

Centre Number						Candidate Number				
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Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
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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**.



J A N 1 2 C H E M 4 0 1

WMP/Jan12/CHEM4

# CHEM4

**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.

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

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

Experiment	Initial [P] / mol dm <sup>-3</sup>	Initial [Q] / mol dm <sup>-3</sup>	Initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
<b>1</b>	0.20	0.30	$1.8 \times 10^{-3}$
<b>2</b>	0.40	0.60	
<b>3</b>	0.60		$5.4 \times 10^{-3}$
<b>4</b>		0.90	$12.2 \times 10^{-3}$

(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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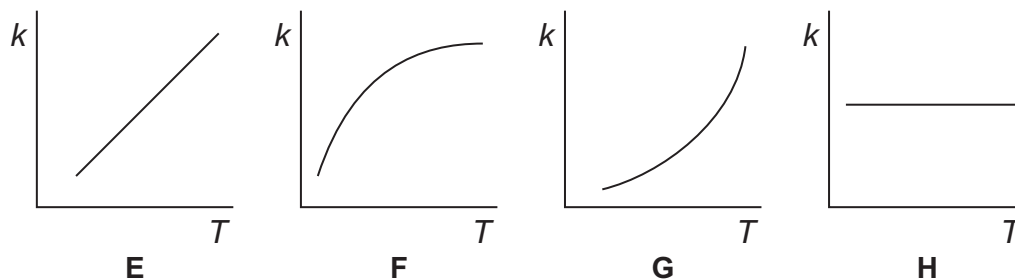
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Units .....

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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.

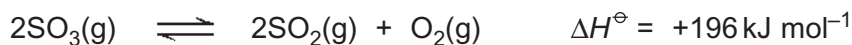
(1 mark)

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Turn over ►



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



- 2 (a) In an experiment, 8.0 mol of sulfur trioxide were placed in a container of volume  $12.0 \text{ dm}^3$  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.

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(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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**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) .....  
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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 ( $\text{CH}_3\text{CH}_2\text{NH}_2$ ) 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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- 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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**Turn over for the next question**

**Turn over ►**







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

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

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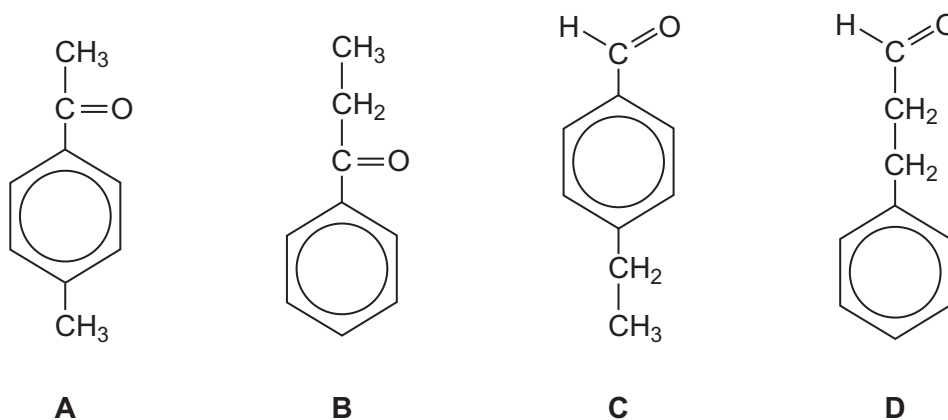
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- 5 Mass spectrometry is used by organic chemists to help distinguish between different compounds.

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



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)



- 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

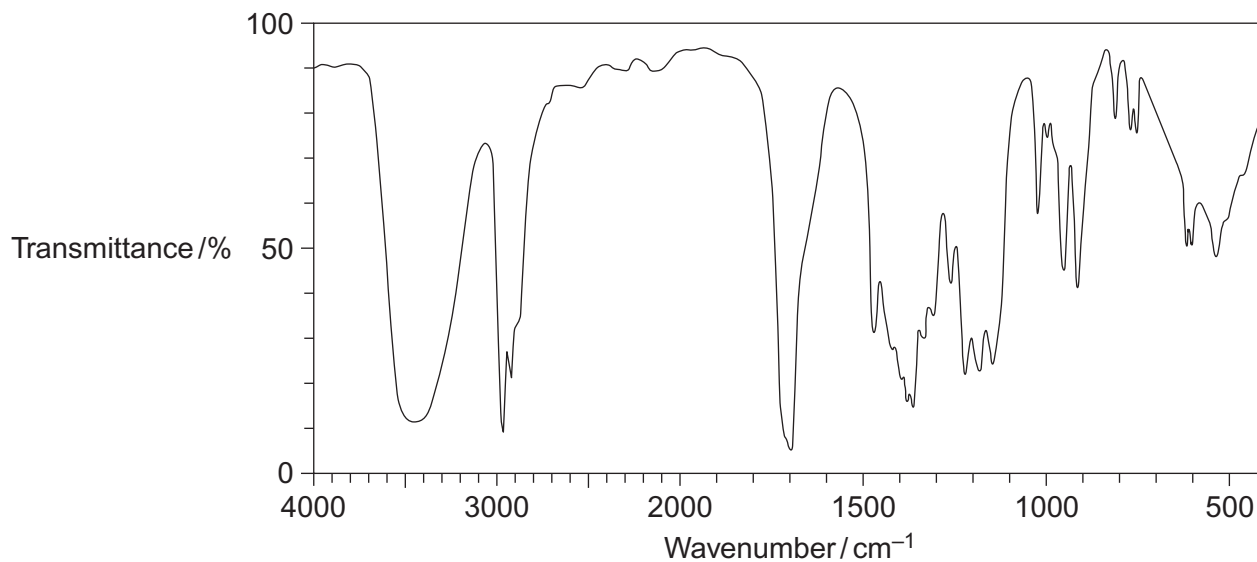
Turn over for the next question

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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  $3450\text{ cm}^{-1}$  in the spectrum.

.....  
(1 mark)



**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.

$\delta$ /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  $\delta = 2.6$

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(1 mark)

**6 (b) (ii)** The peak at  $\delta = 2.2$

.....  
(1 mark)

**6 (b) (iii)** The peak at  $\delta = 1.2$

.....  
(1 mark)

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

(1 mark)

5
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Turn over ►





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)

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Turn over ►



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

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

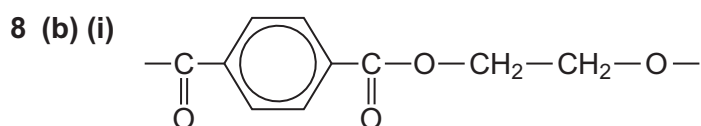
8 (a) (i)  $\text{CH}_3(\text{CH}_2)_{17}\text{COO}^- \text{Na}^+$  .....  
(1 mark)

8 (a) (ii)  $\text{CH}_3(\text{CH}_2)_{19}\text{COOCH}_3$  .....  
(1 mark)

8 (a) (iii)  $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]^+ \text{Br}^-$  .....  
(1 mark)

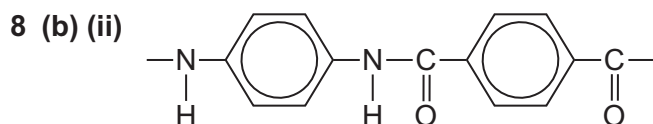
8 (b) The following structures are the repeating units of two different condensation polymers.

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



Type of condensation polymer .....

Common name .....  
(2 marks)



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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(Extra space) ..... (2 marks)

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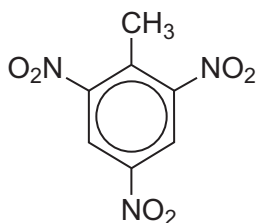
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**Turn over for the next question**

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- 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 .....

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Equation .....

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(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  $^{13}\text{C}$  n.m.r. spectrum of TNT.

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(1 mark)

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

.....  
(1 mark)

9 (d) Using the molecular formula ( $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ ), 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)

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**Turn over for the next question**

**Turn over ►**



### 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  $\text{CH}_3\text{CH}_2\text{COCl}$  and of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  with ammonia.

**10 (a)**    For the reaction of  $\text{CH}_3\text{CH}_2\text{COCl}$  with ammonia, name and outline the mechanism and name the organic product.

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- 10 (b)** For the reaction of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  with an **excess** of ammonia, name and outline the mechanism and name the organic product.

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Question 10 continues on the next page

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

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(Extra space) ..... (1 mark)

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**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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(Extra space) ..... (8 marks)

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**END OF QUESTIONS**

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ANSWER IN THE SPACES PROVIDED**

