Surname		Other Names	
Centre Number			Candidate Number					
Candidate Signature								

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General Certificate of Education
June 2005
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

CHEMISTRY CHM4
Unit 4 Further Physical and Organic Chemistry

Thursday 23 June 2005 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			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 (a) Compound **A**, $HCOOCH_2CH_2CH_3$, is an ester. Name this ester and write an equation for its reaction with aqueous sodium hydroxide.

Name .....

Equation .....

(2 marks)

(b) The initial rate of reaction between ester **A** and aqueous sodium hydroxide was measured in a series of experiments at a constant temperature. The data obtained are shown below.

Experiment	Initial concentration of NaOH / mol dm^{-3}	Initial concentration of **A** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.040	0.030	4.0×10^{-4}
2	0.040	0.045	6.0×10^{-4}
3	0.060	0.045	9.0×10^{-4}
4	0.120	0.060	to be calculated

Use the data in the table to deduce the order of reaction with respect to **A** and the order of reaction with respect to NaOH. Hence calculate the initial rate of reaction in Experiment 4.

Order with respect to A .....

Order with respect to NaOH .....

Initial rate in Experiment 4 .....

.....

(3 marks)

(c) In a further experiment at a different temperature, the initial rate of reaction was found to be 9.0×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of **A** was 0.020 mol dm^{-3} and the initial concentration of NaOH was 2.00 mol dm^{-3}.
Under these new conditions with the much higher concentration of sodium hydroxide, the reaction is first order with respect to **A** and appears to be zero order with respect to sodium hydroxide.

(i) Write a rate equation for the reaction under these new conditions.

.....

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

(ii) Calculate a value for the rate constant under these new conditions and state its units.

Calculation .....

.....

.....

Units .....

(iii) Suggest why the order of reaction with respect to sodium hydroxide appears to be zero under these new conditions.

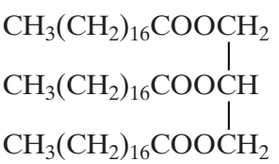
.....

.....

.....

(6 marks)

(d) A naturally-occurring triester, shown below, was heated under reflux with an excess of aqueous sodium hydroxide and the mixture produced was then distilled. One of the products distilled off and the other was left in the distillation flask.



(i) Draw the structure of the product distilled off and give its name.

Structure

Name .....

(ii) Give the formula of the product left in the distillation flask and give a use for it.

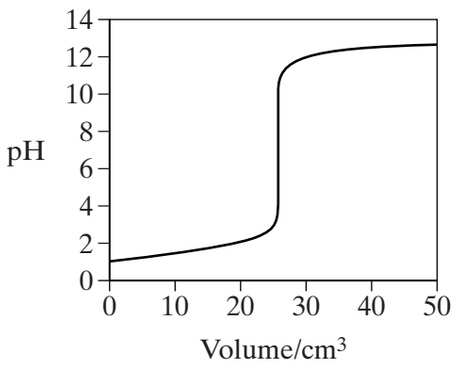
Formula .....

Use .....

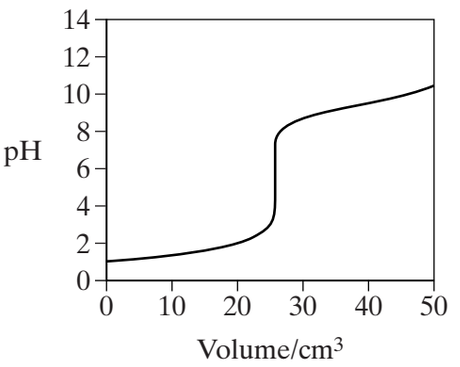
(4 marks)

15

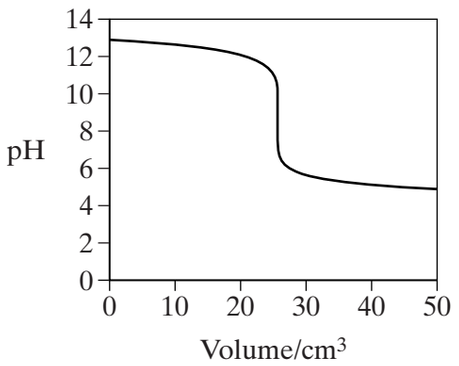
2 (a) Titration curves labelled **A**, **B**, **C** and **D** for combinations of different acids and bases are shown below. All solutions have a concentration of 0.1 mol dm^{-3}.



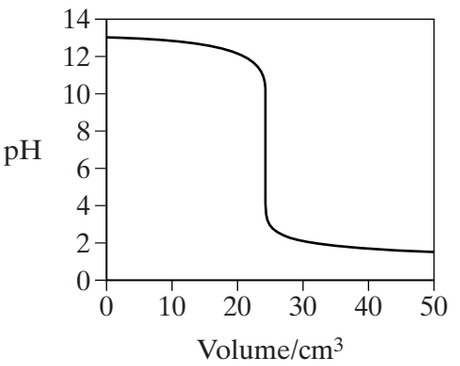
A



B



C



D

(i) Select from **A**, **B**, **C** and **D** the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid .....

ethanoic acid to 25 cm^3 of sodium hydroxide .....

sodium hydroxide to 25 cm^3 of hydrochloric acid .....

(ii) A table of acid–base indicators and the pH ranges over which they change colour is shown below.

Indicator	**pH range**
Thymol blue	1.2 – 2.8
Bromophenol blue	3.0 – 4.6
Methyl red	4.2 – 6.3
Cresolphthalein	8.2 – 9.8
Thymolphthalein	9.3 – 10.5

Select from the table an indicator which could be used in the titration which produces curve **A** but not in the titration which produces curve **B**.

.....

(4 marks)

(b) (i) Write an expression for the term *pH*.

.....

(ii) A solution of potassium hydroxide has a pH of 11.90 at 25 °C. Calculate the concentration of potassium hydroxide in the solution.

.....

.....

.....

.....

(4 marks)

(c) The acid dissociation constant, K_a, for propanoic acid has the value of 1.35×10^{-5} mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

In each of the calculations below, give your answer to 2 decimal places.

(i) Calculate the pH of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

.....

.....

.....

.....

(ii) Calculate the pH of a mixture formed by adding 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of sodium propanoate to 25 cm^3 of a 0.117 mol dm^{-3} aqueous solution of propanoic acid.

.....

.....

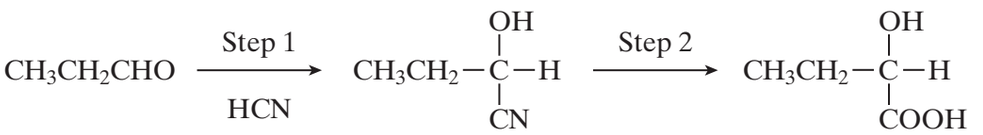
.....

(5 marks)

13

Turn over ▶

3 Consider the reaction sequence shown below.



propanal **Q**

(a) Name and outline a mechanism for the reaction in Step 1.

Name of mechanism .....

Mechanism

(5 marks)

(b) (i) Name compound **Q** formed in Step 2.

.....

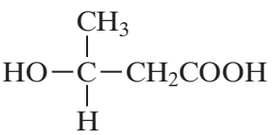
(ii) Two stereoisomers are formed by the dehydration of **Q**. Give the structures of these two isomers and name the type of stereoisomerism shown.

Structures of isomers

Type of stereoisomerism .....

(4 marks)

(c) An isomer of **Q** which has the structure shown below is polymerised to form the biodegradeable polymer known as PHB.



(i) Draw the repeating unit of the polymer PHB.

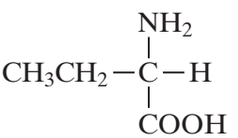
(ii) Suggest a reason why the polymer is biodegradeable.

.....

.....

(2 marks)

(d) The amino acid **R** is shown below.



R

(i) Draw the structure of the zwitterion formed by **R**.

(ii) Draw the structure of the major organic product formed when an excess of **R** is reacted with bromomethane.

(iii) Name the mechanism of the reaction which results in the formation of the product given in part (ii).

.....

(3 marks)

Turn over ▶

4 This question concerns four isomers, **W**, **X**, **Y** and **Z**, with the molecular formula $C_5H_{10}O_2$

(a) The proton n.m.r. spectrum of **W** shows 4 peaks.
The table below gives the chemical shifts, δ values, for each of these peaks, together with their splitting patterns and integration values.

δ/ppm	2.18	2.59	3.33	3.64
Splitting pattern	singlet	triplet	singlet	triplet
Integration value	3	2	3	2

State what can be deduced about the structure of **W** from the presence of the following in its n.m.r. spectrum.

(i) The singlet peak at δ = 2.18

.....

(ii) The singlet peak at δ = 3.33

.....

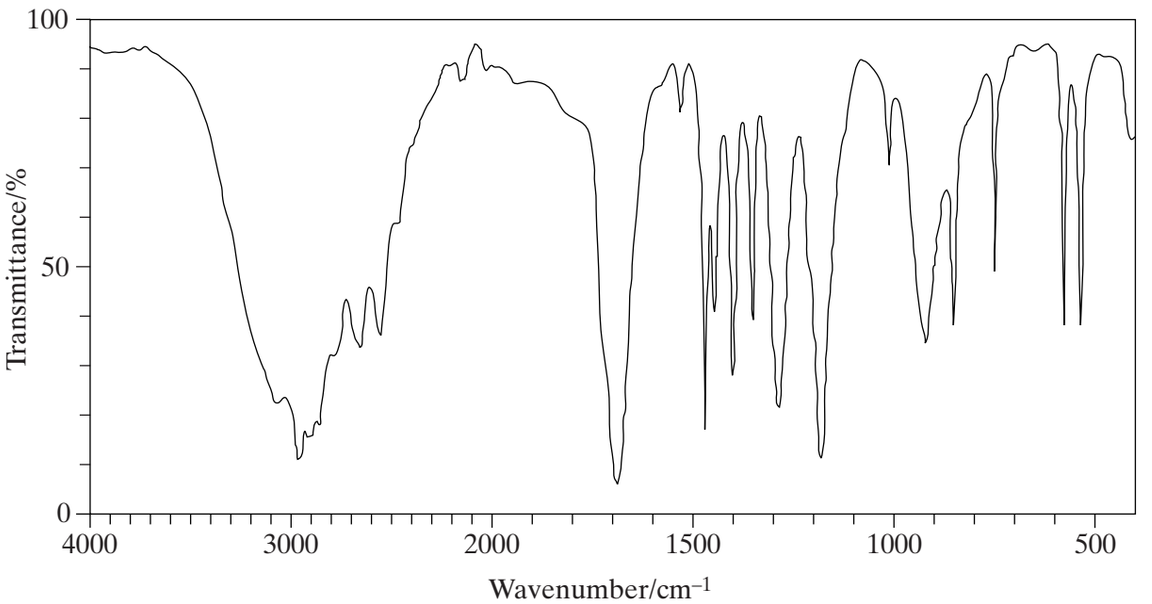
(iii) Two triplet peaks.

.....

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

(4 marks)

(b) The infra-red spectrum of **X** is shown below.



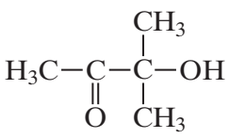
(i) What can be deduced from the broad absorption centred on 3000 cm^{-1} in the infra-red spectrum of **X**?

.....

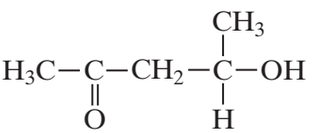
(ii) Given that the proton n.m.r. spectrum of **X** contains only two peaks with the integration ratio 9:1, deduce the structure of **X**.

(2 marks)

(c) Isomers **Y** and **Z** have the structures shown below.



Y



Z

Identify the two reagents you could use in a simple chemical test to distinguish between **Y** and **Z**. State what you would observe when each of **Y** and **Z** is tested with a mixture of these two reagents.

Reagents .....

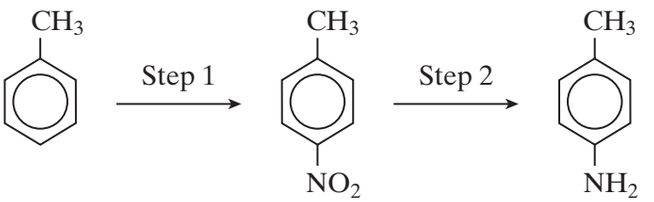
*Observation with **Y*** .....

*Observation with **Z*** .....

(3 marks)

9

5 Consider the following reaction sequence.



methylbenzene **E** **F**

(a) For Step 1, name the mechanism and give the reagents involved.

Name of mechanism .....

Reagents .....

.....

(3 marks)

(b) For Step 2, give a reagent or combination of reagents. Write an equation for this reaction using [H] to represent the reductant.

Reagent(s) .....

Equation .....

(2 marks)

(c) Give the *m/z* value of a major peak which could appear in the mass spectrum of methylbenzene, but not in the spectrum of either **E** or **F**.

.....

(1 mark)

(d) Draw the structure of the species formed by **F** in an excess of hydrochloric acid.

(1 mark)

(e) Compounds **G** and **H** are both monosubstituted benzenes and both are isomers of **F**. **G** is a primary amine and **H** is a secondary amine. Draw the structures of **G** and **H** below.

G

H

(2 marks)

9

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SECTION B

Detach this perforated sheet.
Answer **both** questions in the space provided on pages 14 and 17 to 20 of this booklet.

6 The manufacture of methanol can be achieved in two stages.

(a) In the first stage, methane and steam react according to the following equation.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H^{\ominus} = +210\,kJ\,mol^{-1}$$

Discuss, with reasons, the effects of increasing separately the temperature and the pressure on the yield of the products and on the rate of this reaction. *(6 marks)*

(b) In the second stage, carbon monoxide and hydrogen react according to the following equation.

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

A 62.8 mol sample of carbon monoxide was added to 146 mol of hydrogen. When equilibrium was reached at a given temperature, the mixture contained 26.2 mol of methanol at a total pressure of 9.50 MPa.

Write an expression for the equilibrium constant, K_p, for this reaction. Calculate a value for K_p at this temperature and give its units. *(8 marks)*

7 (a) Name and outline a mechanism for the reaction between propanoyl chloride, CH_3CH_2COCl, and methylamine, CH_3NH_2
Draw the structure of the organic product. *(6 marks)*

(b) Benzene reacts with propanoyl chloride in the presence of aluminium chloride.
Write equations to show the role of aluminium chloride as a catalyst in this reaction.
Outline a mechanism for this reaction of benzene. *(5 marks)*

(c) Write an equation for the reaction of propanoyl chloride with water.
An excess of water is added to 1.48 g of propanoyl chloride. Aqueous sodium hydroxide is then added from a burette to the resulting solution.
Calculate the volume of 0.42 mol dm^{-3} aqueous sodium hydroxide needed to react exactly with the mixture formed. *(5 marks)*

END OF QUESTIONS

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NO QUESTIONS APPEAR ON THIS PAGE

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