16  Main-group chemistry

16.1 (a) Discuss why it is that in the gas phase \( \text{BCl}_3 \) exists as a discrete molecule, whereas \( \text{AlCl}_3 \) forms dimers (illustrated in Fig. 16.16 on page 617).

(b) Explain why \( \text{B}_2\text{H}_6 \) is sometimes described as an ‘electron deficient’ molecule.

(c) Assuming that the Al is \( sp^3 \) hybridized, draw up a description of the bonding in the \( \text{Al}_2\text{Cl}_6 \) dimer. Is this molecule electron deficient?

16.2 Comment on and rationalize the following observations

(a) \( \text{BF}_3 \) is a gas, whereas the other Group 13 trifluorides are all high-melting solids.

(b) \( \text{BF}_3 \) and \( \text{AlF}_3 \) both readily act as Lewis acids toward \( F^- \) ions to give \( [\text{BF}_3]^- \) and \( [\text{AlF}_4]^- \); however, \( \text{TlF}_3 \) does not form an analogous adduct with \( F^- \).

(c) \( \text{GaF} \) and \( \text{InF} \) are known as unstable gaseous species, but \( \text{GaI} \) and \( \text{InI} \) are known as stable solids; all of the thallium(I) halides are known, including \( \text{TlF} \).

16.3 (a) Rationalize the trend in the \( pK_a \) values of the following three aquo ions

\[
\begin{align*}
\text{[K(H}_2\text{O)}_6]^+ \quad pK_a &= 14.5 \\
\text{[Ca(H}_2\text{O)}_6]^{2+} \quad pK_a &= 12.8 \\
\text{[Ga(H}_2\text{O)}_6]^{3+} \quad pK_a &= 2.6
\end{align*}
\]

(b) Use these \( pK_a \) values to discuss: (i) the nature of the metal-containing species which would be present in aqueous solutions of these ions, (ii) what would happen if such solutions were made progressively more basic.

16.4 One of the pieces of evidence that mercury(I) salts contain the species \( [\text{Hg}_2]^{2+} \), rather than a simple \( \text{Hg}^+ \) ion, is that these salts are not paramagnetic (i.e. there are no unpaired electrons). Explain why it is that \( \text{Hg}^+ \) is paramagnetic whereas \( [\text{Hg}_2]^{2+} \) is not. [Hint: draw up a simple MO diagram for \( [\text{Hg}_2]^{2+} \), considering only the 6s electrons].

16.5 Comment on the following

(a) \( \text{AlF}_3 \) is a high melting point solid, whereas \( \text{SiF}_4 \) is a gas at room temperature.

(b) Silicon has fluorides with four, five and six-fold coordination: \( \text{SiF}_4 \), \( [\text{SiF}_3]^- \) and \( [\text{SiF}_6]^{2-} \), but for carbon only the four-coordinate fluoride \( \text{CF}_4 \) is known. However, the gas phase species \( [\text{CH}_3]^- \) has been detected.

(c) The \( \text{Si-F} \) bond lengths in \( \text{SiF}_4 \), \( [\text{SiF}_3]^- \) and \( [\text{SiF}_6]^{2-} \) are 154 pm, 159 pm, and 169 pm, respectively.

16.6 The strength if the \( N≡N \) triple bond is 946 kJ mol\(^{-1}\), whereas that of \( P≡P \) is 490 kJ mol\(^{-1}\); \( N≡N \) and \( P≡P \) single bonds have bond strengths in the range 160 kJ mol\(^{-1}\) to 200 kJ mol\(^{-1}\), depending on the compound. Discuss these data and the consequences they have for the kinds of compounds formed by nitrogen and phosphorus.

16.7 If \( \text{PCl}_3 \) reacts with an excess of water the ultimate product is phosphoric(V) acid, \( \text{H}_3\text{PO}_4 \). However, if equimolar amounts of \( \text{PCl}_3 \) and water react the compound \( \text{POCl}_3 \) is formed. Describe the likely steps by which these two products might be formed, and explain why limiting the amount of water gives a different product.
16.8 Determine the oxidation state of the sulfur in the following compounds or ions

(a) Na₂S  (b) SF₂  (c) S₂F₂  (d) [SO₃]²⁻ (sulfite)  (d) [SSO₃]²⁻ (thiosulfate).

16.9 Discuss the following

(a) The reaction of sulfur with F₂ gives SF₄ and SF₆, but its reaction with Cl₂ gives SCl₂ and S₂Cl₂; there is no evidence for SCl₄ and SCl₆.
(b) The ¹⁹F spectrum of SF₆ consists of a single line, whereas that of SF₄ consists of two 1:2:1 triplets (³²S has spin zero). [Hint: use VSEPR to predict the structures.]
(c) SO₂ exists as a discrete molecule in which the sulfur is two-fold coordinate; solid SeO₂(s) contains chains of the form –O-SeO–O-SeO– in which the Se is three-fold coordinate; TeO₂(s) has a layered structure in which the Te is four-fold coordinate; PbO₂(s) has a three-dimensional structure similar to the fluorite lattice in which the Pb is eight-fold coordinate.

16.10 Use VSEPR to predict the shapes of the following molecules or ions, and predict the form of the ¹⁹F NMR spectrum in each case (ignore any coupling to iodine)

(a) [IF₂]⁺  (b) [IF₂]⁻  (c) IF₃  (d) IF₅  (e) IF₇.

Discuss the reasons why it is that IF₄ has not been prepared but [IF₄]⁻ is well known.

16.11 Explain the following observations

(a) Liquid HF and liquid BF₃ are both very poor conductors of electricity, but a 1:1 mixture of the two liquids is a good conductor.
(b) BF₃ is more resistant to hydrolysis than is BCl₃.
(c) PF₅ is molecular in the solid state, whereas PBr₅ forms an ionic lattice containing [PBr₄]⁺ and Br⁻ ions.
(d) The equilibrium constants for the formation of the adducts A increase as X is changed from F to Cl and then to Br.

16.12 On careful hydrolysis of PF₃ an intermediate compound X is obtained. Accurate mass spectrometry of X gives a parent ion peak at 83.9976. The ³¹P NMR spectrum shows a doublet of doublets with coupling constants 1079 Hz and 756 Hz. The ¹H NMR spectrum shows a very broad peak, and a doublet of doublets with coupling constants 756 Hz and 60 Hz.

Suggest a structure for compound X that is consistent with these data, and predict the form of its ¹⁹F NMR spectrum.

[Relative atomic masses: ³¹P 30.9938; ¹⁹F 18.9984; ¹H 1.0078; ¹⁶O 15.9949. ³¹P, ¹⁹F and ¹H all have spin I = ½]
16.13 The superoxides of Group 1 metals tend to decompose to the peroxide according to the following reaction

\[ 2\text{MO}_2(s) \rightarrow \text{M}_2\text{O}_2(s) + \text{O}_2(g). \]

The energetics of this reaction can be analysed using the following Hess’s Law cycle

\[ \begin{array}{ccc}
\text{2MO}_2(s) & \rightarrow & \text{M}_2\text{O}_2(s) + \text{O}_2(g) \\
\downarrow & & \downarrow \\
\text{2M}^+(g) + 2\text{O}_2^-(g) & \rightarrow & \text{2M}^+(g) + \text{O}_2^{2-}(g) + \text{O}_2(g)
\end{array} \]

\( \Delta_rH^\circ \) for step 1 is \textit{minus twice} the lattice enthalpy of \( \text{MO}_2(s) \), \( \Delta_rH^\circ \) for step 2 is twice the enthalpy of dissociation of the superoxide anion to the peroxide anion, and \( \Delta_rH^\circ \) for step 3 is the lattice enthalpy of \( \text{M}_2\text{O}_2(s) \). Our aim is to use this cycle to work out the value of \( \Delta_rH^\circ \) for step 4, the decomposition of the superoxide.

(a) Use the Kapustinskii equation, Eq. 6.5 on page 197, to write down expressions the lattice enthalpies needed for steps 1 and 3. Write the radius of the cation as \( r_+ \), and assume that of both of the anions \( \text{O}^- \) and \( \text{O}^{2-} \) have the same radius \( r_- \) (this is a fair assumption for this rather crude calculation).

(b) \( \Delta_rH^\circ \) for step 2 does not change with the metal, so we can simply assume a value, which we will call \( C \). Use this value and your answer to (a) to obtain an expression for \( \Delta_rH^\circ \) of step 4.

(c) Carefully explain why your expression predicts that as \( r_+ \) increases, the value of \( \Delta_rH^\circ \) for step 4 increases. Use this result to rationalize why LiO\(_2\) is not known, but RbO\(_2\) is easily formed.

(d) (Requires calculus) Differentiate your expression for \( \Delta_rH^\circ \) of step 4 with respect to \( r_+ \), assuming that \( r_- \) is constant. Argue that the derivative is positive, and hence leads to the same prediction as in (c) as to the way \( \Delta_rH^\circ \) changes with \( r_+ \).

(e) Rather than considering \( \Delta_rH^\circ \) for step 4, we ought really to consider \( \Delta_rG^\circ \) i.e. an entropy term should be included. Discuss whether or not the conclusions of this discussion are likely to be affected by the inclusion of such an entropy term.

16.14 The polyanion I\(_3^-\) forms ionic compounds with Group 1 metals, but these compounds tend to decompose to the iodide and iodine according to the following reaction

\[ \text{MI}_3(s) \rightarrow \text{MI}(s) + \text{I}_2(s). \]

Analyse this decomposition using a Hess’s Law cycle similar to that in the previous question. Use estimates of the lattice energy to show that this reaction becomes less favoured as the radius of the cation increases. (You should assume that the radius of the I\(_3^-\) anion is significantly greater than that of the I\(^-\) anion).
16.15 No compounds in which a Group 2 metal is in the oxidation state +1 are known, and it is speculated that this is because such compounds would disproportionate according to

\[2\text{MgCl}(s) \rightarrow \text{Mg}(s) + \text{MgCl}_2(s),\]

where we have taken MgCl as an example. It is possible to estimate a value for \(\Delta_r H^\circ\) for this reaction using the following Hess’s Law cycle

\[\begin{align*}
\text{Mg}^+(g) + 2\text{Cl}^–(g) &\rightarrow \text{Mg}(g) + \text{Mg}^2+(g) + 2\text{Cl}^–(g) \\
2\text{MgCl}(s) &\rightarrow \text{Mg}(s) + \text{MgCl}_2(s)
\end{align*}\]

\(\Delta_r H^\circ\) for step 1 is twice minus the lattice enthalpy of MgCl, \(\Delta_r H^\circ\) for step 2 is minus the enthalpy of ionization for Mg(g) → Mg\(^{+}\)(g), \(\Delta_r H^\circ\) for step 3 is the enthalpy of ionization for Mg\(^{+}\)(g) → Mg\(^{2+}\)(g), \(\Delta_r H^\circ\) for step 4 is minus the enthalpy of atomization of Mg(s), and \(\Delta_r H^\circ\) for step 5 is the lattice enthalpy of MgCl\(_2\).

(a) Use the Kapustinskii equation, Eq. 6.5 on page 197, to estimate the lattice enthalpies of MgCl and MgCl\(_2\), taking the radius of Mg\(^{+}\) as 100 pm (a guess based on the radius of Na\(^{+}\)), that of Mg\(^{2+}\) as 68 pm, and that of Cl\(^{–}\) as 182 pm.

(b) Given that \(\Delta_r H^\circ\) for atomization of Mg(s) is 148 kJ mol\(^{-1}\), \(\Delta_r H^\circ\) for Mg(g) → Mg\(^{+}\)(g) is 737 kJ mol\(^{-1}\), and \(\Delta_r H^\circ\) for Mg\(^{+}\)(g) → Mg\(^{2+}\)(g) is 1447 kJ mol\(^{-1}\), estimate \(\Delta_r H^\circ\) for step 6, the disproportionation of MgCl.

(c) Explain why \(\Delta_r S^\circ\) for step 6 is expected to be small.

(d) Do your calculations support the contention that MgCl is unstable with respect to disproportionation? Explain in words the origin of this instability.

16.16 High oxidation state metal halides are often unstable with respect to dissociation into a lower oxidation state halide plus the elemental halogen. For example, MX\(_4\) may decompose to MX\(_2\)

\[\text{MX}_4(s) \rightarrow \text{MX}_2(s) + \text{X}_2(g),\]

where M is a metal and X is one of the halogens. This reaction can be analysed using the following Hess’s Law cycle

\[\begin{align*}
\text{M}^{4+}(g) + 4\text{X}^–(g) &\rightarrow \text{M}^{2+}(g) + 4\text{X}^–(g) \\
\text{MX}_4(s) &\rightarrow \text{MX}_2(s) + \text{X}_2(g)
\end{align*}\]

Given the following data, discuss why it is that the higher oxidation state (MX\(_4\)) tends to be more stable for the fluoride than the other halides. A quantitative answer is not expected.

<table>
<thead>
<tr>
<th>electron affinity / kJ mol(^{-1})</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta_r H^\circ(X_2(g) \rightarrow 2X(g)) / kJ mol(^{-1})</td>
<td>158</td>
<td>243</td>
<td>193</td>
<td>151</td>
</tr>
<tr>
<td>(r(X^–) / \text{pm})</td>
<td>133</td>
<td>182</td>
<td>198</td>
<td>220</td>
</tr>
</tbody>
</table>
16.17 The table below gives the values of $\Delta_r H^\circ$ (in kJ mol$^{-1}$) for the processes indicated for the cases where M is K or Ca

<table>
<thead>
<tr>
<th>process</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(s) $\rightarrow$ M(g)</td>
<td>90</td>
<td>193</td>
</tr>
<tr>
<td>M(g) $\rightarrow$ M$^{2+}$(g)</td>
<td>3470</td>
<td>1735</td>
</tr>
<tr>
<td>M$^{2+}$(g) + 2Cl$^-$ (g) $\rightarrow$ MCl$_2$ (s)</td>
<td>$-2210$</td>
<td>$-2226$</td>
</tr>
</tbody>
</table>

$\Delta_r H^\circ$ for Cl$_2$(g) $\rightarrow$ 2Cl(g) is 242 kJ mol$^{-1}$, and the electron affinity of Cl is 349 kJ mol$^{-1}$. Use these data to calculate $\Delta_r H^\circ$ for KCl$_2$(s) and CaCl$_2$(s), and hence predict which of these compounds you would expect to form. What is the principle origin of the difference between the values for these two compounds?