Surname		Other Names	
Centre Number			Candidate Number					
Candidate Signature								

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General Certificate of Education
January 2005
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

CHEMISTRY CHM4
Unit 4 Further Physical and Organic Chemistry

Friday 21 January 2005 Morning 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 $R = 8.31\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$
- 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			
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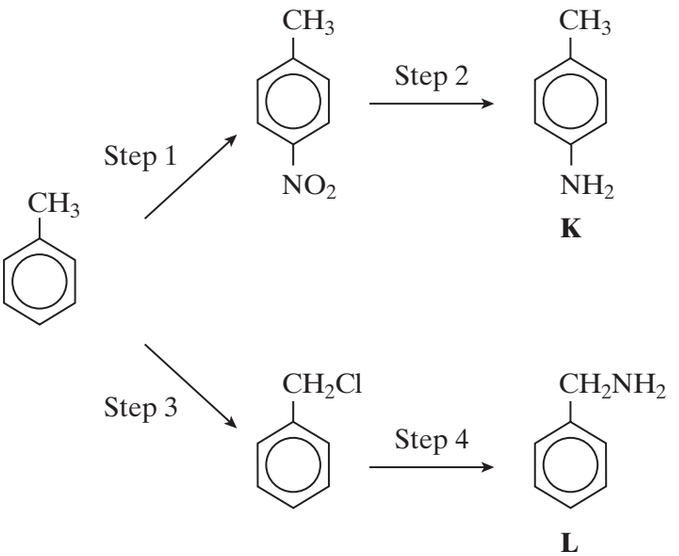
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 The following reaction scheme shows the formation of two amines, **K** and **L**, from methylbenzene.



(a) (i) Give the reagents needed to carry out Step 1. Write an equation for the formation from these reagents of the inorganic species which reacts with methylbenzene.

Reagents .....

.....

Equation .....

(ii) Name and outline a mechanism for the reaction between this inorganic species and methylbenzene.

Name of mechanism .....

Mechanism

(7 marks)

(b) Give a suitable reagent or combination of reagents for Step 2.

.....

(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

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

(c) (i) Give the reagent for Step 4 and state a condition to ensure that the primary amine is the major product.

Reagent .....

Condition .....

(ii) Name and outline a mechanism for Step 4.

Name of mechanism .....

Mechanism

(7 marks)

(d) Explain why amine **K** is a weaker base than ammonia.

.....

.....

.....

(2 marks)

(e) Draw the structure of the organic compound formed when a large excess of bromomethane reacts with amine **L**.

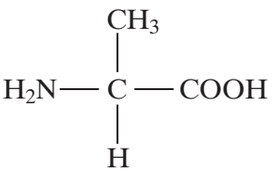
(1 mark)

(f) Draw the structure of the organic compound formed when ethanoyl chloride reacts with amine **L** in an addition–elimination reaction.

(1 mark)

19

2 The amino acid *alanine* is shown below.



(a) A sample of alanine is dissolved in water.

(i) Draw the structure of the main alanine species present in this aqueous solution and give the name of this type of species.

Structure

Type of species .....

(ii) Draw the structure of the alanine species formed when an excess of hydrochloric acid is added to the solution.

(3 marks)

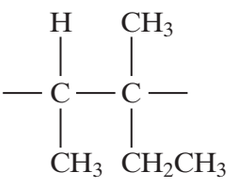
(b) Alanine molecules may be reacted together to form a polypeptide. Give the repeating unit of this polypeptide and name the type of polymerisation involved in its formation.

Repeating unit

Type of polymerisation .....

(2 marks)

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



Give the name of the alkene which is used to form this polymer.

.....

(1 mark)

6

TURN OVER FOR THE NEXT QUESTION

3 Each of the parts (a) to (e) below concerns a different pair of isomers.

Draw one possible structure for each of the species **A** to **J**, using Table 2 on the Data Sheet where appropriate.

(a) Compounds **A** and **B** have the molecular formula C_5H_{10}
A decolourises bromine water but **B** does not.

A **B**

(2 marks)

(b) Compounds **C** and **D** have the molecular formula $C_2H_4O_2$
Each has an absorption in its infra-red spectrum at about 1700 cm^{-1} but only **D** has a broad absorption at 3350 cm^{-1}

C **D**

(2 marks)

(c) Compounds **E** and **F** are esters with the molecular formula $C_5H_{10}O_2$
The proton n.m.r. spectrum of **E** consists of two singlets only whereas that of **F** consists of two quartets and two triplets.

E **F**

(2 marks)

(d) Compounds **G** and **H** have the molecular formula $C_3H_6Cl_2$
G shows optical activity but **H** does not.

G **H**

(2 marks)

(e) Compounds **I** and **J** have the molecular formula C_6H_{12}
Each has an absorption in its infra-red spectrum at about $1650\,cm^{-1}$ and neither shows geometrical isomerism. The proton n.m.r. spectrum of **I** consists of a singlet only whereas that of **J** consists of a singlet, a triplet and a quartet.

I **J**

(2 marks)

10

TURN OVER FOR THE NEXT QUESTION

4 (a) The following table shows the results of three experiments carried out at the same temperature to investigate the rate of the reaction between compounds **P** and **Q**.

	Experiment 1	Experiment 2	Experiment 3
Initial concentration of **P**/mol dm^{-3}	0.50	0.25	0.25
Initial concentration of **Q**/mol dm^{-3}	0.36	0.36	0.72
Initial rate/mol dm^{-3} s^{-1}	7.6×10^{-3}	1.9×10^{-3}	3.8×10^{-3}

Use the data in the table to deduce the order with respect to **P** and the order with respect to **Q**.

*Order with respect to **P*** .....

*Order with respect to **Q*** .....

(2 marks)

(b) In a reaction between **R** and **S**, the order of reaction with respect to **R** is one, the order of reaction with respect to **S** is two and the rate constant at temperature T_1 has a value of 4.2×10^{-4} mol^{-2} dm^6 s^{-1}.

(i) Write a rate equation for the reaction. Calculate a value for the initial rate of reaction when the initial concentration of **R** is 0.16 mol dm^{-3} and that of **S** is 0.84 mol dm^{-3}.

Rate equation .....

Calculation .....

.....

(ii) In a second experiment performed at a different temperature, T_2, the initial rate of reaction is 8.1×10^{-5} mol dm^{-3} s^{-1} when the initial concentration of **R** is 0.76 mol dm^{-3} and that of **S** is 0.98 mol dm^{-3}. Calculate the value of the rate constant at temperature T_2.

.....

.....

.....

(iii) Deduce which of T_1 and T_2 is the higher temperature.

.....

(6 marks)

8

5 Tetrafluoroethene, C_2F_4, is obtained from chlorodifluoromethane, $CHClF_2$, according to the equation:

$$2CHClF_2(g) \rightleftharpoons C_2F_4(g) + 2HCl(g) \qquad \Delta H^{\ominus} = +128\,kJ\,mol^{-1}$$

(a) A 1.0 mol sample of $CHClF_2$ is placed in a container of volume 18.5 dm^3 and heated. When equilibrium is reached, the mixture contains 0.20 mol of $CHClF_2$

(i) Calculate the number of moles of C_2F_4 and the number of moles of HCl present at equilibrium.

Number of moles of C_2F_4 .....

Number of moles of HCl .....

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

.....

(iii) Calculate a value for K_c and give its units.

Calculation .....

.....

.....

.....

Units .....

(6 marks)

(b) (i) State how the temperature should be changed at constant pressure to increase the equilibrium yield of C_2F_4

.....

(ii) State how the total pressure should be changed at constant temperature to increase the equilibrium yield of C_2F_4

.....

(2 marks)

(c) C_2F_4 is used to manufacture the polymer polytetrafluoroethene, PTFE. Name the type of polymerisation involved in the formation of PTFE.

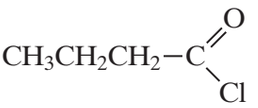
.....

(1 mark)

9

Turn over ▶

6 Compound **U** is shown below.



(a) Name compound **U**.

.....

(1 mark)

(b) (i) State why the mass spectrum of **U** contains two molecular ion peaks.

.....

(ii) Give the *m/z* values of these two peaks.

.....

.....

(2 marks)

(c) Name and outline a mechanism for the reaction of **U** with CH_3OH

Name of mechanism .....

Mechanism

(5 marks)

8

SECTION B

Detach this perforated sheet.
Answer **both** questions in the space provided on pages 15 to 19 of this booklet.

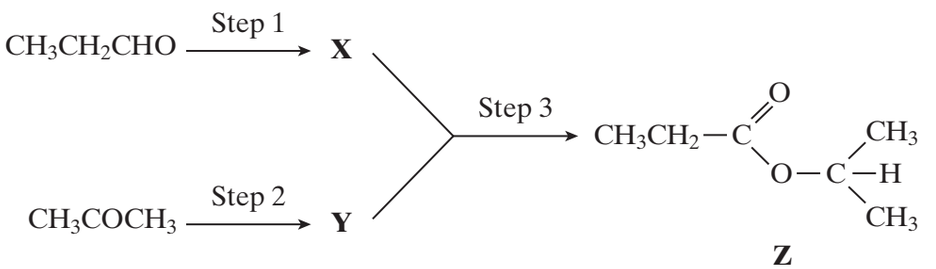
7 (a) Describe how propanal, CH_3CH_2CHO, and propanone, CH_3COCH_3, can be distinguished using

(i) a chemical test and

(ii) the number of peaks in their proton n.m.r. spectra.

(5 marks)

(b) Compound **Z** can be produced by the reaction of compound **X** with compound **Y** as shown in the synthesis outlined below.



Z

Identify compounds **X** and **Y**.
For each of the three steps in the synthesis, name the type of reaction involved and give reagents and conditions. Equations are **not** required.

(10 marks)

Turn over ▶

8 This question concerns the weak acid, ethanoic acid, for which the acid dissociation constant, K_a, has a value of 1.74×10^{-5} mol dm^{-3} at 25 °C.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

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

(a) Write an expression for the term *pH*. Calculate the pH of a 0.150 mol dm^{-3} solution of ethanoic acid.

(4 marks)

(b) A buffer solution is prepared by mixing a solution of ethanoic acid with a solution of sodium ethanoate.

(i) Explain what is meant by the term *buffer solution*.

(ii) Write an equation for the reaction which occurs when a small amount of hydrochloric acid is added to this buffer solution.

(3 marks)

(c) In a buffer solution, the concentration of ethanoic acid is 0.150 mol dm^{-3} and the concentration of sodium ethanoate is 0.100 mol dm^{-3}.

(i) Calculate the pH of this buffer solution.

(ii) A 10.0 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added to 1000 cm^3 of this buffer solution.
Calculate the number of moles of ethanoic acid and the number of moles of sodium ethanoate in the solution after addition of the hydrochloric acid. Hence, find the pH of this new solution.

(8 marks)

END OF QUESTIONS

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