CHEMISTRY
Paper 4 Structured Questions
May/June 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
Total
1  Zinc chloride is one of the most important compounds of zinc. It is used in dry cell batteries, as a flux for soldering and tinning, as a corrosion inhibitor in cooling towers and in the manufacture of rayon.

(a)  Draw a fully labelled diagram to show how you could use a standard hydrogen electrode to measure the standard electrode potential, $E^\circ$, of zinc.

(b)  The electrolysis of zinc chloride can give different electrode products, depending on the conditions used. Suggest the products formed at each electrode in the following cases. One space has been filled in for you.

<table>
<thead>
<tr>
<th>conditions</th>
<th>product at anode</th>
<th>product at cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl$_2$(l)</td>
<td>chlorine</td>
<td></td>
</tr>
<tr>
<td>ZnCl$_2$(concentrated aqueous)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnCl$_2$(dilute aqueous)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c)  Use the following data, together with relevant data from the Data Booklet, to construct a Born-Haber cycle and calculate a value for the lattice energy of zinc chloride.

| Standard enthalpy change of formation of ZnCl$_2$ | $-415 \text{ kJ mol}^{-1}$ |
| Standard enthalpy change of atomisation of Zn(s) | $+131 \text{ kJ mol}^{-1}$ |
| Electron affinity per mole of chlorine atoms    | $-349 \text{ kJ mol}^{-1}$ |

lattice energy = ........................................... kJ mol$^{-1}$ [3]
(d) Zinc is an essential element for plant and animal life. It is often administered in the form of a chelate, which is a complex between a metal ion and a polydentate ligand.

The rate of the reaction between zinc ions and the ligand 4-(2-pyridylazo)resorcinol, PAR, has been studied.

\[
\text{Zn}^{2+} + 2\text{PAR} \rightarrow \text{Zn-PAR} + 2\text{H}^+ 
\]

Both PAR and its zinc complex absorb radiation in the UV-visible region. The figure below shows their absorption spectra.

(i) Devise a suitable experimental technique for studying how the rate of this reaction varies with [Zn\(^{2+}\)(aq)].

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(ii) Describe a reaction you could carry out to show that PAR is a phenol.

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[7]
[Total: 19]
2 (a) Write an equation showing the reaction that occurs when calcium nitrate, \( \text{Ca(NO}_3\text{)}_2 \), is heated.

............................................................................................................................................................[1]

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

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

(c) Gently heating ammonium nitrate, \( \text{NH}_4\text{NO}_3 \), in a test tube produces a mixture of two gases \( \text{A} \) and \( \text{B} \). No residue remains in the tube. The mass spectrum of gas \( \text{A} \) contains peaks at \( m/e \) (mass number) values of 16, 17 and 18, whereas that of gas \( \text{B} \) has peaks at \( m/e \) values of 14, 16, 28, 30 and 44.

(i) Identify the peaks in the mass spectra, and suggest the molecular formulae of the gases \( \text{A} \) and \( \text{B} \).

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............................................................................................................................................................
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(ii) Hence suggest an equation for the thermal decomposition of ammonium nitrate.

............................................................................................................................................................ [5]

[Total: 9]
Carbon forms two stable oxides, CO and CO$_2$. Lead forms three oxides: yellow PbO, black PbO$_2$ and red Pb$_3$O$_4$.

(a) Carbon monoxide burns readily in air. Heating black lead oxide produces oxygen gas, leaving a yellow residue.

(i) Suggest a balanced equation for each reaction.

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(ii) Explain how these two reactions illustrate the relative stabilities of the +2 and +4 oxidation states down Group IV.

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[3]

(b) Red lead oxide contains lead atoms in two different oxidation states.

(i) Suggest what these oxidation states are, and calculate the ratio in which they occur in red lead oxide.

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(ii) Predict the equation for the action of heat on red lead oxide.

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When red lead oxide is heated with dilute nitric acid, HNO$_3$, a solution of lead(II) nitrate is formed and a black solid is left.

(iii) Suggest an equation for this reaction.

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(iv) Explain how this reaction illustrates the relative basicities of the two oxidation states of lead.

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[5]

(c) Both tin(II) oxide and tin(IV) oxide are amphoteric.

Write a balanced equation for the reaction between tin(II) oxide and aqueous sodium hydroxide.

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

[1]

[Total: 9]
The following passage is taken from an A level Chemistry text book.

“In an isolated atom, the five d-orbitals have the same energy. In an octahedral complex ion, however, the presence of the ligands splits the five orbitals into a group of three and a group of two. These two groups have slightly different energies.”

(a) Use the following sets of axes to draw the shape of one d-orbital in each of the two groups mentioned above.

(b) Explain how the presence of the six ligands, $L$, in $[\text{FeL}_6]^{3+}$ splits the 3d orbitals into two groups of different energy, and explain whether the two-orbital group or the three-orbital group has the higher energy.
(c) The following table lists the colours and energies of photons of light of certain wavelengths.

<table>
<thead>
<tr>
<th>wavelength / nm</th>
<th>energy of photon</th>
<th>colour of photon</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>high</td>
<td>violet</td>
</tr>
<tr>
<td>450</td>
<td>↓</td>
<td>blue</td>
</tr>
<tr>
<td>500</td>
<td>lower</td>
<td>green</td>
</tr>
<tr>
<td>600</td>
<td>↓</td>
<td>yellow</td>
</tr>
<tr>
<td>650</td>
<td>low</td>
<td>red</td>
</tr>
</tbody>
</table>

The visible spectra of solutions of two transition metal complexes C and D are shown in the diagram below.

(i) A list of possible colours for these complexes is as follows.

yellow    red    green    blue

Choose one of these words to describe the observed colour of each solution.

solution C ............................................ solution D ............................................

(ii) In which complex, C or D, will the energy gap between the two groups of orbitals be the larger? Explain your answer.

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

[3]

[Total: 8]
5 The following scheme shows some reactions of methylbenzene.

(a) Suggest reagents and conditions for reactions I to IV.

I ........................................................................................................................................
II .......................................................................................................................................
III ......................................................................................................................................
IV .....................................................................................................................................

(b) What type of reaction is each of the following?
reaction I .........................................................................................................................
reaction III ......................................................................................................................

[4]

[2]
(c) Compound F can be converted into 2-phenylethylamine in a two-stage process. Suggest a structure for the intermediate, H, in the box below, and suggest reagents and conditions for the steps V and VI.

\[ \text{CH}_2\text{Cl} \xrightarrow{V} \text{H} \xrightarrow{VI} \text{CH}_2\text{CH}_2\text{NH}_2 \]

reagents and conditions for step V .........................................................
reagents and conditions for step VI .........................................................

[4]

(d) The compounds E, F and G react at different rates with nucleophilic reagents. Draw structures for the products of each compound with the following reagents. If no reaction occurs, write “no reaction” in the box.

<table>
<thead>
<tr>
<th>compound</th>
<th>reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cold water</td>
</tr>
<tr>
<td></td>
<td>hot NaOH(aq)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>E</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td></td>
</tr>
</tbody>
</table>
6 Chemists use skeletal or partial-skeletal formulae to represent larger structures. For example the structure

\[
\begin{align*}
\text{CH}_3 & \text{CH}_2 \\
\text{CH}_2 & \text{CH}_2 \\
\text{CH}_2 & \text{CH}_2 \\
\text{H}_2\text{C} & \text{C} \\
& \text{OH} \\
\text{C} & \text{H} \\
\text{OH} & \text{C} \\
\text{H} & \text{H} \\
\text{OH} & \text{H}
\end{align*}
\]

may also be represented as follows.

Oestradiol is one of the hormones that controls the reproductive cycle in female mammals.

(a) (i) On the above structure of oestradiol, circle one chiral centre.

(ii) What is the total number of chiral centres in the oestradiol molecule? .................

(b) Complete the following part-structures (which have the -OH groups removed) to show the products obtained when oestradiol (above) is reacted with the stated reagents.

(i) sodium metal
(ii) \( \text{Br}_2(\text{aq}) \)

(iii) \( \text{NaOH}(\text{aq}) \)

(iv) \( \text{CH}_3\text{COCl} \)

(v) hot acidified \( \text{K}_2\text{Cr}_2\text{O}_7 \)
7 (a) (i) In a protein, amino acids are joined together by a process called *condensation polymerisation*. *Addition polymerisation* is used in some synthetic polymers, such as poly(propene).

State two important differences between *condensation polymerisation* and *addition polymerisation*.

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(ii) Using the amino acids glycine and alanine shown, draw the displayed formula of the dipeptide ala-gly, clearly labelling the peptide link.

\[
\text{glycine} : H_2\text{N} \quad \text{CO}_2\text{H} \quad \text{alanine} : H_2\text{N} \quad \text{CO}_2\text{HCH}_3
\]

(b) The diagram below shows a section of DNA. Identify the blocks labelled X, Y and Z.
(c) The table below shows the 3-base codes used by RNA.

<table>
<thead>
<tr>
<th>Code</th>
<th>Amino Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>UUU</td>
<td>phe</td>
</tr>
<tr>
<td>UUC</td>
<td>phe</td>
</tr>
<tr>
<td>UUA</td>
<td>leu</td>
</tr>
<tr>
<td>UUG</td>
<td>leu</td>
</tr>
<tr>
<td>CUU</td>
<td>leu</td>
</tr>
<tr>
<td>CUC</td>
<td>leu</td>
</tr>
<tr>
<td>CUA</td>
<td>leu</td>
</tr>
<tr>
<td>CUG</td>
<td>leu</td>
</tr>
<tr>
<td>AUU</td>
<td>ile</td>
</tr>
<tr>
<td>AUC</td>
<td>ile</td>
</tr>
<tr>
<td>AUA</td>
<td>ile</td>
</tr>
<tr>
<td>AUG</td>
<td>met/start</td>
</tr>
<tr>
<td>GUU</td>
<td>val</td>
</tr>
<tr>
<td>GUC</td>
<td>val</td>
</tr>
<tr>
<td>GUA</td>
<td>val</td>
</tr>
<tr>
<td>GUG</td>
<td>val</td>
</tr>
<tr>
<td>UAU</td>
<td>tyr</td>
</tr>
<tr>
<td>UAC</td>
<td>tyr</td>
</tr>
<tr>
<td>UAA</td>
<td>stop</td>
</tr>
<tr>
<td>UAG</td>
<td>stop</td>
</tr>
<tr>
<td>CAU</td>
<td>CAU</td>
</tr>
<tr>
<td>CAC</td>
<td>CAU</td>
</tr>
<tr>
<td>CAA</td>
<td>CAU</td>
</tr>
<tr>
<td>CAG</td>
<td>CAU</td>
</tr>
<tr>
<td>AAU</td>
<td>thr</td>
</tr>
<tr>
<td>AAC</td>
<td>thr</td>
</tr>
<tr>
<td>AAA</td>
<td>thr</td>
</tr>
<tr>
<td>ACG</td>
<td>thr</td>
</tr>
<tr>
<td>GCU</td>
<td>glu</td>
</tr>
<tr>
<td>GCC</td>
<td>glu</td>
</tr>
<tr>
<td>GCA</td>
<td>glu</td>
</tr>
<tr>
<td>GCG</td>
<td>glu</td>
</tr>
<tr>
<td>GAU</td>
<td>glu</td>
</tr>
<tr>
<td>GAC</td>
<td>glu</td>
</tr>
<tr>
<td>GAA</td>
<td>glu</td>
</tr>
<tr>
<td>GAG</td>
<td>glu</td>
</tr>
<tr>
<td>AGU</td>
<td>ser</td>
</tr>
<tr>
<td>AGC</td>
<td>ser</td>
</tr>
<tr>
<td>AGA</td>
<td>ser</td>
</tr>
<tr>
<td>AGG</td>
<td>ser</td>
</tr>
<tr>
<td>GGU</td>
<td>arg</td>
</tr>
<tr>
<td>GGC</td>
<td>arg</td>
</tr>
<tr>
<td>GGA</td>
<td>arg</td>
</tr>
<tr>
<td>GGG</td>
<td>arg</td>
</tr>
<tr>
<td>GGU</td>
<td>cys</td>
</tr>
<tr>
<td>GGC</td>
<td>cys</td>
</tr>
<tr>
<td>GGA</td>
<td>cys</td>
</tr>
<tr>
<td>GGG</td>
<td>cys</td>
</tr>
</tbody>
</table>

(i) What amino acid sequence would the following base code produce? (You may use abbreviations in your answer.)

-AUGUCUAGAGACGGGUAA-

(ii) What would be the effect on the amino acid sequence if a mutation caused the base G at position 13 in the sequence to be replaced by U?

(d) (i) Name a disease which results from a genetic defect.

(ii) Explain how the genetic defect can bring about your named disease.
8 (a) Electrophoresis can be used to separate amino acids which are produced by the hydrolysis of a polypeptide.

Using glycine as an example, explain why the result of electrophoresis depends on pH.

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(b) The diagram below shows the results of electrophoresis in neutral solution. At the start of the experiment a spot of a solution containing a mixture of amino acids P, Q, R and S was placed in the middle of the plate. Following electrophoresis the amino acids had moved to the positions shown in the lower diagram.

![Diagram of electrophoresis results]

(i) Which amino acid existed mainly as a zwitterion in the buffer solution? Explain your answer.

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(ii) Assuming amino acids R and S carry the same charge when in this buffer solution, which is likely to be the larger molecule? Explain your answer.

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(c) Amino acids may also be separated by using two-dimensional paper chromatography. This involves putting a spot of the mixture on the corner of a piece of chromatography paper and allowing a solvent to soak up the paper. The paper is then dried, turned through 90° and placed in a second solvent. This method gives better separation than a one solvent method.

(i) Paper chromatography relies on partition between the solvent applied and another phase.

What is this second phase? .......................................................

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(ii) The table below shows the $R_f$ values for some amino acids in two different solvents.

<table>
<thead>
<tr>
<th>amino acid</th>
<th>$R_f$ solvent 1</th>
<th>$R_f$ solvent 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>B</td>
<td>0.0</td>
<td>0.4</td>
</tr>
<tr>
<td>C</td>
<td>0.3</td>
<td>0.0</td>
</tr>
<tr>
<td>D</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>E</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Use the grid below to plot the positions of the amino acids after two-dimensional paper chromatography using solvent 1 followed by solvent 2.

(iii) Which amino acid travelled fastest in both solvents? ..................................

(iv) Which amino acid did not move at all in solvent 2? ..................................

[Total: 10]
9 (a) Graphite and buckminsterfullerene are two structural forms of carbon. By referring to diagrams of their structures, suggest three differences in their properties.

(b) Nano-sized ‘test-tubes’ can be formed from carbon structures. What is the relationship between the parts of these ‘test tubes’ and the two structural forms of carbon shown above?

(c) Many modern sunscreens contain nano-sized particles of titanium dioxide. This substance does not absorb ultraviolet radiation. Suggest how these nano-particles are able to protect skin from ultraviolet radiation.

[Total: 7]