Surname						Other Names					
Centre Number						Candidate Number					
Candidate Signature											

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General Certificate of Education
January 2002
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

CHEMISTRY CHM4
Unit 4 Further Physical and Organic Chemistry

Thursday 24 January 2002 Morning Session

In addition to this paper you will require:
a Periodic Table;
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 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 marked.

Information

- The maximum mark for this paper is 90.
- Mark allocations are shown in brackets.
- This paper carries 15 per cent of the total marks for Advanced Level.
- You are expected to use a calculator where appropriate.
- The following data may be required.
  Gas constant $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$
- Your answers to questions in Section B should be written 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			
Number	Mark	Number	Mark
1			
2			
3			
4			
5			
6			
7			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **A** and **B** at a constant temperature.

Experiment	Initial concentration of **A**/mol dm^{-3}	Initial concentration of **B**/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
1	0.15	0.24	0.45×10^{-5}
2	0.30	0.24	0.90×10^{-5}
3	0.60	0.48	7.20×10^{-5}

(i) Show how the data in the table can be used to deduce that the reaction is first-order with respect to **A**.

....

....

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

....

....

(2 marks)

(b) The following data were obtained in a second series of experiments on the rate of the reaction between compounds **C** and **D** at a constant temperature.

Experiment	Initial concentration of **C**/mol dm^{-3}	Initial concentration of **D**/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
4	0.75	1.50	9.30×10^{-5}
5	0.20	0.10	To be calculated

The rate equation for this reaction is

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

(i) Use the data from Experiment 4 to calculate a value for the rate constant, k, at this temperature. State the units of k.

Value for k ....

....

....

Units of k ....

....

(ii) Calculate the value of the initial rate in Experiment 5.

....

....

....

(4 marks)

6

TURN OVER FOR THE NEXT QUESTION

Turn over ▶

2 Hydrogen and carbon monoxide were mixed in a 2:1 mole ratio. The mixture was allowed to reach equilibrium according to the following equation at a fixed temperature and a total pressure of 1.75×10^4 kPa.

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

(a) The equilibrium mixture contained 0.430 mol of carbon monoxide and 0.0850 mol of methanol.

(i) Calculate the number of moles of hydrogen present in the equilibrium mixture.

....

(ii) Hence calculate the mole fraction of hydrogen in the equilibrium mixture.

....

....

....

(iii) Calculate the partial pressure of hydrogen in the equilibrium mixture.

....

....

....

(5 marks)

(b) In a different mixture of the three gases at equilibrium, the partial pressure of carbon monoxide was 7550 kPa, the partial pressure of hydrogen was 12300 kPa and the partial pressure of methanol was 2710 kPa.

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

....

(ii) Calculate the value of the equilibrium constant, K_p, for the reaction under these conditions and state its units.

K_p ....

....

Units ....

(3 marks)

(c) Two isomeric esters **E** and **F** formed from methanol have the molecular formula $C_6H_{12}O_2$

Isomer **E** has only 2 singlet peaks in its proton n.m.r. spectrum.

Isomer **F** is optically active.

Draw the structures of these two isomers.

*Isomer **E***

*Isomer **F***

(2 marks)

$\overline{}$ 10

Turn over ▶

3 The value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 298 K.

(a) (i) Write an expression for K_a for ethanoic acid.

....

(ii) Calculate the pH at 298 K of a 0.220 mol dm^{-3} solution of ethanoic acid.

....

....

....

....

....

....

(5 marks)

(b) A sample of the 0.220 mol dm^{-3} solution of ethanoic acid was titrated against sodium hydroxide solution.

(i) Calculate the volume of a 0.150 mol dm^{-3} solution of sodium hydroxide required to neutralise 25.0 cm^3 of the ethanoic acid solution.

....

....

....

....

(ii) From the list below, select the best indicator for this titration and explain your choice.

Name of indicator	**pH range**
bromophenol blue	3.0 – 4.6
methyl red	4.2 – 6.3
bromothymol blue	6.0 – 7.6
thymol blue	8.0 – 9.6

Indicator ....

Explanation ....

....

....

(5 marks)

(c) A buffer solution is formed when 2.00 g of sodium hydroxide are added to 1.00 dm^3 of a 0.220 mol dm^{-3} solution of ethanoic acid.
Calculate the pH at 298 K of this buffer solution.

....

....

....

....

....

....

....

(6 marks)

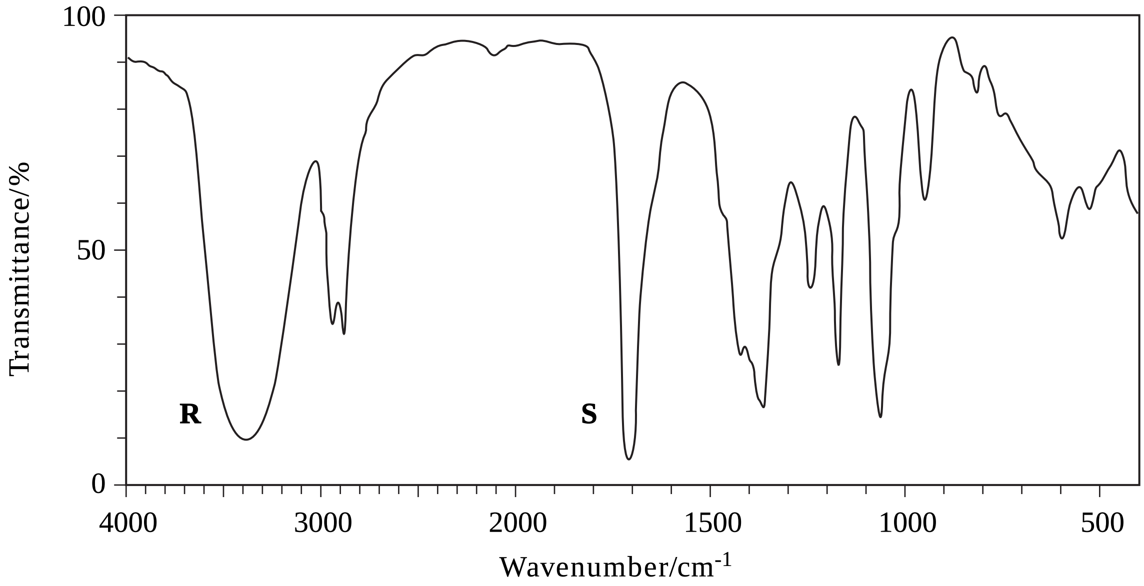
16

Turn over ▶

4 Spectral data for use in this question are printed on the reverse of the Periodic Table provided.

Compound **Q** has the molecular formula $C_4H_8O_2$

(a) The infra-red spectrum of **Q** is shown below.



Identify the type of bond causing the absorption labelled **R** and that causing the absorption labelled **S**.

R ....

S ....

(2 marks)

(b) **Q** does not react with Tollens' reagent or Fehling's solution. Identify a functional group which would react with these reagents and therefore cannot be present in **Q**.

....

(1 mark)

(c) Proton n.m.r. spectra are recorded using a solution of a substance to which tetramethylsilane (TMS) has been added.

(i) Give two reasons why TMS is a suitable standard.

Reason 1 ....

Reason 2 ....

(ii) Give an example of a solvent which is suitable for use in recording an n.m.r. spectrum. Give a reason for your choice.

Solvent ....

Reason ....

(4 marks)

(d) The proton n.m.r. spectrum of **Q** shows 4 peaks.
The table below gives δ values for each of these peaks together with their splitting patterns and integration values.

δ/ppm	2.20	2.69	3.40	3.84
Splitting pattern	singlet	triplet	singlet	triplet
Integration value	3	2	1	2

What can be deduced about the structure of **Q** from the presence of the following in its n.m.r. spectrum?

(i) The singlet peak at δ = 2.20

....

(ii) The singlet peak at δ = 3.40

....

(iii) Two triplet peaks

....

(3 marks)

(e) Using your answers to parts (a), (b) and (d), deduce the structure of compound **Q**.

(1 mark)

11

Turn over ▶

5 (a) Synthetic polyamides are produced by the reaction of dicarboxylic acids with compounds such as $H_2N(CH_2)_6NH_2$

(i) Name the compound $H_2N(CH_2)_6NH_2$

....

(ii) Give the repeating unit in the polyamide nylon 6,6.

....

(2 marks)

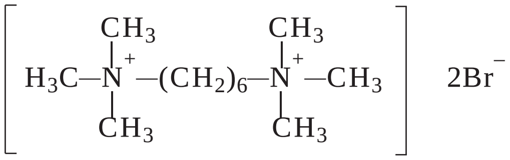
(b) Synthetic polyamides have structures similar to those found in proteins.

(i) Draw the structure of 2-aminopropanoic acid.

(ii) Draw the organic product formed by the condensation of two molecules of 2-aminopropanoic acid.

(2 marks)

(c) Compounds like $H_2N(CH_2)_6NH_2$ are also used to make ionic compounds such as **X**, shown below.



$$\left[H_3C-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-CH_3 \right] \quad 2Br^-$$

Compound **X**

(i) **X** belongs to the same type of compound as $(CH_3)_4N^+Br^-$
Name this **type** of compound.

....

(ii) State a reagent which could produce **X** from $H_2N(CH_2)_6NH_2$ and give a necessary condition to ensure that **X** is the major product.

Reagent ....

Condition ....

(iii) Name the mechanism involved in this reaction to form **X**.

....

(4 marks)

8

Turn over ▶

6 (a) (i) Write an equation for the reduction of pentan-2-one by aqueous $NaBH_4$ to form pentan-2-ol.
Use [H] to represent the reductant.

....

(ii) Name and outline a mechanism for this reduction.

Name of mechanism ....

Mechanism

(iii) State why the pentan-2-ol produced in this reaction is not optically active.

....

....

(7 marks)

(b) Predict the *m/z* values of the two most abundant fragments in the mass spectrum of pentan-2-one.

Fragment 1 ....

Fragment 2 ....

(2 marks)

9

SECTION B

Answer the question below in the space provided on pages 13 to 16 of this booklet.

7 (a) The term *acylation* can be applied to the reaction of ethanoyl chloride with ethylamine and also to the reaction of ethanoyl chloride with benzene in the presence of a catalyst.

For each of these reactions, write an equation for the overall reaction and name the organic product. Name and outline a mechanism for each reaction and identify a suitable catalyst for the reaction with benzene. *(15 marks)*

(b) In the industrial manufacture of aspirin, ethanoic anhydride is used as an acylating agent rather than ethanoyl chloride. Give **two** reasons why ethanoic anhydride is preferred. Describe a simple test to distinguish between a sample of ethanoic anhydride and one of ethanoyl chloride. Write equations for any reactions occurring. *(7 marks)*

(c) Ethylamine can be prepared in a two-step synthesis from bromomethane or in a one-step synthesis from bromoethane.
Give the reagents and conditions for all the reaction steps involved in these syntheses.
State one possible disadvantage for each of these two synthetic routes. *(8 marks)*

END OF QUESTIONS

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Turn over ▶

Turn over ▶

LEAVE
MARGIN
BLANK