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	
9	
TOTAL	

General Certificate of Education
Advanced Level Examination
June 2013

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 12 June 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**.

Do not write outside the box

Section A

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

1 This question involves the use of kinetic data to calculate the order of a reaction and also a value for a rate constant.

1 (a) The data in this table were obtained in a series of experiments on the rate of the reaction between compounds **E** and **F** at a constant temperature.

Experiment	Initial concentration of **E** / mol dm^{-3}	Initial concentration of **F** / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.15	0.24	0.42×10^{-3}
2	0.45	0.24	3.78×10^{-3}
3	0.90	0.12	7.56×10^{-3}

1 (a) (i) Deduce the order of reaction with respect to **E**.

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(1 mark)

(*Space for working*) .....

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1 (a) (ii) Deduce the order of reaction with respect to **F**.

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(1 mark)

(*Space for working*) .....

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1 (b) The data in the following table were obtained in two experiments on the rate of the reaction between compounds **G** and **H** at a constant temperature.

Experiment	Initial concentration of **G** / mol dm^{-3}	Initial concentration of **H** / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
4	3.8×10^{-2}	2.6×10^{-2}	8.6×10^{-4}
5	6.3×10^{-2}	7.5×10^{-2}	To be calculated

The rate equation for this reaction is

$$rate = k[\mathbf{G}]^2[\mathbf{H}]$$

1 (b) (i) Use the data from Experiment **4** to calculate a value for the rate constant k at this temperature. Deduce the units of k.

Calculation .....

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Units .....

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(3 marks)

1 (b) (ii) Calculate a value for the initial rate of reaction in Experiment **5**.

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(1 mark)

6

Turn over ▶

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2 When heated above 100 °C, nitrosyl chloride (NOCl) partly decomposes to form nitrogen monoxide and chlorine as shown in the equation.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

2 (a) A 2.50 mol sample of NOCl was heated in a sealed container and equilibrium was established at a given temperature. The equilibrium mixture formed contained 0.80 mol of NO

Calculate the amount, in moles, of Cl_2 and of NOCl in this equilibrium mixture.

Moles of Cl_2 .....

Moles of NOCl .....

(2 marks)

2 (b) A different mixture of NOCl, NO and Cl_2 reached equilibrium in a sealed container of volume 15.0 dm^3. The equilibrium mixture formed contained 1.90 mol of NOCl and 0.86 mol of NO at temperature *T*.

The value of K_c for the equilibrium at temperature *T* was 7.4×10^{-3} mol dm^{-3}.

2 (b) (i) Write an expression for the equilibrium constant K_c

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(1 mark)

2 (b) (ii) Calculate the amount, in moles, of Cl_2 in this equilibrium mixture.

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(4 marks)

(Extra space) .....

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Do not write outside the box

2 (b) (iii) Consider this alternative equation for the equilibrium at temperature *T*.

$$NOCl(g) \rightleftharpoons NO(g) + \tfrac{1}{2}Cl_2(g)$$

Calculate a value for the different equilibrium constant K_c for the equilibrium as shown in this alternative equation. Deduce the units of this K_c

Calculation .....

.....

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.....

Units .....

.....

(2 marks)

9

Turn over for the next question

Do not write outside the box

3 This question is about Brønsted–Lowry acids of different strengths.

3 (a) State the meaning of the term *Brønsted–Lowry acid*.

.....

(1 mark)

3 (b) (i) Write an expression for the acid dissociation constant K_a for ethanoic acid.

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(1 mark)

3 (b) (ii) The value of K_a for ethanoic acid is 1.75×10^{-5} mol dm^{-3} at 25 ºC.

Calculate the concentration of ethanoic acid in a solution of the acid that has a pH of 2.69

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(4 marks)

3 (c) The value of K_a for chloroethanoic acid ($ClCH_2COOH$) is 1.38×10^{-3} mol dm^{-3} at 25 ºC.

3 (c) (i) Write an equation for the dissociation of chloroethanoic acid in aqueous solution.

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(1 mark)

3 (c) (ii) Suggest why chloroethanoic acid is a stronger acid than ethanoic acid.

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(2 marks)

Do not write outside the box

3 (d) **P** and **Q** are acids. **X** and **Y** are bases. The table shows the strength of each acid and base.

Acids		**Bases**	
strong	weak	strong	weak
P	**Q**	**X**	**Y**

The two acids were titrated separately with the two bases using methyl orange as indicator.
The titrations were then repeated using phenolphthalein as indicator.
The pH range for methyl orange is 3.1–4.4
The pH range for phenolphthalein is 8.3–10.0

For each of the following titrations, select the letter, **A**, **B**, **C**, or **D**, for the correct statement about the indicator(s) that would give a precise end-point.
Write your answer in the box provided.

A Both indicators give a precise end-point.

B **Only** methyl orange gives a precise end-point.

C **Only** phenolphthalein gives a precise end-point.

D Neither indicator gives a precise end-point.

3 (d) (i) Acid **P** with base **X**

(1 mark)

3 (d) (ii) Acid **Q** with base **X**

(1 mark)

3 (d) (iii) Acid **Q** with base **Y**

(1 mark)

Question 3 continues on the next page

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3 (e) Using a burette, 26.40 cm^3 of 0.550 mol dm^{-3} sulfuric acid were added to a conical flask containing 19.60 cm^3 of 0.720 mol dm^{-3} aqueous sodium hydroxide.
Assume that the sulfuric acid is fully dissociated.

Calculate the pH of the solution formed.

Give your answer to 2 decimal places.

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(6 marks)

(Extra space) .....

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18

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4 This question is about acylium ions, $[RCO]^+$

4 (a) The acylium ion $H_3C-\overset{+}{C}=O$ is formed in a mass spectrometer by fragmentation of the molecular ion of methyl ethanoate.

Write an equation for this fragmentation.

Include in your answer a displayed formula for the radical formed.

.....

(2 marks)

4 (b) The acylium ion $H_3C-\overset{+}{C}=O$ can also be formed from ethanoyl chloride. The ion reacts with benzene to form $C_6H_5COCH_3$

4 (b) (i) Write an equation to show the formation of this acylium ion by the reaction of ethanoyl chloride with **one** other substance.

.....

(2 marks)

4 (b) (ii) Name and outline a mechanism for the reaction of benzene with this acylium ion.

Name of mechanism .....

Mechanism

(4 marks)

4 (b) (iii) Ethanoic anhydride also reacts with benzene to form $C_6H_5COCH_3$

Write an equation for this reaction.

.....

(1 mark)

9

Do not write outside the box

5 Lactic acid, $CH_3CH(OH)COOH$, is formed in the human body during metabolism and exercise. This acid is also formed by the fermentation of carbohydrates such as sucrose, $C_{12}H_{22}O_{11}$

5 (a) (i) Give the IUPAC name for lactic acid.

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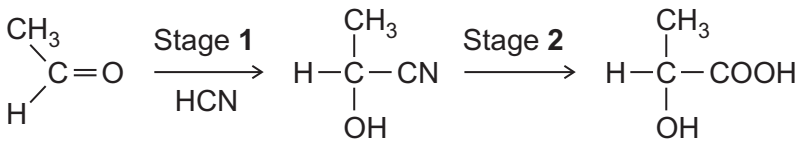
(1 mark)

5 (a) (ii) Write an equation for the formation of lactic acid from sucrose and water.

.....

(1 mark)

5 (b) A molecule of lactic acid contains an asymmetric carbon atom.
The lactic acid in the body occurs as a single enantiomer.
A racemic mixture (racemate) of lactic acid can be formed in the following two-stage synthesis.



5 (b) (i) Name and outline a mechanism for Stage **1**.

Name of mechanism .....

Mechanism

(5 marks)

Do not write outside the box

5 (b) (ii) Give the meaning of the term *racemic mixture (racemate)*.

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(1 mark)

5 (b) (iii) Explain how you could distinguish between a racemic mixture (racemate) of lactic acid and one of the enantiomers of lactic acid.

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(2 marks)

5 (c) A mixture of lactic acid and its salt sodium lactate is used as an acidity regulator in some foods. An acidity regulator makes sure that there is little variation in the pH of food.

5 (c) (i) Write an equation for the reaction of lactic acid with sodium hydroxide.

.....

(1 mark)

5 (c) (ii) The acid dissociation constant K_a for lactic acid has the value 1.38×10^{-4} mol dm^{-3} at 298 K.

Calculate the pH of an equimolar solution of lactic acid and sodium lactate.

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(2 marks)

Question 5 continues on the next page

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5 (c) (iii) Suggest an alternative name for the term *acidity regulator*.
Explain how a mixture of lactic acid and sodium lactate can act as a regulator when natural processes increase the acidity in some foods.

Name .....

Explanation .....

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(3 marks)

(Extra space) .....

.....

5 (d) The cup shown is made from PLA, poly(lactic acid).
PLA is the condensation polymer formed from lactic acid.



The polymer is described as 100% biodegradable and 100% compostable.

Compostable material breaks down slowly in contact with the moist air in a garden bin. This produces compost that can be used to improve soil.

The manufacturers stress that PLA cups differ from traditional plastic cups that are neither biodegradable nor compostable.

5 (d) (i) Draw a section of PLA that shows **two** repeating units.

(2 marks)

Do not write outside the box

5 (d) (ii) Name the type of condensation polymer in PLA.

.....

(1 mark)

5 (d) (iii) An intermediate in the production of PLA is a cyclic compound ($C_6H_8O_4$) that is formed from two PLA molecules.

Draw the structure of this cyclic compound.

(1 mark)

5 (d) (iv) Traditional non-biodegradable plastic cups can be made from poly(phenylethene), commonly known as *polystyrene*.

Draw the repeating unit of poly(phenylethene).

(1 mark)

5 (d) (v) The manufacturers of PLA claim that the material will break down to compost in just 12 weeks.

Suggest **one** reason why PLA in landfill may take longer than 12 weeks to break down.

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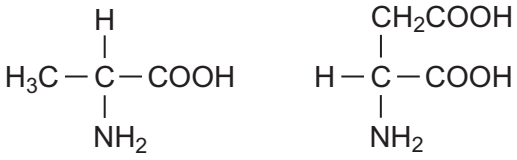
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(1 mark)

22

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6 Alanine and aspartic acid are naturally occurring amino acids.



alanine

aspartic acid

6 (a) Draw the structure of the zwitterion formed by alanine.

(1 mark)

6 (b) Draw the structure of the compound formed when alanine reacts with methanol in the presence of a small amount of concentrated sulfuric acid.

(1 mark)

6 (c) Draw the structure of the species formed by aspartic acid at high pH.

(1 mark)

6 (d) Draw the structure of a dipeptide formed by two aspartic acid molecules.

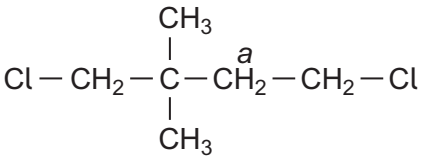
(1 mark)

4

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7 N.m.r. spectroscopy can be used to study the structures of organic compounds.

7 (a) Compound **J** was studied using ^{1}H n.m.r. spectroscopy.



J

7 (a) (i) Identify a solvent in which **J** can be dissolved before obtaining its ^{1}H n.m.r. spectrum.

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(1 mark)

7 (a) (ii) Give the number of peaks in the ^{1}H n.m.r. spectrum of **J**.

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(1 mark)

7 (a) (iii) Give the splitting pattern of the protons labelled *a*.

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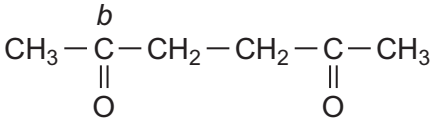
(1 mark)

7 (a) (iv) Give the IUPAC name of **J**.

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(1 mark)

7 (b) Compound **K** was studied using ^{13}C n.m.r. spectroscopy.



K

7 (b) (i) Give the number of peaks in the ^{13}C n.m.r. spectrum of **K**.

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(1 mark)

7 (b) (ii) Use **Table 3** on the Data Sheet to suggest a δ value of the peak for the carbon labelled *b*.

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(1 mark)

7 (b) (iii) Give the IUPAC name of **K**.

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(1 mark)

7

Turn over ▶

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Section B

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

8 This question is about the primary amine $CH_3CH_2CH_2NH_2$

8 (a) The amine $CH_3CH_2CH_2NH_2$ reacts with CH_3COCl

Name and outline a mechanism for this reaction.

Give the IUPAC name of the organic product.

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(6 marks)

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8 (b) Isomers of $CH_3CH_2CH_2NH_2$ include another primary amine, a secondary amine and a tertiary amine.

8 (b) (i) Draw the structures of these **three** isomers.
Label each structure as primary, secondary or tertiary.

(3 marks)

8 (b) (ii) Use **Table 1** on the Data Sheet to explain how you could use infrared spectra in the range outside the fingerprint region to distinguish between the secondary amine and the tertiary amine.

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(2 marks)

Question 8 continues on the next page

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8 (c) The amine $CH_3CH_2CH_2NH_2$ can be prepared by two different routes.

Route **A** is a two-stage process and starts from CH_3CH_2Br

Route **B** is a one-stage process and starts from $CH_3CH_2CH_2Br$

8 (c) (i) Identify the intermediate compound in Route **A**.

Give the reagents and conditions for both stages in Route **A** and the single stage in Route **B**.

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(7 marks)

8 (c) (ii) Give **one** disadvantage of Route **A** and **one** disadvantage of Route **B**.

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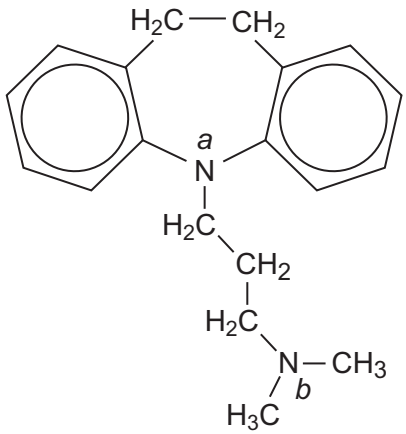
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(2 marks)

20

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9 Imipramine has been prescribed as an antidepressant. The structure of imipramine is shown below.



9 (a) The medicine is usually supplied as a salt. The salt is formed when one mole of imipramine reacts with one mole of hydrochloric acid.

Suggest why the nitrogen atom labelled *b* is more likely to be protonated than the nitrogen atom labelled *a* when the salt is formed.

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(3 marks)

9 (b) Deduce the molecular formula of imipramine and give the number of peaks in its ^{13}C n.m.r. spectrum.

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(2 marks)

END OF QUESTIONS

5

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