Chapter 16

THE GROUP 16 ELEMENTS

Exercises

16.2 (a) $2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$

(b) $FeO(s) + 2\ HCl(aq) \rightarrow FeCl_2(aq) + H_2O(l)$

(c) $FeCl_2(aq) + 2\ NaOH(aq) \rightarrow Fe(OH)_2(s) + 2\ NaCl(aq)$

(d) $H_2S_8(eth.) + S_8Cl_2(eth.) \rightarrow S_{16}(s) + 2\ HCl(g)$

(e) $Na_2SO_4(s) + 2\ C(s) \rightarrow Na_2S(l) + 2\ CO_2(g)$

(f) $SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$

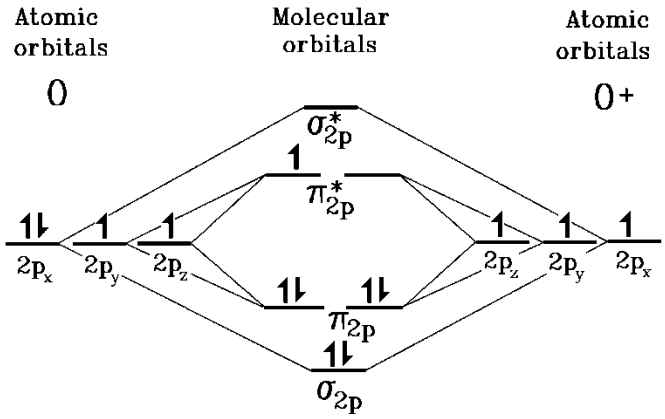
(g) $S_2O_8^{2-}(aq) + S^{2-}(aq) \rightarrow 2\ SO_4^{2-}(aq) + S(s)$

16.4 Oxygen readily forms double bonds, while the other members of the group rarely form multiple bonds; oxygen is limited to four covalent bonds, while the other members of the group often have as many as six.

16.6 (a) Oxide lattices in which there are two or more different metal ions.
(b) The addition of sulfur to rubber and heating to form cross-linked sulfur bridges in the rubber structure.
(c) The reaction sequence used to oxidize hydrogen sulfide to sulfur.

16.8 Dioxygen is more soluble in cold water than in warm water; as a result, there is less available oxygen in warm water for fishes.

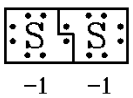
16.10 The bond order should be $2\frac{1}{2}$ (see the diagram) and the ion should have one unpaired electron. The bond length is indeed shorter than that in the dioxygen molecule (bond order 2).



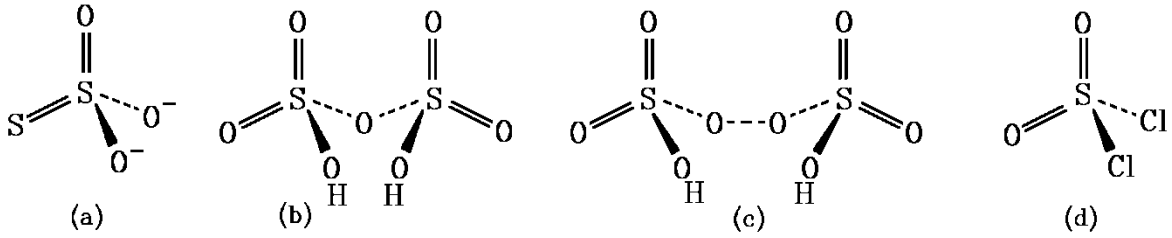
16.12 Oxygen can often cause a higher oxidation state than fluorine because oxygen is able to form a π bond using its full 2*p* orbitals and empty *d* orbitals on the element to which it is bonded. Alternatively one can argue that osmium is not large enough to fit eight fluorine atoms around it.

16.14 We have to assume that the oxygen atom is using *sp* hybrid orbitals to provide the σ bond, while the two other 2*p* orbitals are used to form π bonds with the empty 3*d* orbitals on the silicon atoms.

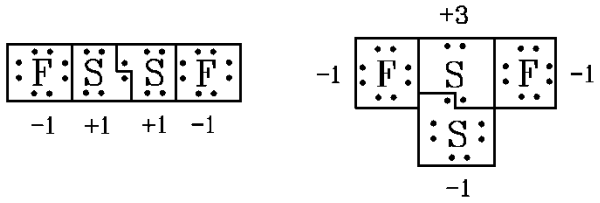
16.16 Barium disulfide would be an ionic compound of formula $Ba^{2+}S_2^{2-}$. The electron-dot structure of the disulfide ion folows, where it can be seen that the oxidation number of each sulfur must be −1. The formation of this compound can be seen as analogous to BaO_2; barium is the only alkaline earth metal to form a dioxide(2−). Thus we use the argument of a low-charge-density cation (large, low charge) stabilizing a large anion.



16.18



16.20 Sulfur rarely, if ever, has an oxidation number of +1, as would be the case in the disulfur difluoride structure. The oxidation numbers of –1 and +3 in the thiothionylfluoride structure resemble the two different ones in the thiosulfate ion.



16.22 (a) Trioxygen is a very toxic gas, causing severe lung damage.
(b) Hydroxide ion is very corrosive, particularly in concentrated solution on the skin causing a white opaque layer.
(c) Hydrogen sulfide is an extremely poisonous gas, causing headaches and nausea in low concentrations and death at higher concentrations.

16.24 Whereas carbon can form four bonds, because sulfur has six valence electrons, it generally forms two bonds in its low oxidation states. Thus when sulfur forms chains, other atoms or ions can attach only to the ends of the chains.

16.26 The Frasch process involves the pumping of compressed air and superheated steam into underground beds of sulfur. The froth of molten sulfur, air, and water rises to the surface and is pumped into gigantic tanks where it is allowed to cool. The solid sulfur is broken by explosives into lumps. The Claus process involves the combustion of hydrogen sulfide to sulfur dioxide:

$$2\ H_2S(g) + 3\ O_2(g) \rightarrow 2\ SO_2(g) + 2\ H_2O(g)$$

The sulfur dioxide is then mixed in a 1:2 mole ratio with more hydrogen sulfide to give powdered sulfur.

$$2\ H_2S(g) + SO_2(g) \rightarrow 3\ S(s) + 2\ H_2O(g)$$

16.28 The sulfide ion is the conjugate base of the very weak acid hydrogen sulfide, so in the presence of traces of water, the following equilibria will occur:

$$S^{2-}(aq) + H_2O(l) \rightarrow HS^-(aq) + OH^-(aq)$$
$$HS^-(aq) + H_2O(l) \rightarrow H_2S(g) + OH^-(aq)$$

16.30 $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(s)$

This reaction involves a decrease in entropy (even if sulfur trioxide gas is formed). Thus the only way it can be spontaneous is if there is a decrease in enthalpy, that is, an exothermic reaction.

16.32 One explanation relates to the decreasing preference for multiple bonds as a group is descended. Thus six single bonds would be energetically preferable to four partially multiple bonds. The other explanation relates to the larger size of the tellurium atom compared to sulfur and selenium atoms, making it feasible to comfortably bond six oxygen atoms around the tellurium atom.

16.34 Sulfates are commonly used in inorganic chemistry because most sulfates are water soluble; the sulfate ion is not oxidizing (unlike nitrate ion) or reducing (unlike sulfite ion); the sulfate ion is the conjugate base of a strong acid, so its solutions are close to neutral; and metal sulfates tend to be thermally stable.

16.36 (a) Sulfur hexafluoride is used mainly as an insulating gas in high-voltage electrical systems.

(b) Sodium thiosulfate was used in classical wet-chemistry photography to react with silver halides.

16.38 The most apparent difference would be the vaporization of the waters in the seas, lakes, and rivers, as non-hydrogen bonded water would be expected to have a boiling point of about –90°C.

16.40 Sulfur tetrafluoride is polar (Figure 16.28) and thus possesses dipole-dipole attractions between neighboring molecules. Sulfur hexafluoride (Figure 16.27) is nonpolar and possesses only dispersion (London) forces.

16.42 For oxygen:

$2\ O(g) \rightarrow O_2(g)$ $\Delta H = 494\ kJ \cdot mol^{-1} = 247\ kJ \cdot mol^{-1}$ per oxygen atom

$8\ O(g) \rightarrow O_8(g)$ $\Delta H = 1656\ kJ \cdot mol^{-1} = 207\ kJ \cdot mol^{-1}$ per oxygen atom

For sulfur:

$2\ S(g) \rightarrow S_2(g)$ $\Delta H = 427\ kJ \cdot mol^{-1} = 213\ kJ \cdot mol^{-1}$ per sulfur atom

$8\ S(g) \rightarrow S_8(g)$ $\Delta H = 2128\ kJ \cdot mol^{-1} = 266\ kJ \cdot mol^{-1}$ per sulfur atom

Thus formation of the dimer is thermodynamically favored for the oxygen molecule, but the octamer is favored for the sulfur compound.

16.44 The reactions follow (sulfur is represented as S rather than S_8 for simplicity).

Oxygen:

$2\ KClO_3(l) \rightarrow 2\ KCl(s) + 3\ O_2(g)$

$2\ H_2O_2(aq) \rightarrow H_2O(l) + O_2(g)$

$C(s) + O_2(g) \rightarrow CO_2(g)$

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

$4\ Li(s) + O_2(g) \rightarrow 2\ Li_2O(s)$

$2\ Na(s) + O_2(g) \rightarrow Na_2O_2(s)$

$K(s) + O_2(s) \rightarrow KO_2(s)$

Sulfur:

$Na_2SO_4(s) + 2\ C(s) \rightarrow Na_2S(l) + 2\ CO_2(g)$

$Na_2S(aq) + 2\ H^+(aq) \rightarrow H_2S(g) + 2\ Na^+(aq)$

$H_2S(g) + Pb^{2+}(aq) \rightarrow PbS(s) + 2\ H^+(aq)$

$2\ H_2S(g) + O_2(g) \rightarrow 2\ S(s) + 2\ H_2O(g)$

$S(s) + 3\ F_2(g) \rightarrow SF_6(g)$

$2\ S(s) + Cl_2(g) \rightarrow S_2Cl_2(l)$

$S_2Cl_2(l) + Cl_2(g) \rightarrow 2\ SCl_2(l)$

$S(s) + O_2(g) \rightarrow SO_2(g)$

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

$H_2SO_3(aq) + OH^-(aq) \rightarrow HSO_3^-(aq) + H_2O(l)$

$HSO_3^-(aq) + OH^-(aq) \rightarrow SO_3^{2-}(aq) + H_2O(l)$

$SO_3^{2-}(aq) + S(s) \rightarrow S_2O_3^{2-}(aq)$

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

$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(s)$

$SO_3(s) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$

$SO_3(s) + H_2O(l) \rightarrow H_2SO_4(aq)$

$H_2S_2O_7(l) + H_2O(l) \rightarrow 2\ H_2SO_4(aq)$

$H_2SO_4(aq) + OH^-(aq) \rightarrow HSO_4^-(aq) + H_2O(l)$

$2\ HSO_4^-(aq) \rightarrow S_2O_8^{2-}(aq) + 2\ H^+(aq) + 2\ e^-$

$HSO_4^-(aq) + OH^-(aq) \rightarrow SO_4^{2-}(aq) + H_2O(l)$

$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

Beyond the Basics

16.46 Using the calculation method,

$$2[N_{ox}(S)] + 10(-1) = 0$$

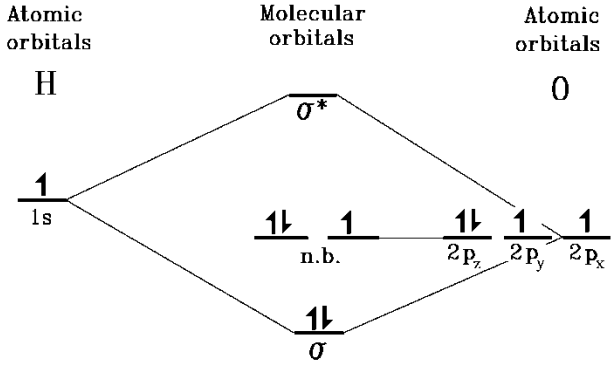
$$[N_{ox}(S)] = +5$$

If the molecule disproportionates as follows—

$$S_2F_{10}(s) \rightarrow SF_6(g) + SF_4(g)$$

—each sulfur atom will acquire a more common oxidation number, +6 and +4, respectively.

16.48 The bond order in the hydroxyl radical is a single bond. Compared to the hydroxyl anion, the "missing" electron is lost from a nonbonding orbital.



16.50 (a) $CsF(s) + SF_4(l) \rightarrow Cs^+(SF_4) + SF_5^-(SF_4)$

(b) $SF_4(l) + BF_3(g) \rightarrow SF_3^+(SF_4) + BF_4^-(SF_4)$

(c) In (b), the B–F bond is much stronger (613 $kJ \cdot mol^{-1}$) than the S–F bond (327 $kJ \cdot mol^{-1}$); thus the boron can abstract a fluorine from the sulfur. In (a), the S–F bond strength must be greater than the energy needed to extract a fluoride ion from the cesium fluoride lattice.

16.52 For nitrogen dioxide:

$\Delta H = [(+249) + (+90) - (+33)]\ kJ \cdot mol^{-1} = +306\ kJ \cdot mol^{-1}$

$E = (306\ kJ \cdot mol^{-1})/(6.02 \times 10^{23}\ mol^{-1}) = 5.08 \times 10^{-19}\ J$

$\nu = E/h = (5.08 \times 10^{-19}\ J)/(6.63 \times 10^{-34}\ J \cdot s) = 7.66 \times 10^{14}\ s^{-1}$

$\lambda = c/\nu = (3.00 \times 10^8\ m \cdot s^{-1})/(7.66 \times 10^{14}\ s^{-1}) = 3.92 \times 10^{-7}\ m = 392\ nm$

For carbon dioxide:

$\Delta H = [(+249) + (-111) - (-394)]\ kJ \cdot mol^{-1} = +532\ kJ \cdot mol^{-1}$

Performing the equivalent calculation gives a wavelength of 225 nm. This wavelength is in the ultraviolet region and thus unavailable in large quantities at sea level.

16.54 $HS^-(aq) \rightarrow S(s) + H^+(aq) + 2\ e^-$ $E_1^o = +0.476$ V

$S(s) + 3\ H_2O(l) \rightarrow SO_3^{2-}(aq) + 6\ H^+(aq) + 4\ e^-$ $E_2^o = +0.659$ V

$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2\ H^+(aq) + 2\ e^-$ $E_3^o = +0.936$ V

Sum:

$HS^-(aq) + 4\ H_2O(l) \rightarrow SO_4^{2-}(aq) + 9\ H^+(aq) + 8\ e^-$ $E^o = ?$

$\Delta G^o = (-n_1FE^o_1) + (-n_2FE^o_2) + (-n_3FE^o_3) = -F(n_1E^o_1 + n_2E^o_2 + n_3E^o_3)$

$= -(9.65 \times 10^4\ C \cdot mol^{-1})[2(+0.476\ V) + 4(+0.659\ V) + 2(+0.936\ V)]$

$= -527\ kJ \cdot mol^{-1}$

This oxidation provides enough free energy to "drive" most biological reduction processes at the deep sea vents.

16.56 The highest possible oxidation state of chromium is +6. This compound must be a peroxy species, like CrO_5, in which several oxygen atoms have the oxidation state of −1.

16.58 Dinitrogen pentoxide, because it is the oxide with the more oxygen atoms that will be the more acidic.

16.60 $$E = E° - \frac{RT}{4F} \ln \frac{1}{[H^+]^4\ pO_2}$$

$$E = +1.229\ V - \frac{(8.31\ C \cdot V \cdot mol^{-1} \cdot K^{-1})(298\ K)}{(4)(9.65 \times 10^4\ C \cdot mol^{-1})} \ln\left(\frac{1}{(1.0 \times 10^{-7})^4 (0.20)}\right)$$

$E = +1.229\ V - 0.424\ V = 0.805\ V$

16.62 (a) [A] Barium; [B] barium hydroxide; [C] dihydrogen; [D] sulfuric acid; [E] barium sulfate.

$Ba(s) + 2\ H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$

$Ba(OH)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2\ H_2O(l)$

(b) [F] Hydrogen peroxide; [G] water; [H] dioxygen.

$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

(c) [I] Sulfur dioxide; [J] sulfur trioxide.

$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(s)$

$SO_3(s) + H_2O(l) \rightarrow H_2SO_4(aq)$

(d) [K] Barium dioxide(2–).

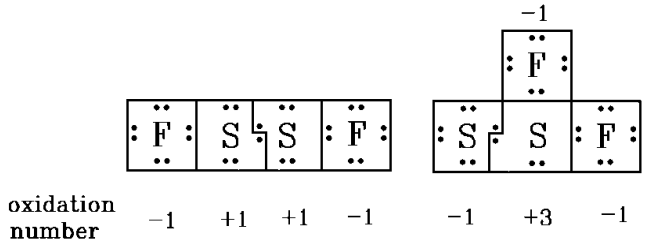
$Ba(s) + O_2(g) \rightarrow BaO_2(s)$

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

16.64 $H_2SO_4(l) + HClO_4(l) \rightarrow H_3SO_4^+(l) + ClO_4^-(l)$

16.66 The fluorine atoms are probably bonded to the sulfur atoms. The highly electronegative fluorine will tend to bond to the lower-electronegativity atom (sulfur).

16.68 The electron-dot structures are:



16.70 For the theoretical reaction:

$2\ O_2(g) \rightarrow O_4(g)$

There would be a decrease in entropy (2 moles of gas to one mole of gas) thus the reaction would need to be significantly exothermic.

Bonds broken = 2(O=O) = 2(494) $kJ \cdot mol^{-1}$ = 988 $kJ \cdot mol^{-1}$

Bonds formed = 4(O–O) = 4(142) $kJ \cdot mol^{-1}$ = 568 $kJ \cdot mol^{-1}$

Thus the reaction would have an enthalpy change of +420 $kJ \cdot mol^{-1}$ rendering it thermodynamically impossible.