Chapter 16

THE GROUP 16 ELEMENTS

Exercises

16.1   (a) $2\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$

      (b) $BaS(s) + 4\ O_3(s) \rightarrow BaSO_4(s) + 4\ O_2(g)$

      (c) $BaO_2(s) + 2\ H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2O_2(aq)$

      (d) $2\ KOH(aq) + CO_2(g) \rightarrow K_2CO_3(aq) + H_2O(l)$

            $K_2CO_3(aq) + CO_2(g) + H_2O(l) \rightarrow 2\ KHCO_3(aq)$

      (e) $Na_2S(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2S(g)$

      (f) $Na_2SO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + SO_2(g) + H_2O(l)$

      (g) $8\ Na_2SO_3(aq) + S_8(s) \rightarrow 8\ Na_2S_2O_3(aq)$

16.3   Polonium is the only element of the group to have an electrical resistivity low enough to be considered metallic.

16.5   (a) Finely divided metals that are spontaneously flammable in air.
(b) Different crystal forms of an element in which identical molecular units are packed differently.
(c) Unusual type of equilibria found with hemoglobin in which addition of one oxygen molecule increases the ease of addition of subsequent oxygen molecules.

16.7   Photosynthesis has resulted in the conversion to dioxygen of most of the carbon dioxide that was in the Earth's atmosphere. On Venus, there is no dioxygen, only carbon dioxide.

16.9   The bond order should be that of ozone itself—about $1\frac{1}{2}$. Using the molecular orbital approach, the electron would be removed from one of the nonbonding orbitals, so there would be no effect on bond order. From simple bonding models, we obtain the same result.
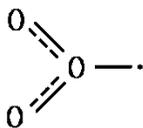
Also, by comparison with the isoelectronic nitrogen dioxide molecule, we would argue that the electron would be lost from the central oxygen's lone pair, opening out the bond angle to greater than 120°.

16.11   We would expect a larger angle for dibromine oxide compared to dichlorine oxide, both from the Bent rule and from consideration of steric crowding by the two large bromine atoms.

16.13   See the diagram. The oxidation number of +1 for oxygen is extremely rare and is a result of each atom being sandwiched between a more electronegative fluorine atom on one side and an identical atom of oxygen on the other.


$$-1 \quad +1 \quad +1 \quad -1$$
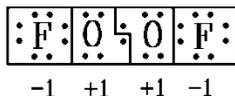
16.15   Among the Group 16 elements, it is only sulfur that readily catenates. With the high stability of oxygen multiple bonds, it is extremely rare to find chains of oxygen atoms. It is probable that the high electronegativity of the end group that "pulls" electron density away from the oxygen chain and in some way stabilizes it.

16.17   The structures are:
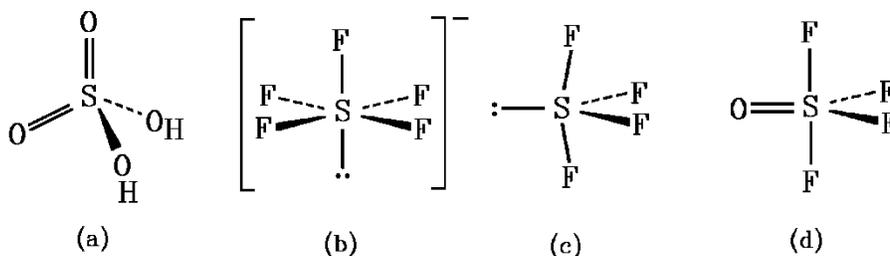
16.19   The structure is probably based on the S_8 ring. As the NH combination has the same number of outer electrons as sulfur, it could simply replace alternate sulfur atoms around the ring and retain the same electron configuration.

16.21 The terminal oxygen atoms have "normal" oxidation states of −2, while sulfur has the common value of +6. The linked oxygen atoms are peroxide-type with oxidation states of −1.
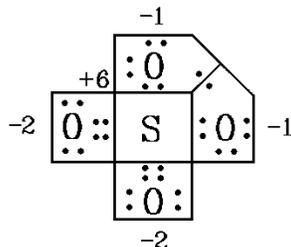
16.23 Whitewash was effective because the calcium hydroxide reacted with carbon dioxide from the air to form opaque calcium carbonate:

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$
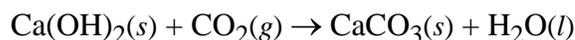
16.25 As the yellow solid sulfur is heated, it first melts to give a low-viscosity, straw-colored liquid. This consists of S_8 molecules. As the temperature is increased, the liquid darkens and becomes very viscous. Over this range, the S_8 rings are breaking open to form long polymer chains. At higher temperatures still, the viscosity decreases as the average chain length decreases. When the liquid boils gaseous green, S_8 molecules are produced, and at even higher temperatures, the gas turns violet as the rings break into S_2 molecules analogous to O_2.

16.27 The closeness of the bond angle in H_2Te to 90° suggests that the central tellurium atom is using pure p orbitals in its bonding.

16.29 Sulfuric acid can act as an acid (usually when dilute); as a dehydrating agent (when concentrated), as an oxidizing agent (when hot and concentrated), as a sulfonating agent (when concentrated), and as a base with stronger acids.

16.31   The most likely formal charge arrangements for sulfur trioxide and the
sulfite ion are shown in (a) and (b), respectively. In the former, the
average bond is $1\frac{2}{3}$, while the average bond in the latter is $1\frac{1}{3}$. Thus sulfur
trioxide will have the stronger bonds (this has been established—the S–O
bond length in sulfur trioxide is 142 pm while that in the sulfite ion is 151
pm).

(a)   (b)
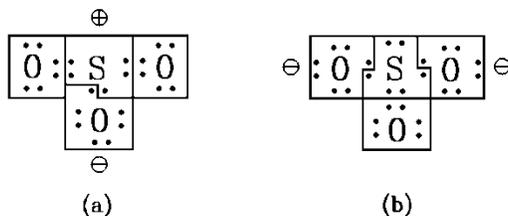
16.33   The formal charge representations are:

(a)   (b)
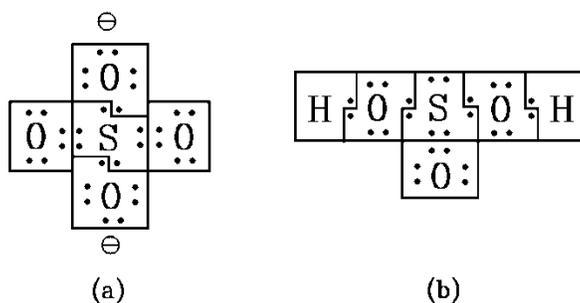
16.35   (a) A black precipitate of lead(II) sulfide is produced from a colorless
lead(II) acetate solution:

$$H_2S(g) + Pb(CH_3COO)_2(aq) \rightarrow PbS(s) + 2\ CH_3COOH(aq)$$
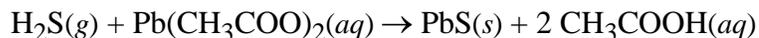
(b) A white precipitate is produced when a solution of barium ion is added
to sulfate ion:

$$Ba^{2+}(aq) + SO_4{}^{2-}(aq) \rightarrow BaSO_4(s)$$
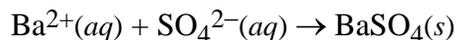
16.37   Though the oxidation of sulfur dioxide to sulfur trioxide is
thermodynamically spontaneous, it is kinetically very slow—or, in other
words, there is a very high activation energy barrier to reaction.

16.39   The large tetramethylammonium cation will stabilize the large, low-charge
ozonide ion.

16.41   The NS_2^+ ion is isoelectronic and isostructural with carbon disulfide, CS_2.

$$\left[\overset{..}{\underset{..}{S}} :: \underset{..}{N} :: \overset{..}{\underset{..}{S}} \right]^+$$
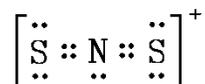
16.43   We require small quantities of selenium for a healthy existence, but in larger quantities it is highly toxic.

Beyond the Basics

16.45   See the diagrams. The value of -668 kJ is much less than the -1209 kJ for sulfur hexafluoride. This difference is accounted for by the chlorine-chlorine bond being stronger than the fluorine-fluorine bond and the sulfur-chlorine bond being weaker than the sulfur-fluorine bond.
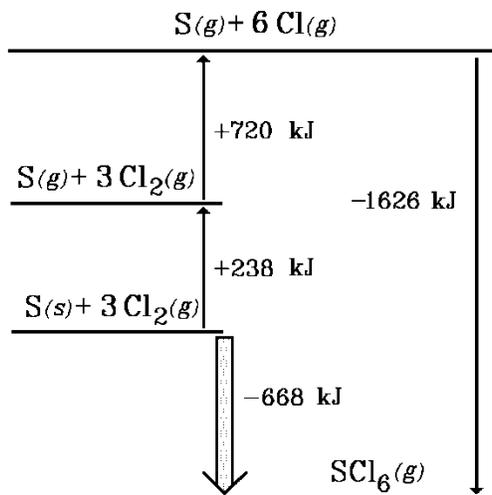
16.47   The ammonium salt will be less basic than the calcium salt because the ammonium ion is the conjugate base of a weak acid, so it reacts with water to produce a hydronium ion, partially neutralizing the hydroxide ion produced from the reaction of the glycollate ion with water to produce its conjugate acid.

$$NH_4^+(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NH_3(aq)$$
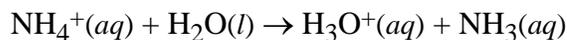
16.49   Concentration in mol·cm^{-3} = $\dfrac{5 \times 10^5 \text{ molecules}}{\text{cm}^3} \times \dfrac{1\,\text{mol}}{6.02 \times 10^{23} \text{ molecules}}$

= 8×10^{-19} mol·cm^{-3} = 8×10^{-16} mol·L^{-1}

At SATP, 1 L of gas contains n = PV/RT mol of gas.

$$n = \frac{100\,kPa \times 1L}{8.31\,kPa \cdot L \cdot mol^{-1} \cdot K^{-1} \times 298\,K} = 0.04\,mol$$

Concentration in ppb = $\dfrac{8 \times 10^{-16}\,mol}{0.04\,mol} \times 10^9 = 2 \times 10^{-5}$ ppb

16.51   (a)   Length of side = 2(74 pm) + 2(126 pm) = 400 pm

(b)   Length of diagonal from mid-edge through center = 2(126)
+ 2(114 pm) = 480 pm

Thus length of side = 1/√2(480 pm) = 339 pm.

16.53   The S=O double bond is preferred according to formal charge principles
(see the diagram). The molecule will be trigonal planar.
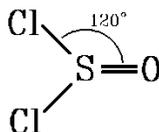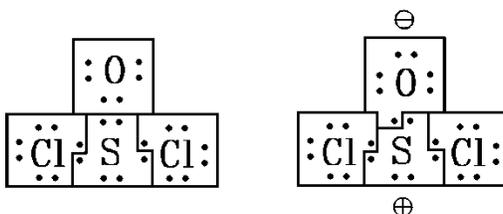
16.55   S(s) + O$_2$(g) → SO$_2$(g)

CaCO$_3$(s) + SO$_2$(g) → CaSO$_3$(s) + CO$_2$(g)

mol S = 1000 tonne coal $\times \dfrac{3 \text{ parts S}}{100 \text{ parts coal}} \times \dfrac{10^6 \text{ g}}{1 \text{ tonne}} \times \dfrac{1 \text{ mol S}}{32.1 \text{ g}} = 9.3 \times 10^5$ mol S

$$\text{mass CaCO}_3 = 9.3 \times 10^5 \text{ mol S} \times \frac{1 \text{ mol SO}_2}{1 \text{ mol S}} \times \frac{1 \text{ mol CaCO}_3}{1 \text{ mol SO}_2} \times \frac{100.1 \text{ g}}{1 \text{ mol CaCO}_3} \times \frac{1 \text{ tonne}}{10^6 \text{ g}}$$

$$= 94 \text{ tonne}$$

16.57 Apparent oxidation number S:
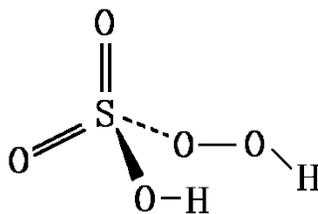
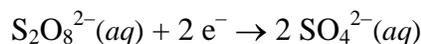$0 = 2[\text{H}] + [\text{S}] + 5[\text{O}]$

$0 = 2[+1] + [\text{S}] + 5[-2]$

$[\text{S}] = +8$, an impossible value because the oxidation number of sulfur cannot exceed 6.

$\text{H}_2\text{SO}_5 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ is the only equation that fits the hint. Thus a likely structure is that of sulfuric acid, $(\text{HO})_2\text{SO}_2$, but with a peroxy- link instead of a hydroxy- link.

16.59 It is most probable that sulfite is oxidized to sulfate while peroxodisulfate is reduced to sulfate.
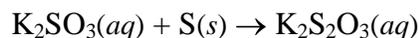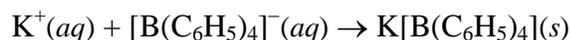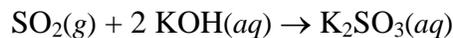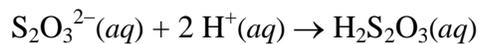
$\text{SO}_3^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{SO}_4^{2-}(aq) + 2\,\text{H}^+(aq) + 2\,\text{e}^-$

$\text{S}_2\text{O}_8^{2-}(aq) + 2\,\text{e}^- \rightarrow 2\,\text{SO}_4^{2-}(aq)$

$\text{SO}_3^{2-}(aq) + \text{S}_2\text{O}_8^{2-}(aq) + \text{H}_2\text{O}(l) \rightarrow 3\,\text{SO}_4^{2-}(aq) + 2\,\text{H}^+(aq)$
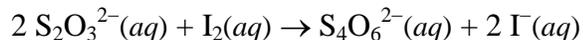
16.61 $E = E° - \dfrac{RT}{2F} \ln \dfrac{1}{[\text{H}^+]^4}$

$E = +0.17 \text{ V} - \dfrac{(8.31 \text{ C} \cdot \text{V} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})}{(2)(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} \ln\left(\dfrac{1}{(1.0 \times 10^{-14})^4} \right)$

$E = +0.17 \text{ V} - 1.65 \text{ V} = -1.48 \text{ V}$

16.63 [A] Sulfur dioxide; [B] potassium hydroxide; [C] potassium sulfite; [D] sulfur; [E] thiosulfate ion; [F] tetrathionate ion; [G] thiosulfuric acid.

$\text{SO}_2(g) + 2\,\text{KOH}(aq) \rightarrow \text{K}_2\text{SO}_3(aq)$

$\text{K}^+(aq) + [\text{B}(\text{C}_6\text{H}_5)_4]^-(aq) \rightarrow \text{K}[\text{B}(\text{C}_6\text{H}_5)_4](s)$

$\text{K}_2\text{SO}_3(aq) + \text{S}(s) \rightarrow \text{K}_2\text{S}_2\text{O}_3(aq)$

$$2\ S_2O_3{}^{2-}(aq) + I_2(aq) \rightarrow S_4O_6{}^{2-}(aq) + 2\ I^-(aq)$$

$$S_2O_3{}^{2-}(aq) + 2\ H^+(aq) \rightarrow H_2S_2O_3(aq)$$

$$H_2S_2O_3(aq) \rightarrow H_2O(l) + S(s) + SO_2(g)$$

16.65   The triple-bond structure is more likely because there are no formal charges in the electron arrangement.
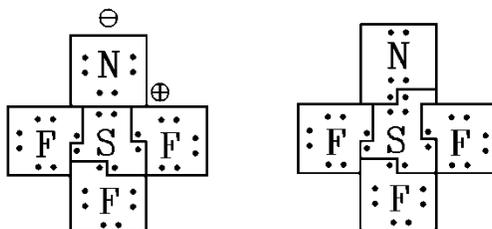
16.67   Rubidium or cesium. A large low-charge cation is necessary to stabilize the low-charge anion.

16.69   In SF_2, the sulfur has a formal oxidation state of +2. In F_3SSF, the sulfur that is surrounded by three fluorines will have the higher oxidation state of +3 (note the lone pair on this sulfur atom), while the sulfur attached to only one fluorine will have an oxidation state of +1.
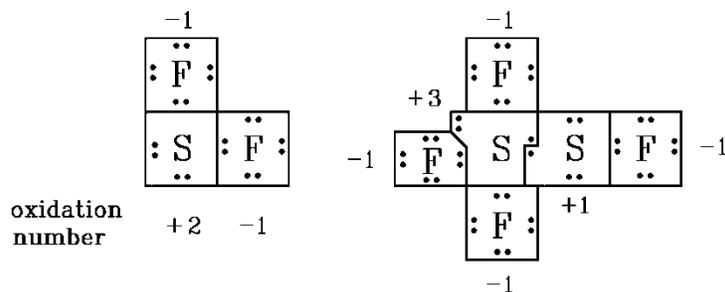
16.71. It could be a trigonal planar molecule. It could hypothetically be formed by reaction of ozone with atomic oxygen:

$$O_3(g) + O(g) \rightarrow O_4(g)$$

The species would be isoelectronic and isostructural with the carbonate ion and the nitrate ion (and isostructural with the gaseous monomeric sulfur trioxide).