Surname		Other Names	
Centre Number			Candidate Number									
Candidate Signature												

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General Certificate of Education
June 2004
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

CHEMISTRY CHM4
Unit 4 Further Physical and Organic Chemistry

Thursday 24 June 2004 Afternoon Session

In addition to this paper you will require:
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.
- 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.
- 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 $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$
- 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			
8			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 (a) The initial rate of the reaction between compounds **A** and **B** was measured in a series of experiments at a fixed temperature. The following rate equation was deduced.

$$\text{rate} = k[\mathbf{A}][\mathbf{B}]^2$$

(i) Complete the table of data below for the reaction between **A** and **B**.

Expt	Initial [**A**] /mol dm^{-3}	Initial [**B**] /mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}
1	4.80×10^{-2}	6.60×10^{-2}	10.4×10^{-3}
2	4.80×10^{-2}	3.30×10^{-2}	
3		13.2×10^{-2}	5.20×10^{-3}
4	1.60×10^{-2}		10.4×10^{-3}

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

Calculation .....

.....

Units .....

(6 marks)

(b) State how the value of the rate constant, k, would change, if at all, if the concentration of **A** were increased in a series of experiments.

.....

(1 mark)

7

The Periodic Table of the Elements

■ The atomic numbers and approximate relative atomic masses shown in the table are for use in the examination unless stated otherwise in an individual question.

I	II										III	IV	V	VI	VII	0
1.0 **H** Hydrogen 1																4.0 **He** Helium 2
6.9 **Li** Lithium 3	9.0 **Be** Beryllium 4										10.8 **B** Boron 5	12.0 **C** Carbon 6	14.0 **N** Nitrogen 7	16.0 **O** Oxygen 8	19.0 **F** Fluorine 9	20.2 **Ne** Neon 10
23.0 **Na** Sodium 11	24.3 **Mg** Magnesium 12										27.0 **Al** Aluminium 13	28.1 **Si** Silicon 14	31.0 **P** Phosphorus 15	32.1 **S** Sulphur 16	35.5 **Cl** Chlorine 17	39.9 **Ar** Argon 18
39.1 **K** Potassium 19	40.1 **Ca** Calcium 20	45.0 **Sc** Scandium 21	47.9 **Ti** Titanium 22	50.9 **V** Vanadium 23	52.0 **Cr** Chromium 24	54.9 **Mn** Manganese 25	55.8 **Fe** Iron 26	58.9 **Co** Cobalt 27	58.7 **Ni** Nickel 28	63.5 **Cu** Copper 29	65.4 **Zn** Zinc 30	69.7 **Ga** Gallium 31	72.6 **Ge** Germanium 32	74.9 **As** Arsenic 33	79.0 **Se** Selenium 34	79.9 **Br** Bromine 35	83.8 **Kr** Krypton 36
85.5 **Rb** Rubidium 37	87.6 **Sr** Strontium 38	88.9 **Y** Yttrium 39	91.2 **Zr** Zirconium 40	92.9 **Nb** Niobium 41	95.9 **Mo** Molybdenum 42	98.9 **Tc** Technetium 43	101.1 **Ru** Ruthenium 44	102.9 **Rh** Rhodium 45	106.4 **Pd** Palladium 46	107.9 **Ag** Silver 47	112.4 **Cd** Cadmium 48	114.8 **In** Indium 49	118.7 **Sn** Tin 50	121.8 **Sb** Antimony 51	127.6 **Te** Tellurium 52	126.9 **I** Iodine 53	131.3 **Xe** Xenon 54
132.9 **Cs** Caesium 55	137.3 **Ba** Barium 56	138.9 **La** Lanthanum 57 *	178.5 **Hf** Hafnium 72	180.9 **Ta** Tantalum 73	183.9 **W** Tungsten 74	186.2 **Re** Rhenium 75	190.2 **Os** Osmium 76	192.2 **Ir** Iridium 77	195.1 **Pt** Platinum 78	197.0 **Au** Gold 79	200.6 **Hg** Mercury 80	204.4 **Tl** Thallium 81	207.2 **Pb** Lead 82	209.0 **Bi** Bismuth 83	210.0 **Po** Polonium 84	210.0 **At** Astatine 85	222.0 **Rn** Radon 86
223.0 **Fr** Francium 87	226.0 **Ra** Radium 88	227 **Ac** Actinium 89 †															

Key

relative atomic mass — 6.9 **Li** Lithium

atomic number — 3

140.1 **Ce** Cerium 58	140.9 **Pr** Praseodymium 59	144.2 **Nd** Neodymium 60	144.9 **Pm** Promethium 61	150.4 **Sm** Samarium 62	152.0 **Eu** Europium 63	157.3 **Gd** Gadolinium 64	158.9 **Tb** Terbium 65	162.5 **Dy** Dysprosium 66	164.9 **Ho** Holmium 67	167.3 **Er** Erbium 68	168.9 **Tm** Thulium 69	173.0 **Yb** Ytterbium 70	175.0 **Lu** Lutetium 71
232.0 **Th** Thorium 90	231.0 **Pa** Protactinium 91	238.0 **U** Uranium 92	237.0 **Np** Neptunium 93	239.1 **Pu** Plutonium 94	243.1 **Am** Americium 95	247.1 **Cm** Curium 96	247.1 **Bk** Berkelium 97	252.1 **Cf** Californium 98	(252) **Es** Einsteinium 99	(257) **Fm** Fermium 100	(258) **Md** Mendelevium 101	(259) **No** Nobelium 102	(260) **Lr** Lawrencium 103

* **58 – 71** Lanthanides

† **90 – 103** Actinides

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

2 The value of the acid dissociation constant, K_a, for the weak acid HA, at 298 K, is 1.45×10^{-4} mol dm^{-3}.

(a) Write an expression for the term K_a for the weak acid HA.

.....

.....

(1 mark)

(b) Calculate the pH of a 0.250 mol dm^{-3} solution of HA at 298 K.

.....

.....

.....

.....

.....

(4 marks)

(c) A mixture of the acid HA and the sodium salt of this acid, NaA, can be used to prepare a buffer solution.

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

.....

.....

.....

(ii) The concentration of HA in a buffer solution is 0.250 mol dm^{-3}. Calculate the concentration of A^- in this buffer solution when the pH is 3.59

.....

.....

.....

.....

.....

.....

(6 marks)

11

3 Sulphur dioxide and oxygen were mixed in a 2:1 mol ratio and sealed in a flask with a catalyst. The following equilibrium was established at temperature T_1

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

The partial pressure of sulphur dioxide in the equilibrium mixture was 24 kPa and the total pressure in the flask was 104 kPa.

(a) Deduce the partial pressure of oxygen and hence calculate the mole fraction of oxygen in the equilibrium mixture.

Partial pressure of oxygen .....

Mole fraction of oxygen .....

.....

.....

(3 marks)

(b) Calculate the partial pressure of sulphur trioxide in the equilibrium mixture.

.....

(1 mark)

(c) Write an expression for the equilibrium constant, K_p, for this reaction. Use this expression to calculate the value of K_p at temperature T_1 and state its units.

Expression for K_p .....

.....

Calculation .....

.....

.....

Units .....

(4 marks)

(d) When equilibrium was established at a different temperature, T_2, the value of K_p was found to have increased. State which of T_1 and T_2 is the lower temperature and explain your answer.

Lower temperature .....

Explanation .....

.....

.....

(3 marks)

(e) In a further experiment, the amounts of sulphur dioxide and oxygen used, the catalyst and the temperature, T_1, were all unchanged, but a flask of smaller volume was used. Deduce the effect of this change on the yield of sulphur trioxide and on the value of K_p.

Effect on yield of SO_3 .....

Effect on K_p .....

(2 marks)

13

TURN OVER FOR THE NEXT QUESTION

4 (a) Name and outline a mechanism for the formation of butylamine, $CH_3CH_2CH_2CH_2NH_2$, by the reaction of ammonia with 1-bromobutane, $CH_3CH_2CH_2CH_2Br$.

Name of mechanism .....

Mechanism

(5 marks)

(b) Butylamine can also be prepared in a two-step synthesis starting from 1-bromopropane, $CH_3CH_2CH_2Br$. Write an equation for each of the two steps in this synthesis.

Step 1

.....

Step 2

.....

(3 marks)

(c) (i) Explain why butylamine is a stronger base than ammonia.

.....

.....

.....

(ii) Identify a substance that could be added to aqueous butylamine to produce a basic buffer solution.

.....

(3 marks)

(d) Draw the structure of a tertiary amine which is an isomer of butylamine.

(1 mark)

12

TURN OVER FOR THE NEXT QUESTION

5 (a) The compound $H_2C{=}CHCN$ is used in the formation of acrylic polymers.

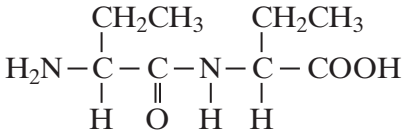
(i) Draw the repeating unit of the polymer formed from this compound.

(ii) Name the type of polymerisation involved in the formation of this polymer.

.....

(2 marks)

(b) When the dipeptide shown below is heated under acidic conditions, a single amino acid is produced.



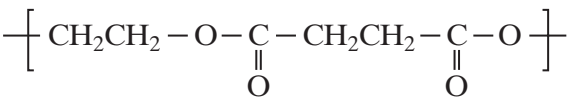
(i) Name this amino acid.

.....

(ii) Draw the structure of the amino acid species present in the acidic solution.

(2 marks)

(c) The repeating unit of a polyester is shown below.



(i) Deduce the empirical formula of the repeating unit of this polyester.

.....

(ii) Draw the structure of the acid which could be used in the preparation of this polyester and give the name of this acid.

Structure .....

Name .....

(iii) Give **one** reason why the polyester is biodegradable.

.....

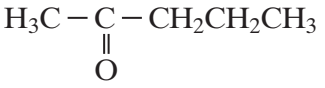
.....

(4 marks)

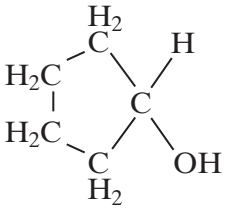
8

TURN OVER FOR THE NEXT QUESTION

6 Compounds **C** and **D**, shown below, are isomers of $C_5H_{10}O$



C



D

(a) Name compound **C**.

.....

(1 mark)

(b) Use **Table 2** on the Data Sheet to help you to answer this question.

(i) Suggest the wavenumber of an absorption which is present in the infra-red spectrum of **C** but not in that of **D**.

.....

(ii) Suggest the wavenumber of an absorption which is present in the infra-red spectrum of **D** but not in that of **C**.

.....

(2 marks)

(c) Deduce the number of peaks in the proton n.m.r. spectrum of **C**.

.....

(1 mark)

(d) Identify a reagent that you could use to distinguish between **C** and **D**. For each of **C** and **D**, state what you would observe when the compound is treated with this reagent.

Reagent .....

Observation with **C** .....

Observation with **D** .....

(3 marks)

(e) Compound **E**, $CH_3CH_2CH_2CH_2CHO$, is also an isomer of $C_5H_{10}O$
Identify a reagent which will react with **E** but not with **C** or **D**. State what you would observe when **E** is treated with this reagent.

Reagent .....

Observation with **E** .....

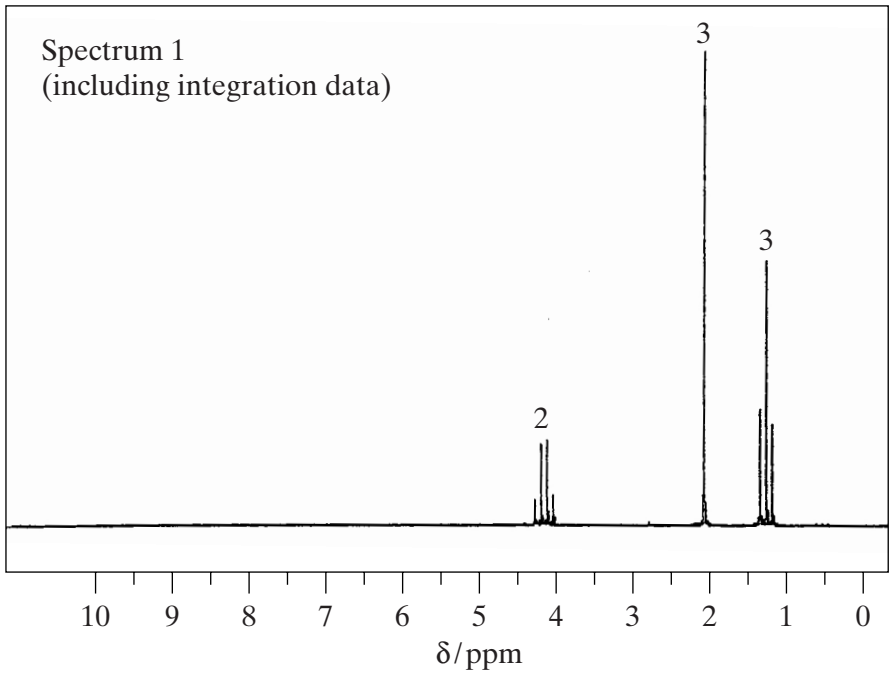
(2 marks)

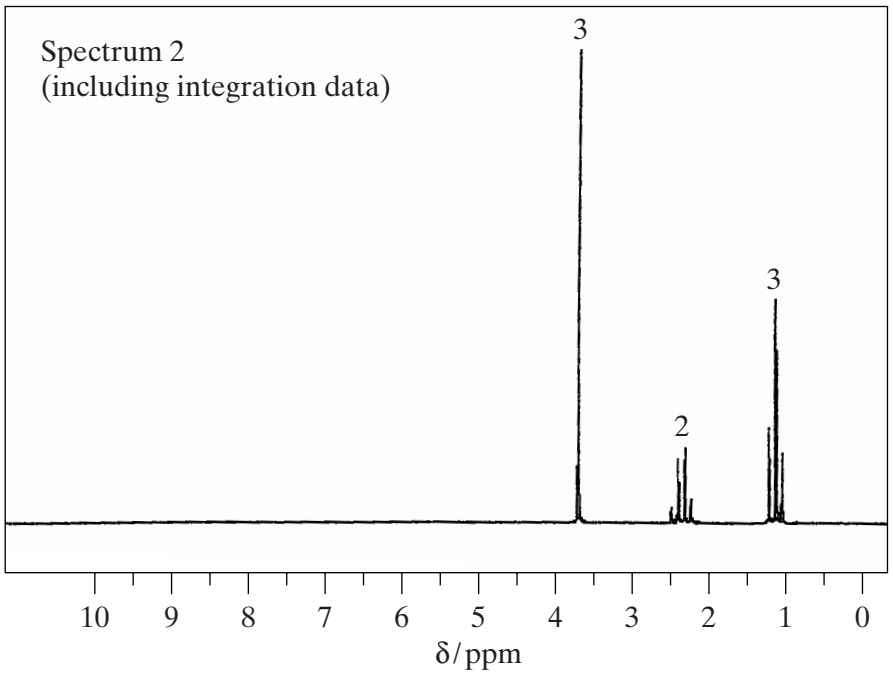
SECTION B

Detach this perforated sheet.
Answer **both** the questions in the space provided on pages 15 to 20 of this booklet.

7 (a) Ester **X**, $CH_3CH_2COOCH_3$, can be produced by the reaction between propanoyl chloride and methanol. Name **X** and outline a mechanism for this reaction. Name the mechanism involved. *(6 marks)*

(b) The proton n.m.r. spectrum of **X** is shown below together with that of an isomeric ester, **Y**. Deduce which of Spectrum 1 and Spectrum 2 is that obtained from **X**. Use **Table 1** on the Data Sheet and the integration data on the spectra to help you to explain your deduction. Suggest a structure for **Y**.

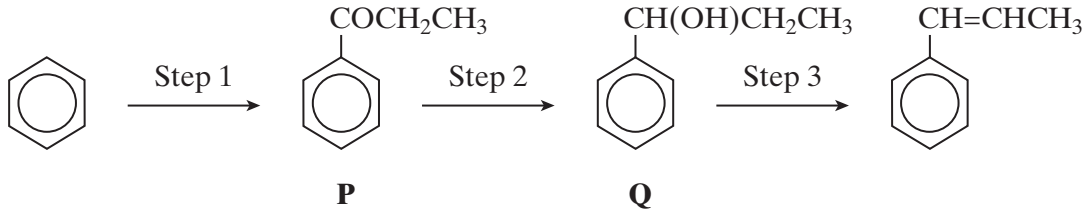




(4 marks)

Turn over ▶

8 Propanoyl chloride can be used, together with a catalyst, in Step 1 of the synthesis of 1-phenylpropene from benzene via compounds **P** and **Q** as shown below.



(a) The mechanism of Step 1 is an electrophilic substitution. Write an equation to show the formation of the electrophile from propanoyl chloride. Outline the mechanism of the reaction of this electrophile with benzene in Step 1. *(5 marks)*

(b) The mass spectrum of **P** contains a molecular ion peak at m/z = 134 and major fragmentation peaks at m/z = 105 and 77. Identify the species responsible for the peak at m/z = 105 and also that responsible for the peak at m/z = 77. Write an equation for the formation, from the molecular ion, of the species responsible for the peak at m/z = 105. *(4 marks)*

(c) $NaBH_4$ can be used in the reaction in Step 2. Name the mechanism involved in this reaction. Molecules of **Q** show optical isomerism but the sample of **Q** formed in Step 2 is optically inactive. State, in terms of their structure, why molecules of **Q** show optical isomerism. Explain, by reference to the mechanism, why the sample of **Q** obtained in Step 2 is not optically active. *(7 marks)*

(d) Identify a suitable reagent for the reaction in Step 3.
Name the type of stereoisomerism shown by the product of this reaction. State what is required in the structure of molecules to allow them to show this type of stereoisomerism. *(4 marks)*

END OF QUESTIONS

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