

Candidate Name	Centre Number	Candidate Number
		2



**GCE A level**

1094/01

**New A2**

**CHEMISTRY CH4**

A.M. WEDNESDAY, 27 January 2010

1<sup>3</sup>/<sub>4</sub> hours

### ADDITIONAL MATERIALS

In addition to this examination paper, you will need:

- a calculator;
- an 8 page answer book;
- a **Data Sheet** which contains a **Periodic Table** supplied by WJEC.  
Refer to it for any **relative atomic masses** you require.

### INSTRUCTIONS TO CANDIDATES

Write your name, centre number and candidate number in the spaces at the top of this page.

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

**Section B** Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

### INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

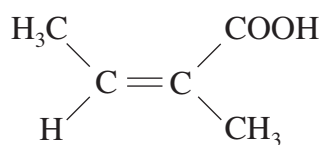
You are reminded that marking will take into account the Quality of Written Communication in all written answers.

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

## SECTION A

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

1. (a) Angelic acid, (2-methylbut-2-enoic acid), is the traditional name for a compound produced by some plants as a defence against attack by beetles.



angelic acid

- (i) This acid is one of a pair of stereoisomers.  
Explain what is meant by the term stereoisomer. [1]

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- (ii) Draw the **skeletal** formula of the **other** stereoisomer of angelic acid. [1]

- (iii) The ethyl esters of these unsaturated acids have uses in the perfume industry.  
State the reagent(s) and the condition(s), apart from heating, that are needed to produce ethyl angelate from angelic acid. [2]

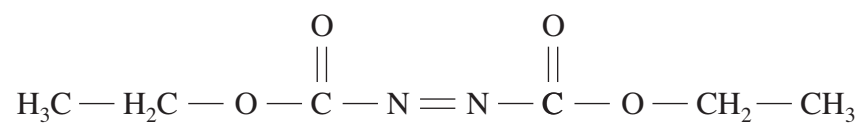
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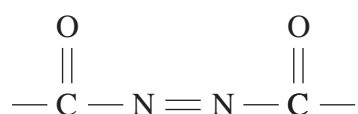


(c) Diethyl azodicarboxylate (abbreviated to DEAD)



is a shock-sensitive, toxic orange liquid.

(i) The conjugated system shown below is present in DEAD and is described as a chromophore.



I. State the meaning of the term chromophore. [1]

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II. Explain why DEAD is an **orange** liquid. [1]

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(ii) The NMR spectrum of DEAD shows two series of peaks – a quartet and a triplet. Explain how the splitting of these peaks arises. [2]

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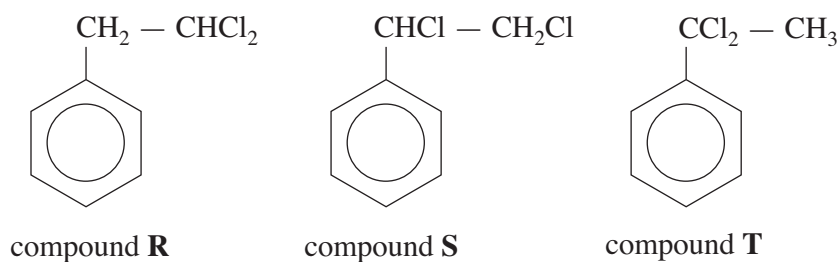
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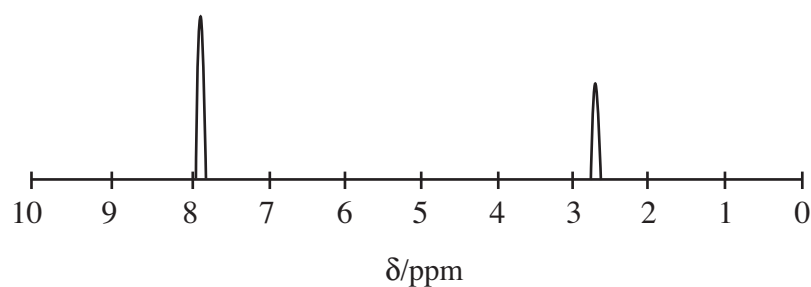
Total [13]



- (b) (2-Chloroethyl)benzene can be made by reacting ethylbenzene with chlorine. During this reaction a number of other compounds, including the following, are produced.



The low resolution NMR spectrum of one of these compounds is shown below.



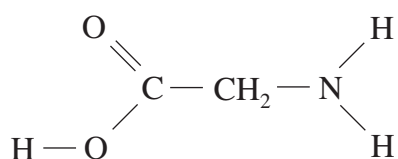
State, giving a reason, which of the three compounds **R**, **S** or **T** will have the low resolution NMR spectrum shown. [2]

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- (c) (i) Aminoethanoic acid (glycine), whose displayed formula is shown below, reacts with ethanoyl chloride.



Give the equation for this reaction, showing the displayed formula of the organic product. [2]

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3. Read the passage below and then answer the question in the spaces provided.

### Carboxylic acids and their esters – versatile materials in industry and in the home

The simplest carboxylic acid, methanoic acid, occurs naturally in stinging nettles and is also used by ants and bees as a form of defence and attack. However, methanoic acid is otherwise limited in its use because of its toxicity, and there is a greater demand for ethanoic acid.

- 5 An aqueous solution of ethanoic acid (vinegar) can be made by the atmospheric oxidation of aqueous ethanol using certain bacteria.

One industrial method for the production of ethanoic acid is to react methanol and carbon monoxide at a temperature of 450 K and a pressure of 30 atmospheres, in the presence of a suitable catalyst. The methanol and carbon monoxide have to be produced from coal, oil or natural gas. The process gives a 99% yield of ethanoic acid.



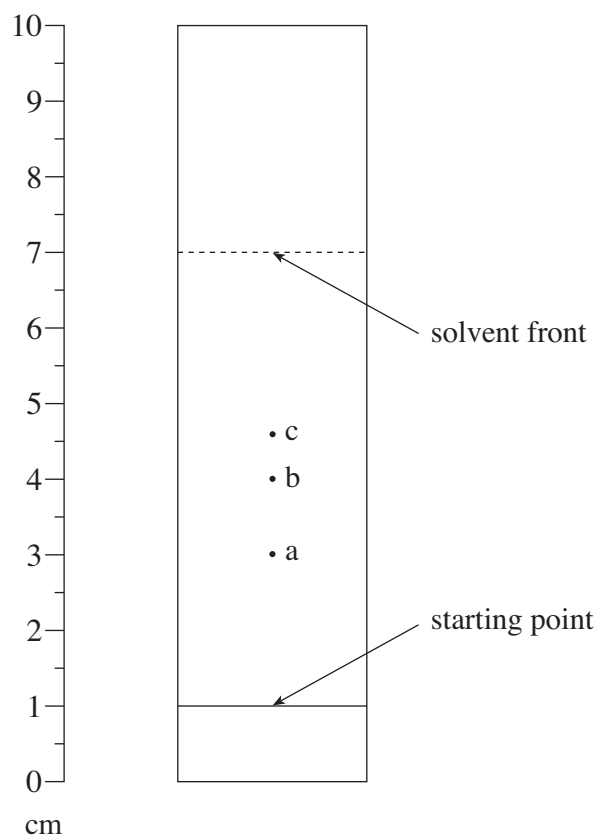
Another industrial process uses the naphtha fraction from petroleum. This process also requires increased temperatures and pressures. Unfortunately, the yield of ethanoic acid is less than 50% and a number of co-products are produced. These include methanoic, propanoic and butane-1,4-dioic acids, as well as propanone.

- 15 Esters of carboxylic acids that have a higher relative molecular mass occur naturally as oils, fats and waxes, and a number of these are used in the perfume industry. Some of these esters are glycerides – esters derived from propane-1,2,3-triol (glycerol). Alkaline hydrolysis of these glycerides produces sodium or potassium salts of large-molecule carboxylic acids that are used as soaps. Many of these oils, fats or waxes contain glycerides of a number of different carboxylic acids and the separation and identification of these is difficult.

- 20 One method of identification is to convert the glyceryl esters to simple ethyl esters and then to separate and identify the ethyl esters by thin layer chromatography (TLC).



A typical TLC chromatogram is shown below.



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Man-made esters have been developed to have specific uses. For example, the polymer PET is used to make bottles and in textiles such as *terylene*, whereas polyvinyl acetate (PVA) is used as an adhesive.

- End of passage -

- (a) By law, the concentration of ethanoic acid present in vinegar has to be within certain limits.

50.00 cm<sup>3</sup> of a sample of vinegar was diluted to exactly 500 cm<sup>3</sup> by the addition of distilled water, using a volumetric flask.

25.00 cm<sup>3</sup> of this **diluted** solution was exactly neutralised by 26.25 cm<sup>3</sup> of a solution of sodium hydroxide of concentration 0.100 mol dm<sup>-3</sup>.

- (i) State a procedure that is essential when diluting a solution, so that the results of the titration are accurate. [1]

- (ii) Use this information and the equation below to calculate the concentration of ethanoic acid present in the **undiluted** vinegar in mol dm<sup>-3</sup>. [4]



- (b) The passage describes two industrial methods for making ethanoic acid (*lines 6 to 14*). These are summarised in the table below.

Method	Starting materials	Temp / K	Pressure / atmosphere	Yield of ethanoic acid / %
1	methanol, carbon monoxide	450	30	99
2	naphtha from petroleum	450	50	< 50

Use the information in the passage and in the table to discuss the relative advantages and disadvantages of **each** process. [4]

(QWC) [1]

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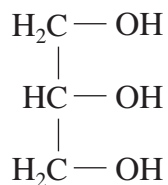
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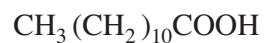
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- (c) The formulae of glycerol (propane-1,2,3-triol) and lauric acid (dodecanoic acid) are given below.



glycerol



lauric acid

Write the structural formula of the tri-ester, glyceryl trilaurate, formed by the reaction of glycerol and lauric acid.

*You need not show the bonds between carbon and hydrogen atoms in your answer.* [1]

- (d) The passage shows a TLC chromatogram of a mixture of three ethyl esters of different carboxylic acids.

The retardation factor ( $R_f$  value) of ethyl palmitate (hexadecanoate) is 0.60.

Use the chromatogram to decide which of the three spots, if any, is given by ethyl palmitate, showing how you arrived at your answer. [2]

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- (e) The polymer PET (*line 24*) is made from ethane-1,2-diol and benzene-1,4-dicarboxylic acid. Give the formula of a section of this polymer, identifying the repeating unit. [2]

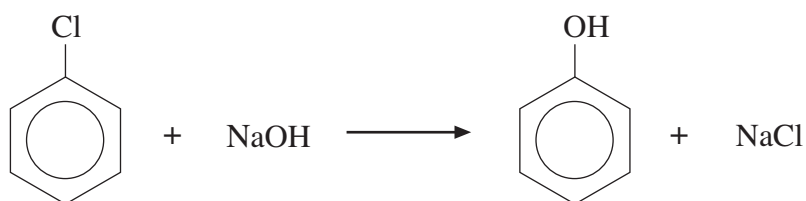
Total [15]

**Section A Total [40]**

## SECTION B

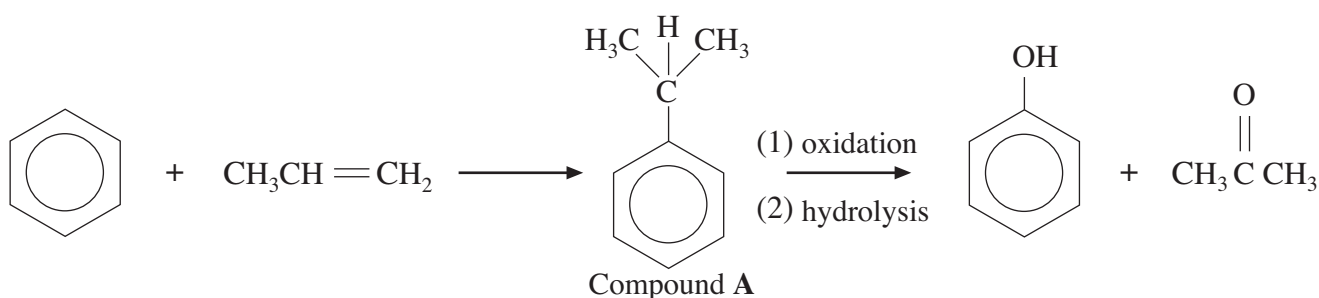
Answer **both** questions in the separate answer book provided.

4. (a) Chlorobenzene,  $C_6H_5Cl$ , is an important industrial chemical. It can be made in the laboratory by reacting benzene and chlorine in the presence of an iron or iron(III) chloride catalyst.  
Give the mechanism for this electrophilic substitution reaction. [4]
- (b) One method for making phenol is by reacting chlorobenzene with aqueous sodium hydroxide, but at a pressure of 200 atmospheres.



Explain why it is difficult to react chlorobenzene with sodium hydroxide. [3]

- (c) Most phenol is now produced from benzene and propene in a three-stage reaction.



- (i) State the name of compound A. [1]
- (ii) Explain why the atom economy of this reaction to make phenol is poor. [2]
- (iii) Using the Data Sheet, describe how an infrared spectrum of a sample of phenol produced in this process would indicate that traces of propanone were also present. [2]
- (iv) At room temperature phenol is a solid. A sample of phenol was dissolved in ethanol and then a few drops of the solution were added to some iron(III) chloride solution. State what was seen and why ethanol is a suitable solvent to use for this reaction. [2]

Turn over.

- (v) Ketones, such as propanone, can be identified by using 2,4-dinitrophenylhydrazine.

In a test, a few drops of a compound suspected to be propanone were added to a solution of 2,4-dinitrophenylhydrazine.

Describe what was seen and how the product of this test could be used to positively identify the compound as propanone.

*You should assume that any compound produced has been separated and purified.* [3]

- (vi) In analytical laboratories, compounds can be separated by gas chromatography and identified by mass spectroscopy.

An impure sample of propanone was obtained in this way and its mass spectrum showed the presence of another ketone, **T**, which showed a molecular ion peak,  $M^+$ , at  $m/z$  86.

In addition, other significant peaks were seen at  $m/z$  values of 29 and 57.

Use this information to show that **T** could be pentan-3-one. [3]

Total [20]

5. (a) (i) Give an equation for the preparation of butylamine from a halogenoalkane. [1]
- (ii) Discuss how the presence of the  $\text{—NH}_2$  group in butylamine results in butylamine having a higher boiling temperature than expected for a molecule of this size. [4]
- (iii) An aqueous solution of butylamine was tested using pH indicator/paper. State the colour that was observed and **explain** why butylamine is able to cause this colour change. [3]

(b) Amides have important pharmacological and commercial uses and there is interest in the development of more economical production methods.

- (i) In the past, the favoured method has been to heat the ammonium salts of carboxylic acids, for example ammonium butanoate gives butanamide.



This is an energy-intensive process, which also gives small amounts of other products.

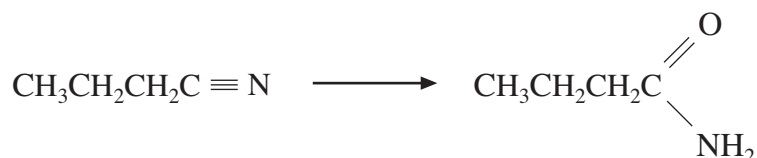
This makes the isolation of pure butanamide difficult.

In a pilot-scale experiment 50.0 kg of ammonium butanoate ( $M_r$  105) was heated to produce 26.9 kg of butanamide ( $M_r$  87).

Calculate the percentage yield of butanamide in this reaction. [3]

- (ii) There is interest in developing processes that use less energy in production and separation, and that also give higher yields.

In one new biochemical experiment, researchers used an enzyme from a suitable bacterium to convert butanenitrile to butanamide.



Details of the method

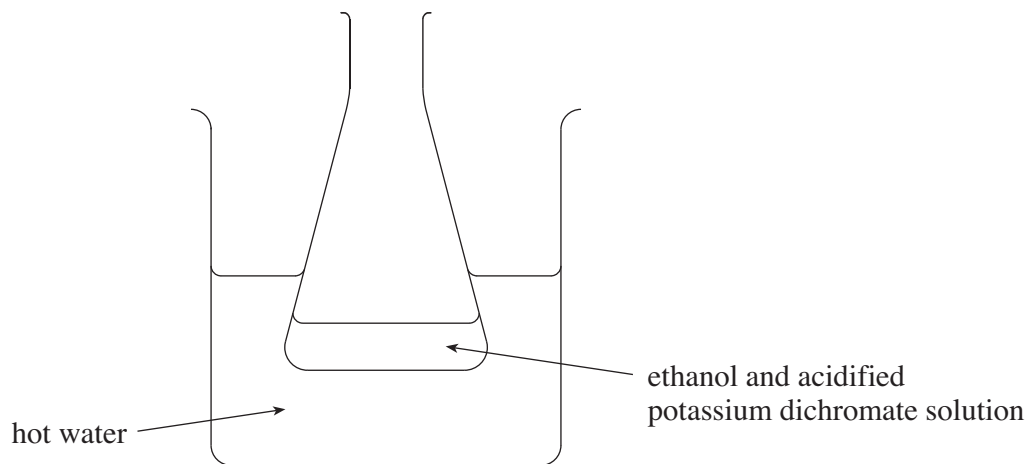
Temperature  $10^\circ\text{C}$

Time taken 6 hours

Yield of butanamide  $> 99\%$

- I Before publishing their results the researchers repeated their experiment. State why this is an essential part of any research work. [1]
- II If you were a member of the research team that discovered this new reaction, suggest what should be the next stage of research before proceeding to a larger scale trial. [1]

- (c) A few  $\text{cm}^3$  of ethanol were added to an acidified solution of potassium dichromate in a small flask and placed in a water bath at  $60^\circ\text{C}$ .



- (i) State what would be seen if the mixture was left for a period of time and explain why this change would occur. [2]
- (ii) Pure samples of the organic products were then isolated. State the names of the organic products and give a chemical test for **each** one, including the expected observations. [4]

(QWC) [1]

Total [20]

**Section B Total [40]**