chromatography. The column is packed with a resin which acts as a polar stationary phase.

Suggest why lysine leaves the column after alanine.

[2 marks]

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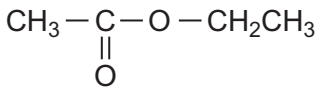
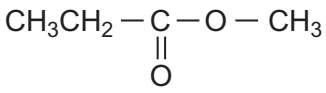
Section B

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

7 (a) **Ester 1** and **Ester 2** were studied by ^{1}H n.m.r. spectroscopy.

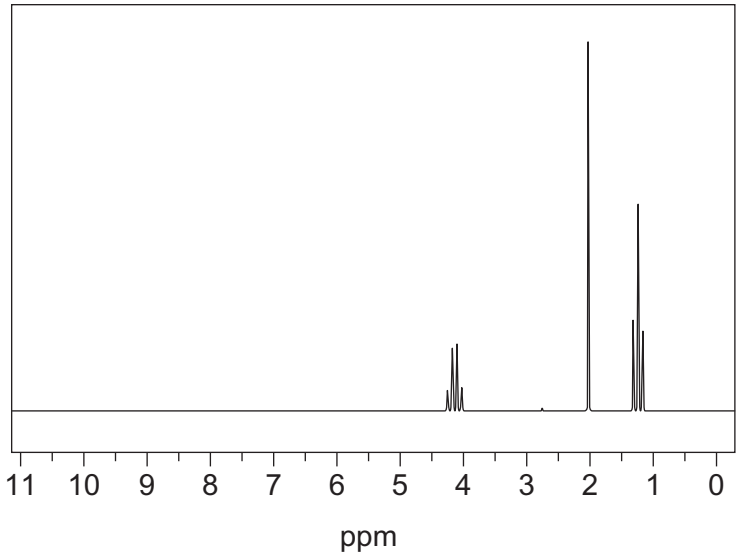


Ester 1



Ester 2

One of the two esters produced this spectrum.



Deduce which of the two esters produced the spectrum shown. In your answer, explain the position and splitting of the quartet peak at δ = 4.1 ppm in the spectrum.

Predict the δ value of the quartet peak in the spectrum of the other ester.

Use **Table B** on the Data Sheet.

[4 marks]

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7 (b) Cetrimide is used as an antiseptic.

$[CH_3(CH_2)_{15}N(CH_3)_3]^+ Br^-$

cetrimide

Name this type of compound.

Give the reagent that must be added to $CH_3(CH_2)_{15}NH_2$ to make cetrimide and state the reaction conditions.

Name the type of mechanism involved in this reaction.

[4 marks]

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7 (c) Give a reagent that could be used in a test-tube reaction to distinguish between benzene and cyclohexene.
Describe what you would see when the reagent is added to each compound and the test tube is shaken.

[3 marks]

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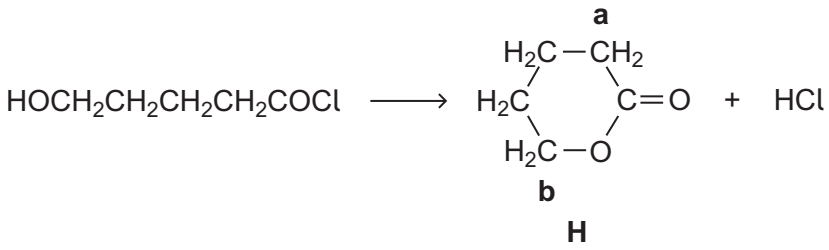
8 This question is about some isomers of $C_5H_8O_2$

8 (a) Compound **H** is a cyclic ester that can be prepared as shown.

On the structure of **H**, two of the carbon atoms are labelled.



8 (a) (i) Name and outline a mechanism for this reaction.

Use **Table C** on the Data Sheet to give the ^{13}C n.m.r. δ value for the carbon atom labelled **a** and the δ value for the carbon atom labelled **b**.

[7 marks]

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8 (a) (ii) $HOCH_2CH_2CH_2CH_2COCl$ can also react to form a polyester in a mechanism similar to that in Question **8 (a) (i)**.

Draw the repeating unit of the polyester and name the type of polymerisation involved.

[2 marks]

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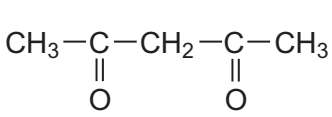
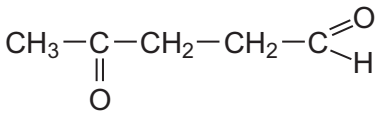
8 (b) State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the ^1H n.m.r. spectrum of each compound.

[5 marks]



J



K

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Question 8 continues on the next page

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8 (c) Draw the structure of each of the following isomers of $C_5H_8O_2$
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

L is methyl 2-methylpropenoate.

M is an ester that shows E-Z stereoisomerism.

N is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

P is an optically active carboxylic acid.

Q is a cyclic compound that contains a ketone group and has only two peaks in its ^1H n.m.r. spectrum.

[5 marks]

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END OF QUESTIONS

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