

Surname						Other Names					
Centre Number						Candidate Number					
Candidate Signature											

For Examiner's Use

General Certificate of Education
January 2007
Advanced Level Examination



CHEMISTRY
Unit 4 Further Physical and Organic Chemistry

CHM4

Tuesday 23 January 2007 9.00 am to 10.30 am

For this paper you must have

- a calculator.

Time allowed: 1 hour 30 minutes

Instructions

- Use blue or black ink or ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- Answer the questions in **Section A** and **Section B** in the spaces provided.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.
- The Periodic Table/Data Sheet is provided on pages 3 and 4. Detach this perforated sheet at the start of the examination.
- **Section B** questions are provided on a perforated sheet. Detach this sheet at the start of the examination.

Information

- The maximum mark for this paper is 90.
- The marks for questions are shown in brackets.
- You are expected to use a calculator where appropriate.
- Write your answers to the question in **Section B** in continuous prose, where appropriate. You will be assessed on your ability to use an appropriate form and style of writing, to organise relevant information clearly and coherently, and to use specialist vocabulary, where appropriate.

Advice

- You are advised to spend about 1 hour on **Section A** and about 30 minutes on **Section B**.

For Examiner's Use			
Question	Mark	Question	Mark
1			
2			
3			
4			
5			
6			
7			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

There are no questions printed on this page

Gas constant $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

Table 1
Proton n.m.r chemical shift data

Type of proton	δ/ppm
RCH_3	0.7–1.2
R_2CH_2	1.2–1.4
R_3CH	1.4–1.6
RCOCH_3	2.1–2.6
ROCH_3	3.1–3.9
RCOOCH_3	3.7–4.1
ROH	0.5–5.0

Table 2
Infra-red absorption data

Bond	Wavenumber/ cm^{-1}
C—H	2850–3300
C—C	750–1100
C=C	1620–1680
C=O	1680–1750
C—O	1000–1300
O—H (alcohols)	3230–3550
O—H (acids)	2500–3000

SECTION A

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

- 1 (a) The following data were obtained by studying the reaction between compounds **A**, **B** and **C** at a constant temperature.

Experiment	Initial concentration of A / mol dm ⁻³	Initial concentration of B / mol dm ⁻³	Initial concentration of C / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.20	0.10	0.40	0.80×10^{-3}
2	0.20	0.40	0.40	3.20×10^{-3}
3	0.10	0.80	0.40	1.60×10^{-3}
4	0.10	0.30	0.20	0.60×10^{-3}

- (i) Deduce the order of reaction with respect to **A**.

.....

- (ii) Deduce the order of reaction with respect to **B**.

.....

- (iii) Deduce the order of reaction with respect to **C**.

.....

(3 marks)

- (b) The rate equation for the reaction between compounds **D** and **E** at a given temperature is

$$\text{rate} = k[\mathbf{D}]^2[\mathbf{E}]$$

The initial rate of reaction is 8.36×10^{-4} mol dm⁻³ s⁻¹ when the initial concentration of **D** is 0.84 mol dm⁻³ and the initial concentration of **E** is 1.16 mol dm⁻³.

Calculate a value for the rate constant, *k*, at this temperature and deduce its units.

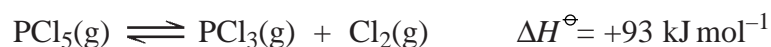
Value of *k*

.....

Units of *k*

.....

- 2 At high temperatures, PCl_5 dissociates according to the following equation.



A 2.60 mol sample of PCl_5 is placed in a sealed container and heated to a fixed temperature. At equilibrium, 1.40 mol of PCl_5 remain unreacted. The total pressure in the container is 125 kPa.

- (a) Calculate the number of moles of Cl_2 and the total number of moles of gas present in the equilibrium mixture.

Moles of Cl_2

Total number of moles
(2 marks)

- (b) Calculate the mole fraction of PCl_5 and the mole fraction of Cl_2 in the equilibrium mixture.

Mole fraction of PCl_5

.....

Mole fraction of Cl_2

.....

(2 marks)

- (c) (i) Write a general expression for the partial pressure of a gas, in a mixture of gases.

.....

.....

- (ii) Calculate the partial pressure of PCl_5 and the partial pressure of Cl_2 in the equilibrium mixture.

Partial pressure of PCl_5

.....

Partial pressure of Cl_2

.....

(3 marks)

- (d) Write an expression for the equilibrium constant, K_p , for this reaction.

.....

.....

- (e) (i) State the effect, if any, on the value of K_p of adding more PCl_5 at a constant temperature.

.....

- (ii) State the effect, if any, on the value of K_p of increasing the temperature of the container.

.....

(2 marks)

- (f) In a further experiment, a second sample of PCl_5 is heated to a different temperature. In the equilibrium mixture produced at this temperature, the partial pressure of PCl_5 is 36.9 kPa and the partial pressure of Cl_2 is 42.6 kPa. Calculate a value for the equilibrium constant, K_p , for this reaction at this temperature and give its units.

Calculation

.....

.....

Units

(3 marks)

Turn over for the next question

3 In this question, give all pH and pK_a values to 2 decimal places.

(a) Hydrochloric acid is described as a strong Brønsted-Lowry acid.

(i) State what is meant by the term *Brønsted-Lowry acid*.

.....

(ii) State why hydrochloric acid is described as *strong*.

.....

(2 marks)

(b) A sample of hydrochloric acid contains 7.05×10^{-3} mol of hydrogen chloride in 50 cm^3 of solution.

(i) Calculate the concentration, in mol dm^{-3} , of this hydrochloric acid.

.....

.....

(ii) Write an expression for the term *pH*.

.....

(iii) Calculate the pH of this hydrochloric acid.

.....

(iv) When water is added to this 50 cm^3 sample of acid the pH increases. Calculate the total volume of the solution when the pH becomes exactly 1.00

.....

.....

.....

.....

(6 marks)

(c) The value of the acid dissociation constant, K_a , for the weak acid HX is $6.10 \times 10^{-5} \text{ mol dm}^{-3}$ at 25°C .

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

.....
.....

(ii) Calculate the pH of a $0.255 \text{ mol dm}^{-3}$ solution of HX at 25°C .

.....
.....
.....
.....

(4 marks)

(d) A given volume of a buffer solution contains $6.85 \times 10^{-3} \text{ mol}$ of the weak acid HY and $2.98 \times 10^{-3} \text{ mol}$ of the salt NaY. The pH of the buffer solution is 3.78

(i) Calculate the value of pK_a for the acid HY at this temperature.

.....
.....
.....
.....
.....
.....

(ii) State and explain the effect on the pH of the buffer solution when a small amount of hydrochloric acid is added.

Effect on pH

Explanation

.....
.....
.....

(7 marks)

- 4 Compounds **J**, **K**, **L** and **M** are structural isomers of $C_4H_{10}O_2$.
Some of these isomers are ethers. Ethers contain the C–O–C linkage.
Isomers **J**, **K**, **L** and **M** can be distinguished using proton n.m.r. spectroscopy and infra-red spectroscopy.

- (a) The substance TMS is used as a standard in recording proton n.m.r. spectra.
Draw the structure of TMS and give two reasons why it is used as a standard.

Structure of TMS

Reason 1

Reason 2

(3 marks)

- (b) State the number of peaks in the proton n.m.r. spectrum of isomer **J**,
 $CH_3OCH_2CH_2OCH_3$

.....
(1 mark)

- (c) (i) Isomer **K**, shown below, has five peaks in its proton n.m.r. spectrum. Predict the splitting pattern of the peaks due to the protons labelled *a* and *b*.



a

b

- (ii) Identify the wavenumber of an absorption which would be present in the infra-red spectrum of **K** but which would not be present in the infra-red spectrum of **J**.

.....
(3 marks)

(d) Isomer **L**, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, can be used to form polyesters.

(i) Give the name of **L**.

.....

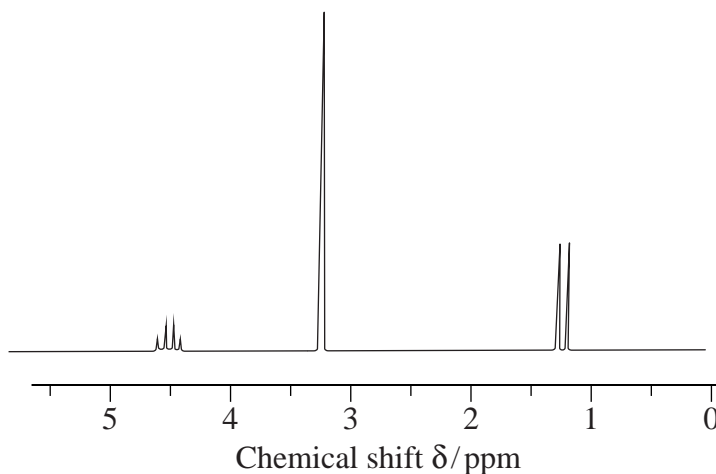
(ii) Isomer **L** reacts with pentanedioic acid to form a polyester. Name the type of polymerisation involved and draw the repeating unit of the polyester formed.

Type of polymerisation

Repeating unit

(4 marks)

(e) The proton n.m.r. spectrum of isomer **M** is shown below. The measured integration trace gives the ratio 0.4 to 2.4 to 1.2 for the peaks at δ 4.6, 3.3 and 1.3, respectively.



(i) State what you can deduce from the integration value for the peak at δ 3.3

.....

(ii) Use **Table 1** on the reverse of the Periodic Table to help you identify the type of proton leading to the peak at δ 3.3

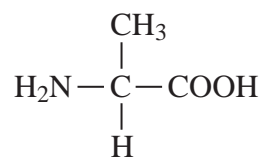
.....

(iii) Draw the part of the structure which can be deduced from the splitting of the peaks at δ 1.3 and δ 4.6 and from their integration values.

.....

(iv) Hence, deduce the structure of **M**.

5 The amino acid *alanine* is shown below.



(a) Give the systematic name for alanine.

.....
(1 mark)

(b) (i) Draw the structure of the dipeptide formed from two alanine molecules, showing clearly the full structure of the peptide link.

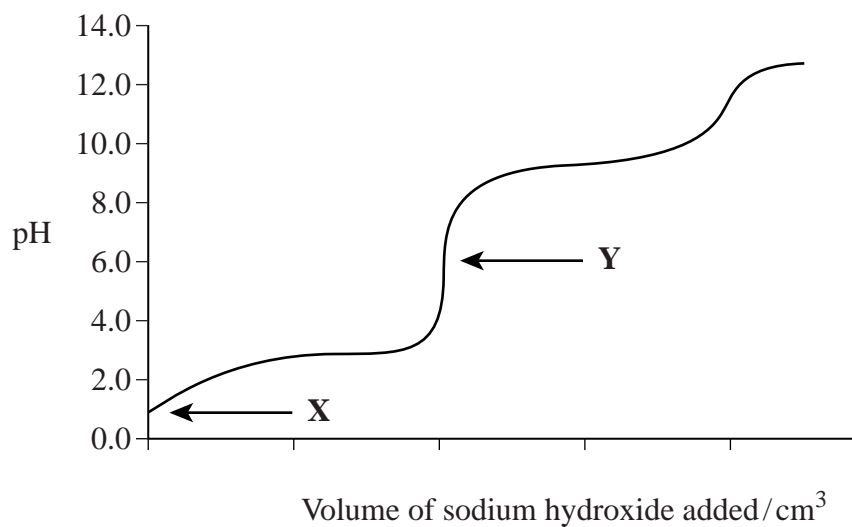
(ii) Draw the structure of the organic compound formed by the reaction of alanine with propan-2-ol in the presence of a small amount of the catalyst concentrated sulphuric acid.

(iii) Draw the structure of the *N*-substituted amide formed by the reaction of alanine with ethanoyl chloride. Name the type of mechanism involved.

Structure

Name of mechanism
(4 marks)

- (c) A solution was prepared by reacting alanine with an equal number of moles of hydrochloric acid. This solution was titrated with aqueous sodium hydroxide. The titration curve obtained is shown below.



- (i) Draw the structure of the alanine species present at point X on the curve.
- (ii) Draw the structure of the alanine species present at point Y on the curve.

(2 marks)

7

SECTION B

Detach this perforated sheet.

Answer **both** questions 6 and 7 in the space provided on page 14 and pages 17-20.

- 6 (a) An acylium ion has the structure $\text{R}-\overset{+}{\text{C}}=\text{O}$ where R is any alkyl group.

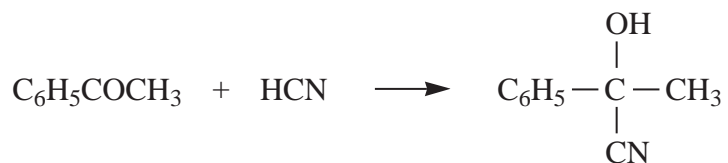
In the conversion of benzene into phenylethanone, $\text{C}_6\text{H}_5\text{COCH}_3$, an acylium ion $\text{CH}_3\overset{+}{\text{C}}\text{O}$ reacts with a benzene molecule.

Write an equation to show the formation of this acylium ion from ethanoyl chloride and one other substance.

Name and outline the mechanism of the reaction of this acylium ion with benzene.

(6 marks)

- (b) Phenylethanone, $\text{C}_6\text{H}_5\text{COCH}_3$, reacts with HCN according to the equation below.



Name and outline the mechanism of this reaction.

The product formed exists as a racemic mixture. State the meaning of the term *racemic mixture* and explain why such a mixture is formed in this reaction.

(8 marks)

- (c) Acylium ions are also formed by the fragmentation of molecular ions in a mass spectrometer.

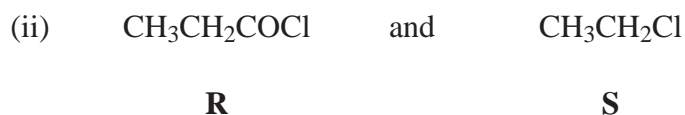
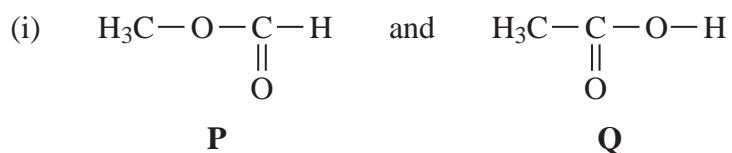
Give the name of compound **Z**, $\text{CH}_3\text{CH}_2\text{COCH}(\text{CH}_3)_2$

Draw the structures of the **two** possible acylium ions formed in the fragmentation of the molecular ion of **Z** in a mass spectrometer.

Write an equation for the formation of **one** of these acylium ions from the molecular ion of **Z**.

(5 marks)

- 7 (a) Describe, by giving reagents and stating observations, how you could distinguish between the compounds in the following pairs using simple test-tube reactions.



(6 marks)

- (b) (i) Give the reagents needed for the reduction of nitrobenzene to form phenylamine. Write an equation for the reaction. Use [H] to represent the reductant.
- (ii) Name the type of mechanism for the reaction between phenylamine and bromomethane. Draw the structure of the product of the reaction of phenylamine with a large excess of bromomethane.

(5 marks)

END OF QUESTIONS

