Surname		Other Names	
Centre Number			Candidate Number					
Candidate Signature								

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General Certificate of Education
January 2006
Advanced Level Examination

ASSESSMENT and QUALIFICATIONS ALLIANCE

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

Monday 23 January 2006 9.00 am to 10.30 am

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.
- 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 $R = 8.31$ J K^{-1} mol^{-1}
- Your answers to the question 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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5			
6			
7			
8			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

There are no questions printed on this page

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

SECTION A

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

1 The initial rate of the reaction between the gases NO and H_2 was measured in a series of experiments at a constant temperature and the following rate equation was determined.

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

(a) Complete the table of data below for the reaction between NO and H_2

Experiment	Initial [NO] / mol dm^{-3}	Initial [H_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	3.0×10^{-3}	1.0×10^{-3}	1.8×10^{-5}
2	3.0×10^{-3}		7.2×10^{-5}
3	1.5×10^{-3}	1.0×10^{-3}	
4		0.50×10^{-3}	8.1×10^{-5}

(3 marks)

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

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(3 marks)

6

2 In this question, give all pH values to 2 decimal places.

(a) (i) Write expressions for the ionic product of water, K_w, and for pH.

K_w = ...

pH = ...

(ii) At 318 K, the value of K_w is 4.02×10^{-14} mol^2 dm^{-6} and hence the pH of pure water is 6.70
State why pure water is not acidic at 318 K.

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.....

(iii) Calculate the number of moles of sodium hydroxide in 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide.

.....

.....

(iv) Use the value of K_w given above and your answer to part (a)(iii) to calculate the pH of the solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 998 cm^3 of pure water at 318 K.

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(6 marks)

(b) At 298 K, the acid dissociation constant, K_a, for propanoic acid, CH_3CH_2COOH, has the value 1.35×10^{-5} mol dm^{-3}.

(i) Write an expression for K_a for propanoic acid.

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(ii) Calculate the pH of 0.125 mol dm^{-3} aqueous propanoic acid at 298 K.

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(4 marks)

(c) Sodium hydroxide reacts with propanoic acid as shown in the following equation.

$$NaOH + CH_3CH_2COOH \longrightarrow CH_3CH_2COONa + H_2O$$

A buffer solution is formed when sodium hydroxide is added to an excess of aqueous propanoic acid.

(i) Calculate the number of moles of propanoic acid in 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

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.....

(ii) Use your answers to part (a)(iii) and part (c)(i) to calculate the number of moles of propanoic acid in the buffer solution formed when 2.00 cm^3 of 0.500 mol dm^{-3} aqueous sodium hydroxide are added to 50.0 cm^3 of 0.125 mol dm^{-3} aqueous propanoic acid.

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(iii) Hence calculate the pH of this buffer solution at 298 K.

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(6 marks)

16

Turn over ▶

3 (a) The expression for an equilibrium constant, K_c, for a homogeneous equilibrium reaction is given below.

$$K_c = \frac{[A]^2[B]}{[C][D]^3}$$

(i) Write an equation for the forward reaction.

.....

(ii) Deduce the units of K_c

.....

(iii) State what can be deduced from the fact that the value of K_c is larger when the equilibrium is established at a lower temperature.

.....

(3 marks)

(b) A 36.8 g sample of N_2O_4 was heated in a closed flask of volume 16.0 dm^3. An equilibrium was established at a constant temperature according to the following equation.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The equilibrium mixture was found to contain 0.180 mol of N_2O_4

(i) Calculate the number of moles of N_2O_4 in the 36.8 g sample.

.....

.....

(ii) Calculate the number of moles of NO_2 in the equilibrium mixture.

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(iii) Write an expression for K_c and calculate its value under these conditions.

Expression for K_c .....

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Calculation .....

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(iv) Another 36.8 g sample of N_2O_4 was heated to the same temperature as in the original experiment, but in a larger flask. State the effect, if any, of this change on the position of equilibrium and on the value of K_c compared with the original experiment.

Effect on the position of equilibrium .....

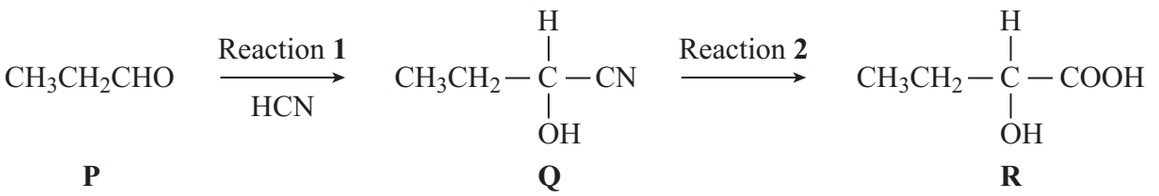
Effect on the value of K_c .....

(9 marks)

12

Turn over for the next question

4 Consider the sequence of reactions below.



P **Q** **R**

(a) Name and outline a mechanism for Reaction **1**.

Name of mechanism .....

Mechanism

(5 marks)

(b) (i) Name compound **Q**

.....

(ii) The molecular formula of **Q** is C_4H_7NO. Draw the structure of the isomer of **Q** which shows geometrical isomerism and is formed by the reaction of ammonia with an acyl chloride.

(3 marks)

(c) Draw the structure of the main organic product formed in each case when **R** reacts separately with the following substances:

(i) methanol in the presence of a few drops of concentrated sulphuric acid;

(ii) acidified potassium dichromate(VI);

(iii) concentrated sulphuric acid in an elimination reaction.

(3 marks)

11

5 (a) Name the compound $(CH_3)_2NH$

.....

(1 mark)

(b) $(CH_3)_2NH$ can be formed by the reaction of an excess of CH_3NH_2 with CH_3Br. Name and outline a mechanism for this reaction.

Name of mechanism .....

Mechanism

(5 marks)

(c) Name the type of compound produced when a large excess of CH_3Br reacts with CH_3NH_2
Give a use for this type of compound.

Type of compound .....

Use .....

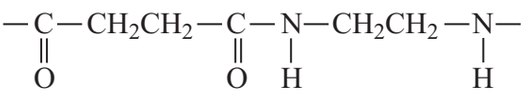
(2 marks)

(d) Draw the structures of the two compounds formed in the reaction of CH_3NH_2 with ethanoic anhydride.

(2 marks)

10

6 (a) The structure below shows the repeating unit of a polymer.



By considering the functional group formed during polymerisation, name this type of polymer and the type of polymerisation involved in its formation.

Type of polymer .....

Type of polymerisation .....

(2 marks)

(b) Draw the structure of the species present in solid aminoethanoic acid, H_2NCH_2COOH

(1 mark)

(c) Explain why the melting point of aminoethanoic acid is much higher than that of hydroxyethanoic acid, $HOCH_2COOH$

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(2 marks)

5

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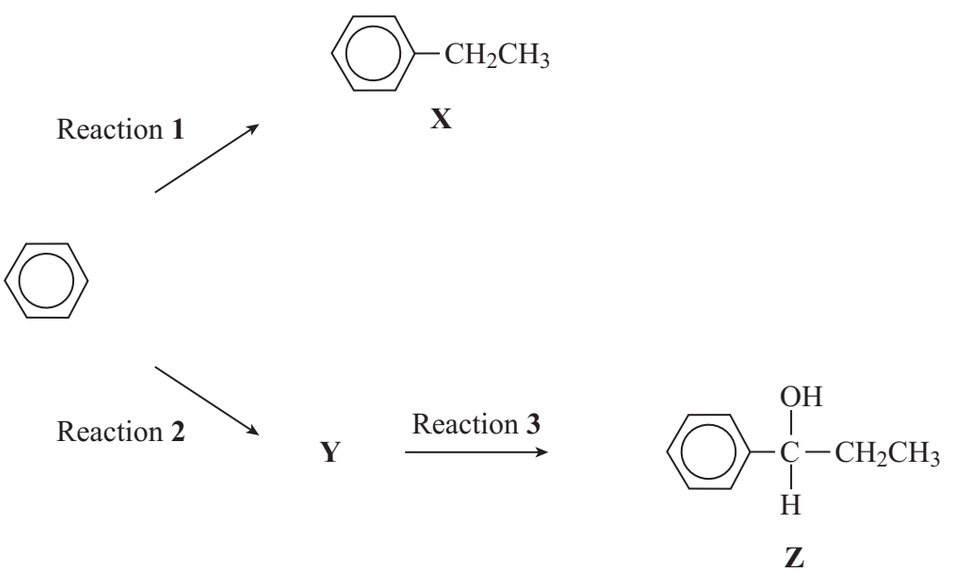
SECTION B

Detach this perforated sheet.
Answer both questions in the spaces provided.

7 Two reactions of benzene are shown below.



(a) Name **X** and give the reagent and catalyst required for Reaction **1**.
Write an equation for the formation of the reactive intermediate involved in this reaction.
Name and outline a mechanism for the reaction of this reactive intermediate with benzene to form **X**.

(8 marks)

(b) (i) Deduce the structure of **Y** and give the organic reagent needed for Reaction **2**.

(ii) Give the reagent(s) needed for Reaction **3**.

(3 marks)

11

8 (a) The reaction of but-1-ene with chlorine produces 1,2-dichlorobutane, $C_4H_8Cl_2$

(i) Given that chlorine exists as a mixture of two isotopes, ^{35}Cl and ^{37}Cl, predict the number of molecular ion peaks and their *m/z* values in the mass spectrum of $C_4H_8Cl_2$

(ii) The mass spectrum of 1,2-dichlorobutane contains peaks at *m/z* = 77 and 79. Draw the structure of the fragment ion which produces the peak at *m/z* = 77 and write an equation showing its formation from the molecular ion.

(6 marks)

(b) The reaction of but-2-ene with hydrogen chloride forms a racemic mixture of the stereoisomers of 2-chlorobutane.

(i) Name the type of stereoisomerism shown by 2-chlorobutane and give the meaning of the term *racemic mixture*. State how separate samples of the stereoisomers could be distinguished.

(ii) By considering the shape of the reactive intermediate involved in the mechanism of this reaction, explain how a racemic mixture of the two stereoisomers of 2-chlorobutane is formed.

(7 marks)

(c) The reaction of but-2-ene with chlorine produces 2,3-dichlorobutane, $C_4H_8Cl_2$

(i) State the number of peaks, their integration ratio and any splitting of peaks in the proton n.m.r. spectrum of 2,3-dichlorobutane.

(ii) Compound **S**, an isomer of $C_4H_8Cl_2$, produces a proton n.m.r. spectrum which consists only of a singlet, a triplet and a quartet with an integration ratio of 3:3:2 respectively.

Compound **T**, also an isomer of $C_4H_8Cl_2$, produces a proton n.m.r. spectrum which consists only of two singlets with an integration ratio of 3:1

Draw the structures of **S** and of **T**.

(6 marks)

19

END OF QUESTIONS

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