Surname		Other Names	
Centre Number			Candidate Number									
Candidate Signature												

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General Certificate of Education
June 2006
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

CHEMISTRY **CHM4**
Unit 4 Further Physical and Organic Chemistry

Monday 19 June 2006 1.30 pm to 3.00 pm

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 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			
Number	Mark	Number	Mark
1			
2			
3			
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5			
6			
7			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 (a) Write an equation for the formation of methyl propanoate, $CH_3CH_2COOCH_3$, from methanol and propanoic acid.

.....

(1 mark)

(b) Name and outline a mechanism for the reaction between methanol and propanoyl chloride to form methyl propanoate.

Name of mechanism .....

Mechanism

(5 marks)

(c) Propanoic anhydride could be used instead of propanoyl chloride in the preparation of methyl propanoate from methanol. Draw the structure of propanoic anhydride.

(1 mark)

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

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

(d) (i) Give **one** advantage of the use of propanoyl chloride instead of propanoic acid in the laboratory preparation of methyl propanoate from methanol.

.....

.....

(ii) Give **one** advantage of the use of propanoic anhydride instead of propanoyl chloride in the industrial manufacture of methyl propanoate from methanol.

.....

.....

(2 marks)

(e) An ester contains a benzene ring. The mass spectrum of this ester shows a molecular ion peak at $m/z = 136$.

(i) Deduce the molecular formula of this ester.

.....

.....

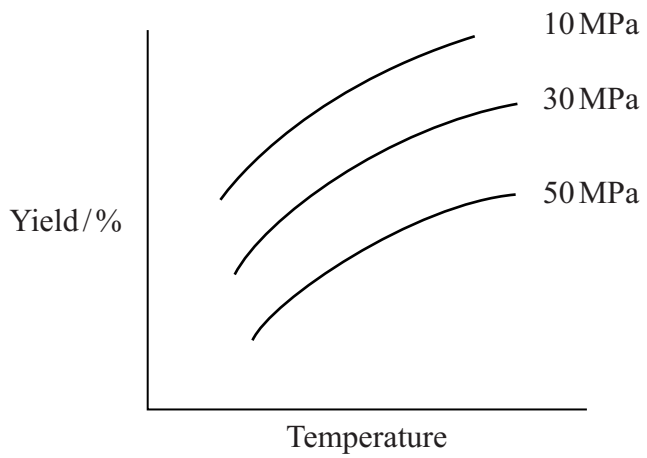
.....

(ii) Draw **two** possible structures for this ester.

(3 marks)

12

2 (a) The diagram below shows the effect of temperature and pressure on the equilibrium yield of the product in a gaseous equilibrium.



(i) Use the diagram to deduce whether the forward reaction involves an increase or a decrease in the number of moles of gas. Explain your answer.

Change in number of moles .....

Explanation .....

.....

.....

(ii) Use the diagram to deduce whether the forward reaction is exothermic or endothermic. Explain your answer.

The forward reaction is .....

Explanation .....

.....

.....

(6 marks)

(b) When a 0.218 mol sample of hydrogen iodide was heated in a flask of volume V dm^3, the following equilibrium was established at 700 K.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The equilibrium mixture was found to contain 0.023 mol of hydrogen.

(i) Calculate the number of moles of iodine and the number of moles of hydrogen iodide in the equilibrium mixture.

Number of moles of iodine .....

Number of moles of hydrogen iodide .....

.....

(ii) Write an expression for K_c for the equilibrium.

.....

.....

(iii) State why the volume of the flask need not be known when calculating a value for K_c.

.....

.....

(iv) Calculate the value of K_c at 700 K.

.....

.....

.....

.....

(v) Calculate the value of K_c at 700 K for the equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

.....

.....

(7 marks)

13

3 (a) A sample of hydrochloric acid has a pH of 2.34
Write an expression for pH and calculate the concentration of this acid.

pH .....

Concentration .....

.....

(2 marks)

(b) A 0.150 mol dm^{-3} solution of a weak acid, HX, also has a pH of 2.34

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

.....

.....

(ii) Calculate the value of K_a for this acid and state its units.

Calculation .....

.....

.....

Units .....

(iii) Calculate the value of pK_a for the acid HX. Give your answer to two decimal places.

.....

(5 marks)

(c) A 30.0 cm^3 sample of a 0.480 mol dm^{-3} solution of potassium hydroxide was partially neutralised by the addition of 18.0 cm^3 of a 0.350 mol dm^{-3} solution of sulphuric acid.

(i) Calculate the initial number of moles of potassium hydroxide.

.....

.....

(ii) Calculate the number of moles of sulphuric acid added.

.....

.....

(iii) Calculate the number of moles of potassium hydroxide remaining in excess in the solution formed.

.....

.....

(iv) Calculate the concentration of hydroxide ions in the solution formed.

.....

.....

.....

(v) Hence calculate the pH of the solution formed. Give your answer to two decimal places.

.....

.....

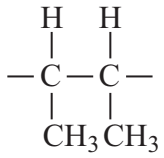
.....

(6 marks)

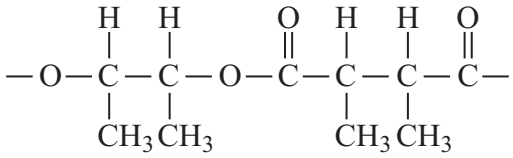
13

Turn over for the next question

4 (a) The repeating units of two polymers, **P** and **Q**, are shown below.



P



Q

(i) Draw the structure of the monomer used to form polymer **P**. Name the type of polymerisation involved.

Structure of monomer

Type of polymerisation .....

(ii) Draw the structures of **two** compounds which react together to form polymer **Q**. Name these **two** compounds and name the type of polymerisation involved.

Structure of compound 1

Name of compound 1 .....

Structure of compound 2

Name of compound 2 .....

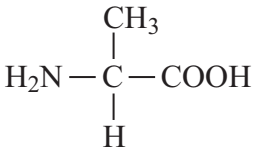
Type of polymerisation .....

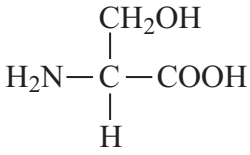
(iii) Identify a compound which, in aqueous solution, will break down polymer **Q** but not polymer **P**.

.....

(8 marks)

(b) Draw the structures of the **two** dipeptides which can form when one of the amino acids shown below reacts with the other.





Structure 1 *Structure 2*

(2 marks)

(c) Propylamine, $CH_3CH_2CH_2NH_2$, can be formed either by nucleophilic substitution or by reduction.

(i) Draw the structure of a compound which can undergo nucleophilic substitution to form propylamine.

(ii) Draw the structure of the nitrile which can be reduced to form propylamine.

(iii) State and explain which of the two routes to propylamine, by nucleophilic substitution or by reduction, gives the less pure product. Draw the structure of a compound formed as an impurity.

Route giving the less pure product .....

Explanation .....

.....

Structure of an impurity

(5 marks)

15

Turn over ▶

5 The hydrolysis of methyl propanoate was studied in acidic conditions at 25 °C and the rate equation was found to be

$$\text{rate} = k[CH_3CH_2COOCH_3][H^+]$$

(a) Use the data below to calculate the value of the rate constant, k, at this temperature. Deduce its units.

Initial rate of reaction / mol dm^{-3} s^{-1}	Initial concentration of methyl propanoate / mol dm^{-3}	Initial concentration of hydrochloric acid / mol dm^{-3}
1.15×10^{-4}	0.150	0.555

Rate constant .....

.....

.....

Units .....

.....

(3 marks)

(b) The reaction in part (a) was repeated at the same temperature, but water was added so that the volume of the reaction mixture was doubled. Calculate the initial rate of reaction under these conditions.

.....

.....

(1 mark)

(c) A third experiment was carried out at a different temperature. Some data from this experiment are shown in the table below.

Initial rate of reaction / mol dm^{-3} s^{-1}	Value of rate constant at this different temperature	Initial concentration of methyl propanoate / mol dm^{-3}
4.56×10^{-5}	8.94×10^{-4}	0.123

Calculate the initial pH of the reaction mixture. Give your answer to two decimal places.

.....

.....

.....

.....

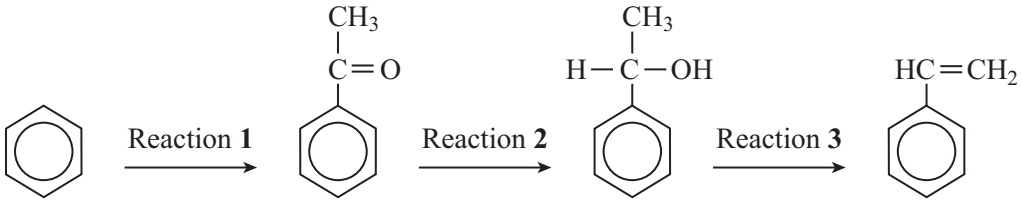
(3 marks)

7

SECTION B

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

6 A possible synthesis of phenylethene *(styrene)* is outlined below.

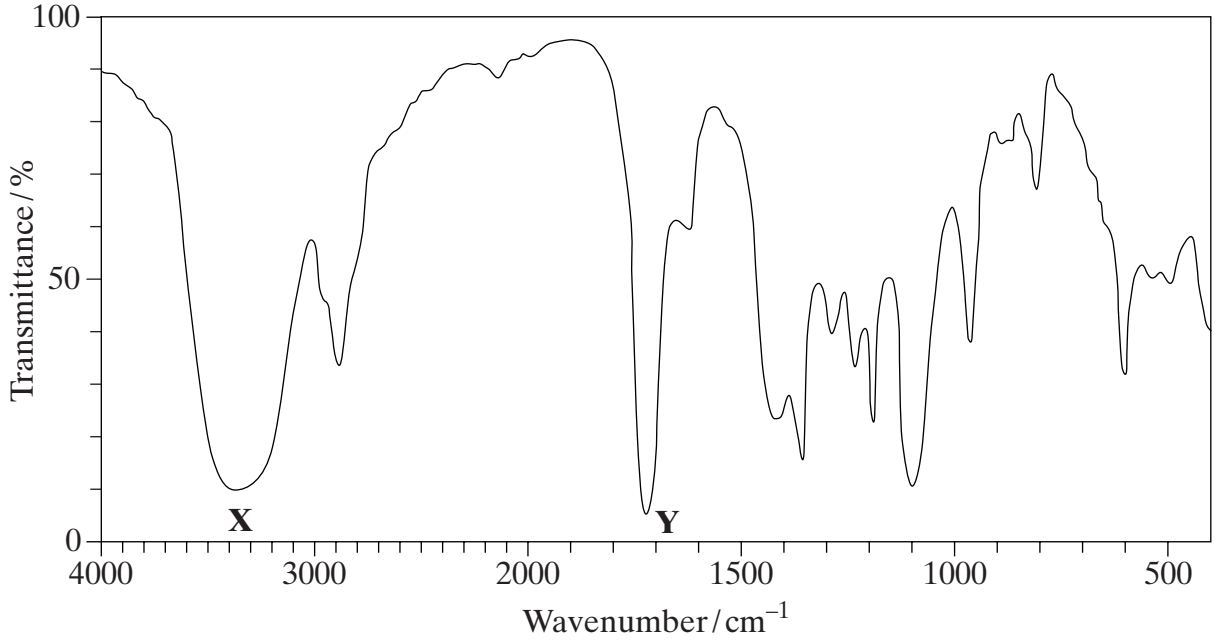


(a) In Reaction **1**, ethanoyl chloride and aluminium chloride are used to form a reactive species which then reacts with benzene.
Write an equation to show the formation of the reactive species.
Name and outline the mechanism by which this reactive species reacts with benzene.
(6 marks)

(b) $NaBH_4$ is a possible reagent for Reaction **2**.
Name and outline the mechanism for the reaction with $NaBH_4$ in Reaction **2**.
Name the product of Reaction **2**.
(6 marks)

(c) Name the type of reaction involved in Reaction **3** and give a reagent for the reaction.
(2 marks)

7 (a) The infra-red spectrum of compound **A**, $C_3H_6O_2$, is shown below.



Identify the functional groups which cause the absorptions labelled **X** and **Y**.

Using this information draw the structures of the three possible structural isomers for **A**.

Label as **A** the structure which represents a pair of optical isomers.

(6 marks)

(b) Draw the structures of the three **branched-chain** alkenes with molecular formula C_5H_{10}

Draw the structures of the three dibromoalkanes, $C_5H_{10}Br_2$, formed when these three alkenes react with bromine.

One of these dibromoalkanes has only three peaks in its proton n.m.r. spectrum. Deduce the integration ratio and the splitting patterns of these three peaks.

(10 marks)

END OF QUESTIONS

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