Surname		Other Names	
Centre Number			Candidate Number									
Candidate Signature												

For Examiner's Use

General Certificate of Education
January 2010
Advanced Level Examination

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

Wednesday 27 January 2010 9.00 am to 10.30 am

For this paper you must have
- a calculator.

Time allowed: 1 hour 30 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- Answer the questions in **Section A** and **Section B** in the spaces provided. Answers written in margins or on blank pages will not be marked.
- Show all your working.
- Do all rough work in this book. Cross through any work you do not want to be 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 questions in **Section B** in continuous prose, where appropriate.
- You will be assessed on your ability to use good English, to organise relevant information clearly 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			
Question	Mark	Question	Mark
1			
2			
3			
4			
5			
6			
7			
8			
9			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

SECTION A

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

1 (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds **W** and **X** at a constant temperature.

Experiment	Initial concentration of **W** / mol dm^{-3}	Initial concentration of **X** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.25	0.12	0.15×10^{-5}
2	0.50	0.12	0.30×10^{-5}
3	1.00	0.24	2.40×10^{-5}

1 (a) (i) Show how the data in the table can be used to deduce that the reaction is first-order with respect to **W**.

.....

.....

1 (a) (ii) Deduce the order with respect to **X**.

.....

.....

(2 marks)

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

1 (b) The following data were obtained in a second series of experiments on the rate of the reaction between compounds **Y** and **Z** at a constant temperature.

Experiment	Initial concentration of **Y** / mol dm^{-3}	Initial concentration of **Z** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
4	0.25	0.50	6.20×10^{-5}
5	0.35	0.10	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\mathbf{Y}]^2[\mathbf{Z}]$$

1 (b) (i) Use the data from Experiment 4 to calculate a value for the rate constant, k, at this temperature. State the units of k.

Value for k .....

.....

.....

Units of k .....

.....

1 (b) (ii) Calculate the value of the initial rate in Experiment 5.

.....

.....

.....

(4 marks)

6

Turn over ▶

2 Nitrogen dioxide dissociates according to the following equation.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

When 5.75 g of nitrogen dioxide were heated to a constant temperature, *T*, in a flask of volume 5.0 dm^3, an equilibrium mixture was formed which contained 1.60 g of oxygen.

2 (a) (i) Calculate the amount, in moles, of oxygen present in this equilibrium mixture and deduce the amount, in moles, of nitrogen monoxide also present in this equilibrium mixture.

Moles of O_2 at equilibrium .....

.....

Moles of NO at equilibrium .....

2 (a) (ii) Calculate the amount, in moles, in the original 5.75 g of nitrogen dioxide and hence calculate the amount, in moles, of nitrogen dioxide present in this equilibrium mixture.

Original moles of NO_2 .....

.....

Moles of NO_2 at equilibrium .....

.....

(4 marks)

2 (b) Write an expression for the equilibrium constant, K_c, for this reaction. Calculate the value of this constant at temperature *T* and give its units.

Expression for K_c .....

.....

Calculation .....

.....

.....

.....

.....

(4 marks)

2 (c) State the effect on the equilibrium yield of oxygen and on the value of K_c when the same mass of nitrogen dioxide is heated to the same temperature T, but in a different flask of greater volume.

Yield of oxygen .....

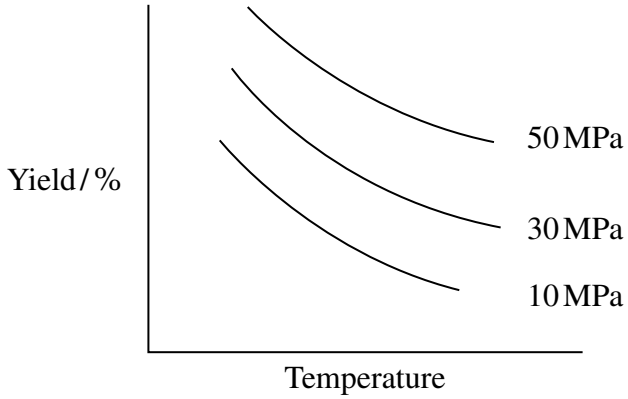
Value of K_c .....

(2 marks)

10

Turn over for the next question

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



3 (a) 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 .....

.....

.....

(3 marks)

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

The forward reaction is .....

Explanation .....

.....

.....

(3 marks)

6

4 The value of the acid dissociation constant, K_a, for the weak acid HA, at 298 K, is 2.54×10^{-5} mol dm^{-3}.

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

.....

.....

(1 mark)

4 (b) Calculate the pH of a 0.300 mol dm^{-3} solution of HA at 298 K.

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.....

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.....

.....

(4 marks)

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

4 (c) (i) State and explain the effect on the pH of this buffer solution when a small amount of sodium hydroxide solution is added.

Effect on pH .....

Explanation .....

.....

4 (c) (ii) The concentration of HA in a buffer solution is 0.300 mol dm^{-3}. Calculate the concentration of A^- in this buffer solution when the pH is 4.82

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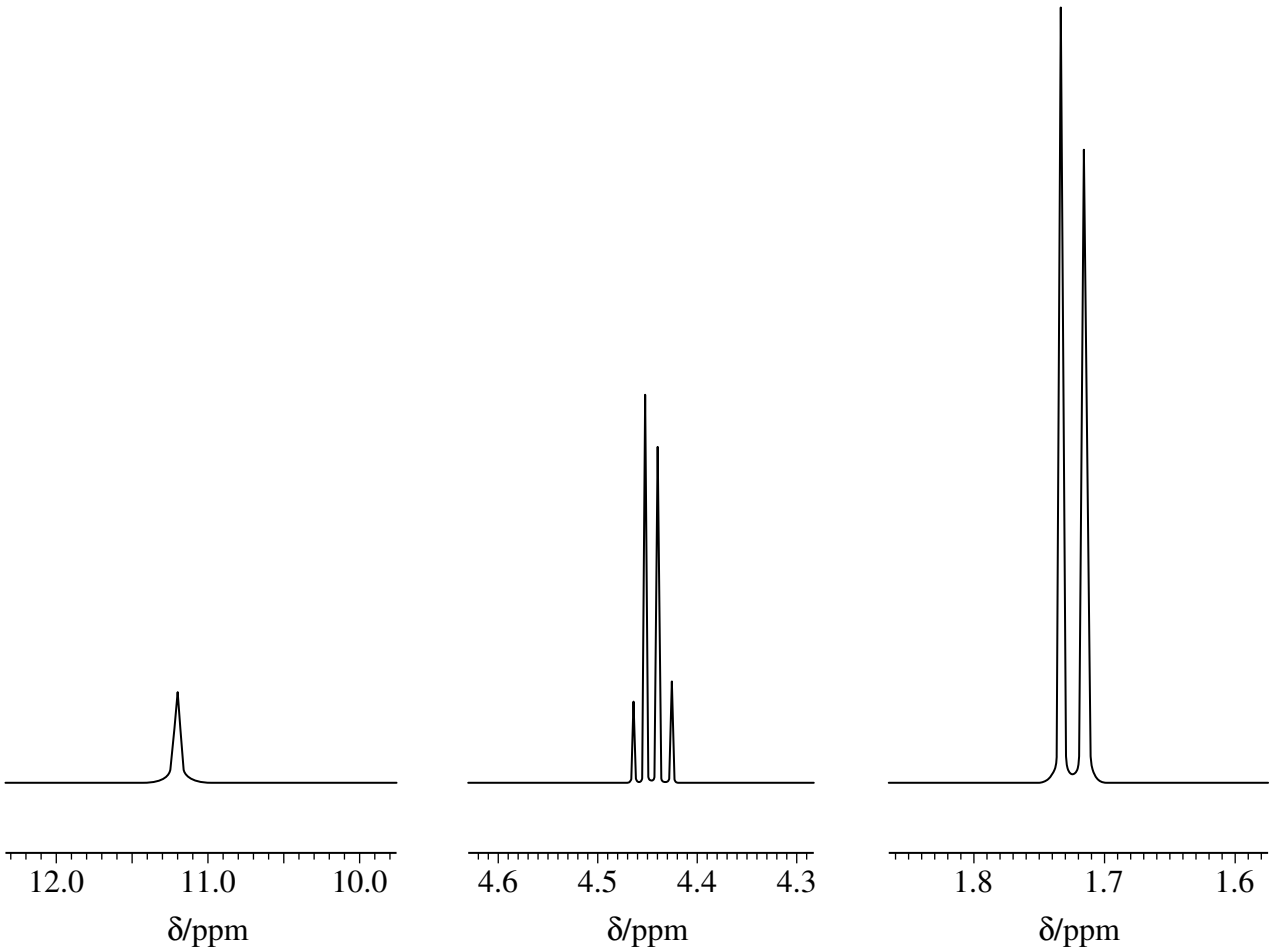
(6 marks)

11

Turn over ▶

5 Three sections of the proton n.m.r. spectrum of $CH_3CHClCOOH$ are shown below.



5 (a) Name the compound $CH_3CHClCOOH$

.....

(1 mark)

5 (b) Explain the splitting patterns in the peaks at δ 1.72 and δ 4.44

Peak at δ 1.72 .....

.....

Peak at δ 4.44 .....

.....

(2 marks)

5 (c) Predict the splitting pattern that would be seen in the proton n.m.r. spectrum of the isomeric compound $ClCH_2CH_2COOH$

.....

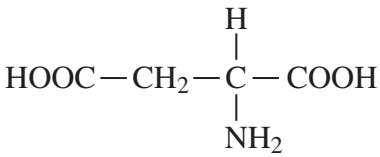
.....

(1 mark)

5 (d) The amino acid *alanine* is formed by the reaction of $CH_3CHClCOOH$ with an excess of ammonia. The mechanism is nucleophilic substitution. Outline this mechanism, showing clearly the structure of *alanine*.

(5 marks)

5 (e) The amino acid *aspartic acid* has the structure



Draw structures to show the product formed in each case when aspartic acid reacts with

5 (e) (i) an excess of aqueous HCl,

5 (e) (ii) an excess of aqueous NaOH,

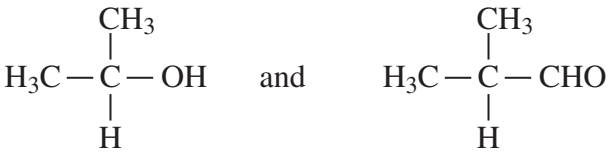
5 (e) (iii) another molecule of aspartic acid.

(3 marks)

12

6 (a) Describe, by giving reagents and stating observations, how you could distinguish between the compounds in the following pairs using a simple test-tube reaction for each pair.

6 (a) (i)



A and **B**

Reagent .....

*Observation with **A*** .....

*Observation with **B*** .....

(3 marks)

6 (a) (ii) CH_3COOCH_3 and CH_3CH_2COOH

C **D**

Reagent .....

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

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

(3 marks)

6 (b) Explain how *fingerprinting* is used to identify a compound using infra-red spectroscopy.

.....

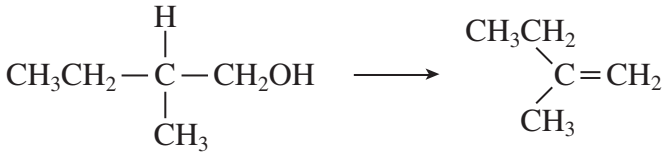
.....

.....

(2 marks)

8

7 Consider the reaction shown below.



J **K**

7 (a) (i) Name compound **J**

.....

7 (a) (ii) Compound **J** exists as a pair of stereoisomers. Name this type of stereoisomerism.

.....

(2 marks)

7 (b) (i) Name the type of mechanism for this reaction.

.....

7 (b) (ii) Draw the repeating unit of the polymer formed by **K** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation .....

7 (b) (iii) Draw the structure of an isomer of **K** which shows stereoisomerism.

7 (b) (iv) Draw the structure of an isomer of **K** which has only one peak in its proton n.m.r. spectrum.

(5 marks)

7

Turn over ▶

SECTION B

Detach this perforated sheet.
Answer both Questions **8** and **9** in the space provided on page 14 and pages 17–20.

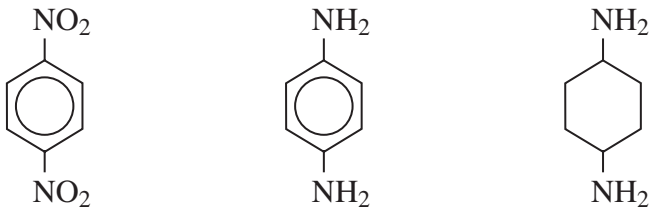
8 The term *acylation* can be applied to the reaction of ethanoyl chloride with ethylamine and also to the reaction of ethanoyl chloride with benzene in the presence of a catalyst.

For each of these reactions, write an equation for the overall reaction and name the organic product. Name and outline a mechanism for each reaction and identify a suitable catalyst for the reaction with benzene. *(15 marks)*

9 (a) Give reagents and conditions and write equations to show the formation of nitrobenzene from benzene.

Name and outline a mechanism for this reaction of benzene. *(8 marks)*

9 (b) Compounds **R**, **S** and **T** are shown below.



R **S** **T**

Name **R** and give reagents for the conversion of **R** into **S**. Write an equation for this reaction using [H] to represent the reductant.

Explain why **S** is a weaker base than **T**. *(6 marks)*

9 (c) Draw the repeating unit of the polymer formed by the reaction of **S** with hexanedioic acid. *(1 mark)*

END OF QUESTIONS

There are no questions printed on this page

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ANSWER IN THE SPACES PROVIDED