CHEMISTRY
Paper 4 Structured Questions
May/June 2010
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.
1 (a) Phosphorus and sulfur are two non-metallic elements on the right hand side of the Periodic Table. For each of these elements describe the observations you would make when it burns in air, and write a balanced equation for the reaction.

**phosphorus**

observation ......................................................................................................................

equation ...........................................................................................................................

**sulfur**

observation ......................................................................................................................

equation ...........................................................................................................................

1 (b) White phosphorus, P$_4$, is produced commercially by heating calcium phosphate(V) rock with a mixture of silica, SiO$_2$, and coke in an electric furnace at 1400 °C. Calcium silicate, CaSiO$_3$, and carbon monoxide are the other products.

(i) Balance the following equation which represents the overall process.

$$\text{Ca}_3(\text{PO}_4)_2 + \text{SiO}_2 + \text{C} \rightarrow \text{P}_4 + \text{CaSiO}_3 + \text{CO}$$

When heated to 400 °C in the absence of air, white phosphorus is changed into the red form of the element. The following table lists some of the properties of the two forms, which are known as allotropes.

<table>
<thead>
<tr>
<th>allotrope</th>
<th>electrical conductivity</th>
<th>melting point /°C</th>
<th>solubility in water</th>
<th>solubility in benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>white</td>
<td>none</td>
<td>44</td>
<td>insoluble</td>
<td>soluble</td>
</tr>
<tr>
<td>red</td>
<td>none</td>
<td>500</td>
<td>insoluble</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

(ii) Suggest the type of structure and bonding in each allotrope.

<table>
<thead>
<tr>
<th>allotrope</th>
<th>type of structure</th>
<th>type of bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>white</td>
<td></td>
<td></td>
</tr>
<tr>
<td>red</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(iii) In both allotropes, phosphorus has a valency of 3. Suggest by means of diagrams how the phosphorus atoms might be joined together in each allotrope.

[7]

[Total: 11]
2 (a) Describe three characteristic chemical properties of transition elements that are not shown by Group II elements.

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......................................................................................................................................[3]

(b) When NH₃(aq) is added to a green solution containing Ni²⁺(aq) ions, a grey-green precipitate is formed. This precipitate dissolves in an excess of NH₃(aq) to give a blue-violet solution.
Suggest an explanation for these observations, showing your reasoning and including equations for the reactions you describe.

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......................................................................................................................................[4]

(c) Dimethylglyoxime, DMG, is a useful reagent for the quantitative estimation of nickel. It forms an insoluble salt with nickel ions according to the following equation.

\[
\text{Ni}^{2+}(aq) + C_4H_8N_2O_2 \rightarrow \text{NiC}_4\text{H}_6\text{N}_2\text{O}_2(s) + 2H^+(aq)
\]

A small coin of mass 3.40 g was dissolved in nitric acid and an excess of DMG was added. The precipitated Ni-DMG was filtered off, washed and dried. Its mass was 4.00 g.
Calculate the % of nickel in the coin.

percentage of nickel = ..................................% [3]

[Total: 10]
3 (a) Describe how the behaviour of the oxides of tin and lead in their +4 oxidation states differ on heating.

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(b) Explain the following by using data from the Data Booklet where appropriate, and writing equations for all reactions.

(i) A sample of liquid PbCl₄ is placed in a flask and the flask is gently warmed. A gas is evolved and a white solid is produced. When the gas is bubbled through KI(aq), purple fumes are produced.

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(ii) Repeating the same experiment using liquid SnCl₄ instead of PbCl₄ results in no evolution of gas, and no reaction with KI(aq).

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(c) The molecule dichlorocarbene, CC₁₂, can be produced under certain conditions. It is highly unstable, reacting with water to produce carbon monoxide and a strongly acidic solution.

(i) Suggest the electron arrangement in CC₁₂ and draw a dot-and-cross diagram showing this. Predict the shape of the molecule.

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(ii) Construct an equation for the reaction of CC₁₂ with water.

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[Total: 8]
Ethanolamine and phenylamine are two organic bases that are industrially important. Ethanolamine is a useful solvent with basic properties, whilst phenylamine is an important starting material in the manufacture of dyes and pharmaceuticals.

The following table lists some of their properties, together with those of propylamine.

<table>
<thead>
<tr>
<th>compound</th>
<th>formula</th>
<th>$M_r$</th>
<th>boiling point/°C</th>
<th>solubility in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>propylamine</td>
<td>$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$</td>
<td>59</td>
<td>48</td>
<td>fairly soluble</td>
</tr>
<tr>
<td>ethanolamine</td>
<td>$\text{HOCH}_2\text{CH}_2\text{NH}_2$</td>
<td>61</td>
<td>170</td>
<td>very soluble</td>
</tr>
<tr>
<td>phenylamine</td>
<td><img src="image" alt="Phenylamine structure" /></td>
<td>93</td>
<td>184</td>
<td>sparingly soluble</td>
</tr>
</tbody>
</table>

(a) Suggest why the boiling point of ethanolamine is much higher than that of propylamine. Draw a diagram to illustrate your answer.

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(b) Describe and explain the relative basicities of propylamine and phenylamine.

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(c) Write an equation showing ethanolamine acting as a Brønsted-Lowry base.

...........................................................................................................................................[1]
(d) Propylamine can be synthesised from bromoethane by the following route.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{Br} & \quad \text{step 1} \quad \xrightarrow{\text{X}} \quad \text{X} \\
& \quad \text{step 2} \quad \xrightarrow{} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2
\end{align*}
\]

(i) Draw the structure of the intermediate compound X in the box above.

(ii) Suggest reagents and conditions for

- step 1: ........................................................................................................................................
- step 2: ........................................................................................................................................

[3]

(e) Apart from their relative basicities, ethanolamine and phenylamine differ in many of their reactions.

For each of these two compounds, describe one test that would give a positive result with the stated compound, but a negative result with the other.

**ethanolamine**

- test: ........................................................................................................................................
- observation: .............................................................................................................................

**phenylamine**

- test: ........................................................................................................................................
- observation: .............................................................................................................................

[4]

[Total: 12]
5 Although standard electrode potentials are measured for solutions where the concentrations of ions are 1.0 mol dm\(^{-3}\), cells used as sources of battery power tend to operate with more concentrated solutions. This question concerns the electrode reactions involved in the hydrogen-oxygen fuel cell and the lead-acid car battery.

(a) In the hydrogen-oxygen fuel cell, H\(_2\)(g) and O\(_2\)(g) are fed onto two inert electrodes dipping into NaOH(aq).

The following reactions take place.

left hand electrode (cathode): \[ \text{H}_2(g) + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O}(l) + 2\text{e}^- \]

right hand electrode (anode): \[ \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4\text{e}^- \rightarrow 4\text{OH}^- \]

(i) Use the Data Booklet to calculate \(E^{\circ}_{\text{cell}}\) for this reaction.

(ii) Construct an equation for the overall reaction.

(iii) By using one of the phrases more positive, more negative or no change, deduce the effect of increasing [OH\(^-\)(aq)] on the electrode potential of

- the left hand electrode .................................................................
- the right hand electrode .................................................................

(iv) Hence deduce whether the overall \(E_{\text{cell}}\) is likely to increase, decrease or remain the same, when [OH\(^-\)(aq)] increases. Explain your answer.

(v) Suggest one other reason why a high [NaOH(aq)] is used in the fuel cell.
(b) In the cells of a lead-acid car battery the following reactions take place.

\[
\text{cathode: } \text{Pb}(s) \rightarrow \text{Pb}^{2+}(aq) + 2e^- \\
\text{anode: } \text{PbO}_2(s) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{Pb}^{2+}(aq) + 2\text{H}_2\text{O}(l)
\]

(i) Use the \textit{Data Booklet} to calculate \(E^{\circ}_{\text{cell}}\) for this reaction.

(ii) Construct an equation for the overall reaction.

The electrolyte in a lead-acid cell is \(\text{H}_2\text{SO}_4(aq)\). Most of the \(\text{Pb}^{2+}(aq)\) ions that are produced at the electrodes are precipitated as the highly insoluble \(\text{PbSO}_4(s)\).

(iii) Construct an equation for the overall cell reaction in the presence of \(\text{H}_2\text{SO}_4\).

(iv) By considering the effect of decreasing \([\text{Pb}^{2+}(aq)]\) on the electrode potentials of the cathode and the anode, deduce the effect of the presence of \(\text{H}_2\text{SO}_4(aq)\) in the electrolyte on the overall \(E_{\text{cell}}\). State whether \(E_{\text{cell}}\) will increase, decrease or remain the same.

Overall \(E_{\text{cell}}\) will ..........................................

Explain your answer.

[Total: 11]
6 Acyl chlorides are useful intermediates in organic syntheses.

(a) (i) State a suitable reagent for converting carboxylic acids into acyl chlorides.

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(ii) Construct an equation for the reaction between ethanoic acid, CH₃CO₂H, and the reagent you have stated in (i).

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(b) (i) In the boxes provided draw the structures of the compounds formed when benzoyl chloride undergoes the following reactions.

C₂H₅OH

COCI

A

B

C₂H₅OH

NH₃

II

(iii) Name the functional group in

• compound A .................................................................

• compound B .................................................................

(iii) What type of reaction is reaction II?

..................................................................................................................................

[2]

[5]
(c) (i) Suggest suitable acyl chlorides to use in the following reaction. Draw their structures in the boxes provided.

\[ C + H_{2}NCH_{2}CH_{2}NH_{2} \rightarrow E \]

Compound E dissolves in, but does not react with, cold water.

(ii) Suggest the major type of intermolecular interaction that occurs between E and water.

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(iii) A solution of the diamine \( H_{2}NCH_{2}CH_{2}NH_{2} \) in water has pH = 11 but a solution of E in water has pH = 7. Suggest why this is the case.

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(iv) What type of polymer is compound F?

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[5]
[Total: 12]
Predict the products of the following reactions and draw their structures in the boxes provided. Note that the molecular formula of the final product is given in each case.

1. \( \text{Cl}_2 + \text{light} \rightarrow \)  

2. \( \text{Cl}_2 + \text{AlCl}_3 \rightarrow \)  

3. \( \text{KMnO}_4 + \text{OH}^- + \text{heat} \rightarrow \) then \( \text{H}^+ \rightarrow \)

4. \( \text{NaOH} \rightarrow \text{heat} \rightarrow \)  

5. \( \text{HNO}_3 + \) then \( \text{H}_2\text{SO}_4 \rightarrow 55^\circ \text{C} \rightarrow \)  

6. \( \text{CH}_3\text{OH} + \text{conc. H}_2\text{SO}_4 \rightarrow \text{heat} \rightarrow \)  

[Total: 6]
8 The molecule that contains the genetic information for an individual organism is called deoxyribonucleic acid, DNA.

(a) The diagram shows part of a DNA molecule. Study the diagram and identify the blocks labelled J, K, L and M as accurately as you can.

(b) The DNA molecule is formed from two polymer strands. What stops these strands from separating from each other?
(c) List three differences between the structures of DNA and RNA.

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2. ......................................................................................................................................
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3. ......................................................................................................................................
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[3]

(d) Outline the different roles of mRNA and tRNA in the processes of transcription and translation.

mRNA ......................................................................................................................................
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   ..........................................................................................................................................

tRNA ................................................................................................................................
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   ..........................................................................................................................................

[2]

[Total: 10]
A range of modern analytical techniques has made the identification of molecules, and atoms in compounds, much more rapid than traditional laboratory analysis.

(a) One instrumental technique is NMR spectroscopy, which uses the fact that under certain conditions protons can exist in two different energy states. Explain how these different energy states arise.

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(b) When methanol, CH$_3$OH, is examined using NMR spectroscopy, it absorbs at two different frequencies. Explain why, and predict the relative areas of the two peaks.

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(c) The NMR spectrum below is that of one of three possible isomers of molecular formula C$_3$H$_6$O$_2$. 

![NMR Spectrum Diagram]
The compound could be propanoic acid, methyl ethanoate or ethyl methanoate.

(i) In the boxes provided, draw the structures of the three compounds.

![propanoic acid](image1)
![methyl ethanoate](image2)
![ethyl methanoate](image3)

(ii) Explain which compound produced the spectrum shown, indicating which protons are responsible for each of the peaks A and B.

(iii) The NMR spectrum of another of the compounds has a peak at δ11.0. State which compound this would be, and identify the proton(s) responsible for this peak.

compound ..................................................
proton(s) ..................................................

(d) X-ray crystallography is a technique used to identify the relative positions of atoms in a crystal of a compound.

(i) What further information about organic macromolecules can be deduced by the use of X-ray crystallography?

(ii) Which atoms cannot be located by X-ray crystallography?

[Total: 10]
The nature and variety of drugs that are available to treat diseases or life-threatening conditions has never been greater. At the same time, we are much better able to deliver drugs to their targets in the body.

(a) Some drugs have to be given by injection, rather than by mouth. Name a functional group in a drug molecule that might be broken down by the acid in the stomach.

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(b) The anti-cancer drug Taxol could be broken down if taken by mouth.

\[\text{Taxol}\]

Circle two bonds, each in a different functional group, that could be hydrolysed in the digestive system. [2]
(c) One way of protecting drug molecules that are taken by mouth is to enclose them in liposomes. These are artificially created spheres made from phospholipids which have an ionic phosphate ‘head’ and two hydrocarbon ‘tails’.

(i) State in which area of the liposome, A, B or C, each of the following types of drug would be carried.

a hydrophilic drug ......................

a hydrophobic drug ......................

(ii) For the remaining position, A, B or C, explain why this would not be a suitable area for carrying a drug.

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[3]

(d) One way of carrying drugs in the bloodstream is to attach them by a chemical bond to a polymer. One such polymer is polyethylene glycol or PEG.

\[ \text{HO} - (\text{CH}_2 - \text{CH}_2 - \text{O})_n - \text{H} \]

(i) Where would a drug be attached to a molecule of PEG?

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(ii) Suggest why a liposome can carry more drug molecules than a molecule of PEG.

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[2]
(e) Better-targeted delivery of drugs allows smaller amounts to be used, which brings significant advantages. Suggest two advantages of using smaller drug doses.

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[Total: 10]