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
June 2012

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 13 June 2012 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.
- 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 accurate scientific terminology.

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

Do not write outside the box

Section A

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

1 (a) A mixture of 1.50 mol of hydrogen and 1.20 mol of gaseous iodine was sealed in a container of volume V dm^3. The mixture was left to reach equilibrium as shown by the following equation.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At a given temperature, the equilibrium mixture contained 2.06 mol of hydrogen iodide.

1 (a) (i) Calculate the amounts, in moles, of hydrogen and of iodine in the equilibrium mixture.

Moles of hydrogen .....

Moles of iodine .....

(2 marks)

1 (a) (ii) Write an expression for the equilibrium constant (K_c) for this equilibrium.

.....

.....

(1 mark)

1 (a) (iii) K_c for this equilibrium has no units.
State why the units cancel in the expression for K_c

.....

.....

(1 mark)

1 (a) (iv) A different mixture of hydrogen, iodine and hydrogen iodide was left to reach equilibrium at the same temperature in a container of the same volume.
This second equilibrium mixture contained 0.38 mol of hydrogen, 0.19 mol of iodine and 1.94 mol of hydrogen iodide.

Calculate a value for K_c for this equilibrium at this temperature.

.....

.....

.....

.....

(2 marks)

(Extra space) .....

.....

Do not write outside the box

1 (b) This question concerns changes made to the four equilibria shown in parts **(b) (i)** to **(b) (iv)**.
In each case, use the information in the table to help you choose from the letters **A** to **E** the best description of what happens as a result of the change described. Write your answer in the box.

Each letter may be used once, more than once or not at all.

	Position of equilibrium	Value of equilibrium constant, K_c
A	remains the same	same
B	moves to the right	same
C	moves to the left	same
D	moves to the right	different
E	moves to the left	different

1 (b) (i) Change: increase the temperature of the equilibrium mixture at constant pressure.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\quad \Delta H^{\ominus} = +52\,kJ\,mol^{-1}$

(1 mark)

1 (b) (ii) Change: increase the total pressure of the equilibrium mixture at constant temperature.

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ $\quad \Delta H^{\ominus} = -92\,kJ\,mol^{-1}$

(1 mark)

1 (b) (iii) Change: add a catalyst to the equilibrium mixture at constant temperature.

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\quad \Delta H^{\ominus} = -41\,kJ\,mol^{-1}$

(1 mark)

1 (b) (iv) Change: add chlorine to the equilibrium mixture at constant temperature.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\quad \Delta H^{\ominus} = +93\,kJ\,mol^{-1}$

(1 mark)

10

Do not write outside the box

2 Gases **P** and **Q** react as shown in the following equation.

$$2P(g) + 2Q(g) \longrightarrow R(g) + S(g)$$

The initial rate of the reaction was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\mathbf{P}]^2[\mathbf{Q}]$$

2 (a) Complete the table of data for the reaction between **P** and **Q**.

Experiment	Initial [**P**] / mol dm^{-3}	Initial [**Q**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	2.5×10^{-2}	1.8×10^{-2}	5.0×10^{-5}
2	7.5×10^{-2}	1.8×10^{-2}	
3	5.0×10^{-2}		5.0×10^{-5}
4		5.4×10^{-2}	4.5×10^{-4}

(3 marks)

(Space for working) .....

.....

.....

.....

2 (b) Use the data from Experiment **1** to calculate a value for the rate constant (k) at this temperature. Deduce the units of k.

Calculation .....

.....

.....

.....

Units .....

.....

(3 marks)

6

Do not write outside the box

3 This question is about several Brønsted–Lowry acids and bases.

3 (a) Define the term *Brønsted–Lowry* acid.

.....

.....

(1 mark)

3 (b) Three equilibria are shown below. For each reaction, indicate whether the substance immediately **above** the box is acting as a Brønsted–Lowry acid (**A**) or a Brønsted–Lowry base (**B**) by writing **A** or **B** in each of the six boxes.

3 (b) (i) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

(1 mark)

3 (b) (ii) $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$

(1 mark)

3 (b) (iii) $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$

(1 mark)

3 (c) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker. Distilled water was added until the pH of the solution was 1.25

Calculate the total volume of the solution formed. State the units.

.....

.....

.....

.....

.....

(3 marks)

(*Extra space*) .....

.....

.....

Question 3 continues on the next page

Do not write outside the box

3 (d) At 298 K, the value of the acid dissociation constant (K_a) for the weak acid HX in aqueous solution is 3.01×10^{-5} mol dm^{-3}.

3 (d) (i) Calculate the value of pK_a for HX at this temperature.
Give your answer to 2 decimal places.

.....

.....

(1 mark)

3 (d) (ii) Write an expression for the acid dissociation constant (K_a) for the weak acid HX.

.....

.....

.....

(1 mark)

3 (d) (iii) Calculate the pH of a 0.174 mol dm^{-3} solution of HX at this temperature.
Give your answer to 2 decimal places.

.....

.....

.....

.....

.....

(3 marks)

(Extra space) .....

.....

.....

Do not write outside the box

3 (e) An acidic buffer solution is formed when 10.0 cm^3 of 0.125 mol dm^{-3} aqueous sodium hydroxide are added to 15.0 cm^3 of 0.174 mol dm^{-3} aqueous HX.
The value of K_a for the weak acid HX is 3.01×10^{-5} mol dm^{-3}.

Calculate the pH of this buffer solution at 298 K.
Give your answer to 2 decimal places.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(6 marks)

(Extra space) .....

18

.....

.....

.....

.....

.....

Do not write outside the box

4 Acyl chlorides and acid anhydrides are important compounds in organic synthesis.

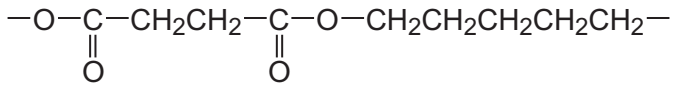
4 (a) Outline a mechanism for the reaction of CH_3CH_2COCl with CH_3OH and name the organic product formed.

Mechanism

Name of organic product .....

(5 marks)

4 (b) A polyester was produced by reacting a diol with a diacyl chloride. The repeating unit of the polymer is shown below.



4 (b) (i) Name the diol used.

.....

(1 mark)

4 (b) (ii) Draw the displayed formula of the diacyl chloride used.

(1 mark)

Do not write outside the box

4 (b) (iii) A shirt was made from this polyester. A student wearing the shirt accidentally splashed aqueous sodium hydroxide on a sleeve. Holes later appeared in the sleeve where the sodium hydroxide had been.

Name the type of reaction that occurred between the polyester and the aqueous sodium hydroxide. Explain why the aqueous sodium hydroxide reacted with the polyester.

Type of reaction .....

Explanation .....

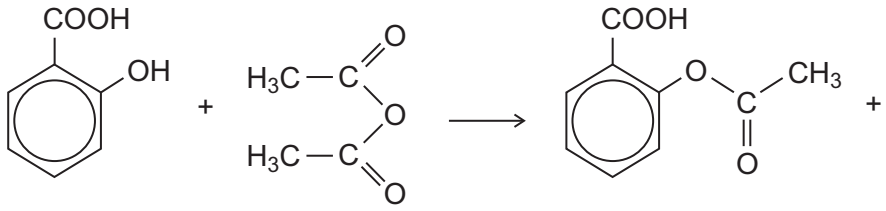
.....

.....

.....

(3 marks)

4 (c) (i) Complete the following equation for the preparation of aspirin using ethanoic anhydride by writing the structural formula of the missing product.



.....

aspirin

(1 mark)

4 (c) (ii) Suggest a name for the mechanism for the reaction in part **(c) (i)**.

.....

(1 mark)

4 (c) (iii) Give **two** industrial advantages, other than cost, of using ethanoic anhydride rather than ethanoyl chloride in the production of aspirin.

Advantage 1 .....

.....

.....

Advantage 2 .....

.....

.....

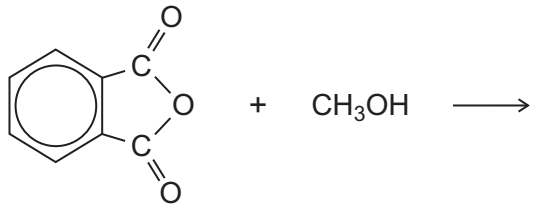
(2 marks)

Question 4 continues on the next page

Turn over ▶

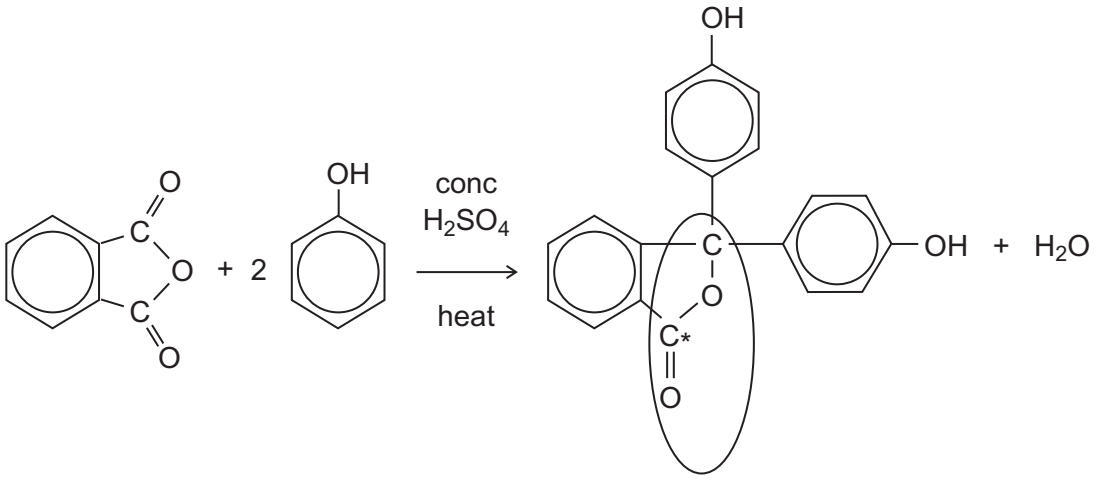
Do not write outside the box

4 (d) Complete the following equation for the reaction of one molecule of benzene-1,2-dicarboxylic anhydride (phthalic anhydride) with one molecule of methanol by drawing the structural formula of the single product.



(1 mark)

4 (e) The indicator phenolphthalein is synthesised by reacting phthalic anhydride with phenol as shown in the following equation.



phenol phenolphthalein

4 (e) (i) Name the functional group ringed in the structure of phenolphthalein.

.....

(1 mark)

4 (e) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of phenolphthalein.

.....

(1 mark)

4 (e) (iii) One of the carbon atoms in the structure of phenolphthalein shown above is labelled with an asterisk (*).
Use **Table 3** on the Data Sheet to suggest a range of δ values for the peak due to this carbon atom in the ^{13}C n.m.r. spectrum of phenolphthalein.

.....

(1 mark)

Do not write outside the box

4 (f) Phenolphthalein can be used as an indicator in some acid–alkali titrations.
The pH range for phenolphthalein is 8.3 – 10.0

4 (f) (i) For **each** acid–alkali combination in the table below, put a tick (✓) in the box if phenolphthalein could be used as an indicator.

Acid	Alkali	Tick box (✓)
sulfuric acid	sodium hydroxide	
hydrochloric acid	ammonia	
ethanoic acid	potassium hydroxide	
nitric acid	methylamine	

(2 marks)

4 (f) (ii) In a titration, nitric acid is added from a burette to a solution of sodium hydroxide containing a few drops of phenolphthalein indicator.
Give the colour **change** at the end-point.

.....

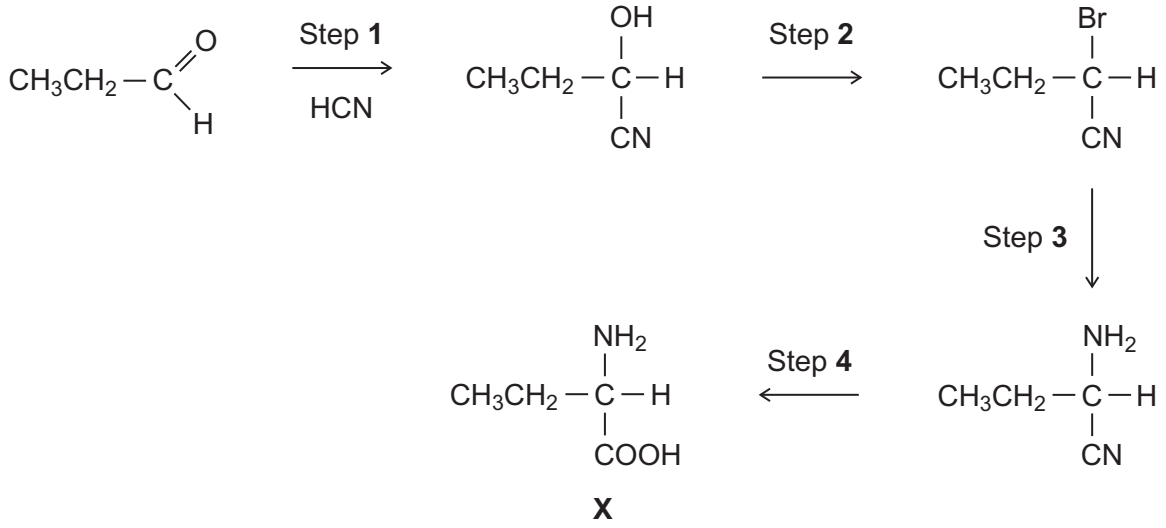
(1 mark)

21

Turn over for the next question

Do not write outside the box

5 A possible synthesis of the amino acid **X** is shown below.



X

5 (a) Name and outline a mechanism for Step **1**.

Name of mechanism .....

Mechanism

(5 marks)

5 (b) Give the IUPAC name of the product of Step **2**.

.....

(1 mark)

Do not write outside the box

5 (c) For Step **3**, give the reagent, give a necessary condition and name the mechanism.

Reagent .....

Condition .....

Name of mechanism .....

(3 marks)

5 (d) At room temperature, the amino acid **X** exists as a solid.

5 (d) (i) Draw the structure of the species present in the solid amino acid.

(1 mark)

5 (d) (ii) With reference to your answer to part **(d) (i)**, explain why the melting point of the amino acid **X** is higher than the melting point of $CH_3CH_2CH(OH)COOH$

.....

.....

.....

.....

.....

(2 marks)

(Extra space) .....

.....

Question 5 continues on the next page

Do not write outside the box

5 (e) There are many structural isomers of **X**, $CH_3CH_2CH(NH_2)COOH$

5 (e) (i) Draw a structural isomer of **X** that is an ethyl ester.

(1 mark)

5 (e) (ii) Draw a structural isomer of **X** that is an amide and also a tertiary alcohol.

(1 mark)

5 (e) (iii) Draw a structural isomer of **X** that has an unbranched carbon chain and can be polymerised to form a polyamide.

(1 mark)

5 (f) Draw the structure of the tertiary amine formed when **X** reacts with bromomethane.

(1 mark)

16

Turn over for the next question

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED

Do not write outside the box

Section B

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

6 Benzene reacts with ethanoyl chloride in a substitution reaction to form $C_6H_5COCH_3$
This reaction is catalysed by aluminium chloride.

6 (a) Write equations to show the role of aluminium chloride as a catalyst in this reaction.

Outline a mechanism for the reaction of benzene.

Name the product, $C_6H_5COCH_3$

.....

.....

.....

(6 marks)

Do not write outside the box

6 (b) The product of the substitution reaction ($C_6H_5COCH_3$) was analysed by mass spectrometry. The most abundant fragment ion gave a peak in the mass spectrum with $m/z = 105$
Draw the structure of this fragment ion.

(1 mark)

6 (c) When methylbenzene reacts with ethanoyl chloride and aluminium chloride, a similar substitution reaction occurs but the reaction is faster than the reaction of benzene.
Suggest why the reaction of methylbenzene is faster.

.....

.....

.....

.....

.....

.....

(2 marks)

9

Turn over for the next question

Do not write outside the box

7 (a) A chemist discovered four unlabelled bottles of liquid, each of which contained a different pure organic compound. The compounds were known to be propan-1-ol, propanal, propanoic acid and 1-chloropropane.

Describe four **different** test-tube reactions, one for each compound, that could be used to identify the four organic compounds.
Your answer should include the name of the organic compound, the reagent(s) used and the expected observation for each test.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(8 marks)

(*Extra space*) .....

.....

.....

.....

Do not write outside the box

7 (b) A fifth bottle was discovered labelled propan-2-ol. The chemist showed, using infrared spectroscopy, that the propan-2-ol was contaminated with propanone.

The chemist separated the two compounds using column chromatography. The column contained silica gel, a polar stationary phase.

The contaminated propan-2-ol was dissolved in hexane and poured into the column. Pure hexane was added slowly to the top of the column. Samples of the eluent (the solution leaving the bottom of the column) were collected.

- Suggest the chemical process that would cause a sample of propan-2-ol to become contaminated with propanone.
- State how the infrared spectrum showed the presence of propanone.
- Suggest why propanone was present in samples of the eluent collected first (those with shorter retention times), whereas samples containing propan-2-ol were collected later.

.....

.....

.....

.....

.....

.....

.....

.....

.....

(4 marks)

(*Extra space*) .....

12

.....

.....

.....

.....

.....

.....

.....

Turn over for the next question

Do not write outside the box

8 When the molecular formula of a compound is known, spectroscopic and other analytical techniques can be used to distinguish between possible structural isomers.

Draw **one** possible structure for each of the compounds described in parts **(a)** to **(d)**.

8 (a) Compounds **F** and **G** have the molecular formula $C_6H_4N_2O_4$ and both are dinitrobenzenes.
F has two peaks in its ^{13}C n.m.r. spectrum.
G has three peaks in its ^{13}C n.m.r. spectrum.

F **G**

(2 marks)

(Space for working)

Do not write outside the box

8 (b) Compounds **H** and **J** have the molecular formula C_6H_{12}
Both have only one peak in their ^1H n.m.r. spectra.
H reacts with aqueous bromine but **J** does not.

H **J**

(2 marks)

(Space for working)

Question 8 continues on the next page

Do not write outside the box

8 (c) **K** and **L** are cyclic compounds with the molecular formula $C_6H_{10}O$
Both have four peaks in their ^{13}C n.m.r. spectra.
K is a ketone and **L** is an aldehyde.

K **L**

(2 marks)

(Space for working)

Do not write outside the box

8 (d) Compounds **M** and **N** have the molecular formula $C_6H_{15}N$
M is a tertiary amine with only two peaks in its ^1H n.m.r. spectrum.
N is a secondary amine with only three peaks in its ^1H n.m.r. spectrum.

M **N**

(2 marks)

(Space for working)

8

END OF QUESTIONS

There are no questions printed on this page

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED

Copyright © 2012 AQA and its licensors. All rights reserved.