16 Main-group chemistry

16.1 (a) Discuss why it is that in the gas phase BCl_3 exists as a discrete molecule, whereas $AlCl_3$ forms dimers (illustrated in Fig. 16.16 on page 617).

(b) Explain why B_2H_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 Al_2Cl_6 dimer. Is this molecule electron deficient?

16.2 Comment on and rationalize the following observations

(a) BF_3 is a gas, whereas the other Group 13 trifluorides are all high-melting solids.

(b) BF_3 and AlF_3 both readily act as Lewis acids toward F^- ions to give $[BF_4]^-$and $[AlF_4]^-$; however, TlF_3 does not form an analogous adduct with F^-.

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

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

$$[K(H_2O)_6]^+ \ pK_a = 14.5 \quad [Ca(H_2O)_6]^{2+} \ pK_a = 12.8 \quad [Ga(H_2O)_6]^{3+} \ pK_a = 2.6$$

(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 $[Hg_2]^{2+}$, rather than a simple Hg^+ ion, is that these salts are not paramagnetic (i.e. there are no unpaired electrons). Explain why it is that Hg^+ is paramagnetic whereas $[Hg_2]^{2+}$ is not. [Hint: draw up a simple MO diagram for $[Hg_2]^{2+}$, considering only the 6*s* electrons].

16.5 Comment on the following

(a) AlF_3 is a high melting point solid, whereas SiF_4 is a gas at room temperature.

(b) Silicon has fluorides with four, five and six-fold coordination: SiF_4, $[SiF_5]^-$ and $[SiF_6]^{2-}$, but for carbon only the four-coordinate fluoride CF_4 is known. However, the gas phase species $[CH_5]^+$ has been detected.

(c) The Si–F bond lengths in SiF_4, $[SiF_5]^-$ and $[SiF_6]^{2-}$ 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 PCl_5 reacts with an excess of water the ultimate product is phosphoric(V) acid, H_3PO_4. However, if equimolar amounts of PCl_5 and water react the compound $POCl_3$ 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) Na_2S (b) SF_2 (c) S_2F_2 (d) $[SO_3]^{2-}$ (sulfite) (d) $[SSO_3]^{2-}$ (thiosulfate).

16.9 Discuss the following

(a) The reaction of sulfur with F_2 gives SF_4 and SF_6, but its reaction with Cl_2 gives SCl_2 and S_2Cl_2; there is no evidence for SCl_4 and SCl_6.

(b) The ^{19}F spectrum of SF_6 consists of a single line, whereas that of SF_4 consists of two 1:2:1 triplets (^{32}S has spin zero). [Hint: use VSEPR to predict the structures.]

(c) SO_2 exists as a discrete molecule in which the sulfur is two-fold coordinate; solid SeO_2(s) contains chains of the form –O–SeO–O–SeO– in which the Se is three-fold coordinate; TeO_2(s) has a layered structure in which the Te is four-fold coordinate; PbO_2(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 ^{19}F NMR spectrum in each case (ignore any coupling to iodine)

(a) $[IF_2]^+$ (b) $[IF_2]^-$ (c) IF_3 (d) IF_5 (e) IF_7.

Discuss the reasons why it is that IF_4 has not been prepared but $[IF_4]^-$ is well known.

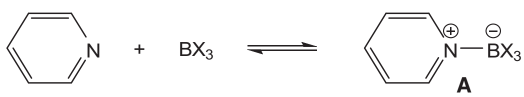
16.11 Explain the following observations

(a) Liquid HF and liquid BF_3 are both very poor conductors of electricity, but a 1:1 mixture of the two liquids is a good conductor.

(b) BF_3 is more resistant to hydrolysis than is BCl_3.

(c) PF_5 is molecular in the solid state, whereas PBr_5 forms an ionic lattice containing $[PBr_4]^+$ 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 PF_3 an intermediate compound **X** is obtained. Accurate mass spectrometry of **X** gives a parent ion peak at 83.9976. The ^{31}P NMR spectrum shows a doublet of doublets with coupling constants 1079 Hz and 756 Hz. The ^{1}H NMR spectrum shows a very broad peak, and a doublet of doublets with coupling constants 756 Hz and 60 Hz.

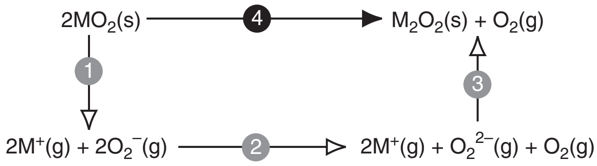
Suggest a structure for compound **X** that is consistent with these data, and predict the form of its ^{19}F NMR spectrum.

[Relative atomic masses: ^{31}P 30.9938; ^{19}F 18.9984; ^{1}H 1.0078; ^{16}O 15.9949. ^{31}P, ^{19}F and ^{1}H all have spin $I = \frac{1}{2}$]

16.13 The superoxides of Group 1 metals tend to decompose to the peroxide according to the following reaction

$$2MO_2(s) \longrightarrow M_2O_2(s) + O_2(g).$$

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



$\Delta_r H^\circ$ for step 1 is *minus twice* the lattice enthalpy of $MO_2(s)$, $\Delta_r H^\circ$ for step 2 is twice the enthalpy of dissociation of the superoxide anion to the peroxide anion, and $\Delta_r H^\circ$ for step 3 is the lattice enthalpy of $M_2O_2(s)$. Our aim is to use this cycle to work out the value of $\Delta_r H^\circ$ 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 O_2^- and O_2^{2-} have the same radius r_- (this is a fair assumption for this rather crude calculation).

(b) $\Delta_r H^\circ$ 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 $\Delta_r H^\circ$ of step 4.

(c) Carefully explain why your expression predicts that as r_+ increases, the value of $\Delta_r H^\circ$ 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 $\Delta_r H^\circ$ 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 $\Delta_r H^\circ$ changes with r_+.

(e) Rather than considering $\Delta_r H^\circ$ for step 4, we ought really to consider $\Delta_r G^\circ$ 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

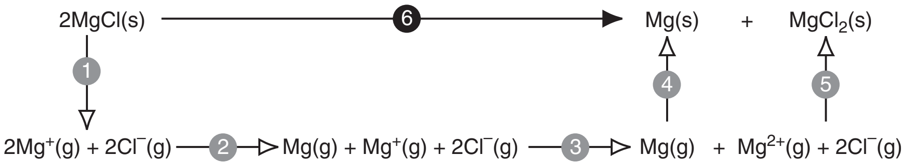
$$MI_3(s) \longrightarrow MI(s) + I_2(s).$$

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

$$2MgCl(s) \longrightarrow Mg(s) + MgCl_2(s),$$

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



$\Delta_r H^\circ$ 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 $Mg(g) \rightarrow Mg^+(g)$, $\Delta_r H^\circ$ for step 3 is the enthalpy of ionization for $Mg^+(g) \rightarrow Mg^{2+}(g)$, $\Delta_r H^\circ$ 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 $Mg(g) \rightarrow Mg^+(g)$ is 737 kJ mol^{-1}, and $\Delta_r H^\circ$ for $Mg^+(g) \rightarrow Mg^{2+}(g)$ is 1447 kJ mol^{-1}, estimate $\Delta_r H^\circ$ for step 6, the disproportionation of MgCl.

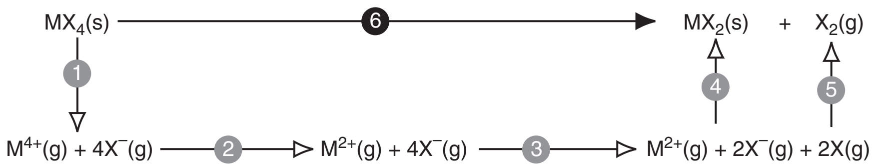
(c) Explain why $\Delta_r S^\circ$ for step 6 is expected to be small.

(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

$$MX_4(s) \longrightarrow MX_2(s) + X_2(g),$$

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



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.

	F	Cl	Br	I
electron affinity / kJ mol^{-1}	328	349	325	295
$\Delta_r H^\circ(X_2(g) \rightarrow 2X(g))$ / kJ mol^{-1}	158	243	193	151
$r(X^-)$ / pm	133	182	198	220

The definition of the electron affinity is given in section 8.4.2 on page 275.

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

process	K	Ca
$M(s) \rightarrow M(g)$	90	193
$M(g) \rightarrow M^{2+}(g)$	3470	1735
$M^{2+}(g) + 2Cl^-(g) \rightarrow MCl_2(s)$	−2210	−2226

$\Delta_r H^\circ$ 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 $\Delta_f H^\circ$ 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?