Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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10	
11	
TOTAL	

General Certificate of Education
Advanced Level Examination
January 2012

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Thursday 26 January 2012 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.
- 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 80 minutes on **Section A** and about 25 minutes on **Section B**.

Section A

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

1 The initial rate of the reaction between two gases **P** and **Q** was measured in a series of experiments at a constant temperature. The following rate equation was determined.

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

1 (a) Complete the table of data below 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	0.20	0.30	1.8×10^{-3}
2	0.40	0.60	
3	0.60		5.4×10^{-3}
4		0.90	12.2×10^{-3}

(3 marks)

(*Space for working*) ....

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

Calculation ....

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Units ....

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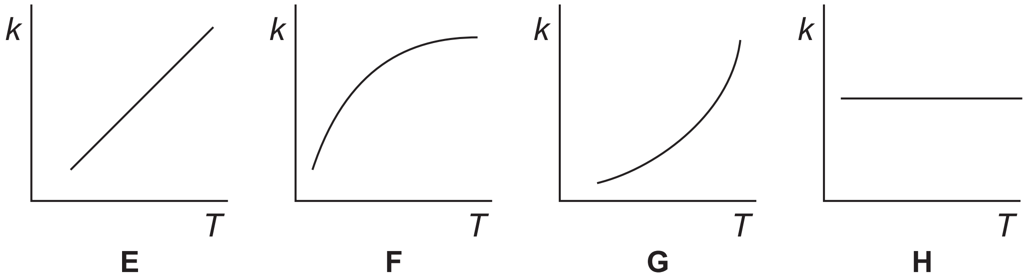
(3 marks)

1 (c) Consider the graphs **E**, **F**, **G** and **H** below.



Write in the box below the letter of the graph that shows how the rate constant *k* varies with temperature.

[ ]

(1 mark)

7

2 At high temperatures and in the presence of a catalyst, sulfur trioxide decomposes according to the following equation.

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad \Delta H^\ominus = +196\,\text{kJ mol}^{-1}$$

2 (a) In an experiment, 8.0 mol of sulfur trioxide were placed in a container of volume 12.0 dm^3 and allowed to come to equilibrium.
At temperature T_1 there were 1.4 mol of oxygen in the equilibrium mixture.

2 (a) (i) Calculate the amount, in moles, of sulfur trioxide and of sulfur dioxide in the equilibrium mixture.

Amount of sulfur trioxide ....

Amount of sulfur dioxide ....

(2 marks)

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

....

....

(1 mark)

2 (a) (iii) Deduce the units of K_c for this equilibrium.

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(1 mark)

2 (a) (iv) Calculate a value of K_c for this equilibrium at temperature T_1

(If you were unable to complete the calculations in part **(a) (i)** you should assume that the amount of sulfur trioxide in the equilibrium mixture was 5.8 mol and the amount of sulfur dioxide was 2.1 mol. These are **not** the correct values.)

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(3 marks)

(Extra space) ....

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Do not write outside the box

2 (b) The experiment was repeated at the same temperature using the same amount of sulfur trioxide but in a larger container.
State the effect, if any, of this change on:

2 (b) (i) the amount, in moles, of oxygen in the new equilibrium mixture

....

(1 mark)

2 (b) (ii) the value of K_c

....

(1 mark)

2 (c) The experiment was repeated in the original container but at temperature T_2
The value of K_c was smaller than the value at temperature T_1
State which is the higher temperature, T_1 or T_2
Explain your answer.

Higher temperature ....

Explanation ....

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(3 marks)

(Extra space) ....

....

12

Turn over ▶

3 Ammonia and ethylamine are examples of weak Brønsted–Lowry bases.

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

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(1 mark)

3 (b) (i) Write an equation for the reaction of ethylamine ($CH_3CH_2NH_2$) with water to form a weakly alkaline solution.

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(1 mark)

3 (b) (ii) In terms of this reaction, state why the solution formed is **weakly** alkaline.

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(1 mark)

3 (c) State which is the stronger base, ammonia or ethylamine. Explain your answer.

Stronger base ....

Explanation ....

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(3 marks)

(Extra space) ....

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Do not write outside the box

3 (d) Give the formula of an organic compound that forms an alkaline buffer solution when added to a solution of ethylamine.

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(1 mark)

3 (e) Explain qualitatively how the buffer solution in part **(d)** maintains an almost constant pH when a small amount of hydrochloric acid is added to it.

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(2 marks)

(Extra space) ....

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9

Turn over for the next question

4 This question involves calculations about two strong acids and one weak acid.
All measurements were carried out at 25 °C.

4 (a) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker and 100 cm^3 of distilled water were added.
Calculate the pH of the new solution formed.
Give your answer to 2 decimal places.

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(2 marks)

(Extra space) ....

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4 (b) HX is a weak monobasic acid.

4 (b) (i) Write an expression for the acid dissociation constant, K_a, for HX.

....

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(1 mark)

4 (b) (ii) The pH of a 0.0850 mol dm^{-3} solution of HX is 2.79
Calculate a value for the acid dissociation constant, K_a, of this acid.
Give your answer to 3 significant figures.

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(3 marks)

(Extra space) ....

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Do not write outside the box

4 (c) A 25.0 cm^3 sample of 0.620 mol dm^{-3} nitric acid was placed in a beaker and 38.2 cm^3 of 0.550 mol dm^{-3} aqueous sodium hydroxide were added.
Calculate the pH of the solution formed.
Give your answer to 2 decimal places.

The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C.

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(6 marks)

(Extra space) ....

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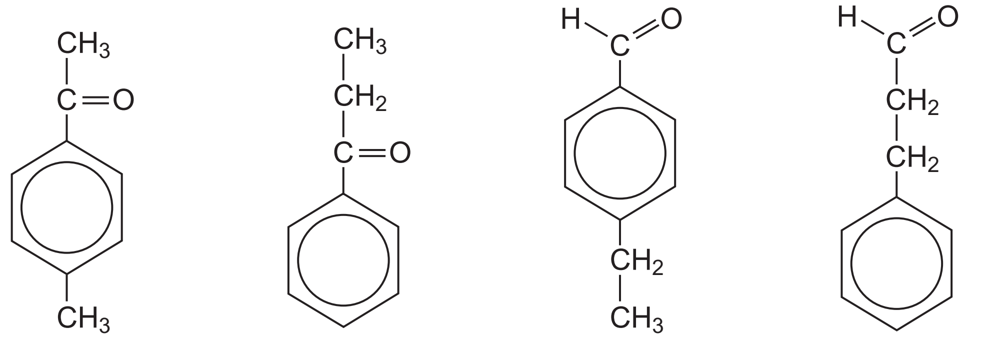
12

5 Mass spectrometry is used by organic chemists to help distinguish between different compounds.

Four isomers of $C_9H_{10}O$, shown below, were analysed by mass spectrometry.



A **B** **C** **D**

The mass spectra obtained from these four isomers were labelled in random order as I, II, III and IV.

Each spectrum contained a molecular ion peak at *m*/*z* = 134

The data in the table below show the *m*/*z* values greater than 100 for the **major** peaks in each spectrum due to fragmentation of the molecular ion. The table also shows where no major peaks occurred.

Spectrum	*m*/*z* values for major peaks	No major peak at *m*/*z*
I	119	133, 105
II	133, 119 and 105	
III	133, 105	119
IV	105	133, 119

5 (a) Two of the molecular ions fragmented to form an ion with *m*/*z* = 133 by losing a radical. Identify the radical that was lost.

....

(1 mark)

5 (b) Two of the molecular ions fragmented to form an ion with *m*/*z* = 119 by losing a radical. Identify the radical that was lost.

....

(1 mark)

Do not write outside the box

5 (c) Three of the molecular ions fragmented to form ions with *m*/*z* = 105 by losing a radical with M_r = 29

Identify **two** different radicals with M_r = 29 that could have been lost.

Radical 1 ....

Radical 2 ....

(2 marks)

5 (d) Consider the structures of the four isomers and the fragmentations indicated in parts **(a)** to **(c)**.
Write the letter **A**, **B**, **C** or **D**, in the appropriate box below, to identify the compound that produces each spectrum.

Spectrum I ☐

Spectrum II ☐

Spectrum III ☐

Spectrum IV ☐

(4 marks)

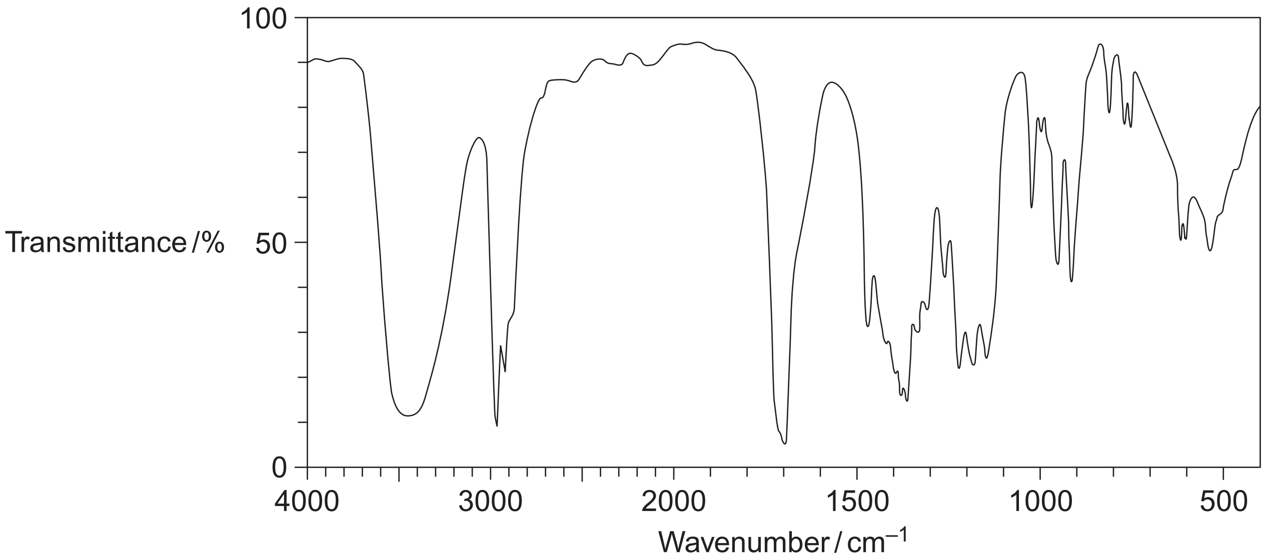
8

Turn over for the next question

Do not write outside the box

6 Compound **X** ($C_6H_{12}O_2$) was analysed by infrared spectroscopy and by proton nuclear magnetic resonance spectroscopy.

6 (a) The infrared spectrum of **X** is shown below.
Use **Table 1** on the Data Sheet to help you answer the question.



Identify the functional group that causes the absorption at 3450 cm^{-1} in the spectrum.

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(1 mark)

Do not write outside the box

6 (b) The proton n.m.r. spectrum of **X** consists of 4 singlet peaks.

The table below gives the chemical shift for each of these peaks, together with their integration values.

δ/ppm	1.2	2.2	2.6	3.8
Integration value	6	3	2	1

Use **Table 2** on the Data Sheet to help you answer the following questions.

Use the chemical shift and the integration data to show what can be deduced about the structure of **X** from the presence of the following in its proton n.m.r. spectrum.

6 (b) (i) The peak at δ = 2.6

....

(1 mark)

6 (b) (ii) The peak at δ = 2.2

....

(1 mark)

6 (b) (iii) The peak at δ = 1.2

....

(1 mark)

6 (b) (iv) Deduce the structure of **X** ($C_6H_{12}O_2$)

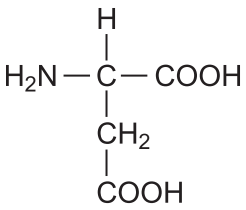
(1 mark)

5

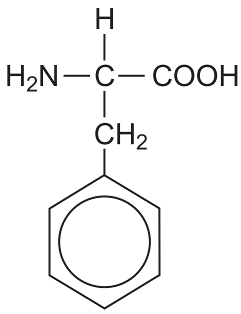
Turn over ▶

Do not write outside the box

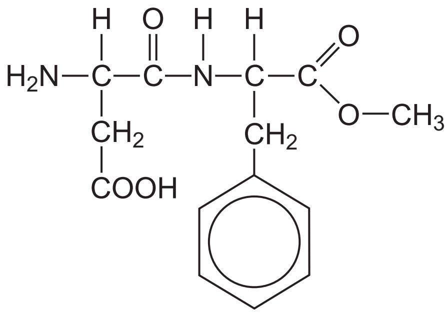
7 The amino acids aspartic acid and phenylalanine react together to form a dipeptide. This dipeptide can be converted into a methyl ester called aspartame.



aspartic acid



phenylalanine



aspartame

Aspartame has a sweet taste and is used in soft drinks and in sugar-free foods for people with diabetes.

Hydrolysis of aspartame forms methanol initially. After a longer time the peptide link breaks to form the free amino acids. Neither of these amino acids tastes sweet.

7 (a) Apart from the release of methanol, suggest why aspartame is **not** used to sweeten foods that are to be cooked.

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(1 mark)

(Extra space) ....

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7 (b) Give the IUPAC name of aspartic acid.

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(1 mark)

7 (c) Draw the organic species formed by aspartic acid at high pH.

(1 mark)

7 (d) Draw the zwitterion of phenylalanine.

(1 mark)

7 (e) Phenylalanine exists as a pair of stereoisomers.

7 (e) (i) State the meaning of the term *stereoisomers*.

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(2 marks)

7 (e) (ii) Explain how a pair of stereoisomers can be distinguished.

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(2 marks)

(Extra space) ....

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8

Do not write outside the box

8 Common substances used in everyday life often contain organic compounds.

8 (a) State an everyday use for each of the following compounds.

8 (a) (i) $CH_3(CH_2)_{17}COO^- Na^+$ ....

(1 mark)

8 (a) (ii) $CH_3(CH_2)_{19}COOCH_3$ ....

(1 mark)

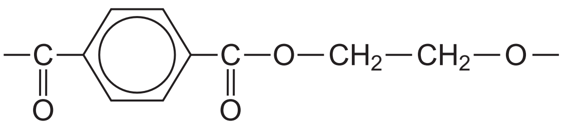
8 (a) (iii) $[C_{16}H_{33}N(CH_3)_3]^+ Br^-$ ....

(1 mark)

8 (b) The following structures are the repeating units of two different condensation polymers.

For each example, name the type of condensation polymer. Give a common name for a polymer of this type.

8 (b) (i)

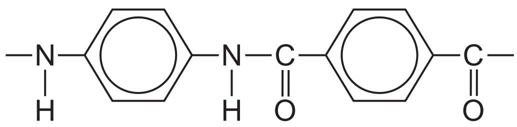


Type of condensation polymer ....

Common name ....

(2 marks)

8 (b) (ii)



Type of condensation polymer ....

Common name ....

(2 marks)

8 (b) (iii) Explain why the polymer in part **(b) (ii)** has a higher melting point than the polymer in part **(b) (i)**.

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(2 marks)

(Extra space) ....

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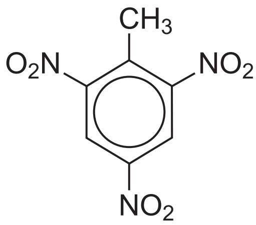
9

Turn over for the next question

9 Many aromatic nitro compounds are used as explosives. One of the most famous is 2-methyl-1,3,5-trinitrobenzene, originally called trinitrotoluene or TNT. This compound, shown below, can be prepared from methylbenzene by a sequence of nitration reactions.



9 (a) The mechanism of the nitration of methylbenzene is an electrophilic substitution.

9 (a) (i) Give the reagents used to produce the electrophile for this reaction.
Write an equation or equations to show the formation of this electrophile.

Reagents ....

....

Equation ....

....

(3 marks)

9 (a) (ii) Outline a mechanism for the reaction of this electrophile with methylbenzene to produce 4-methylnitrobenzene.

(3 marks)

9 (b) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TNT.

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(1 mark)

9 (c) Deduce the number of peaks in the ^{1}H n.m.r. spectrum of TNT.

....

(1 mark)

9 (d) Using the molecular formula ($C_7H_5N_3O_6$), write an equation for the decomposition reaction that occurs on the detonation of TNT. In this reaction equal numbers of moles of carbon and carbon monoxide are formed together with water and nitrogen.

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(1 mark)

9

Turn over for the next question

Section B

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

10 The reactions of molecules containing the chlorine atom are often affected by other functional groups in the molecule.

Consider the reaction of CH_3CH_2COCl and of $CH_3CH_2CH_2Cl$ with ammonia.

10 (a) For the reaction of CH_3CH_2COCl with ammonia, name and outline the mechanism and name the organic product.

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(6 marks)

(Extra space) ....

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Do not write outside the box

10 (b) For the reaction of $CH_3CH_2CH_2Cl$ with an **excess** of ammonia, name and outline the mechanism and name the organic product.

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(6 marks)

(Extra space) ....

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Question 10 continues on the next page

Turn over ▶

10 (c) Suggest **one** reason why chlorobenzene (C_6H_5Cl) does **not** react with ammonia under normal conditions.

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(1 mark)

(Extra space) ....

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13

Do not write outside the box

11 Chemists have to design synthetic routes to convert one organic compound into another.

Propanone can be converted into 2-bromopropane by a three-step synthesis.

Step 1: propanone is reduced to compound **L**.
Step 2: compound **L** is converted into compound **M**.
Step 3: compound **M** reacts to form 2-bromopropane.

Deduce the structure of compounds **L** and **M**.

For each of the three steps, suggest a reagent that could be used and name the mechanism.

Equations and curly arrow mechanisms are **not** required.

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(8 marks)

(Extra space) ....

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8

END OF QUESTIONS

There are no questions printed on this page

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED