Surname		Other Names	
Centre Number		Candidate Number	
Candidate Signature			

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General Certificate of Education
January 2003
Advanced Level Examination

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

Wednesday 22 January 2003 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.

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 $R = 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$
- 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			
8			
Total (Column 1) →			
Total (Column 2) →			
TOTAL			
Examiner's Initials			

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.

Key

relative atomic mass — 6.9
Li Lithium
atomic number — 3

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 †															

* **58 – 71** Lanthanides	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
† **90 – 103** Actinides	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

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

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SECTION A

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

1 (a) The initial rate of the reaction between substances **P** and **Q** was measured in a series of experiments and the following rate equation was deduced.

$$\text{rate} = k[\mathbf{P}]^2[\mathbf{Q}]$$

(i) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [**P**] / mol dm^{-3}	Initial [**Q**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.30	4.8×10^{-3}
2	0.10	0.10	
3	0.40		9.6×10^{-3}
4		0.60	19.2×10^{-3}

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

....

....

....

....

....

(6 marks)

(b) What change in the reaction conditions would cause the value of the rate constant to change?

....

(1 mark)

7

Turn over ▶

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2 Nitrogen dioxide dissociates according to the following equation.

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

When 21.3 g of nitrogen dioxide were heated to a constant temperature, T, in a flask of volume 11.5 dm^3, an equilibrium mixture was formed which contained 7.04 g of oxygen.

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

Number of moles of O_2 at equilibrium ....

....

Number of moles of NO at equilibrium ....

(ii) Calculate the number in moles in the original 21.3 g of nitrogen dioxide and hence calculate the number of moles of nitrogen dioxide present in this equilibrium mixture.

Original number of moles of NO_2 ....

....

Number of moles of NO_2 at equilibrium ....

....

(4 marks)

(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)

(c) The total number of moles of gas in the flask is 0.683. Use the ideal gas equation to determine the temperature T at which the total pressure in the flask is 3.30×10^5 Pa. (The gas constant $R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$)

....

....

....

....

....

(3 marks)

(d) 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 ....

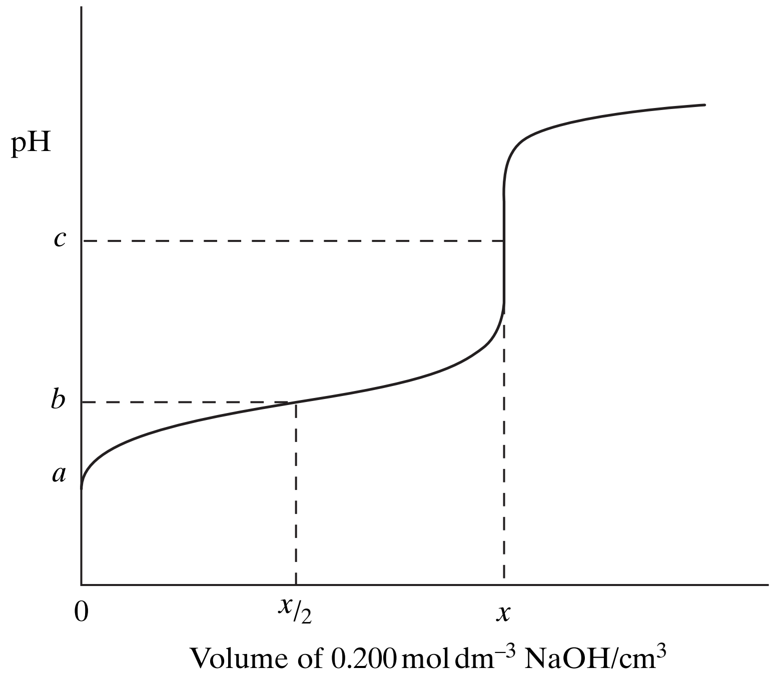
(2 marks)

13

TURN OVER FOR THE NEXT QUESTION

Turn over ▶

3 The sketch below shows the change in pH when a 0.200 mol dm^{-3} solution of sodium hydroxide is added from a burette to 25.0 cm^3 of a 0.150 mol dm^{-3} solution of the weak acid HA at 25 °C.



(a) The volume of sodium hydroxide solution added at the equivalence point is x cm^3. Calculate the value of x.

....

....

....

(2 marks)

(b) (i) Define the term pH.

....

(ii) The pH at the equivalence point is c. Suggest a value for c.

....

(iii) Identify a suitable indicator for detecting the equivalence point of the titration.

....

(3 marks)

LEAVE MARGIN BLANK

(c) The value of K_a for the weak acid HA at 25 °C is 2.75×10^{-5} mol dm^{-3}.

(i) Explain the term *weak* as applied to the acid HA.

....

(ii) Write an expression for K_a for the acid HA.

....

....

(iii) Calculate the pH of the 0.150 mol dm^{-3} solution of acid HA before any sodium hydroxide is added, i.e. the pH at point *a*.

....

....

....

....

....

(5 marks)

(d) Calculate the pH of the solution formed when $x/2$ cm^3 of the 0.200 mol dm^{-3} solution of sodium hydroxide are added to 25.0 cm^3 of the 0.150 mol dm^{-3} solution of HA, i.e. the pH at point *b*.

....

....

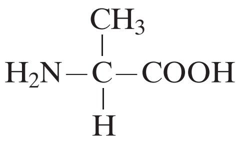
....

(3 marks)

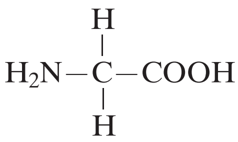
13

TURN OVER FOR THE NEXT QUESTION

4 The structures of the amino acids *alanine* and *glycine* are shown below.



alanine



glycine

(a) Give the systematic name for *alanine*.

(1 mark)

(b) *Alanine* exists as a pair of stereoisomers.

(i) Explain the meaning of the term *stereoisomers*.

(ii) State how you could distinguish between the stereoisomers.

(4 marks)

(c) Give the structural formula of the species formed by *glycine* at pH 14.

(1 mark)

LEAVE MARGIN BLANK

(d) When two amino acids react together, a dipeptide is formed. Give the structural formulae of the **two** dipeptides which are formed when *alanine* and *glycine* react together.

Dipeptide 1

Dipeptide 2

(2 marks)

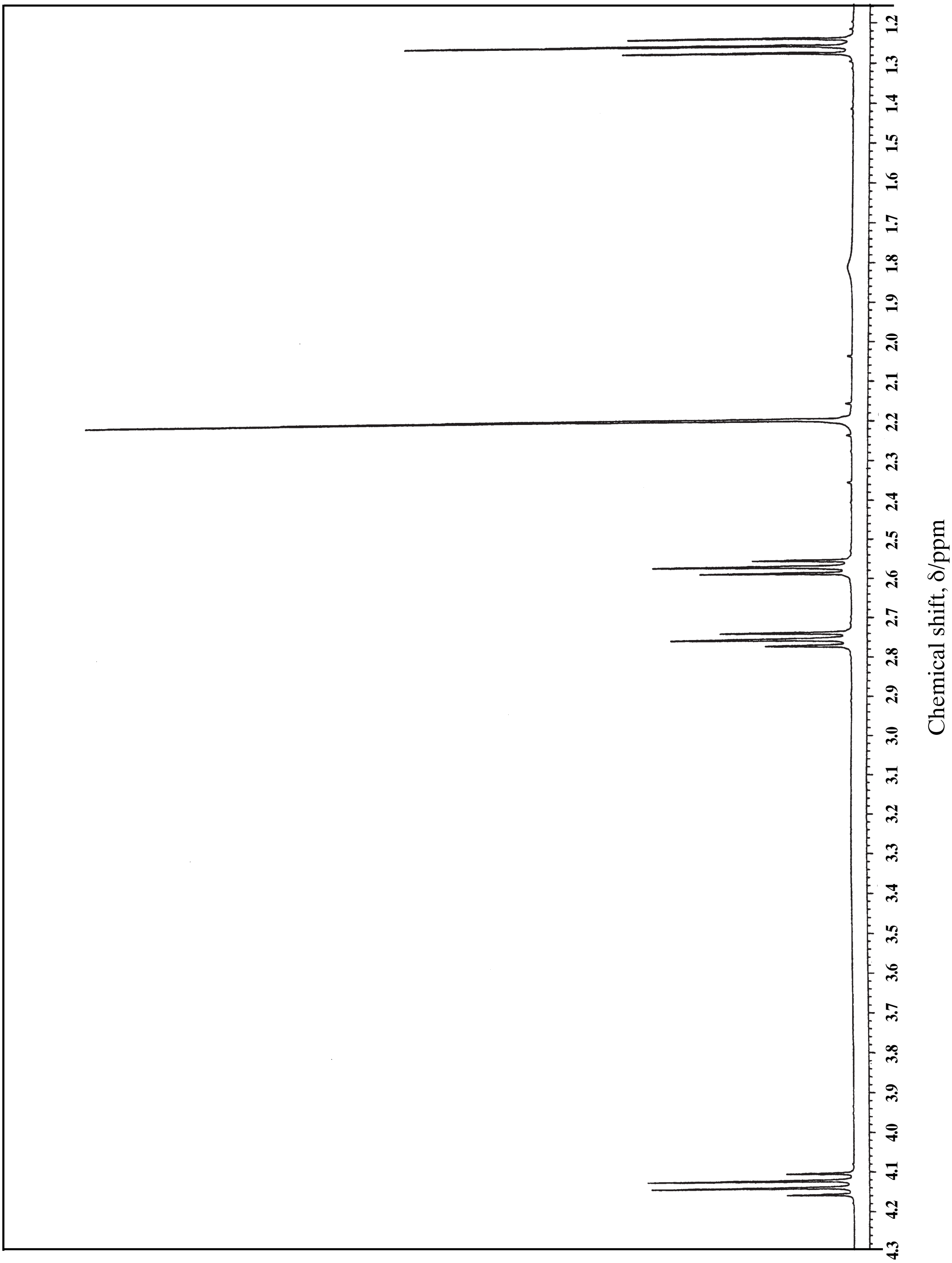
(e) Give the structural formula of the organic compound formed when *glycine* reacts with methanol in the presence of a small amount of concentrated sulphuric acid.

(1 mark)

9

Turn over ▶

5 The proton n.m.r. spectrum of compound **X** is shown below.



Compound **X**, $C_7H_{12}O_3$, contains both a ketone and an ester functional group. The measured integration trace for the peaks in the n.m.r. spectrum of **X** gives the ratio shown in the table below.

Chemical shift, δ/ppm	4.13	2.76	2.57	2.20	1.26
Integration ratio	0.8	0.8	0.8	1.2	1.2

Refer to the spectrum, the information given above and the data on the reverse of the Periodic Table provided to answer the following questions.

(a) How many different types of proton are present in compound **X**?

....

(1 mark)

(b) What is the whole-number ratio of each type of proton in compound **X**?

....

(1 mark)

(c) Draw the part of the structure of **X** which can be deduced from the presence of the peak at δ 2.20.

....

(1 mark)

(d) The peaks at δ 4.13 and δ 1.26 arise from the presence of an alkyl group. Identify the group and explain the splitting pattern.

Alkyl group ....

Explanation ....

....

....

(3 marks)

(e) Draw the part of the structure of **X** which can be deduced from the splitting of the peaks at δ 2.76 and δ 2.57.

....

(1 mark)

(f) Deduce the structure of compound **X**.

....

(2 marks)

9

Turn over ▶

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6 (a) Methylamine is a weak Brønsted–Lowry base and can be used in aqueous solution with one other substance to prepare a basic buffer.

(i) Explain the term *Brønsted–Lowry base* and write an equation for the reaction of methylamine with water to produce an alkaline solution.

Brønsted–Lowry base ....

Equation ....

(ii) Suggest a substance that could be added to aqueous methylamine to produce a basic buffer.

....

(iii) Explain how the buffer solution in part (a)(ii) is able to resist a change in pH when a small amount of sodium hydroxide is added.

....

....

....

(5 marks)

(b) Explain why methylamine is a stronger base than ammonia.

....

....

....

(2 marks)

(c) A cation is formed when methylamine reacts with a large excess of bromoethane. Name the mechanism involved in the reaction and draw the structure of the cation formed.

Name of mechanism ....

Structure

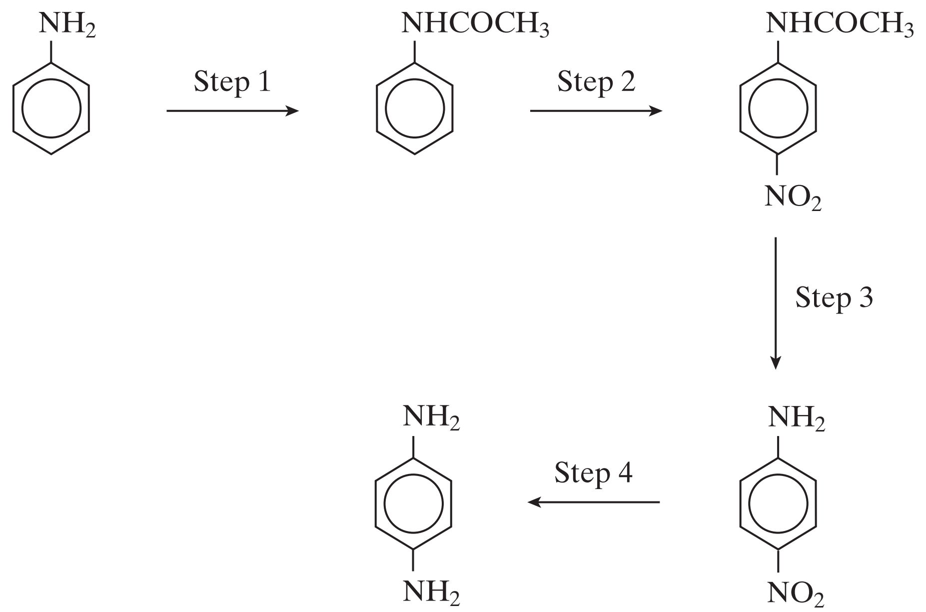
(2 marks)

9

SECTION B

Answer **both** questions in the space provided on pages 16 to 20 of this booklet.

7 A possible synthesis of 1,4-diaminobenzene is shown below.



(a) Identify a suitable reagent or combination of reagents for Step 1. Name and outline a mechanism for the reaction. *(6 marks)*

(b) Identify a suitable reagent or combination of reagents for Step 2. Name and outline a mechanism for the reaction. *(6 marks)*

(c) Identify a suitable reagent or combination of reagents for Step 4. Draw the repeating unit of the polymer formed by reaction of 1,4-diaminobenzene with pentanedioic acid. *(3 marks)*

TURN OVER FOR THE NEXT QUESTION

Turn over ▶

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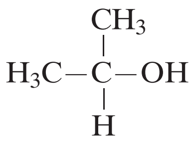
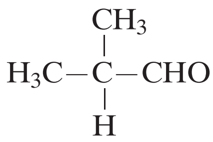
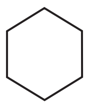
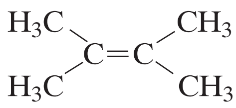
8 (a) Describe, by giving reagents and stating observations, how you could distinguish between the compounds in the following pairs using a simple test-tube reaction for each pair.

(i)  and 

A **B**

(ii)  and 

C **D**

(iii) CH_3COOCH_3 and CH_3CH_2COOH

E **F**

(8 marks)

(b) State how compounds **E** and **F** in part (a)(iii) above could be distinguished by their infra-red spectra, without using the fingerprint region. Explain how *fingerprinting* is used to identify a compound. *(3 marks)*

(c) Suggest the structure of the fragment responsible for the major peak in the mass spectrum of compound **E** and state its *m/z* value. Write an equation showing the formation of this fragment from the molecular ion. *(4 marks)*

END OF QUESTIONS