UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Subsidiary Level and Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

*5027796699*

**CHEMISTRY** **9701/04**

Paper 4 Structured Questions **October/November 2007**

**1 hour 45 minutes**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

**Section A**
Answer **all** questions.

**Section B**
Answer **all** questions.

You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

| For Examiner's Use | |
|---|---|
| 1 | |
| 2 | |
| 3 | |
| 4 | |
| 5 | |
| 6 | |
| 7 | |
| 8 | |
| 9 | |
| 10 | |
| Total | |

This document consists of **15** printed pages and **1** blank page.




UNIVERSITY of CAMBRIDGE International Examinations

For Examiner's Use

## Section A

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

**1** **(a)** Use the general formula of a carboxylic acid, $RCO_2H$, to write equations to explain the following terms.

**(i)** $K_a$ .....

**(ii)** p$K_a$ .....

[2]

**(b)** The p$K_a$ values of four carboxylic acids are listed in the table below.

| acid | formula of acid | p$K_a$ |
|---|---|---|
| 1 | $CH_3CH_2CO_2H$ | 4.9 |
| 2 | $CH_3CHClCO_2H$ | 2.8 |
| 3 | $CH_3CCl_2CO_2H$ | 1.4 |
| 4 | $CH_2ClCH_2CO_2H$ | 4.1 |

**(i)** Describe and explain the trend in acid strength shown by acids 1, 2 and 3.

.....

.....

.....

.....

**(ii)** Suggest an explanation for the difference in the p$K_a$ values for acids 2 and 4.

.....

.....

**(iii)** Calculate the pH of a 0.010 mol $dm^{-3}$ solution of propanoic acid (acid 1).

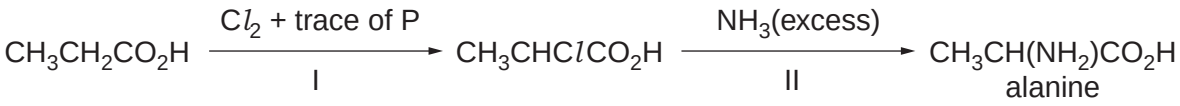
.....

.....

.....

[6]

**(c)** A good way of making synthetic amino acids uses chloro-acids as intermediates.




**(i)** Suggest the role that the trace of phosphorus plays in reaction I.

.....

**(ii)** Write a fully balanced equation for reaction I.

.....

**(iii)** State the *type of mechanism* of reaction II.

.....

**(iv)** When 10.0 g of propanoic acid was used in this 2-stage synthesis, a yield of 9.5 g of alanine was obtained.
Calculate the overall percentage yield.

.....

[5]

**(d)** In the solid state and in aqueous solutions, alanine exists as a zwitterion.
Draw the structural formula of this zwitterion.

[2]

[Total: 15]

**2** **(a)** Describe and explain the trend in the solubilities of the sulphates of the Group II elements.

.....

.....

.....

.....

.....[4]

**(b)** The salts formed by the Group II elements with other divalent anions show a similar trend in their solubilities, whereas most of their salts with monovalent anions are very soluble.

Use this information to predict the identities of compounds **A** and **B** in the following description of some reactions of Group II compounds, and write balanced equations for the reactions.

Magnesium hydroxide, $Mg(OH)_2$, is almost insoluble in water. Stirring a mixture of magnesium hydroxide and aqueous ethanedioic acid, $H_2C_2O_4$, produces a clear colourless solution containing **A**. When a solution of calcium nitrate, $Ca(NO_3)_2$, is added, a white precipitate of **B** is formed.

identity of **A** ..... identity of **B** .....

equations .....

.....[3]

**(c)** The solubility product, $K_{sp}$, of magnesium hydroxide has a numerical value of $2.0 \times 10^{-11}$.

**(i)** Write an expression for the $K_{sp}$ of magnesium hydroxide, stating its units.

.....

**(ii)** Use the value of $K_{sp}$ given to calculate the concentration of $Mg(OH)_2$ in a saturated solution.

.....

.....

**(iii)** Explain whether magnesium hydroxide would be more or less soluble in $0.1\,mol\,dm^{-3}$ $MgSO_4(aq)$ than in water.

.....

.....

[5]

[Total: 12]

For Examiner's Use

**3** The following account describes the preparation of Péligot's salt, named after the 19th century French chemist who first made it.

Place 6.0 g of potassium dichromate(VI) in a 100 $cm^3$ beaker and add 8.0 g of concentrated hydrochloric acid and 1.0 $cm^3$ water. Warm the mixture gently; if carefully done the dichromate(VI) will dissolve without the evolution of chlorine. On cooling the beaker in an ice bath the solution will deposit long orange-red crystals of Péligot's salt.

An analysis of Péligot's salt showed that it contained the following percentages by mass:
K, 22.4%; Cr, 29.8%; C*l*, 20.3%; O, 27.5%.

**(a)** Calculate the empirical formula of Péligot's salt.

[2]

**(b)** Suggest a balanced equation for the formation of Péligot's salt.

.....[1]

**(c)** The instructions suggest that strong heating might cause chlorine to be evolved.

**(i)** What *type of reaction* would produce chlorine in this system?

.....

**(ii)** Use the *Data Booklet* to identify relevant half equations and $E^{\ominus}$ values for the production of chlorine from the reaction between $K_2Cr_2O_7$ and HC*l*.

.....

.....

Use these equations to write the overall full ionic equation for this reaction.

.....

**(iii)** The use of **dilute** HC*l*(aq) does not result in the production of chlorine. Suggest why this is so.

.....

**(iv)** Use the *Data Booklet* to suggest a reason why it is **not** possible to prepare the bromine analogue of Péligot's salt by using HBr(aq) instead of HC*l*(aq).

.....

[6]

[Total: 9]

**4** **(a)** By choosing the chlorides of **two** of the Group IV elements as examples, describe the trend in the reactions of these chlorides with water. Suggest an explanation for any differences, and write equations for any reactions that occur.

.....

.....

.....

.....[3]

**(b)** The standard enthalpy changes of formation of lead(II) chloride and lead(IV) chloride are given in the following table.

| compound | $\Delta H_f^\ominus$ / kJ mol$^{-1}$ |
|---|---|
| $PbCl_2(s)$ | –359 |
| $PbCl_4(l)$ | –329 |

Use these data, and also bond energy data from the *Data Booklet*, to calculate the enthalpy changes for the following two reactions.

**(i)** $CCl_2(g) + Cl_2(g) \longrightarrow CCl_4(g)$

$\Delta H^\ominus$ = ..... kJ mol$^{-1}$

**(ii)** $PbCl_2(s) + Cl_2(g) \longrightarrow PbCl_4(l)$

$\Delta H^\ominus$ = ..... kJ mol$^{-1}$

**(iii)** Make use of your answers to parts **(i)** and **(ii)** to suggest how the relative stabilities of the two oxidation states vary down the Group.

.....

.....
[3]

[Total: 6]

**5** Potassium manganate(VII) can be used to estimate the percentage of hydrogen peroxide in household bleach. The following unbalanced equation represents the reaction between them.

..... $MnO_4^-$ + ..... $H_2O_2$ + ..... $H^+$ ⟶ ..... $Mn^{2+}$ + ..... $H_2O$ + ..... $O_2$

**(a)** Balance this equation by putting the appropriate numbers in the spaces above. [1]

**(b)** Use data from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for the reaction.

.....[1]

**(c)** When 0.020 mol $dm^{-3}$ $KMnO_4$(aq) was added from a burette into an acidified 25.0 $cm^3$ sample of $H_2O_2$, 15.0 $cm^3$ of $KMnO_4$ was required to reach the end-point.

**(i)** Describe what you would see during this titration, and also at the end-point.

.....

.....

**(ii)** Calculate the concentration of $H_2O_2$ in the sample.

.....

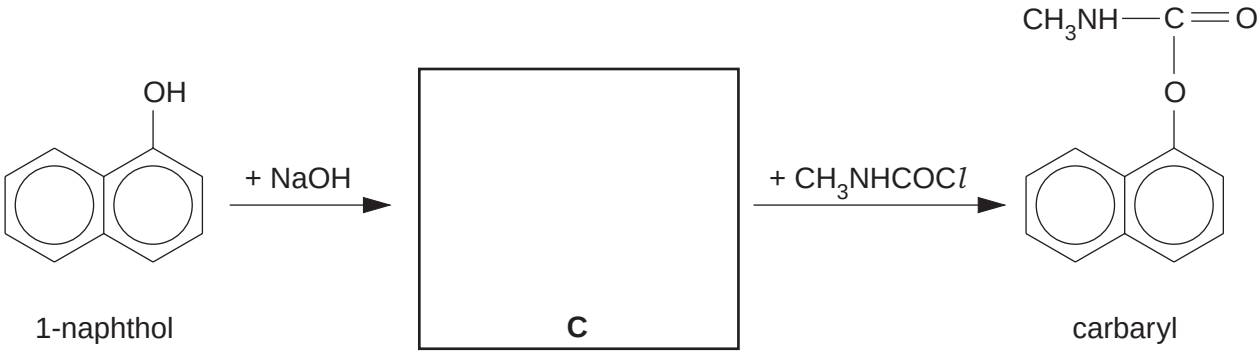
.....

.....

[4]

[Total: 6]

**6** The phenol 1-naphthol is a starting point for the manufacture of carbaryl, an insecticide and a plant growth inhibitor.




**(a)** **(i)** Suggest a structure for the intermediate **C** and draw it in the box above.

**(ii)** Name the functional groups in carbaryl.

.....

.....

**(iii)** Suggest structures for the three products formed when carbaryl is hydrolysed.

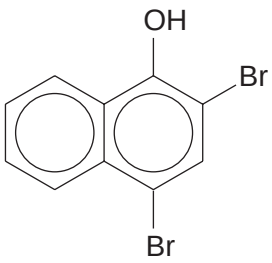
**(iv)** What reagents and conditions would you use for this hydrolysis?

.....

[7]

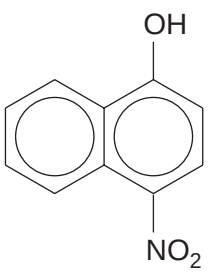
**(b)** Suggest reagents and conditions for converting 1-naphthol into each of the following compounds.

**(i)**




.....

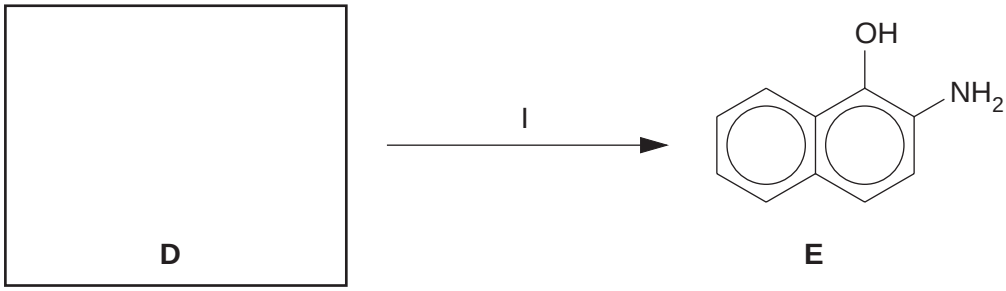
**(ii)**




.....

[2]

**(c)** Compound **D** is an isomer of 4-nitro-1-naphthol. **D** is formed as a by-product during the reaction in **b(ii)**. It can be converted into 2-amino-1-naphthol, **E**.




**(i)** Suggest the structural formula of the isomer **D**.

**(ii)** Suggest reagents needed for reaction I.

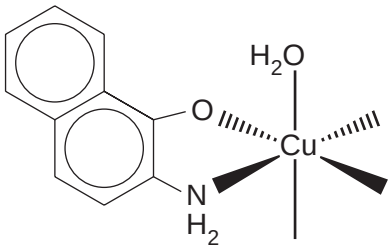
.....

**(iii)** Suggest the structural formula of the compound formed when compound **E** reacts with an excess of $CH_3COCl$.

[3]

**(d)** When an alkaline solution of compound **E** is added to a solution containing $Cu^{2+}(aq)$ ions, a pale green-blue precipitate **F** forms. Analysis of **F** shows that its formula is $Cu(C_{10}H_8NO)_2(H_2O)_2$.

**(i)** Complete the following structural formula of **F**.




When an excess of concentrated $NH_3(aq)$ is added to **F**, the precipitate dissolves to form a deep blue solution.

**(ii)** State the formula of the ion responsible for the deep blue colour.

.....

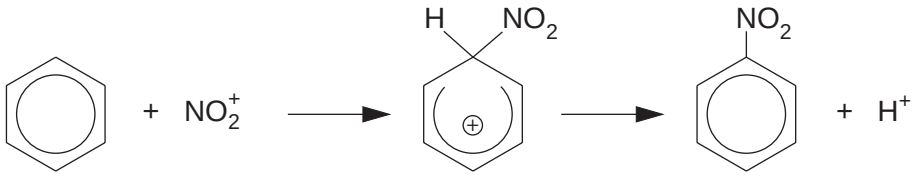
**(iii)** What type of reaction is occurring here?

.....

[3]

[Total: 15]

**7** The nitration of benzene occurs in the following steps.



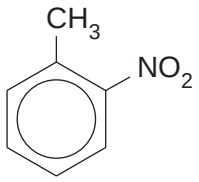

**(a)** What reagents and conditions are needed for this reaction?

.....[2]

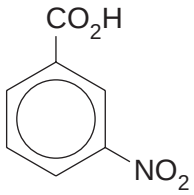
**(b)** Write an equation showing how the electrophile $NO_2^+$ is formed from the reagents.

.....[1]

**(c)** The nitration of methylbenzene produces mainly 2-nitromethylbenzene, whereas the nitration of benzoic acid produces mainly 3-nitrobenzoic acid.

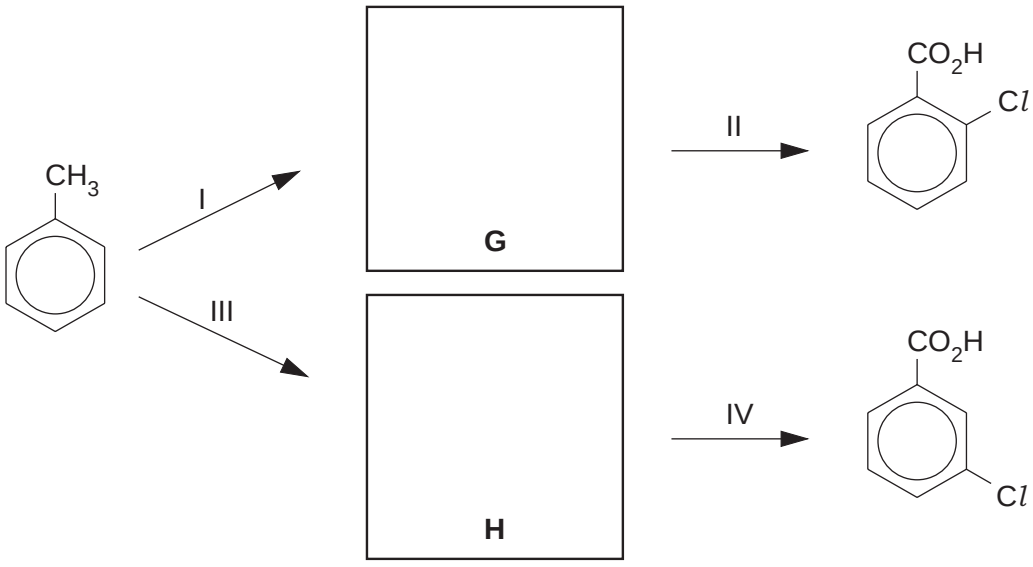



2-nitromethylbenzene




3-nitrobenzoic acid

Use this information to suggest suitable intermediates **G** and **H** in the following two 2-stage syntheses of chlorobenzoic acids, and suggest suitable reagents for reactions I to IV.




reagents:

reaction I ..... reaction II .....

reaction III ..... reaction IV .....

[4]

[Total: 7]

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## Section B – Applications of Chemistry

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

**8** **(a)** DNA carries the genetic code in living organisms and consists of a double helix.

**(i)** Describe what is meant by a *double helix*.

.....

.....

**(ii)** How are the strands of the double helix held together?

.....

..... [2]

**(b)** In replicating the genetic code two RNA molecules, mRNA and tRNA, are used to perform functions called *transcription* and *translation*.
Describe the role of the RNA molecules in these two functions.

transcription .....

.....

.....

translation .....

.....

.....[4]

**(c)** When an egg is boiled, the protein changes from a viscous liquid to a solid.

**(i)** Suggest what causes this change as the protein is heated.

.....

.....

**(ii)** Why is there no change to the primary structure of the protein under these conditions?

.....

..... [2]

**(d)** Describe in outline how energy is provided in animal cells.

.....

.....

.....

.....

.....

.....[3]

[Total: 11]

**9** **(a)** Explain with reference to energy states how $^{1}H$ NMR can supply information about the structure of molecules.

.....

.....

.....

.....[3]

**(b)** Nuclear magnetic resonance is used in magnetic resonance imaging scanners. These scanners are increasingly used in hospitals to detect tumours. Suggest why magnetic resonance techniques are better than X-rays.

.....

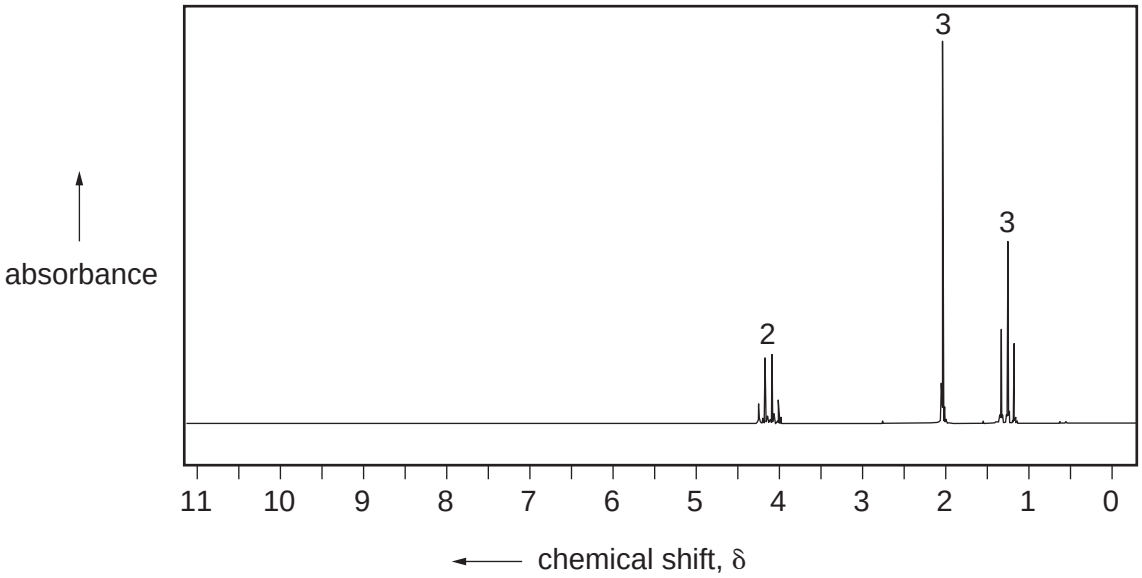
.....

.....

.....[2]

For Examiner's Use

**(c)** The NMR spectrum shown below was obtained from a simple organic molecule, **G**, $C_xH_yO_2$. When a sample of **G** was placed in a mass spectrometer, the ratio of the M : M+1 peaks for the molecule was 14.5 : 0.66.




**(i)** Calculate how many carbon atoms there are in the molecule.

**(ii)** Use the NMR spectrum and the *Data Booklet* to work out the structure of **G**.

[5]

[Total: 10]

**10** Read the following article about the use of bacteria in mining, and then answer the questions that follow it.

The discovery that bacteria could 'mine' metals for us was made in Spain. The Rio Tinto mine, in the southwest corner of Spain, was originally mined for copper by the Romans some 2,000 years ago. In 1752, some mining engineers looked over the mine to see if it could possibly be re-opened. They noticed streams of a blue-green liquid running from spoil heaps of the processed rock that lay around the mine. When this blue-green liquid ran over iron, it coated the iron with a brown film. The brown film was metallic copper.

There was still some copper left in the spoil heaps. At the time, everybody thought that the copper was being dissolved in the liquid through a simple chemical reaction. But in 1947, US scientists discovered that the copper was being 'mined' by a bacterium called *Thiobacillus ferrooxidans*.

The bacterium *Thiobacillus ferrooxidans* lives off the chemical energy trapped in metal sulphides. In the ore, the copper exists as copper sulphide. The bacteria gain energy by converting the copper sulphide to copper sulphate, which is then excreted. At the same time, they absorb the difference in energy in the chemical bonds. These bacteria can also obtain energy in similar reactions with ores of zinc, lead and uranium.

**(a)** Use the *Data Booklet* to explain why the blue-green liquid coated the iron with copper. Write an equation for the reaction.

.....

.....

[2]

**(b)** Suggest **two** reasons why this method of extracting copper might be useful for ore containing only a small percentage of copper.

**(i)** .....

.....

**(ii)** .....

.....

[2]

**(c)** Suggest **one** disadvantage of using bacteria rather than traditional mining and smelting methods.

.....

.....[1]

**(d)** In conventional copper mining, the ore will typically contain 0.5 – 2.0% copper, which gives an idea of what a valuable resource copper is.

**(i)** The ore from a particular mine contains 0.75% copper, and 150 000 tonnes of ore are mined each year. From this ore about 60% of the copper is extracted, and the remainder is left in the 'spoil heaps' of processed ore.

What mass of copper is extracted each year?

**(ii)** If the use of bacteria can recover a further 17% of copper from the spoil heaps, what is the extra mass of copper produced?

[2]

**(e)** Suggest why bacteria are unlikely to be used in the extraction of aluminium.

.....

.....[1]

**(f)** Metals like copper and zinc from abandoned mines can contaminate ground-water. Suggest **one** way of removing these contaminants.

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.....[1]

[Total: 9]

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