

Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

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General Certificate of Education  
January 2008  
Advanced Level Examination



**CHEMISTRY**  
**Unit 4 Further Physical and Organic Chemistry**

**CHM4**

Tuesday 22 January 2008 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 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 questions 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**.

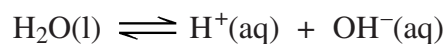
For Examiner's Use			
Question	Mark	Question	Mark
1			
2			
3			
4			
5			
6			
7			
8			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

## SECTION A

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

1 In this question give all values of pH to 2 decimal places.

(a) The dissociation of water can be represented by the following equilibrium.



(i) Write an expression for the ionic product of water,  $K_w$

.....

(ii) The pH of a sample of pure water is 6.63 at 50 °C.

Calculate the concentration in  $\text{mol dm}^{-3}$  of  $\text{H}^+$  ions in this sample of pure water.

.....

(iii) Deduce the concentration in  $\text{mol dm}^{-3}$  of  $\text{OH}^-$  ions in this sample of pure water.

.....

(iv) Calculate the value of  $K_w$  at this temperature.

.....

.....

.....

(4 marks)

(b) At 25 °C the value of  $K_w$  is  $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ .

Calculate the pH of a  $0.136 \text{ mol dm}^{-3}$  solution of KOH at 25 °C.

.....

.....

.....

.....

(2 marks)



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

**Table 1**  
Proton n.m.r chemical shift data

Type of proton	$\delta/\text{ppm}$
$\text{RCH}_3$	0.7–1.2
$\text{R}_2\text{CH}_2$	1.2–1.4
$\text{R}_3\text{CH}$	1.4–1.6
$\text{RCOCH}_3$	2.1–2.6
$\text{ROCH}_3$	3.1–3.9
$\text{RCOOCH}_3$	3.7–4.1
$\text{ROH}$	0.5–5.0

**Table 2**  
Infra-red absorption data

Bond	Wavenumber/ $\text{cm}^{-1}$
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

2 In this question give all values of pH to 2 decimal places.

The acid dissociation constant,  $K_a$ , for propanoic acid has the value  $1.35 \times 10^{-5} \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ .

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$$

(a) Calculate the pH of a  $0.169 \text{ mol dm}^{-3}$  solution of propanoic acid.

.....

.....

.....

.....

.....

(3 marks)

(b) A buffer solution contains  $0.250 \text{ mol}$  of propanoic acid and  $0.190 \text{ mol}$  of sodium propanoate in  $1000 \text{ cm}^3$  of solution.

A  $0.015 \text{ mol}$  sample of solid sodium hydroxide is then added to this buffer solution.

(i) Write an equation for the reaction of propanoic acid with sodium hydroxide.

.....

(ii) Calculate the number of moles of propanoic acid and of propanoate ions present in the buffer solution after the addition of the sodium hydroxide.

*Moles of propanoic acid present* .....

.....

*Moles of propanoate ions present* .....

.....

(iii) Hence, calculate the pH of the buffer solution after the addition of the sodium hydroxide.

.....

.....

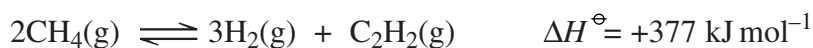
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.....

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(6 marks)

3 Under suitable conditions the equilibrium represented below was established.



(a) Write an expression for the equilibrium constant,  $K_c$ , for this reaction.

.....  
 .....  
 (1 mark)

(b) At a given temperature and pressure, the equilibrium mixture contained 0.44 mol of methane, 0.28 mol of hydrogen and 0.12 mol of ethyne ( $\text{C}_2\text{H}_2$ ) in a container of volume  $0.25 \text{ dm}^3$ .

Calculate the value of  $K_c$  under these conditions and deduce its units.

*Calculation* .....

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

*Units* .....  
 (4 marks)

(c) State the effect of an increase in temperature on the position of this equilibrium and on the value of  $K_c$  for this reaction.

*Effect on position of equilibrium* .....

*Effect on the value of  $K_c$*  .....  
 (2 marks)

(d) State the effect of an increase in pressure on the position of this equilibrium and on the value of  $K_c$  for this reaction.

*Effect on position of equilibrium* .....

*Effect on the value of  $K_c$*  .....  
 (2 marks)

- (e) Calculate the mole fraction of ethyne ( $\text{C}_2\text{H}_2$ ) in this equilibrium mixture.

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

(2 marks)

- (f) Calculate the partial pressure of ethyne in this mixture, given that the total pressure is  $2.78 \times 10^4$  kPa.

.....  
 .....

(1 mark)

- (g) A different equilibrium mixture was produced starting from methane alone.



When 3.0 mol of methane were used, the equilibrium mixture formed contained 1.6 mol of methane. Calculate the number of moles of hydrogen and the number of moles of ethyne present in this equilibrium mixture.

*Moles of hydrogen* .....

.....

*Moles of ethyne* .....

.....

(2 marks)

14
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**Turn over for the next question**

**Turn over ►**

- 4 (a) Each part below concerns a different pair of isomers.

Draw one possible structure for each of the compounds **A** to **J**.

Use **Table 2** on the Data Sheet where appropriate.

- (i) Compounds **A** and **B** have the molecular formula  $C_6H_{12}$   
Both have only one peak in their proton n.m.r. spectra.  
**A** has an absorption at  $1650\text{ cm}^{-1}$  in its infra-red spectrum but **B** does not.

**A**

**B**

- (ii) Compounds **C** and **D** have the molecular formula  $C_5H_{10}O$  and both have only two peaks in their proton n.m.r. spectra.  
**C** forms a silver mirror with Tollens' reagent but **D** does not.

**C**

**D**

- (iii) Compounds **E** and **F** have the molecular formula  $C_3H_6O_2$  and both have only a quartet, a triplet and a singlet peak in their proton n.m.r. spectra.  
**E** gives an effervescence with aqueous sodium hydrogencarbonate but **F** does not.

**E**

**F**



- (iv) Compounds **G** and **H** have the molecular formula  $C_6H_{12}$   
**G** shows geometrical isomerism but not optical isomerism.  
**H** shows optical isomerism but not geometrical isomerism.

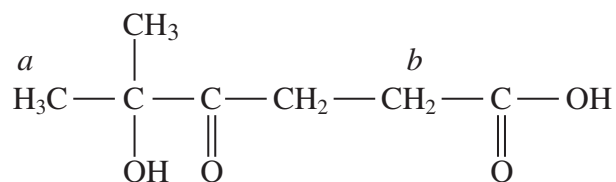
**G****H**

- (v) Compounds **I** and **J** have the molecular formula  $C_5H_{12}O$   
**I** cannot be oxidised by acidified potassium dichromate(VI) but can be dehydrated to form an alkene.  
**J** can be oxidised by acidified potassium dichromate(VI) but cannot be dehydrated to form an alkene.

**I****J**

(10 marks)

- (b) Consider the compound below.



- (i) Predict the number of peaks in its proton n.m.r. spectrum.

.....

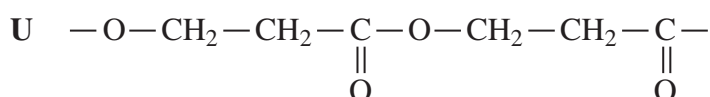
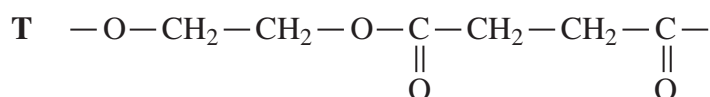
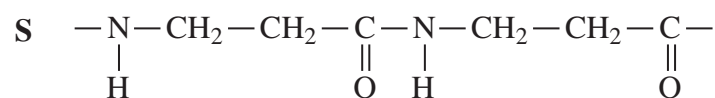
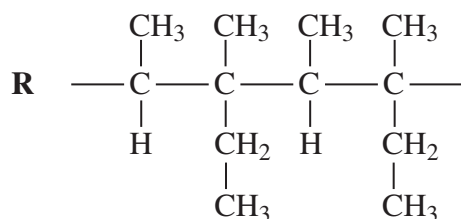
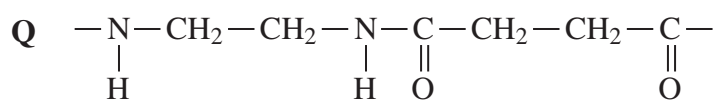
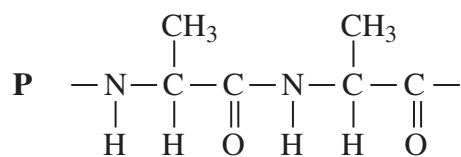
- (ii) The protons labelled *a* and *b* each produce a peak in the proton n.m.r. spectrum.  
Name the splitting pattern for each of these peaks.

Splitting pattern for the protons labelled *a* .....

Splitting pattern for the protons labelled *b* .....

(3 marks)

5 Sections of different polymers **P** to **U** are shown below.



- (a) (i) Polymer **P** is formed from the single amino acid, 2-aminopropanoic acid.  
Draw the structure of the zwitterion of this amino acid.

- (ii) One other polymer represented above is formed from a single amino acid.  
Give the formula of this amino acid.

.....

- (iii) Name the monomers used in the formation of polymer **Q**.

Name of first monomer .....

Name of second monomer .....

(4 marks)

(b) Polymer **R** is formed from an alkene monomer.

(i) Name the type of polymerisation involved in the formation of polymer **R**.

.....

(ii) Name the alkene monomer.

.....

(2 marks)

(c) Polymers **T** and **U** are polyesters.

(i) Draw the structures of the monomers used to produce polymer **T**.

*First monomer*

*Second monomer*

(ii) Draw the structure of the species formed when polymer **U** is hydrolysed by heating with aqueous sodium hydroxide.

(3 marks)

(d) (i) Name the strongest type of intermolecular force in polymer **R**.

.....

(ii) Name the strongest type of intermolecular force in polymer **T**.

.....

(2 marks)

- 6 (a) The initial rate of the reaction between compounds X and Y was measured in a series of experiments at a fixed temperature. The following rate equation was deduced.

$$\text{rate} = k[\text{X}]^2[\text{Y}]^0$$

- (i) Complete the table of data below for the reaction between X and Y.

Expt	Initial [X] /mol dm <sup>-3</sup>	Initial [Y] /mol dm <sup>-3</sup>	Initial rate /mol dm <sup>-3</sup>
1	$1.20 \times 10^{-3}$	$3.30 \times 10^{-3}$	$2.68 \times 10^{-4}$
2	$1.20 \times 10^{-3}$	$6.60 \times 10^{-3}$	
3	$2.40 \times 10^{-3}$	$6.60 \times 10^{-3}$	
4		$9.90 \times 10^{-3}$	$8.04 \times 10^{-4}$

- (ii) Using the data for experiment 1, calculate a value for the rate constant,  $k$ , and deduce its units.

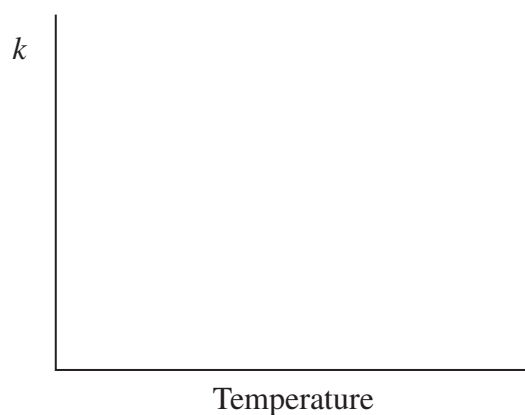
*Calculation* .....

.....

*Units* .....

(6 marks)

- (b) Sketch a graph to show how the value of the rate constant,  $k$ , varies with temperature.

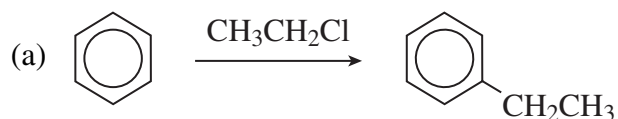


(1 mark)

**SECTION B**

Answer **both** questions 7 and 8 in the space provided on pages 15–20.

7 Chloroethane ( $\text{CH}_3\text{CH}_2\text{Cl}$ ) can be used as a reagent in each of the following reactions.

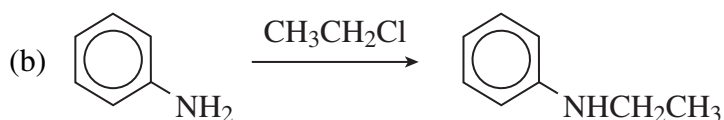


Identify a catalyst for this reaction and show how the catalyst reacts and is regenerated.

Name and outline a mechanism for this reaction.

Name the product shown and identify an important industrial chemical manufactured from it.

(9 marks)



Name and outline a mechanism for this reaction and name the product shown.

(6 marks)

15
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**Turn over for the next question**

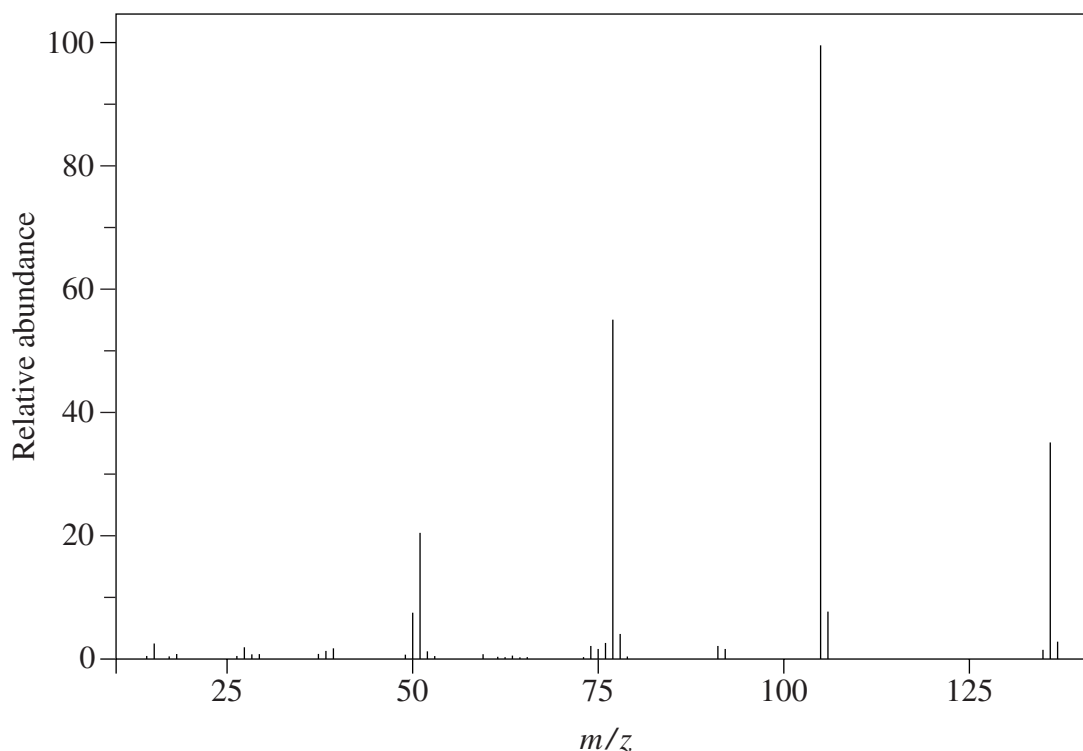
**Turn over ►**

8 The ester methyl benzenecarboxylate ( $C_6H_5COOCH_3$ ) can be prepared by the reaction of methanol with benzenecarbonyl chloride,  $C_6H_5COCl$

(a) Name and outline a mechanism for this reaction.

(5 marks)

(b) The mass spectrum of methyl benzenecarboxylate is shown below.



Suggest structures for the fragment ions which produce peaks at  $m/z = 105$  and  $m/z = 77$  in the mass spectrum above.

Write an equation for the fragmentation of the molecular ion to give the ion which produces the peak at  $m/z = 105$ .

(4 marks)

(c) Esters **V** and **W** are isomers of methyl benzenecarboxylate and both contain a benzene ring.

**V** has a major peak at  $m/z = 43$  in its mass spectrum. Suggest a structure for the fragment ion which produces this peak and hence suggest a structure for **V**.

**W** has a major peak at  $m/z = 91$  in its mass spectrum. Suggest a structure for the fragment ion which produces this peak and hence suggest a structure for **W**.

(4 marks)

(d) (i) Infra-red spectroscopy can be used to distinguish between esters and carboxylic acids. Identify an absorption that would enable you to distinguish between methyl benzenecarboxylate and its isomer 4-methylbenzenecarboxylic acid.

(ii) State how infra-red spectroscopy can be used to show that an unknown ester is definitely methyl benzenecarboxylate.

(2 marks)

END OF QUESTIONS













