This document consists of 16 printed pages.
1 (a) Describe and explain the variation in the solubilities of the hydroxides of the Group 2 elements.

The table lists the standard enthalpy changes of formation, $\Delta H^\circ_f$, for some compounds and aqueous ions.

<table>
<thead>
<tr>
<th>species</th>
<th>$\Delta H^\circ_f / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$^{2+}$(aq)</td>
<td>–538</td>
</tr>
<tr>
<td>OH$^-$ (aq)</td>
<td>–230</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>–394</td>
</tr>
<tr>
<td>BaCO$_3$(s)</td>
<td>–1216</td>
</tr>
<tr>
<td>H$_2$O(l)</td>
<td>–286</td>
</tr>
</tbody>
</table>

(b) (i) Reaction 1 occurs when CO$_2$(g) is bubbled through an aqueous solution of Ba(OH)$_2$.

Use the data in the table to calculate the standard enthalpy change for reaction 1, $\Delta H^\circ_r$.

$$\text{Ba(OH)}_2(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{BaCO}_3(\text{s}) + \text{H}_2\text{O(}l) \quad \text{reaction 1}$$

$$\Delta H^\circ_r = \text{............................ kJ mol}^{-1} \quad [2]$$
If CO\(_2\)(g) is bubbled through an aqueous solution of Ba(OH)\(_2\) for a long time, the precipitated BaCO\(_3\)(s) dissolves, as shown in reaction 2.

\[
\text{BaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{Ba(HCO}_3\text{)}_2(aq) \quad \text{reaction 2}
\]

The standard enthalpy change for reaction 2, \(\Delta H_{r2}^\circ\), = -26 kJ mol\(^{-1}\).

(ii) Use this information and the data in the table to calculate the standard enthalpy change of formation of the HCO\(_3\)\(^-\)(aq) ion.

\[
\Delta H_{f}^\circ \text{HCO}_3^-\text{(aq)} = ....................... \text{kJ mol}^{-1} \quad [2]
\]

(iii) The overall process is shown by reaction 3.

Use your answer to (ii), and the data given in the table, to calculate the standard enthalpy change for reaction 3, \(\Delta H_{r3}^\circ\).

\[
\text{Ba(OH)}_2(aq) + 2\text{CO}_2(g) \rightarrow \text{Ba(HCO}_3\text{)}_2(aq) \quad \text{reaction 3}
\]

\[
\Delta H_{r3}^\circ = ....................... \text{kJ mol}^{-1} \quad [1]
\]

(iv) How would the value of \(\Delta H_{r3}^\circ\) compare with the value of \(\Delta H_{r4}^\circ\) for the similar reaction with Ca(OH)\(_2\)(aq) as shown in reaction 4?

Explain your answer.

\[
\text{Ca(OH)}_2(aq) + 2\text{CO}_2(g) \rightarrow \text{Ca(HCO}_3\text{)}_2(aq) \quad \text{reaction 4}
\]

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

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

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

(c) The standard entropy change for reaction 1 is \(\Delta S_{r1}^\circ\).

Suggest, with a reason, how the standard entropy change for reaction 3 might compare with \(\Delta S_{r3}^\circ\).

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

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

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

[Total: 13]
2 (a) One atom of each of the four elements H, C, N and O can bond together in different ways. Two examples are molecules of cyanic acid, HOCN, and isocyanic acid, HNCO. The atoms are bonded in the order they are written.

(i) Draw ‘dot-and-cross’ diagrams of these two acids, showing outer shell electrons only.

HOCN, cyanic acid

HNCO, isocyanic acid

(ii) Suggest the values of the bond angles HNC and NCO in isocyanic acid.

HNC ...................... NCO ...................... [1]

(iii) Suggest which acid, cyanic or isocyanic, will have the shorter C–N bond length. Explain your answer.

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

(b) (i) Isocyanic acid is a weak acid.

\[
\text{HNCO} \rightleftharpoons \text{H}^+ + \text{NCO}^-
\]

\[
K_a = 1.2 \times 10^{-4} \text{ mol dm}^{-3}
\]

Calculate the pH of a 0.10 mol dm\(^{-3}\) solution of isocyanic acid.

\[
pH = .........................  \quad [2]
\]

(ii) Sodium cyanate, NaNCO, is used in the production of isocyanic acid. Sodium cyanate is prepared commercially by reacting urea, \((\text{NH}_2)_2\text{CO}\), with sodium carbonate. Other products in this reaction are carbon dioxide, ammonia and steam.

Write an equation for the production of NaNCO by this method.

............................................................................................................................................  [1]
(c) Barium hydroxide, \( \text{Ba(OH)}_2 \), is completely ionised in aqueous solutions. During the addition of 30.0 cm\(^3\) of 0.100 mol dm\(^{-3}\) \( \text{Ba(OH)}_2 \) to 20.0 cm\(^3\) of 0.100 mol dm\(^{-3}\) isocyanic acid, the pH was measured.

(i) Calculate the [OH\(^-\)] at the end of the addition.

\[
[\text{OH}^-] = \ldots \ldots \ldots \ldots \ldots \ldots \text{mol dm}^{-3} [2]
\]

(ii) Use your value in (i) to calculate \([H^+]\) and the pH of the solution at the end of the addition.

\[
\text{final } [H^+] = \ldots \ldots \ldots \ldots \ldots \ldots \text{mol dm}^{-3} \\
\text{final pH} = \ldots \ldots \ldots \ldots \ldots \ldots [2]
\]

(iii) On the following axes, sketch how the pH changes during the addition of a total of 30.0 cm\(^3\) of 0.100 mol dm\(^{-3}\) \( \text{Ba(OH)}_2 \) to 20.0 cm\(^3\) of 0.100 mol dm\(^{-3}\) isocyanic acid.
(d) The cyanate ion, NCO⁻, can act as a **monodentate ligand**.

(i) State what is meant by the terms

**monodentate**, .................................................................................................................................................

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

**ligand**. .................................................................................................................................................

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

(ii) Silver ions, Ag⁺, react with cyanate ions to form a linear complex.

(ii) Suggest the formula of this complex, including its charge.

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

[2]

(e) When heated with HCl(aq), organic isocyanates, RNCO, are hydrolysed to the amine salt, RNH₃Cl, and CO₂.

RNCO + H₂O + HCl → RNH₃Cl + CO₂

A 1.00 g sample of an organic isocyanate, RNCO, was treated in this way, and the CO₂ produced was absorbed in an excess of aqueous Ba(OH)₂ according to the equation shown. The solid BaCO₃ precipitated weighed 1.66 g.

Ba(OH)₂(aq) + CO₂(g) → BaCO₃(s) + H₂O(l)

(i) Calculate the number of moles of BaCO₃ produced.

moles of BaCO₃ = ......................................... [1]

(ii) Hence calculate the \( M_r \) of the organic isocyanate RNCO.

\[ M_r \text{ of RNCO} = ......................................... \] [1]
The R group in RNCO and RNH₃Cl contains carbon and hydrogen only.

(iii) Use your $M_r$ value calculated in (ii) to suggest the molecular formula of the organic isocyanate RNCO.

molecular formula of RNCO ........................................................................................................ [1]

(iv) Suggest a possible structure of the amine RNH₂, which forms the amine salt, RNH₃Cl.

[1]

[Total: 23]
Bubbling air through different aqueous mixtures of CoCl₂, NH₄Cl and NH₃ produces various complex ions with the general formula [Co(NH₃)₆−nClₙ]³−n.

(a) (i) Determine the oxidation state of the cobalt in these complex ions.

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

(ii) Name the two types of reaction undergone by the cobalt ions during the formation of these complex ions.

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

(iii) The complex [Co(NH₃)₄Cl₂]⁺ shows isomerism.

Draw three-dimensional structures of the two isomers, and suggest the type of isomerism shown here.

Type of isomerism ..........................................................................................................................................................  [3]

(b) (i) What is meant by the term co-ordination number?

...........................................................................................................................................................................  [1]
(ii) Complete the table by predicting appropriate co-ordination numbers, formulae and charges for the complexes C, D, E and F.

<table>
<thead>
<tr>
<th>complex</th>
<th>metal ion</th>
<th>ligand</th>
<th>co-ordination number</th>
<th>formula of complex</th>
<th>charge on complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Cr$^{3+}$</td>
<td>CN$^-$</td>
<td>3–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Ni$^{2+}$</td>
<td>H$_2$NCH$_2$CH$_2$NH$_2$</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Pt$^{2+}$</td>
<td>Cl$^-$</td>
<td>2–</td>
<td>[Fe(O$_2$CCO$_2$)$_3$]</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Fe$^{3+}$</td>
<td>O$_2$C–CO$_2^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) Iron(III) forms complexes in separate reactions with both SCN$^-$ ions and Cl$^-$ ions.

Fe$^{3+}$(aq) + SCN$^-$(aq) $\rightleftharpoons$ [FeSCN]$^{2+}$(aq) \hspace{1cm} equilibrium 1

Fe$^{3+}$(aq) + 4Cl$^-$(aq) $\rightleftharpoons$ [FeCl$_4$]$^{-}$ (aq) \hspace{1cm} equilibrium 2

(i) Write the expressions for the stability constants, $K_{stab}$, for these two equilibria. Include units in your answers.

$K_{stab1} =$

\hspace{1cm} units = ........................................

$K_{stab2} =$

\hspace{1cm} units = ........................................ [3]

(ii) An equilibrium can be set up between these two complexes as shown in equilibrium 3.

[FeCl$_4$]$^{-}$ (aq) + SCN$^-$(aq) $\rightleftharpoons$ [FeSCN]$^{2+}$(aq) + 4Cl$^-$(aq) \hspace{1cm} equilibrium 3

Write an expression for $K_{eq3}$ in terms of $K_{stab1}$ and $K_{stab2}$.

$K_{eq3} =$ ........................................................................................................... [1]

(iii) The numerical values for these stability constants are shown.

$K_{stab1} = 1.4 \times 10^2 \hspace{1cm} K_{stab2} = 8.0 \times 10^{-2}$

Calculate the value of $K_{eq3}$ stating its units.

$K_{eq3} =$ ........................................................ units = ........................................................... [2]

[Total: 19]
Carvone occurs in spearmint and a stereoisomer of carvone occurs in caraway seeds. Treating either isomer with hydrogen over a nickel catalyst produces a mixture of isomers with the structural formula $X$.

\[ \text{carvone} \xrightarrow{H_2 + Ni} X \]

(a) (i) State the type of stereoisomerism carvone can show. Explain your answer.
.............................................................................................................................................
............................................................................................................................................. [1]

(ii) Write an equation, using molecular formulae, for this conversion of carvone to $X$.
............................................................................................................................................. [2]

$X$ can be synthesised from methylbenzene by the following route.

\[ \text{methylbenzene} \]

\[ \xrightarrow{\text{step 1}} \]

\[ \xrightarrow{\text{step 2}} \]

\[ \xrightarrow{\text{step 3}} \]

\[ \xrightarrow{\text{step 4}} \]

\[ \xrightarrow{\text{step 5}} \]

\[ \xrightarrow{\text{step 6}} X \]
(b) (i) Name the mechanism in step 1.

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

(ii) What type of reaction is occurring in the following steps?

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

step 5 ...........................................................................................................................................

(iii) Suggest reagents and conditions for each of the following steps.

step 1 ...........................................................................................................................................

step 2 ...........................................................................................................................................

step 3 ...........................................................................................................................................

step 4 ........................................................................................................................................... [6]

(c) During step 6, hydrogen is added to the benzene ring to produce the cyclohexane ring in X. The six hydrogen atoms are all added to the same side of the benzene ring.

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

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

(ii) Complete the part structure to show the structure of the isomer of X that would most likely be obtained during this reaction.

X

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

[Total: 15]
Compounds J, K, L and M are isomers of each other with the molecular formula C₉H₁₁NO. All four isomers contain a benzene ring. Two of the isomers contain a chiral centre. The results of six tests carried out on J, K, L and M are shown in the table.

<table>
<thead>
<tr>
<th>test</th>
<th>observations with each isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>J</td>
</tr>
<tr>
<td>add cold HCl(aq)</td>
<td>soluble</td>
</tr>
<tr>
<td>2</td>
<td>add 2,4-DNPH reagent</td>
</tr>
<tr>
<td>3</td>
<td>add NaOH(aq) + I₂(aq)</td>
</tr>
<tr>
<td>4</td>
<td>warm with Fehling’s solution</td>
</tr>
<tr>
<td>5</td>
<td>heat with NaOH(aq)</td>
</tr>
<tr>
<td>6</td>
<td>diazotization and addition of alkaline phenol</td>
</tr>
</tbody>
</table>

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in each of the four isomers J, K, L and M.

Complete the table below, identifying the group(s) present in each isomer.

<table>
<thead>
<tr>
<th>group(s) in compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>L</td>
</tr>
<tr>
<td>M</td>
</tr>
</tbody>
</table>

[5]
(b) (i) Name the type of reaction occurring in test 5 that converts M into P + Q.

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

(ii) Suggest structures for compounds P and Q.

P (C₆H₇N)  
Q (C₃H₅O₂Na)  [2]

(c) Isomers J, K, L and M all have the molecular formula C₉H₁₁NO.

Use the information in (a) to suggest a structure for each of these isomers and draw these in the boxes. Draw circles around all chiral centres in K and L.

J  
K  
L  
M  [5]

(d) Compound N is another isomer which has the same molecular formula C₉H₁₁NO and also contains a benzene ring.
N contains the same functional group as M.
When heated with NaOH(aq), N produces ethylamine and a sodium salt W. Suggest the structure of W.

W  [1]

[Total: 14]
The reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol is:

\[
\text{C}_6\text{H}_5\text{CHClCH}_3 + \text{OH}^- \rightarrow \text{C}_6\text{H}_5\text{CH(OH)CH}_3 + \text{Cl}^-
\]

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

(a) Describe a suitable method for studying the rate of this reaction at a temperature of 40°C, given the following.

- a solution of 0.10 mol dm\(^{-3}\) 1-chloro-1-phenylethane, labelled A
- a solution of 0.10 mol dm\(^{-3}\) sodium hydroxide, labelled B
- 0.10 mol dm\(^{-3}\) \(\text{HCl}\)
- volumetric glassware
- ice-cold solvent
- stopclock
- access to standard laboratory equipment and chemicals

(b) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

<table>
<thead>
<tr>
<th>experiment</th>
<th>([\text{C}_6\text{H}_5\text{CHClCH}_3]/\text{mol dm}^{-3})</th>
<th>([\text{OH}^-]/\text{mol dm}^{-3})</th>
<th>relative rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>0.10</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
<td>0.10</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>0.15</td>
<td>to be calculated</td>
</tr>
</tbody>
</table>

(i) Deduce the order of reaction with respect to each of \([\text{C}_6\text{H}_5\text{CHClCH}_3]\) and \([\text{OH}^-]\). Explain your reasoning.

order with respect to \([\text{C}_6\text{H}_5\text{CHClCH}_3]\) ............................................................................................

order with respect to \([\text{OH}^-]\) ............................................................................................

[2]
(ii) Write the rate equation for this reaction, stating the units of the rate constant, \( k \).

\[
\text{rate} = \frac{\text{mol dm}^{-3}}{\text{s}^{-1}}
\]

units of \( k \) = .......................................................................................................................... [1]

(iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = .................................................. [1]

c) (i) Use your answers in (b)(i) to help you to draw the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structures of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane.

Use your mechanism in (i) to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

...............................................................................................................................................
............................................................................................................................................... [1]
(d) The proton NMR spectrum of a sample of 1-phenylethanol shows four peaks: a multiplet for the C₆H₅ protons and three other peaks as shown in the table. When the sample is shaken with D₂O and the proton NMR spectrum recorded, fewer peaks are seen.

Complete the table for the proton NMR spectrum of 1-phenylethanol, C₆H₅CH(OH)CH₃. Use of the Data Booklet might be helpful.

<table>
<thead>
<tr>
<th>δ/ppm</th>
<th>number of ¹H atoms responsible for the peak</th>
<th>group responsible for the peak</th>
<th>splitting pattern</th>
<th>result on shaking with D₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>1</td>
<td>C₆H₅CH(OH)CH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>1</td>
<td>C₆H₅CH₂OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>1</td>
<td>C₆H₅CH₂OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2-7.4</td>
<td>5</td>
<td>C₆H₅</td>
<td>multiplet</td>
<td>peak remains</td>
</tr>
</tbody>
</table>

[Total: 16]