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	
TOTAL	

General Certificate of Education
Advanced Level Examination
January 2011

Chemistry — CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 26 January 2011 9.00 am to 10.45 am

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.
- 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 accurate scientific terminology.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

Section A

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

1 The rate of hydrolysis of an ester **X** ($HCOOCH_2CH_2CH_3$) was studied in alkaline conditions at a given temperature. The rate was found to be first order with respect to the ester and first order with respect to hydroxide ions.

1 (a) (i) Name ester **X**.

....

(1 mark)

1 (a) (ii) Using **X** to represent the ester, write a rate equation for this hydrolysis reaction.

....

(1 mark)

1 (a) (iii) When the initial concentration of **X** was 0.024 $mol\,dm^{-3}$ and the initial concentration of hydroxide ions was 0.035 $mol\,dm^{-3}$, the initial rate of the reaction was 8.5×10^{-5} $mol\,dm^{-3}\,s^{-1}$.
Calculate a value for the rate constant at this temperature and give its units.

Calculation ....

....

....

....

Units ....

....

(3 marks)

1 (a) (iv) In a second experiment at the same temperature, water was added to the original reaction mixture so that the total volume was doubled.
Calculate the initial rate of reaction in this second experiment.

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(1 mark)

Do not write outside the box

1 (a) (v) In a third experiment at the same temperature, the concentration of **X** was half that used in the experiment in part **1 (a) (iii)** and the concentration of hydroxide ions was three times the original value.
Calculate the initial rate of reaction in this third experiment.

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(1 mark)

1 (a) (vi) State the effect, if any, on the value of the rate constant *k* when the temperature is lowered but all other conditions are kept constant. Explain your answer.

Effect ....

Explanation ....

....
(2 marks)

1 (b) Compound **A** reacts with compound **B** as shown by the overall equation

$$A + 3B \rightarrow AB_3$$

The rate equation for the reaction is

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

A suggested mechanism for the reaction is

Step **1** $A + B \rightarrow AB$

Step **2** $AB + B \rightarrow AB_2$

Step **3** $AB_2 + B \rightarrow AB_3$

Deduce which one of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step ....

Explanation ....

....
(2 marks)

11

Turn over ▶

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ANSWER IN THE SPACES PROVIDED

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2 This question is about the pH of several solutions.

Give all values of pH to 2 decimal places.

2 (a) (i) Write an expression for pH.

....

(1 mark)

2 (a) (ii) Calculate the pH of 0.154 mol dm^{-3} hydrochloric acid.

....

....

(1 mark)

2 (a) (iii) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} hydrochloric acid are added to 990 cm^3 of water.

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(2 marks)

2 (b) The acid dissociation constant, K_a, for the weak acid HX has the value 4.83 x 10^{-5} mol dm^{-3} at 25 °C.
A solution of HX has a pH of 2.48

Calculate the concentration of HX in the solution.

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(4 marks)

Question 2 continues on the next page

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2 (c) Explain why the pH of an acidic buffer solution remains almost constant despite the addition of a small amount of sodium hydroxide.

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(2 marks)

2 (d) The acid dissociation constant, K_a, for the weak acid HY has the value 1.35×10^{-5} mol dm^{-3} at 25 °C.

A buffer solution was prepared by dissolving 0.0236 mol of the salt NaY in 50.0 cm^3 of a 0.428 mol dm^{-3} solution of the weak acid HY

2 (d) (i) Calculate the pH of this buffer solution.

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(4 marks)

2 (d) (ii) A 5.00×10^{-4} mol sample of sodium hydroxide was added to this buffer solution.

Calculate the pH of the buffer solution after the sodium hydroxide was added.

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(4 marks)

18

Turn over for the next question

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3 Synthesis gas is a mixture of carbon monoxide and hydrogen. Methanol can be manufactured from synthesis gas in a reversible reaction as shown by the following equation.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H^\ominus = -91\ \text{kJ mol}^{-1}$$

3 (a) A sample of synthesis gas containing 0.240 mol of carbon monoxide and 0.380 mol of hydrogen was sealed together with a catalyst in a container of volume 1.50 dm^3. When equilibrium was established at temperature T_1 the equilibrium mixture contained 0.170 mol of carbon monoxide.

Calculate the amount, in moles, of methanol and the amount, in moles, of hydrogen in the equilibrium mixture.

Methanol ....

Hydrogen ....

(2 marks)

3 (b) A different sample of synthesis gas was allowed to reach equilibrium in a similar container of volume 1.50 dm^3 at temperature T_1

At equilibrium, the mixture contained 0.210 mol of carbon monoxide, 0.275 mol of hydrogen and 0.0820 mol of methanol.

3 (b) (i) Write an expression for the equilibrium constant K_c for this reaction.

....

....

(1 mark)

3 (b) (ii) Calculate a value for K_c for the reaction at temperature T_1 and state its units.

Calculation ....

....

....

....

....

Units ....

....

(4 marks)

3 (b) (iii) State the effect, if any, on the value of K_c of adding more hydrogen to the equilibrium mixture.

....

(1 mark)

3 (c) The temperature of the mixture in part **3 (b)** was changed to T_2 and the mixture was left to reach a new equilibrium position. At this new temperature the equilibrium concentration of methanol had increased.
Deduce which of T_1 or T_2 is the higher temperature and explain your answer.

Higher temperature ....

Explanation ....

....

....
(3 marks)

3 (d) The following reaction has been suggested as an alternative method for the production of methanol.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

The hydrogen used in this method is obtained from the electrolysis of water.

Suggest **one** possible environmental disadvantage of the production of hydrogen by electrolysis.

....

....
(1 mark)

3 (e) One industrial use of methanol is in the production of biodiesel from vegetable oils such as

$$\begin{array}{l} CH_2OOCC_{17}H_{35} \\ | \\ CHOOCC_{17}H_{31} \\ | \\ CH_2OOCC_{17}H_{29} \end{array}$$

Give the formula of **one** compound in biodiesel that is formed by the reaction of methanol with the vegetable oil shown above.

....
(1 mark)

13

4 (a) Name compound **Y**, $HOCH_2CH_2COOH$

....

(1 mark)

4 (b) Under suitable conditions, molecules of **Y** can react with each other to form a polymer.

4 (b) (i) Draw a section of the polymer showing **two** repeating units.

(1 mark)

4 (b) (ii) Name the type of polymerisation involved.

....

(1 mark)

4 (c) When **Y** is heated, an elimination reaction occurs in which one molecule of **Y** loses one molecule of water. The organic product formed by this reaction has an absorption at 1637 cm^{-1} in its infrared spectrum.

4 (c) (i) Identify the bond that causes the absorption at 1637 cm^{-1} in its infrared spectrum.

....

(1 mark)

4 (c) (ii) Write the displayed formula for the organic product of this elimination reaction.

(1 mark)

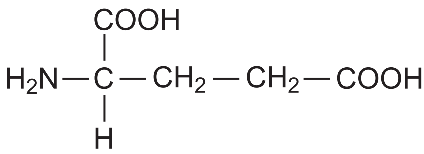
4 (c) (iii) The organic product from part **4 (c) (ii)** can also be polymerised.
Draw the repeating unit of the polymer formed from this organic product.

(1 mark)

4 (d) At room temperature, 2-aminobutanoic acid exists as a solid.
Draw the structure of the species present in the solid form.

(1 mark)

4 (e) The amino acid, glutamic acid, is shown below.



Draw the structure of the organic species formed when glutamic acid reacts with each of the following.

4 (e) (i) an excess of sodium hydroxide

(1 mark)

4 (e) (ii) an excess of methanol in the presence of concentrated sulfuric acid

(1 mark)

4 (e) (iii) ethanoyl chloride

(1 mark)

Question 4 continues on the next page

Turn over ▶

4 (f) A tripeptide was heated with hydrochloric acid and a mixture of amino acids was formed. This mixture was separated by column chromatography.
Outline briefly why chromatography is able to separate a mixture of compounds.
Practical details are **not** required.

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(3 marks)

13

Turn over for the next question

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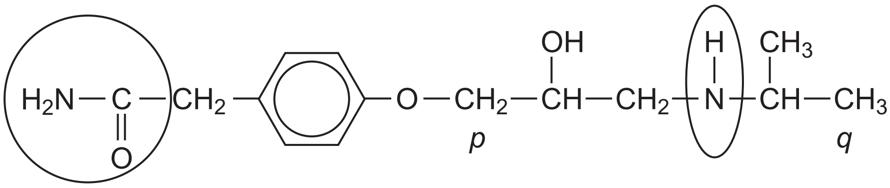
ANSWER IN THE SPACES PROVIDED

5 Atenolol is an example of the type of medicine called a beta blocker. These medicines are used to lower blood pressure by slowing the heart rate. The structure of atenolol is shown below.



J **K**

5 (a) Give the name of each of the circled functional groups labelled **J** and **K** on the structure of atenolol shown above.

Functional group labelled **J** ....

Functional group labelled **K** ....

(2 marks)

5 (b) The ^{1}H n.m.r. spectrum of atenolol was recorded.

One of the peaks in the ^{1}H n.m.r. spectrum is produced by the CH_2 group labelled *p* in the structure of atenolol.
Use **Table 2** on the Data Sheet to suggest a range of δ values for this peak.
Name the splitting pattern of this peak.

Range of δ values ....

Name of splitting pattern ....

(2 marks)

5 (c) N.m.r. spectra are recorded using samples in solution.
The ^{1}H n.m.r. spectrum was recorded using a solution of atenolol in $CDCl_3$

5 (c) (i) Suggest why $CDCl_3$ and **not** $CHCl_3$ was used as the solvent.

....

....

(1 mark)

5 (c) (ii) Suggest why $CDCl_3$ is a more effective solvent than CCl_4 for polar molecules such as atenolol.

....

....

(1 mark)

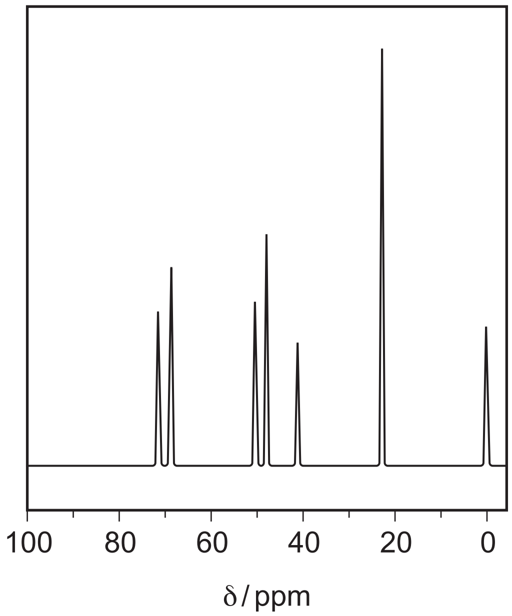
5 (d) The ^{13}C n.m.r. spectrum of atenolol was also recorded.

Use the structure of atenolol given to deduce the total number of peaks in the ^{13}C n.m.r. spectrum of atenolol.

....

(1 mark)

5 (e) Part of the ^{13}C n.m.r. spectrum of atenolol is shown below. Use this spectrum and **Table 3** on the Data Sheet, where appropriate, to answer the questions which follow.



5 (e) (i) Give the formula of the compound that is used as a standard and produces the peak at δ = 0 ppm in the spectrum.

....

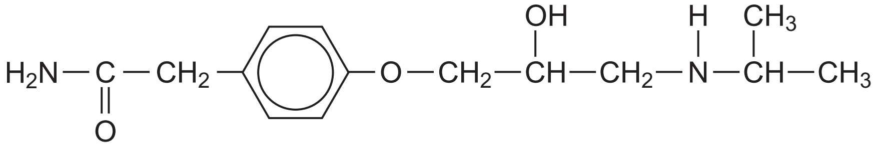
(1 mark)

5 (e) (ii) One of the peaks in the ^{13}C n.m.r. spectrum above is produced by the CH_3 group labelled *q* in the structure of atenolol.
Identify this peak in the spectrum by stating its δ value.

....

(1 mark)

5 (e) (iii) There are three CH_2 groups in the structure of atenolol. One of these CH_2 groups produces the peak at δ = 71 in the ^{13}C n.m.r. spectrum above.
Draw a circle around this CH_2 group in the structure of atenolol shown below.



(1 mark)

Question 5 continues on the next page

Turn over ▶

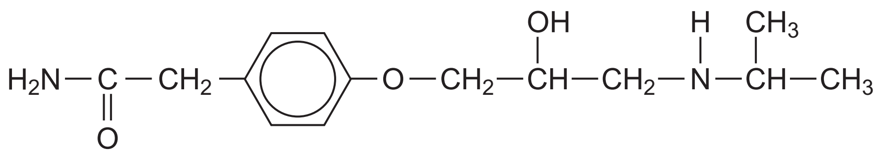
5 (f) Atenolol is produced industrially as a racemate (an equimolar mixture of two enantiomers) by reduction of a ketone. Both enantiomers are able to lower blood pressure. However, recent research has shown that one enantiomer is preferred in medicines.

5 (f) (i) Suggest a reducing agent that could reduce a ketone to form atenolol.

....

(1 mark)

5 (f) (ii) Draw a circle around the asymmetric carbon atom in the structure of atenolol shown below.



(1 mark)

5 (f) (iii) Suggest how you could show that the atenolol produced by reduction of a ketone was a racemate and **not** a single enantiomer.

....

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....

....

(2 marks)

5 (f) (iv) Suggest **one** advantage and **one** disadvantage of using a racemate rather than a single enantiomer in medicines.

Advantage ....

....

Disadvantage ....

....

(2 marks)

16

Turn over for the next question

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Section B

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

6 Many synthetic routes need chemists to increase the number of carbon atoms in a molecule by forming new carbon–carbon bonds. This can be achieved in several ways including

- reaction of an aromatic compound with an acyl chloride
- reaction of an aldehyde with hydrogen cyanide.

6 (a) Consider the reaction of benzene with CH_3CH_2COCl

6 (a) (i) Write an equation for this reaction and name the organic product.
Identify the catalyst required in this reaction.
Write equations to show how the catalyst is used to form a reactive intermediate and how the catalyst is reformed at the end of the reaction.

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(5 marks)

(*Extra space*) ....

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6 (a) (ii) Name and outline a mechanism for the reaction of benzene with this reactive intermediate.

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(4 marks)

(Extra space) ....

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Question 6 continues on the next page

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6 (b) Consider the reaction of propanal with HCN

6 (b) (i) Write an equation for the reaction of propanal with HCN and name the product.

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(2 marks)

(*Extra space*) ....

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6 (b) (ii) Name and outline a mechanism for the reaction of propanal with HCN

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(5 marks)

(Extra space) ....

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6 (b) (iii) The rate-determining step in the mechanism in part **6 (b) (ii)** involves attack by the nucleophile.
Suggest how the rate of reaction of propanone with HCN would compare with the rate of reaction of propanal with HCN
Explain your answer.

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(2 marks)

(Extra space) ....

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18

Turn over for the next question

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7 The compound $(CH_3CH_2)_2NH$ can be made from ethene in a three-step synthesis as shown below.

$$\text{ethene} \xrightarrow{\text{Step } \mathbf{1}} \mathbf{F} \xrightarrow{\text{Step } \mathbf{2}} \mathbf{G} \xrightarrow{\text{Step } \mathbf{3}} (CH_3CH_2)_2NH$$

7 (a) Name the compound $(CH_3CH_2)_2NH$

....

(1 mark)

7 (b) Identify compounds **F** and **G**.

Compound **F** ....

Compound **G** ....

(2 marks)

7 (c) For the reactions in Steps **1**, **2** and **3**,

- give a reagent or reagents
- name the mechanism.

Balanced equations and mechanisms using curly arrows are **not** required.

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(6 marks)

(*Extra space*) ....

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Do not write outside the box

7 (d) Identify **one** organic impurity in the product of Step **3** and give a reason for its formation.

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(2 marks)

(Extra space) ....

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11

END OF QUESTIONS

There are no questions printed on this page

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