CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CHEMISTRY
PAPER 4

MAY/JUNE SESSION 2002
1 hour

Candidates answer on the question paper.
Additional materials:
Data Booklet

INSTRUCTIONS TO CANDIDATES
Write your name, Centre number and candidate number in the spaces at the top of this page.
Answer all questions.
Write your answers in the spaces provided on the question paper.

INFORMATION FOR CANDIDATES
The number of marks is given in brackets [ ] at the end of each question or part question.
You may lose marks if you do not show your working or if you do not use appropriate units.
1 (a) Write an expression for $K_w$.

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

(b) Use your expression to help you calculate the pH of 0.200 mol dm$^{-3}$ NaOH(aq).

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

(c) The pH of 0.200 mol dm$^{-3}$ NH$_3$(aq) is 11.3. Explain why this answer differs from your answer in (b).

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

(d) A 20.0 cm$^3$ sample of 0.200 mol dm$^{-3}$ NH$_3$(aq) was titrated with 0.100 mol dm$^{-3}$ HCl. On the following axes, sketch how the pH changes during this titration. Mark clearly where the end point occurs.

![Graph showing pH changes during titration]
(e) 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.

<table>
<thead>
<tr>
<th>indicator</th>
<th>pH at which colour changes</th>
<th>place one tick only in this column</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl violet</td>
<td>0.0 - 1.6</td>
<td></td>
</tr>
<tr>
<td>methyl orange</td>
<td>3.1 - 4.4</td>
<td></td>
</tr>
<tr>
<td>bromothymol blue</td>
<td>6.0 - 7.6</td>
<td></td>
</tr>
<tr>
<td>phenolphthalein</td>
<td>8.3 - 10.0</td>
<td></td>
</tr>
</tbody>
</table>

(f) A solution containing NH₃(aq) and NH₄Cl(aq) acts as a buffer solution, resisting changes in pH when acids or alkalies are added.

Explain with the help of equations how this mixture acts as a buffer.

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

[Total: 10]
2 The ester 4-nitrophenyl ethanoate hydrolyses in alkaline solution according to the following equation.

\[
\text{CH}_3\text{C}^\text{O} = \text{O}^+ \text{NO}_2 + 2\text{OH}^- \rightarrow \text{CH}_3\text{C}^\text{O}^- + \text{O}^+ \text{NO}_2 + \text{H}_2\text{O}
\]

colourless \hspace{1cm} yellow

(a) Suggest, and briefly describe, a suitable experimental technique for studying the rate of this reaction.

(b) The reaction rate was studied using two solutions of different hydroxide ion concentrations.

run A: \([\text{OH}^-] = 0.20 \text{ mol dm}^{-3}\)
run B: \([\text{OH}^-] = 0.40 \text{ mol dm}^{-3}\)

The following graphs show how the concentration of the ester, 4-nitrophenyl ethanoate, varied over time in the two runs.
(i) By drawing tangents on the graphs, measure and calculate the initial rates of reaction during the two runs. Give the units in each case.

initial rate of run A ....................................................................................................
initial rate of run B .................................................................................................... [3]

(ii) By using your results, calculate the overall order of reaction with respect to [OH⁻].
............................................................................................................................ [1]

(iii) From the curve of run B, determine the order of reaction with respect to [ester].
............................................................................................................................ [1]

(iv) Explain how you arrived at you answer in (iii).
............................................................................................................................ [1]

(v) Write a rate equation for the reaction.
............................................................................................................................ [1]

(vi) Use your rate equation and the initial rates to calculate a value for the rate constant, including units.
............................................................................................................................ [2]

[Total: 13]
3  (a) Write an equation to represent the thermal decomposition of calcium nitrate, Ca(NO₃)₂.

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

(b) Describe and explain how the thermal stabilities of the Group II nitrates vary down the group.

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

(c) When a molten nitrate of a Group I metal is heated strongly, it evolves oxygen and leaves the metal nitrite, MNO₂ (M = Na, K, Rb or Cs).

(i) Write a balanced equation for this reaction.

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

(ii) When a particular Group I metal nitrate was heated in this way until no further change occurred, it lost 10.85% of its mass. Calculate the Aᵣ of the metal and hence identify it.

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

[Total: 7]
4 (a) Complete the electronic configuration of the Fe$^{3+}$ ion.

\[ 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \] .................................................. [1]

(b) By quoting suitable data from the *Data Booklet*, explain how $E^o$ values can be used to show the relative oxidising abilities of

(i) the halogens Cl$_2$, Br$_2$, I$_2$.

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

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

(ii) the transition metal ions Cr$^{3+}$, Fe$^{3+}$, Co$^{3+}$.

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

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

[3]

c) Use these $E^o$ values to predict whether a reaction will occur when the following pairs of aqueous solutions are mixed. If a reaction occurs, write a balanced equation and calculate the $E^o_{\text{cell}}$.

(i) Fe$^{3+}$(aq) and Cl$^-$ (aq)

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

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

(ii) Co$^{3+}$(aq) and Br$^-$ (aq)

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

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

(iii) Cr$^{2+}$(aq) and I$_2$(aq)

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

[4]

[Total: 8]
The common analgesic drug paracetamol has the following structure.

\[
\text{CH}_3\text{CONH-} - \text{OH}
\]

(a) Name the two functional groups in the paracetamol molecule

............................................................................................................................... and ............................................................................................................................. [2]

(b) Draw the structural formulae of the molecules or ions formed when paracetamol reacts with

(i) \( \text{Br}_2(\text{aq}) \),

(ii) \( \text{NaOH}(\text{aq}) \) in the cold,

(iii) \( \text{NaOH}(\text{aq}) \) under reflux.

[3]

(c) Paracetamol can be synthesised by reacting 4-aminophenol with compound \( X \).

\[
\text{H}_2\text{N-} - \text{OH} + X \rightarrow \text{paracetamol}
\]

(i) Suggest a possible identity of \( X \).

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

(ii) What reagent would you use to convert ethanoic acid, \( \text{CH}_3\text{CO}_2\text{H} \), into \( X \)?

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

[2]

[Total: 7]
Methylbenzene can react with chlorine in two ways, depending on the conditions of the reaction.

(a) State the condition needed for
(i) reaction I,
..................................................................................................................................
..................................................................................................................................
(ii) reaction II.
..................................................................................................................................
..................................................................................................................................

(b) One of the two compounds A and B reacts with NaOH(aq), but the other is inert.

(i) Which one (A or B) does not react? Give a reason for your answer.
..................................................................................................................................
..................................................................................................................................
..................................................................................................................................

(ii) Write an equation for the reaction with NaOH(aq) that does occur.

[2]

[Total: 4]
7 Phenylamine is an important intermediate compound for the production of dyes.

Phenylamine

(a) Phenylamine can be synthesised from benzene in two steps. Draw the structural formula of the intermediate Y in the scheme below, and suggest reagents and conditions for steps I and II.

\[
\begin{array}{c}
\text{benzene} \\
\rightarrow \text{Y} \\
\rightarrow \text{Phenylamine} \\
\end{array}
\]

reagent + conditions for step I .................................................................
reagent + conditions for step II ................................................................. [4]

(b) Phenylamine is a weak base.

(i) Write an equation showing phenylamine acting as a base.

(ii) How would you expect its basicity to compare with that of ammonia?

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

(iii) Explain the reasoning for your answer in (ii).

....................................................................................................................... [3]
Dyes can be made from phenylamine by first converting it into benzenediazonium chloride, and then coupling this with a phenol.

\[
\text{NH}_2 \quad \xrightarrow{\text{III}} \quad \text{N}_2\text{Cl}^- \quad \xrightarrow{\text{IV}} \quad \text{dye} + \text{a phenol}
\]

(i) State the reagents and condition needed for step III.
..................................................................................................................................

(ii) What reagent is the phenol dissolved in for step IV to be effective?
..................................................................................................................................

(iii) Suggest the structural formula of the dye formed when benzenediazonium chloride is coupled with 2-methylphenol.

[4]

[Total: 11]