

Cambridge

International

Cambridge International Examinations

Cambridge International Advanced Level

| CANDIDATE NAME | | | | |
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| CENTRE NUMBER | | CANDIDATE NUMBER | | |

CHEMISTRY 9701/42

Paper 4 Structured Questions

May/June 2014

2 hours

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 an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO NOT WRITE IN ANY BARCODES.

Section A

Answer all questions.

Section B

Answer all questions.

Electronic calculators may be used.

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 Exam | iner's Use |
|----------|------------|
| 1 | |
| 2 | |
| 3 | |
| 4 | |
| 5 | |
| 6 | |
| 7 | |
| 8 | |
| Total | |

This document consists of 19 printed pages and 1 blank page.

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[Turn over

Section A

Answer all the questions in the spaces provided.

| 1 | (a) | (i) | On the diagrams below, show the outer electron arrangements of the atoms and ions |
|---|-----|-----|--|
| | | | indicated. (Use the symbol $\uparrow\downarrow$ to represent a pair of electrons in an orbital.) |

| 4s | 4s | 4s |
|--|--|---------------|
| 3d | 3d { | 3d { |
| Fe | Fe ²⁺ (aq) | |
| (ii) Use the above diagrams to are colourless. | explain why Fe ²⁺ (aq) ions a | are coloured, |

| (ii) | Use the above diagrams to explain why $Fe^{2+}(aq)$ ions are coloured, whereas $Zn^{2+}(aq)$ ions are colourless. | | | | |
|------|---|-------|--|--|--|
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| | l de la companya de | 4 | | | |

Zn2+(aq)

(b) When concentrated HCl is added to a solution of $Cu^{2+}(aq)$ ions, the solution turns yellow.

| . , | State the formula of the species responsible for the yellow colour and name the <i>type of reaction</i> that has occurred. |
|-----|--|
| | |

(ii) Ammonia can react as a base or as a ligand.

Describe the colour changes that occur when $NH_3(aq)$ is **gradually** added, with stirring, to the yellow solution, until the $NH_3(aq)$ is in excess.

Identify the **three** ions or compounds responsible for the new colours.

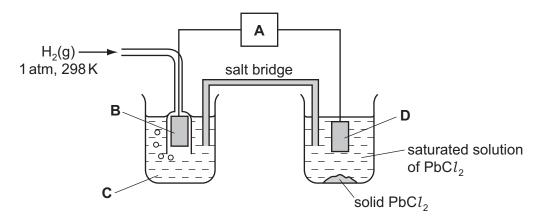
| ••••• | ••••• | |
|-------|-------|------|
| | | |
| | | |
| | | |

[7]

| (c) | When aqueous solutions of KI and $\rm K_2S_2O_8$ are mixed almost no reaction occurs, but when a few drops of $\rm Fe^{2^+}(aq)$ or $\rm Fe^{3^+}(aq)$ are added, iodine, $\rm I_2(aq)$, is produced at a steady rate. | | | | | |
|-----|---|---|--|--|--|--|
| | (i) | Write an equation for the overall reaction. | | | | |
| | (ii) | State the precise role of the iron ions during this reaction. | | | | |
| | (iii) | By means of equations or otherwise, explain why the presence of <i>either</i> Fe ²⁺ <i>or</i> Fe ³⁺ is able to speed up the reaction. | | | | |
| | | | | | | |
| | | | | | | |
| | | [3] | | | | |
| | | [Total: 14] | | | | |

2 Lead(II) chloride, PbC l_2 , can be used in the manufacture of some types of coloured glass.

 $PbCl_2$ is only sparingly soluble in water. The $[Pb^{2+}]$ in a saturated solution of $PbCl_2$ can be estimated by measuring the cell potential, E_{cell} , of the following cell.



| (| (a) | In the spaces below, | , identify what t | the four letters | A-D in the | above diagram | represent |
|----|-----|----------------------|-------------------|------------------|------------|---------------|-----------|
| ٠, | | | , | | | | |

| Α | В |
|---|-----|
| C | D |
| | [4] |

- **(b)** In a saturated solution of PbC l_2 , [PbC l_2 (aq)] = 3.5×10^{-2} mol dm⁻³.
 - (i) The E° for the Pb²⁺/Pb electrode is -0.13 V. Predict the potential of the right-hand electrode in the diagram above. Indicate this by placing a tick in the appropriate box in the table below.

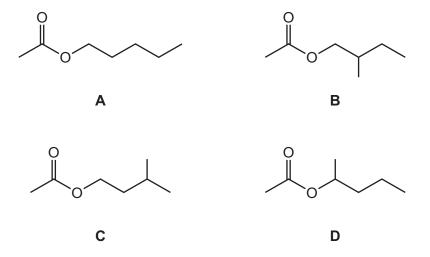
| electrode potential/V | place one tick only in this column |
|--------------------------|---|
| -0.17 | |
| -0.13 | |
| -0.09 | |
| 0.00 | |

| Explain your answer | | |
|---------------------|------|------|
| | | |
| | | |

| | (ii) | Write an expression for the solubility product, $K_{\rm sp}$, of PbC l_2 . | | | | | | | |
|-----|-------|---|--|--|--|--|--|--|--|
| | (iii) | Calculate the value of $K_{\rm sp}$, including units. | | | | | | | |
| | | K _{sp} = units | | | | | | | |
| | | [5] | | | | | | | |
| (c) | | behaviours of ${\rm PbC}l_2$ and ${\rm SnC}l_2$ towards reducing agents are similar, but their behaviours ards oxidising agents are very different. | | | | | | | |
| | (i) | Illustrate this comparison by quoting and comparing relevant E° values for the two metals and their ions. Explain what the relative E° values mean in terms of the ease of oxidation or reduction of these compounds. | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| | (ii) | Writing a balanced molecular or ionic equation in each case, suggest a reagent to carry out each of the following reactions. | | | | | | | |
| | | the reduction of $PbCl_2$ | | | | | | | |
| | | the oxidation of $\mathrm{SnC}l_2$ | | | | | | | |
| | | [5] | | | | | | | |

| | | 6 |
|-----|-------|--|
| (d) | (i) | Write an equation to represent the lattice energy of ${\rm PbC}\it{l}_{2}$. Show state symbols. |
| | | |
| | (ii) | Use the following data, together with appropriate data from the $\it Data\ Booklet$, to calculate a value for the lattice energy of ${\rm PbC}\it{l}_{\it{2}}$. |
| | | electron affinity of chlorine = $-349 \text{kJ} \text{mol}^{-1}$ enthalpy change of atomisation of lead = $+195 \text{kJ} \text{mol}^{-1}$ enthalpy change of formation of PbC $l_2(s)$ = $-359 \text{kJ} \text{mol}^{-1}$ |
| | | |
| | | |
| | | |
| | | |
| | | lattice energy =kJ mol⁻¹ |
| | (iii) | How might the lattice energy of $PbCl_2$ compare to that of $PbBr_2$? Explain your answer. |
| | | |
| | | |
| | | [6] |
| | | [Total: 20] |

3 The following four isomeric esters with the molecular formula $C_7H_{14}O_2$ are used as artificial flavours in drinks and sweets to give a pear, banana or plum taste to foodstuffs.



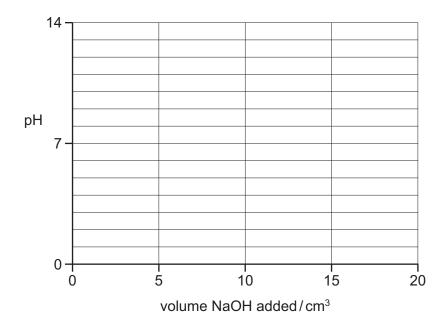
(a) In each of the spaces below, write one or more of the letters A-D, as appropriate.

| (i) | Which of these compounds can exist as optical isomers? | | | | | | |
|------|---|-----|--|--|--|--|--|
| (ii) | On hydrolysis, which of these compounds produce(s) a secondary alcohol? | | | | | | |
| | | [3] | | | | | |
| | e hydrolysis of all these compounds produces ethanoic acid, $\mathrm{CH_3CO_2H}$, as one of ducts. | the | | | | | |
| Sta | te the reagents and conditions needed for this hydrolysis. | | | | | | |

(b)

| (c) | c) The acid dissociation constant, K_a , of ethanoic acid is $1.75 \times 10^{-5} \text{mol dm}^{-3}$. | | | | | | | | |
|-----|--|---|--|--|--|--|--|--|--|
| | (i) | Explain why this value of $K_{\rm a}$ is | | | | | | | |
| | | much larger than that of ethanol, CH₃CH₂OH, | | | | | | | |
| | | a maller than that of chloroothanoic said CICH CO H | | | | | | | |
| | | • smaller than that of chloroethanoic acid, C1CH2CO2H. | | | | | | | |
| | (ii) | Calculate the pH of a 0.100 mol dm ⁻³ solution of ethanoic acid. | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| | | [- | | | | | | | |
| (d) | | $0\mathrm{cm^3}$ of $0.100\mathrm{moldm^{-3}}$ NaOH were slowly added to a $10.0\mathrm{cm^3}$ sample of $0.100\mathrm{moldm}$ anoic acid, and the pH was measured throughout the addition. | | | | | | | |
| | (i) | Calculate the number of moles of NaOH remaining at the end of the addition. | | | | | | | |
| | | | | | | | | | |
| | (ii) | Calculate the [OH-] at the end of the addition. | | | | | | | |
| | | | | | | | | | |
| | (iii) | Using the expression $K_w = [H^+][OH^-]$ and your value in (ii), calculate $[H^+]$ and the pH of the solution at the end of the addition. | | | | | | | |
| | | | | | | | | | |

(iv) On the following axes, sketch how the pH will change during the addition of a total of 20.0 cm³ of 0.100 mol dm⁻³ NaOH. Mark clearly where the end point occurs.



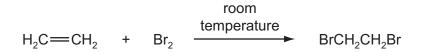
(v) From the following list of indicators, put a tick in the box by the side of the indicator you consider most suitable for this titration.

| indicator | pH at which colour changes | place one tick only in this column |
|------------------|----------------------------|---|
| malachite green | 0-1 | |
| thymol blue | 1-2 | |
| bromophenol blue | 3-4 | |
| thymolphthalein | 9-10 | |

[7]

[Total: 15]

4 Both ethene and benzene react with bromine.



- (a) What type of reaction is the reaction of bromine with
 - (i) ethene,

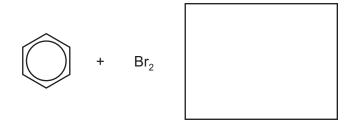
(ii) benzene?

(b) Write an equation to show the formation of the electrophile during the reaction between bromine and benzene.

......[1]

- (c) Each of these reactions involves an intermediate.
 - (i) Draw the structure of the intermediate in each reaction.

$$H_2C \longrightarrow CH_2 + Br_2 \rightarrow$$



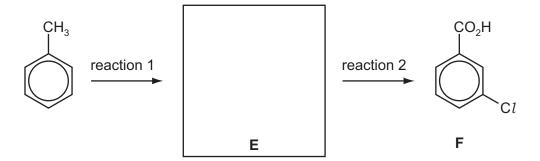
(ii) Suggest why the product of the reaction between bromine and benzene, bromobenzene, is still unsaturated.

[3]

(d) When methylbenzene is nitrated, 4-nitromethylbenzene is formed, but when benzoic acid is nitrated, 3-nitrobenzoic acid is produced.

Consider the following synthesis of 3-chlorobenzoic acid, **F**, from methylbenzene. Use the information given above to suggest

- the structure of the intermediate E,
- the reagents and conditions needed for reactions 1 and 2.



reagents and conditions for reaction 1

reagents and conditions for reaction 2

[3]

- **(e)** Consider the following synthesis of 3-chlorophenylmethylamine, **H**, from **F**. Suggest
 - the structure of the intermediate **G**,
 - the reagents for reactions 3 and 4.

reagents for reaction 3

reagents for reaction 4

[3]

[Total: 11]

| 5 | Although now remembered for his music, the Russian composer Alexander Borodin was a chemist. |
|---|--|
| | He is credited with the discovery of the <i>aldol reaction</i> , a product of which is compound J . |
| | J shows the following properties: |

| • | its molecular | formula | is | C4H8O2 |
|---|---------------|---------|----|--------|
|---|---------------|---------|----|--------|

| • | it | is | nei | utra | ı |
|---|----|----|------|------|----|
| _ | 1. | 10 | 1100 | aua | ١, |

- it reacts with sodium metal,
- it reacts with Fehling's solution,
- it does not react with aqueous bromine.

| (a) | Sug | ggest which functional groups are res | pon | sible for the reactions with | |
|-----|------|---|-----|---|----------|
| | (i) | sodium, | | | |
| | (ii) | Fehling's solution. | | | |
| | | | | | [2] |
| (b) | | e result of the bromine test shows a fogest the identity of this functional gro | | onal group is absent from compound J . | |
| | | | | | [1] |
| (c) | | he boxes below, draw three possibults, and that are structural isomers of | | traight-chain structures for J that fit th | ne above |
| | | | | | |
| | | | | | |
| | | K | | L | |
| | | | | | |
| | | | | | |
| | | M | | | |

[3]

| (d) | Cor | impound ${f J}$ reacts with alkaline aqueous iodine to give a pale yellow precipitate. | | | | | |
|-----|--|--|--------|---|-----|--|--|
| | (i) | Which functional group does this re | action | n show that J contains? | | | |
| | (ii) | Which of your three structures K , L | or M | contains this group and is therefore J ? | | | |
| | | | | | [2] | | |
| (e) | Cor | mpound J exists as stereoisomers. | | | | | |
| | (i) Name the type of stereoisomerism shown by J . | | | | | | |
| | (ii) | Draw two structures of J to illustrate | e this | stereoisomerism. | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | [2] | | |

Section B

Answer all the questions in the spaces provided.

- **6** This question looks at the formation and breakdown of protein chains in the body.
 - (a) Proteins are formed from chains of amino acid monomers joined together. The structures of two amino acids, valine and serine are shown.

$$CH_3$$
 OH OH_2 OH_2 OH_2 OH_2 OH_3 OH_4 OH_2 OH_4 OH_5 OH_5 OH_5 OH_6 OH_6 OH_7 OH_8 OH_8 OH_9 OH_9

(i) Draw the structure of the dipeptide val-ser, showing the peptide bond in displayed form.

- (ii) What type of reaction has taken place in order to form this dipeptide?
- (iii) Identify the other molecule produced in this reaction.

.....[4]

(b) Both DNA and RNA are involved in protein synthesis.

Complete the table to show three differences between the structures of DNA and RNA.

| | DNA | RNA |
|---|-----|-----|
| 1 | | |
| 2 | | |
| 3 | | |

[3]

(c) In protein synthesis, sections of the DNA are copied by mRNA and this, in turn, is read by the ribosome in order to assemble the amino acids for the new protein chain. Each group of three bases codes for one amino acid, with some amino acids having several codes. The codes are summarised in the table.

| UUU | phe | UCU | ser | UAU | tyr | UGU | cys |
|--------------------------|------------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| UUC | phe | UCC | ser | UAC | tyr | UGC | cys |
| UUA | leu | UCA | ser | UAA | stop | UGA | stop |
| UUG | leu | UCG | ser | UAG | stop | UGG | trp |
| CUU CUC CUA CUG | leu leu leu leu | CCU CCC CCA CCG | pro pro pro | CAU CAC CAA CAG | his his gln gln | CGU CGC CGA CGG | arg arg arg arg |
| AUU AUC AUA AUG | ile ile ile met/ start | ACU ACC ACA ACG | thr thr thr thr | AAU AAC AAA AAG | asn asn lys lys | AGU AGC AGA AGG | ser ser arg arg |
| GUU | val | GCU | ala | GAU | asp | GGU | gly |
| GUC | val | GCC | ala | GAC | asp | GGC | gly |
| GUA | val | GCA | ala | GAA | glu | GGA | gly |
| GUG | val | GCG | ala | GAG | glu | GGG | gly |

In general the amino acid chains start with the code AUG, and end with one of the three 'stop' codes shown in the table.

(i) Use the abbreviations to show the sequence of amino acids in the peptide for the base

| | sequence shown. |
|------|--|
| | - AUGCUAACACCGGAGUAA - |
| | |
| (ii) | Sometimes an error can occur in the base sequence. |
| | What are these errors called? |
| | |
| | |

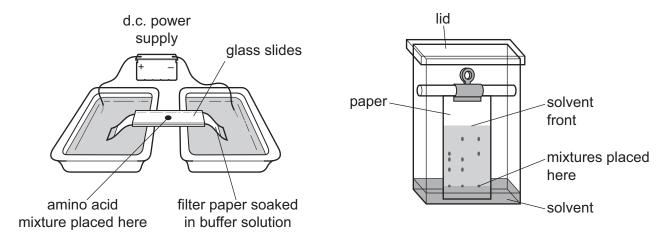
(iii) This type of error can lead to the formation of a protein with a different structure from the original, as in *sickle cell anaemia*. In this case the amino acid glutamic acid (glu) is replaced by valine (val) in the protein as a result of one base being changed in a three base code.

| |
|------|
| [3] |

[Total: 10]

Use the table to suggest the change of base that causes this.

- **7** Modern methods of chemical analysis often rely on the interpretation of data gathered from instrumental techniques.
 - (a) Electrophoresis and paper chromatography can both be used to separate amino acids from a mixture obtained from polypeptides.



electrophoresis

paper chromatography

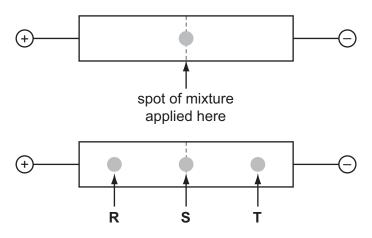
| | In each case, give one property of the amino acids that causes their separation. |
|-----|--|
| | electrophoresis |
| | |
| | paper chromatography |
| | [2] |
| (b) | Amino acids are colourless. |
| | How are the positions of the different amino acids made visible so that measurements can be made? |
| | |
| | [1] |
| (c) | Which measurements need to be made in order to identify individual amino acids in paper chromatography? |
| | [1] |
| | II |

(d) The diagram shows the results of electrophoresis on a mixture of the amino acids glycine, lysine and glutamic acid at pH 7.0. The structures of the amino acids at pH 7.0 are shown.

glycine: H₃N⁺CH₂CO₂⁻

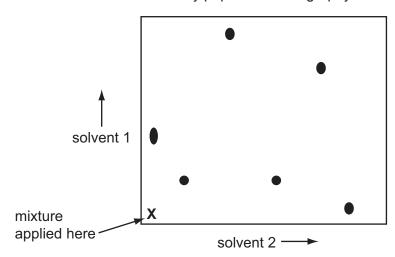
lysine: $H_3N^+CH(CH_2CH_2CH_2CH_2NH_3^+)CO_2^-$

glutamic acid: H₃N⁺CH(CH₂CH₂CO₂⁻)CO₂⁻



Identify the amino acids responsible for the spots labelled R, S and T.

(e) This diagram shows the results of two-way paper chromatography of a mixture of amino acids.



To answer these questions you need to indicate clearly on the diagram above as directed in the questions.

- (i) Put a **U** next to the amino acid that travelled furthest in solvent 2.
- (ii) Put a ring around the **two** amino acids that were **not** separated in solvent 1.
- (iii) Put a **W** next to the amino acid that was very soluble in **both** solvents.

[3]

[Total: 10]

| Pol | ymers consist of monomers joined by either addition or condensation reactions. | |
|-----|---|-----|
| (a) | Name an example of a synthetic addition polymer and a synthetic condensation polymer. | |
| | addition polymer | |
| | condensation polymer | |
| | | [2] |
| (b) | Addition polymers are long-term pollutants in the environment but condensation polymers a often biodegradable. | re |
| | (i) What type of reaction occurs when condensation polymers biodegrade? | |
| | (ii) Identify two functional groups that could undergo this type of reaction. | |
| | | [2] |
| (c) | Petroleum is a non-renewable resource from which a wide range of useful polymers is current produced. Current polymer research is looking at renewable plant material as a potent source of monomers. | • |
| | Two monomers obtained from plants are shown. | |
| | CH ₃ CH(OH)COOH HOCH ₂ COOH | |
| | Draw the displayed formula of the repeat unit of a polymer using both monomers. | |
| | | |
| | | |
| | | |
| | | |
| | | [2] |
| (d) | Monomers obtained from plant sources do not usually form addition polymers. Suggest why this is. | |
| | | |
| | | ן י |

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8

(e) The diagrams show sections of two polymers ${\bf Y}$ and ${\bf Z}$.

| | O N H | N | O N H |
|---|-------------|---|-------|
| Υ | | Z | |

| (i) | What would be the main force between the chains in each polymer? |
|------|--|
| | Υ |
| | |
| | Z |
| (ii) | Which is likely to be the more hydrophilic of these two polymers? Explain your answer. |
| | |
| | |
| | |

[Total: 10]

[3]

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