UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME

CENTRE NUMBER CANDIDATE NUMBER

CHEMISTRY 9701/43
Paper 4 Structured Questions
October/November 2011 2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Centre number and candidate number 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 ON 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
Total

This document consists of 17 printed pages and 3 blank pages.
Section A

Answer all questions in the spaces provided.

1 (a) Complete the electronic configurations of the following ions.

\[ \text{Cr}^{3+}: \quad 1s^22s^22p^6 \]
\[ \text{Mn}^{2+}: \quad 1s^22s^22p^6 \]

(b) Both KMnO\(_4\) and K\(_2\)Cr\(_2\)O\(_7\) are used as oxidising agents, usually in acidic solution.

(i) Use information from the Data Booklet to explain why their oxidising power increases as the [H\(^+\)(aq)] in the solution increases.

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(ii) What colour changes would you observe when each of these oxidising agents is completely reduced?

• KMnO\(_4\) from ........................................ to .........................................

• K\(_2\)Cr\(_2\)O\(_7\) from ........................................ to .........................................

(c) Manganese(IV) oxide, MnO\(_2\), is a dark brown solid, insoluble in water and dilute acids. Passing a stream of SO\(_2\)(g) through a suspension of MnO\(_2\) in water does, however, cause it to dissolve, to give a colourless solution.

(i) Use the Data Booklet to suggest an equation for this reaction, and explain what happens to the oxidation states of manganese and of sulfur during the reaction.

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(ii) The pH of the suspension of MnO\(_2\) is reduced. Explain what effect, if any, this would have on the extent of this reaction.

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(d) The main ore of manganese, pyrolusite, is mainly MnO$_2$. A solution of SnCl$_2$ can be used to estimate the percentage of MnO$_2$ in a sample of pyrolusite, using the following method.

- A known mass of pyrolusite is warmed with an acidified solution containing a known amount of SnCl$_2$.
- The excess Sn$^{2+}$(aq) ions are titrated with a standard solution of KMnO$_4$.

In one such experiment, 0.100 g of pyrolusite was warmed with an acidified solution containing $2.00 \times 10^{-3}$ mol Sn$^{2+}$. After the reaction was complete, the mixture was titrated with 0.0200 mol dm$^{-3}$ KMnO$_4$, and required 18.1 cm$^3$ of this solution to reach the end point.

The equation for the reaction between Sn$^{2+}$(aq) and MnO$_4^-$(aq) is as follows.

$$2\text{MnO}_4^- + 5\text{Sn}^{2+} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{Sn}^{4+} + 8\text{H}_2\text{O}$$

(i) Use the *Data Booklet* to construct an equation for the reaction between MnO$_2$ and Sn$^{2+}$ ions in acidic solution.

(ii) Calculate the percentage of MnO$_2$ in this sample of pyrolusite by the following steps.

- number of moles of MnO$_4^-$ used in the titration
- number of moles of Sn$^{2+}$ this MnO$_4^-$ reacted with
- number of moles of Sn$^{2+}$ that reacted with the 0.100 g sample of pyrolusite
- number of moles of MnO$_2$ in 0.100 g pyrolusite. Use your equation in (i).
- mass of MnO$_2$ in 0.100 g pyrolusite
- percentage of MnO$_2$ in pyrolusite

percentage = ..................................................% 

[6]
2 (a) (i) What is meant by the term *ligand* as applied to the chemistry of the transition elements?

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(ii) Describe the type of bonding that occurs between a ligand and a transition element.

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[2]

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.

\[
\text{Cr(CO)}_6 + \text{PR}_3 \rightarrow \text{Cr(CO)}_5\text{PR}_3 + \text{CO}
\]

Two separate experiments were carried out to study the rate of this reaction. In the first experiment, the ligand \(\text{PR}_3\) was in a large excess and \([\text{Cr(CO)}_6]\) was measured with time. The results are shown on the graph below.

![Graph showing the concentration of \([\text{Cr(CO)}_6]\) vs. time/s.]

In the second experiment, \(\text{Cr(CO)}_6\) was in a large excess, and \([\text{PR}_3]\) was measured with time. The following results were obtained.

<table>
<thead>
<tr>
<th>time / s</th>
<th>([\text{PR}_3]/\text{mol dm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0100</td>
</tr>
<tr>
<td>120</td>
<td>0.0076</td>
</tr>
<tr>
<td>200</td>
<td>0.0060</td>
</tr>
<tr>
<td>360</td>
<td>0.0028</td>
</tr>
</tbody>
</table>

(i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.
(ii) Use the graphs to determine the order of reaction with respect to Cr(CO)$_6$ and PR$_3$. In each case explain how you arrived at your answer.

Cr(CO)$_6$

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PR$_3$

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(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, using the method of initial rates, or any other method you prefer.

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(iv) State the units of the rate constant.

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(v) Four possible mechanisms for this reaction are given below. Draw a circle around the letter next to the one mechanism which is consistent with the rate equation you have written in (iii).

A  Cr(CO)$_6$ $\rightarrow$ Cr(CO)$_5$ + CO  fast 
    Cr(CO)$_5$ + PR$_3$ $\rightarrow$ Cr(CO)$_5$PR$_3$  slow

B  Cr(CO)$_6$ $\rightarrow$ Cr(CO)$_5$ + CO  slow 
    Cr(CO)$_5$ + PR$_3$ $\rightarrow$ Cr(CO)$_5$PR$_3$  fast

C  Cr(CO)$_6$ + PR$_3$ $\rightarrow$ [OC•••Cr(CO)$_4$•••PR$_3$] $\rightarrow$ Cr(CO)$_5$PR$_3$ + CO (transition state)

D  Cr(CO)$_6$ + PR$_3$ $\rightarrow$ Cr(CO)$_6$PR$_3$  slow 
    Cr(CO)$_6$PR$_3$ $\rightarrow$ Cr(CO)$_6$PR$_3$ + CO  fast

Explain your answer.

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[9]

[Total: 11]
3 (a) Amino acids such as alanine are essential building blocks for making proteins. They can be synthesised by a general reaction of which the following is an example.

\[
\text{CH}_3\text{CHO} \xrightarrow{\text{NaCN + NH}_4\text{Cl/}} \xrightarrow{\text{(i) H}_3\text{O}^+ + \text{heat}} \xrightarrow{\text{neutralise}} \text{CH}_3\text{CH(NH}_2\text{)CO}_2\text{H}
\]

(i) Suggest the structure of the intermediate compound E by drawing its structural formula in the box above.

(ii) Suggest, in the box below, the structural formula of the starting material needed to synthesise phenylalanine by the above general reaction.

(b) (i) What is a protein?

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(ii) Using alanine as an example, draw a diagram to show how proteins are formed from amino acids. Show two repeat units in your answer.

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(c) The hydrolysis of compound F produces two compounds G and H.

(i) State the reagents and conditions needed for this hydrolysis.

(ii) Draw the structures of the two products G and H in the boxes above.

(d) (i) Draw the zwitterionic structure of alanine.

(ii) Suggest the structural formulae of the zwitterions that could be formed from the following compounds.

<table>
<thead>
<tr>
<th>compound</th>
<th>zwitterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂N− phen− CO₂H</td>
<td></td>
</tr>
<tr>
<td>OH phen− NHCH₃</td>
<td></td>
</tr>
<tr>
<td>HO− S− NH₂</td>
<td></td>
</tr>
</tbody>
</table>
(e) Solutions of amino acids are good buffers.

(i) What is meant by the term buffer?
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(ii) Write an equation to show how a solution of alanine, CH$_3$CH(NH$_2$)CO$_2$H, behaves as a buffer in the presence of an acid such as HCl(aq).
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(iii) Briefly describe how the pH of blood is controlled.
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(iv) Calculate the pH of the buffer formed when 10.0 cm$^3$ of 0.100 mol dm$^{-3}$ NaOH is added to 10.0 cm$^3$ of 0.250 mol dm$^{-3}$ CH$_3$CO$_2$H, whose $pK_a = 4.76$.

\[
pH = \ ......................................................
\]

[7]

[Total: 19]
4 (a) Write an equation representing the action of heat on calcium nitrate, Ca(NO$_3$)$_2$.

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[1]

(b) Describe and explain the trend in the thermal stabilities of the nitrates of the Group II elements.

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[3]

(c) Sodium carbonate is stable to heat, but heating lithium carbonate readily produces CO$_2$(g).

(i) Suggest an equation for the action of heat on lithium carbonate.

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(ii) Suggest a reason for the difference in reactivity of these two carbonates.

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(iii) Predict what you would see if a sample of lithium nitrate was heated. Explain your answer.

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[4]

[Total: 8]
Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H₂SO₄, and K₂Cr₂O₇.

(a) Suggest a reason why these reagents do not attack an alkane such as CH₄.

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(b) When a mixture of chlorine and ethane gas is exposed to strong sunlight, an explosion can occur due to the fast exothermic reaction. Under more controlled conditions, however, the following reaction occurs.

\[ \text{C}_2\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{HCl} \]

(i) What is the name of this type of reaction?

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(ii) Use equations to describe the mechanism of this reaction, naming the steps involved.

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(iii) This reaction can produce organic by-products, in addition to C₂H₅Cl.

Draw the structural formulae of three possible organic by-products. Two of your by-products should contain 4 carbon atoms per molecule. Briefly describe how each by-product could be formed.

<table>
<thead>
<tr>
<th>structural formula of by-product</th>
<th>formed by</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(iv) It is found by experiment that, during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

<table>
<thead>
<tr>
<th>reaction</th>
<th>relative rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH₃ → RCH₂Cl</td>
<td>1</td>
</tr>
<tr>
<td>R₂CH₂ → R₂CHCl</td>
<td>7</td>
</tr>
<tr>
<td>R₃CH → R₃CCl</td>
<td>21</td>
</tr>
</tbody>
</table>

Using this information, and considering the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule, predict the relative ratio of the two possible products J and K from the chlorination of 2-methylpropane. Explain your answer.

\[
\text{2-methylpropane} \quad \xrightarrow{\text{C/Cl}_2} \quad \text{J} + \text{K}
\]

ratio \( J/K = \) ..............................................................

explanation:
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(c) In the boxes below draw the skeletal formulae of four different structural isomers of \( \text{C}_5\text{H}_{11}\text{Cl} \) that could be obtained from the chlorination of 2-methylbutane. Indicate any chiral centres in your structures by an asterisk (*).

\[
\text{2-methylbutane} \quad + \text{C/Cl}_2 \quad \xrightarrow{} \quad \text{C}_5\text{H}_{11}\text{Cl} + \text{HCl}
\]

[Total: 16]
6 The formation of proteins is a key process in the growth and repair of tissues in living organisms.

(a) (i) Study the structures of the three molecules below. One of the molecules could be a building block for a protein while the other two could be building blocks for other biological polymers.

Which of the three could be a building block for a protein? Explain your answer.
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(ii) For which biological polymer could one of the other molecules form a building block?

molecule ...................... polymer ................................................................. [2]

(b) Protein molecules have four levels of structure as the long molecules fold and take shape.

(i) The primary structure is the sequence of amino acids in the protein chain. What type of bonding exists between the amino acids in this chain?
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(ii) What type of bonding can exist in all of the other types of structure?
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(iii) Name one type of bonding that does not occur in the primary or secondary structure of the protein.
................................................................................................................................................ [3]
(c) Many proteins play an important role in catalysing chemical reactions in living organisms.

(i) What name is given to these catalysts?
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(ii) Give two changes in conditions under which these catalysts may be inactivated, explaining the chemical reason for this in each case.
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[4]
[Total: 9]
Different analytical techniques are used to build up a picture of complex molecules. Each technique on its own provides different information about complex molecules but together the techniques can give valuable structural information.

(a) Complete the table, identifying the technique which can provide the appropriate structural information.

<table>
<thead>
<tr>
<th>structural information</th>
<th>analytical technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>three-dimensional arrangement of atoms and bonds in a molecule</td>
<td></td>
</tr>
<tr>
<td>chemical environment of protons in a molecule</td>
<td></td>
</tr>
<tr>
<td>identity of amino acids present in a polypeptide</td>
<td></td>
</tr>
</tbody>
</table>

(b) One general method of separating organic molecules is chromatography. Briefly explain the chemical principles involved in each of the following techniques.

(i) paper chromatography

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(ii) thin-layer chromatography

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[3]

[2]
(c) A combination of mass spectrometry and NMR spectroscopy is often enough to determine the structure of a simple organic compound. The organic compound $N$ produced a mass spectrum in which the ratio of the $M:M+1$ peaks was 5.9:0.20, and which had an $M+2$ peak of similar height to the $M$ peak.

(i) Calculate how many carbon atoms are present in one molecule of $N$.

(ii) Deduce which element, other than carbon and hydrogen, is present in $N$.

(iii) Explain how many atoms of this element are present in one molecule of $N$.

The NMR spectrum of $N$ is shown.

(iv) State the empirical formula of $N$ and, using the NMR data, suggest the structural formula of $N$, explaining your reasons.
8 Drugs can be delivered in a number of ways. The method chosen depends both on the nature of the drug, and the problem it is being used to treat.

(a) Many common drugs are taken by mouth in forms similar to those shown.

\[
\text{P} \quad \text{Q}
\]

digestible gel casing

(i) Some drugs are available in solution. How would the speed of action of this form compare with P and Q? Explain your answer.

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(ii) Explain which of the two forms, P or Q, would act the most rapidly when taken by mouth.

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(iii) Some drugs are broken down before they can be absorbed by the intestine. Suggest how the design of Q prevents this.

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[3]

(b) After an abdominal operation drugs are often delivered by means of a ‘drip’ inserted into a blood vessel in the patient's arm. Explain why this is more effective than taking painkillers by mouth.

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[2]
One of the molecules that has found a variety of uses in drug delivery is poly(ethylene glycol) or PEG. It is formed from dihydroxyethane, HOCH₂CH₂OH.

\[
2n \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{H–(OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_n\text{–OH} + (2n–1) \text{H}_2\text{O}
\]

(i) What type of reaction is this?

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Attaching a PEG molecule to a drug increases the time that it takes for the drug to be broken down and flushed from the body. There are thought to be two major reasons for this: firstly the PEG can form bonds to slow the passage of the drug around the body; secondly it may reduce the efficiency of breakdown of the drug by enzymes.

(ii) What type of bonds would the PEG part of the molecule form with molecules in the body?

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(iii) Suggest why attaching a PEG molecule to a drug molecule would reduce the rate of the drug's decomposition by enzymes.

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(iv) Drugs are often protein or polypeptide molecules. What type of reaction might occur in the breakdown of such a drug?

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[Total: 5]