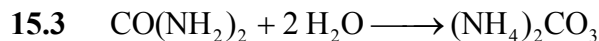
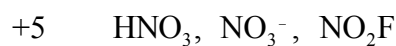
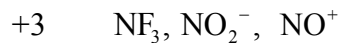
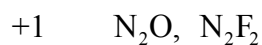
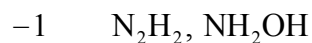
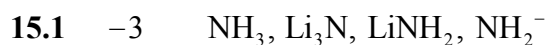


# CHAPTER 15

## THE ELEMENTS:

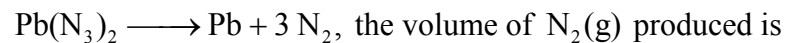
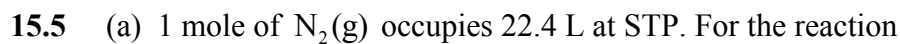
### THE LAST FOUR MAIN GROUPS



$$\text{mass of } (\text{NH}_4)_2\text{CO}_3 = (5.0 \text{ kg urea}) \left( \frac{10^3 \text{ g}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol}}{60.06 \text{ g}} \right)$$

$$\left( \frac{1 \text{ mol } (\text{NH}_4)_2\text{CO}_3}{1 \text{ mol urea}} \right) \left( \frac{96.09 \text{ g } (\text{NH}_4)_2\text{CO}_3}{1 \text{ mol } (\text{NH}_4)_2\text{CO}_3} \right)$$

$$= 8.0 \times 10^3 \text{ g (or 8.0 kg)} (\text{NH}_4)_2\text{CO}_3$$

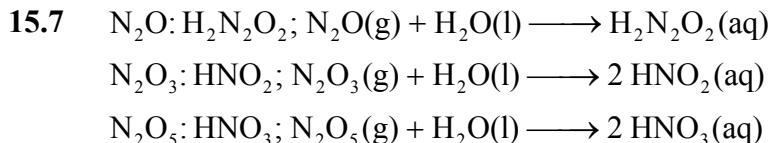


$$(1.5 \text{ g Pb(N}_3)_2) \left( \frac{1 \text{ mol Pb(N}_3)_2}{291.25 \text{ g Pb(N}_3)_2} \right) \left( \frac{3 \text{ mol N}_2}{1 \text{ mol Pb(N}_3)_2} \right) \left( \frac{22.4 \text{ L N}_2}{1 \text{ mol N}_2} \right)$$

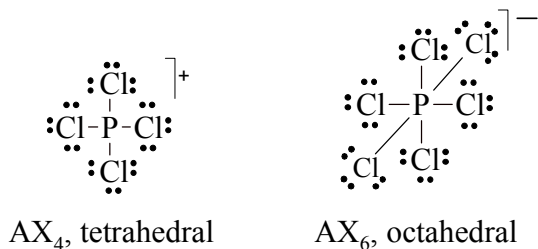
$$= 0.35 \text{ L N}_2(\text{g})$$

(b)  $\text{Hg(N}_3)_2$  would produce a larger volume, because its molar mass is less. Note that molar mass occurs in the denominator in this calculation.

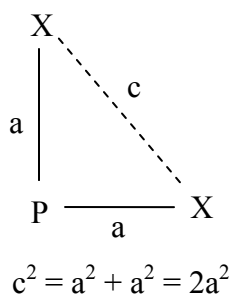
(c) Metal azides are good explosives because the azid ion is thermodynamically unstable with respect to the production of  $\text{N}_2(\text{g})$ . This is because the N—N triple bond is so strong and also because the production of a gas is favored entropically.



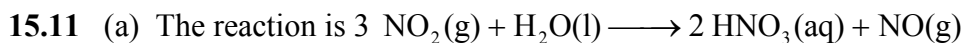
**15.9** (a)



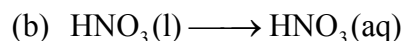
(b) and (c) The  $\text{PX}_6^-$  ions (where X = halogen) are octahedral. The calculation of the X—X separation can easily be done using the Pythagorean theorem.



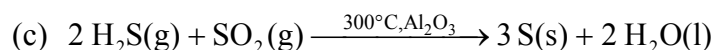
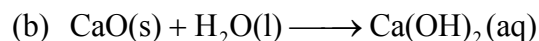
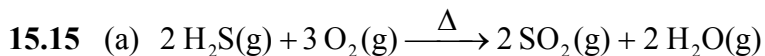
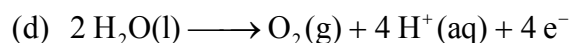
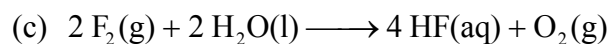
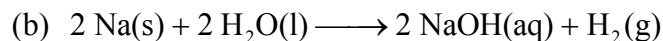
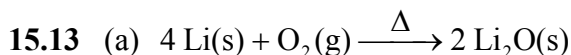
For Br,  $a = 220$  pm, giving  $c = 311$  pm. For Cl,  $a = 204$  pm, giving  $c = 288$  pm. Both these distances are much shorter than twice the van der Waals radius (Cl, 362 pm; Br, 390 pm) but are substantially longer than twice the atomic radius (Cl, 198; Br, 228 pm). It is not clear from these numbers that the steric interaction is the main consideration. Weaker P—Br bond energies may also play a role in the nonobservation of the  $\text{PBr}_6^-$  ion.

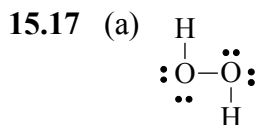


$$\begin{aligned}\Delta H^\circ_{\text{r}} &= 2(-207.36 \text{ kJ} \cdot \text{mol}^{-1}) + 90.25 \text{ kJ} \cdot \text{mol}^{-1} \\ &\quad - [3(33.18 \text{ kJ} \cdot \text{mol}^{-1}) + (285.83 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -138.18 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$



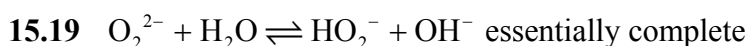
$$\begin{aligned}\Delta H^\circ_{\text{r}} &= -207.36 \text{ kJ} \cdot \text{mol}^{-1} - (-174.10 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -33.26 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$





Each O in  $\text{H}_2\text{O}_2$  is an  $\text{AX}_2\text{E}_2$  structure; therefore, the bond angle is predicted to be  $< 109.5^\circ$ . In actuality, it is  $97^\circ$ .

(b)–(e), The reduction potential of  $\text{H}_2\text{O}_2$  is  $+1.78 \text{ V}$  in acidic solution. It should, therefore, be able to oxidize any ion that has a reduction potential that is less than  $+1.78 \text{ V}$ . For the ions listed,  $\text{Cu}^+$  and  $\text{Mn}^{2+}$  will be oxidized. It would require an input of  $1.98 \text{ V}$  to oxidize  $\text{Ag}^+$  to  $\text{Ag}^{2+}$  and  $2.87 \text{ V}$  to oxidize  $\text{F}^-$ .



$$\text{HO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O}_2 + \text{OH}^- \quad K_b = \frac{K_w}{K_{a1}}$$

$$K_{a1} = 1.8 \times 10^{-12} \quad K_b = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-12}} = 5.6 \times 10^{-3}$$

Because this  $K_b$  is relatively small, we can assume that essentially all the  $\text{OH}^-$  is formed in the first ionization; therefore,

$$[\text{OH}^-] = \left( \frac{2.00 \text{ g Na}_2\text{O}_2}{0.200 \text{ L}} \right) \left( \frac{1 \text{ mol Na}_2\text{O}_2}{77.98 \text{ g Na}_2\text{O}_2} \right) \left( \frac{1 \text{ mol OH}^-}{1 \text{ mol Na}_2\text{O}_2} \right) \\ = 0.128 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(0.128) = 0.893 \quad \text{pH} = 14.00 - 0.893 = 13.11$$

If we do not ignore the second ionization, then the additional contribution to  $[\text{OH}^-]$  can be approximately calculated as follows:

$$K_b = \frac{[\text{H}_2\text{O}_2][\text{OH}^-]}{[\text{HO}_2^-]} = \frac{x(0.128 + x)}{(0.128 - x)} = 5.6 \times 10^{-3}$$

To a first approximation,  $x = 5.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$

$$\text{To a second approximation, } x = \frac{K_b(0.128 - 0.0056)}{(0.128 + 0.0056)} = 0.005$$

Then  $[\text{OH}^-] = 0.128 + 0.005 = 0.133$ ;  $\text{pOH} = -\log(0.133) = 0.876$ ; and  $\text{pH} = 13.12$ . The difference between calculations is slight.

- 15.21** The weaker the H—X bond, the stronger the acid.  $\text{H}_2\text{Te}$  has the weakest bond;  $\text{H}_2\text{O}$ , the strongest. Therefore, the acid strengths are  $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$

- 15.23** (a) The reaction is  $\text{H}_2\text{SO}_4(\text{l}) \longrightarrow \text{H}_2\text{SO}_4(\text{aq})$

where  $\text{H}_2\text{SO}_4(\text{aq})$  is  $\text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$  because  $\text{H}_2\text{SO}_4$  is a strong acid. (Note:  $\Delta H^\circ_f(\text{H}^+)$  is defined as 0).

$$\Delta H^\circ_r = -887.34 \text{ kJ} \cdot \text{mol}^{-1} - (-813.99 \text{ kJ} \cdot \text{mol}^{-1}) = -73.35 \text{ kJ} \cdot \text{mol}^{-1}$$

- (b) The number of moles of  $\text{H}_2\text{SO}_4$  is

$$10.00 \div 98.07 \text{ g} \cdot \text{mol}^{-1} = 0.1020 \text{ mol}$$

The amount of heat generated should be

$$0.1020 \text{ mol} \times -73.35 \text{ kJ} \cdot \text{mol}^{-1} = -7.482 \text{ kJ}.$$

The heat capacity of water is  $4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1}$ . Adding 7.482 kJ of heat to the water should raise the temperature by

$$\Delta t = \frac{7.482 \text{ kJ} \times 1000 \text{ J} \cdot \text{kJ}^{-1}}{4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1} \times 500.0 \text{ g}} = 3.56^\circ$$

The final temperature should be  $25.0^\circ\text{C} + 3.56^\circ\text{C} = 28.6^\circ\text{C}$ .

- 15.25** Fluorine comes from the minerals fluorspar,  $\text{CaF}_2$ ; cryolite,  $\text{Na}_3\text{AlF}_6$ ; and the fluorapatites,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ . The free element is prepared from HF and the KF by electrolysis, but the HF and KF needed for the electrolysis are prepared in the laboratory. Chlorine primarily comes from the mineral rock salt, NaCl. The pure element is obtained by electrolysis of liquid NaCl.

Bromine is found in seawater and brine wells as the  $\text{Br}^-$  ion; it is also found as a component of saline deposits; the pure element is obtained by oxidation of  $\text{Br}^-(\text{aq})$  by  $\text{Cl}_2(\text{g})$ .

Iodine is found in seawater, seaweed, and brine wells as the  $\text{I}^-$  ion; the pure element is obtained by oxidation of  $\text{I}^-(\text{aq})$  by  $\text{Cl}_2(\text{g})$ .

**15.27** (a)  $\text{HIO}(\text{aq})$   $\text{H} = +1$ ,  $\text{O} = -2$ ; therefore,  $\text{I} = +1$

(b)  $\text{ClO}_2$   $\text{O} = -2$ ; therefore,  $\text{Cl} = +4$

(c)  $\text{Cl}_2\text{O}_7$   $\text{O} = -2$ ; therefore,  $\text{Cl} = +14/2 = +7$

(d)  $\text{NaIO}_3$   $\text{Na} = +1$ ,  $\text{O} = -2$ ; therefore,  $\text{I} = +5$

**15.29** (a)  $4 \text{KClO}_3(\text{l}) \xrightarrow{\Delta} 3 \text{KClO}_4(\text{s}) + \text{KCl}(\text{s})$

(b)  $\text{Br}_2(\text{l}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{HBrO}(\text{aq}) + \text{HBr}(\text{aq})$

(c)  $\text{NaCl}(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \longrightarrow \text{NaHSO}_4(\text{aq}) + \text{HCl}(\text{g})$

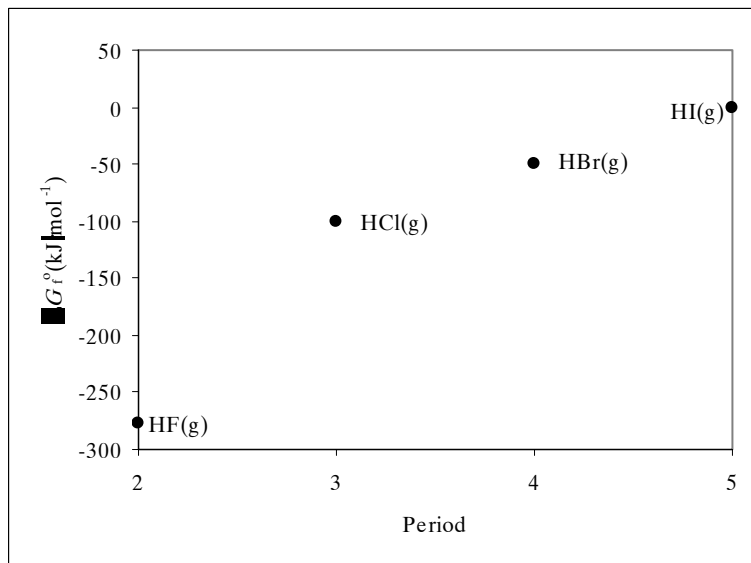
(d) (a) and (b) are redox reactions. In (a), Cl is both oxidized and reduced. In (b), Br is both oxidized and reduced. (c) is a Brønsted acid-base reaction;  $\text{H}_2\text{SO}_4$  is the acid, and  $\text{Cl}^-$  the base.

**15.31** (a)  $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$  ( $\text{HClO}_4$  is strongest;  $\text{HClO}$ , weakest)

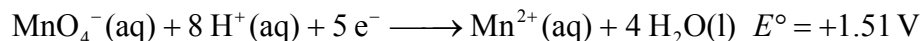
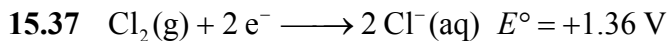
(b) The oxidation number of Cl increases from  $\text{HClO}$  to  $\text{HClO}_4$ . In  $\text{HClO}_4$ , chlorine has its highest oxidation number of +7, so  $\text{HClO}_4$  will be the strongest oxidizing agent.

**15.33**  $\text{AX}_2\text{E}_2$ , angular, slightly less than  $109^\circ$

15.35

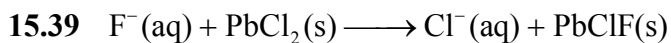


The thermodynamic stability of the hydrogen halides decreases down the group. The  $\Delta G^\circ_f$  values of HCl, HBr, and HI fit nicely on a straight line; whereas HF is anomalous. In other properties, HF is also the anomalous member of the group, in particular, its acidity. Also see Exercise 15.42.



$$E^\circ_{\text{cell}} = (1.36 - 1.51) \text{ V} = -0.15 \text{ V}$$

Because  $E^\circ_{\text{cell}}$  is negative,  $\text{Cl}_2(\text{g})$  will not oxidize  $\text{Mn}^{2+}$  to form the permanganate ion in an acidic solution.



$$\begin{aligned} \text{molarity of F}^- \text{ ions} &= \left( \frac{0.765 \text{ g PbClF}}{0.0250 \text{ L}} \right) \left( \frac{1 \text{ mol PbClF}}{261.64 \text{ g PbClF}} \right) \left( \frac{1 \text{ mol F}^-}{1 \text{ mol PbClF}} \right) \\ &= 0.117 \text{ mol} \cdot \text{L}^{-1} \end{aligned}$$



The number of moles of  $\text{NH}_4\text{ClO}_4$  is

$$1.00 \text{ kg} \times 1000 \text{ g} \cdot \text{kg}^{-1} \div 117.49 \text{ g} \cdot \text{mol}^{-1} = 8.51 \text{ mol}$$

The number of moles of Al is

$$1.00 \text{ kg} \times 1000 \text{ g} \cdot \text{kg}^{-1} \div 26.98 \text{ g} \cdot \text{mol}^{-1} = 37.06 \text{ mol}$$

The limiting reagent is the  $\text{NH}_4\text{ClO}_4$ .

The standard enthalpy for the reaction is given by

$$\begin{aligned} \Delta H^\circ_{\text{r}} &= (-1675.7 \text{ kJ} \cdot \text{mol}^{-1}) + (-704.2 \text{ kJ} \cdot \text{mol}^{-1}) + 6(-241.82 \text{ kJ} \cdot \text{mol}^{-1}) \\ &\quad + 3(90.25 \text{ kJ} \cdot \text{mol}^{-1}) - [3(-295.31 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -2674.1 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

This value is the amount of heat released for 3 mol  $\text{NH}_4\text{ClO}_4$ . The amount released for 8.51 mol will be

$$8.51 \text{ mol NH}_4\text{ClO}_4 \times \frac{-2674.1 \text{ kJ} \cdot \text{mol}^{-1}}{3 \text{ mol NH}_4\text{ClO}_4} = -7.59 \times 10^3 \text{ kJ}$$

There will be  $7.59 \times 10^3 \text{ kJ}$  of heat released.

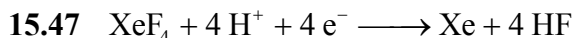
**15.43** Helium occurs as a component of natural gases found under rock formations in certain locations, especially some in Texas. Argon is obtained by distillation of liquid air.

**15.45** (a)  $\text{KrF}_2$ :F = -1; therefore, Kr = +2

(b)  $\text{XeF}_6$ :F = -1; therefore, Xe = +6

(c)  $\text{KrF}_4$ :F = -1; therefore, Kr = +4

(d)  $\text{XeO}_4^{2-}$ :O = -2,  $N_{\text{ox}}(\text{Xe}) - 8 = -2$ ; therefore,  $N_{\text{ox}}(\text{Xe}) = +6$





**15.49** Because  $\text{H}_4\text{XeO}_6$  has more highly electronegative O atoms bonded to Xe, we predict that  $\text{H}_4\text{XeO}_6$  is more acidic than  $\text{H}_2\text{XeO}_4$ .

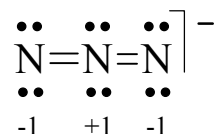
**15.51** A sol is colloid comprised of solid particles suspended in a liquid. Muddy water is a type of sol. A foam is a suspension of a gas in a solid or liquid. Styrofoam, foam rubber, soapsuds, and aerogels are all types of foams.

**15.53** (a) both a sol and an emulsion (b) a foam (c) a sol

**15.55** In fluorescence, the light that is emitted is of lower energy than the light that is absorbed, and the fluorescence stops as soon as the exciting radiation is stopped. In phosphorescence, the phosphorescing molecules remain excited for a period of time after the stimulus has stopped.

**15.57** The mercury atoms are an energy transfer agent. They absorb the energy from a high-voltage discharge and emit ultraviolet light in the region of 254 and 185 nm. This emitted light then excites a fluorescent material that emits radiation in the visible region of the spectrum, which is the light observed when the lamp is turned on.

**15.59** (a) and (b). The formal charges are given under each atom.

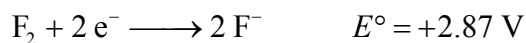


(c) The value of  $-\frac{1}{3}$  is an average oxidation number based solely upon the number of nitrogen atoms and the overall charge. From the Lewis structure, we can see that the molecule is asymmetric and it is possible that the different nitrogen atoms may have different oxidation numbers. It would be extreme to state that the terminal nitrogens have oxidation numbers of  $-1$  and the central nitrogen atom has an oxidation number of

+1, but assigning the same oxidation number of  $-\frac{1}{3}$  to all three atoms is also not strictly accurate.

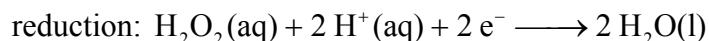
(d) This situation most often arises when an element has bonds to other atoms of the same type.

**15.61** The larger the value of  $E^\circ$  for the reduction  $X_2 + 2 e^- \longrightarrow 2 X^-$ , the greater the oxidizing strength of the halogen  $X_2$ . From Appendix 2B,



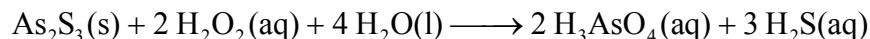
Thus,  $I_2 < Br_2 < Cl_2 < F_2$ .

**15.63** oxidation:



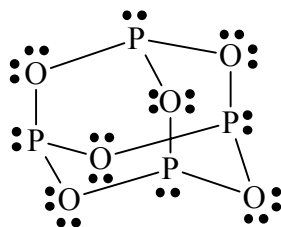
Multiply the reduction reaction by 2, cancel electrons, and add.

overall:

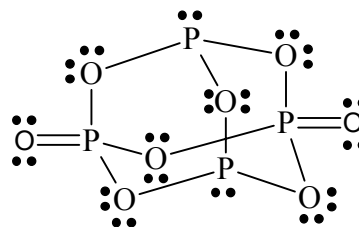


**15.65** This ratio,  $\Delta H_{\text{vap}}/T_b$ , is the entropy of vaporization. Hydrogen bonding is much stronger in  $H_2O(l)$  than in  $H_2S(l)$ . Thus  $H_2O(l)$  has a more ordered arrangement than  $H_2S(l)$ . Consequently, the change in entropy upon transformation to the gaseous state is greater for  $H_2O$  than for  $H_2S$ .

**15.67** The two molecules are shown below:



Phosphorous(III) oxide



Phosphorous(V) oxide

The basic structure of the two molecules is the same. The phosphorus atoms lie in a tetrahedral arrangement in which there are bridging oxygen atoms to the other phosphorus atoms. In phosphorus(V) oxide, there is an additional terminal oxygen atom bonded to each phosphorus atom. In phosphorus(III) oxide, each oxygen atom has a formal charge of 0 as does each phosphorus atom. In phosphorus(V) oxide, this is also true.

According to the Lewis structures, all P—O bonds in phosphorus(III) oxide have a bond order of 1, while in phosphorus(V) oxide, the terminal oxygen atoms have a bond order of 2 between them and the phosphorus atoms to which they are attached. If one examines the molecular parameters, one sees that all of the P—O<sub>bridging</sub> distances for phosphorus(III) oxide are slightly longer than those of phosphorus(V) oxide

(163.8 pm versus 160.4 pm). This is expected because the radius of phosphorus(V) should be smaller than that of phosphorus(III). The terminal PRO distances for phosphorus(V) oxide are considerably shorter (142.9 pm); this agrees with the higher bond order between phosphorus and these atoms.

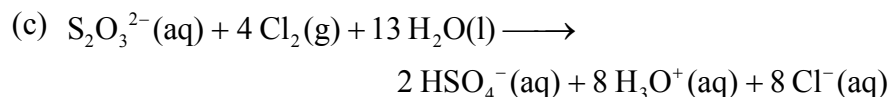
**15.69** (a)  $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{SO}_3(\text{l})$  This is Lewis acid-base reaction.

$\text{SO}_2$  is the acid and  $\text{H}_2\text{O}$  is the base.

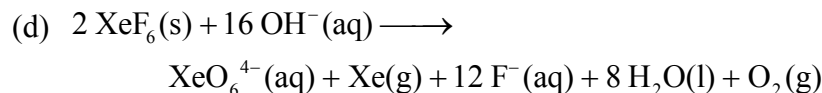
(b)  $2 \text{F}_2(\text{g}) + 2 \text{NaOH}(\text{aq}) \longrightarrow \text{OF}_2(\text{g}) + 2 \text{NaF}(\text{aq}) + \text{H}_2\text{O}(\text{l})$  This is a redox reaction illustrating the oxidizing ability of  $\text{F}_2$  in basic solution and

is used for the preparation of  $\text{OF}_2(\text{g})$ .

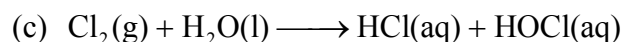
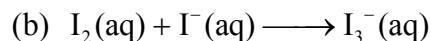
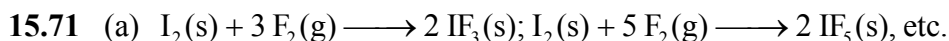
O is oxidized and F is reduced.



This is a redox reaction illustrating the oxidizing power of  $\text{Cl}_2(\text{g})$  in acidic solution. S is oxidized and Cl is reduced.

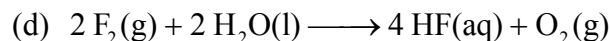


This is a redox reaction that is also a disproportionation reaction in that Xe goes from oxidation number +6 to +8 and to 0. Xe is both oxidized and reduced.



But there are competing reactions, such as

$\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2 \text{HCl}(\text{aq}) + \frac{1}{2} \text{O}_2(\text{g})$ . The predominant reaction is determined by the temperature and pH.



To determine how much product is formed, we must first identify the limiting reagent:

$$\text{moles of XeF}_4(\text{s}) = \frac{330.0 \text{ g}}{207.29 \text{ g} \cdot \text{mol}^{-1}} = 1.592 \text{ mol}$$

$$\text{moles of SF}_4(\text{s}) = \frac{250.0 \text{ g}}{108.07 \text{ g} \cdot \text{mol}^{-1}} = 2.313 \text{ mol}$$

Given the 1:2 stoichiometry of the reaction,  $\text{SF}_4(\text{s})$  is the limiting reagent and 2.313 mol of  $\text{SF}_6(\text{s})$  will be produced.

$$(2.313 \text{ mol})(146.07 \text{ g} \cdot \text{mol}^{-1}) = 337.9 \text{ g of } \text{SF}_6(\text{s}) \text{ produced.}$$

**15.75** Orpiment is  $\text{As}_2\text{S}_3$  and realgar is  $\text{As}_4\text{S}_4$ . Orpiment is yellow and realgar is orange-red. They are both used as pigments.



$\text{AX}_2$ , linear  $180^\circ$

(b)  $\text{F}^-$ , 133 pm;  $\text{N}_3^-$ , 148 pm;  $\text{Cl}^-$ , 181 pm; therefore, between fluorine and chlorine.

(c)  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{HI}$  are all strong acids. For  $\text{HF}$ ,  $K_a = 3.5 \times 10^{-4}$ , so  $\text{HF}$  is slightly more acidic than  $\text{HN}_3$ . The small size of the azide ion suggests that the  $\text{H}-\text{N}$  bond in  $\text{HN}_3$  is similar in strength to that of the  $\text{H}-\text{F}$  bond, so it is expected to be a weak acid.

(d) ionic:  $\text{NaN}_3$ ,  $\text{Pb}(\text{N}_3)_2$ ,  $\text{AgN}_3$ , etc.

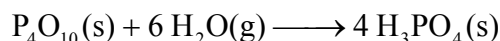
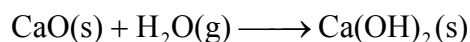
covalent:  $\text{HN}_3$ ,  $\text{B}(\text{N}_3)_3$ ,  $\text{FN}_3$ , etc.

$$\begin{aligned} \mathbf{15.79} \quad [\text{ClO}^-] &= (0.02834 \text{ L}) \left( \frac{0.110 \text{ mol } \text{S}_2\text{O}_3^{2-}}{1 \text{ L } \text{Na}_2\text{S}_2\text{O}_3} \right) \\ &\quad \left( \frac{1 \text{ mol } \text{I}_2}{2 \text{ mol } \text{S}_2\text{O}_3^{2-}} \right) \left( \frac{1 \text{ mol } \text{ClO}^-}{1 \text{ mol } \text{I}_2} \right) \left( \frac{1}{0.01000 \text{ L } \text{ClO}^-} \right) \\ &= 0.156 \text{ mol} \cdot \text{L}^{-1} \end{aligned}$$

**15.81** The solubility of the ionic halides is determined by a variety of factors, especially the lattice enthalpy and enthalpy of hydration. There is a delicate balance between the two factors, with the lattice enthalpy usually being the determining one. Lattice enthalpies decrease from chloride to

iodide, so water molecules can more readily separate the ions in the latter. Less ionic halides, such as the silver halides, generally have a much lower solubility, and the trend in solubility is the reverse of the more ionic halides. For the less ionic halides, the covalent character of the bond allows the ion pairs to persist in water. The ions are not easily hydrated, making them less soluble. The polarizability of the halide ions, and thus, the covalency of their bonding, increases down the group.

**15.83** To answer this question, we can compare equilibrium “vapor pressures” of water over each of these reagents. The one with the lowest equilibrium vapor pressure will be the better drying agent. The two reactions of interest are



First, the free energies of the reactions are calculated and from these the equilibrium pressure of water can be obtained.

For CaO:

$$\begin{aligned}\Delta G^\circ_r &= -898.49 \text{ kJ} \cdot \text{mol}^{-1} - [(-604.03 \text{ kJ} \cdot \text{mol}^{-1}) + (-228.57 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -65.89 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$\Delta G^\circ_r = -RT \ln K$$

$$K = e^{\frac{\Delta G^\circ}{RT}} = e^{\frac{-65890 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}} = 3.5 \times 10^{11}$$

$$K = \frac{1}{P_{\text{H}_2\text{O}}} = 3.5 \times 10^{11}$$

$$P_{\text{H}_2\text{O}} = 2.8 \times 10^{-12} \text{ bar}$$

For  $\text{P}_4\text{O}_{10}$ :

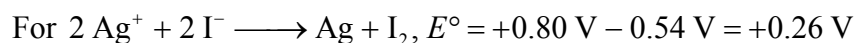
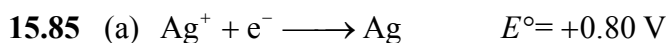
$$\begin{aligned}\Delta G^\circ_r &= 4(-1119.2 \text{ kJ} \cdot \text{mol}^{-1}) \\ &\quad - [(-2697.0 \text{ kJ} \cdot \text{mol}^{-1}) + 6(-228.57 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -408.4 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$K = e^{\frac{\Delta G^\circ}{RT}} = e^{\frac{-408\,400 \text{ J}\cdot\text{mol}^{-1}}{(8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298 \text{ K})}} = 3.9 \times 10^{71}$$

$$K = \frac{1}{(P_{\text{H}_2\text{O}})^6} = 3.9 \times 10^{71}$$

$$P_{\text{H}_2\text{O}} = 1.2 \times 10^{-12} \text{ bar}$$

Because the pressure of water possible above CaO is greater than that above  $\text{P}_4\text{O}_{10}$ , CaO will be a poorer drying agent.



The process should be spontaneous.

(b) The formation of AgI precipitate means that the concentration of  $\text{Ag}^+$  ions is never high enough to achieve the conditions necessary for the redox reaction to take place. The solubility product  $K_{\text{sp}}$  limits the concentrations in solution, so that the actual redox potential is not the value calculated, which represents the values when

$[\text{Ag}^+] = 1 \text{ M}$  and  $[\text{I}^-] = 1 \text{ M}$ . If we use the concentrations established by the solubility equilibrium and the Nernst equation, we can calculate the actual redox potential:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

where, in this case,  $Q = \frac{1}{K_{\text{sp}}^2}$  for the reaction as written

$$K_{\text{sp}} = 1.5 \times 10^{-16} \text{ for AgI}$$

$$\begin{aligned}
E &= +0.26 \text{ V} - \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{(2)(96485 \text{ J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1})} \ln \frac{1}{(1.5 \times 10^{-16})^2} \\
&= +0.26 \text{ V} - \frac{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{(96485 \text{ J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1})} \ln \frac{1}{(1.5 \times 10^{-16})} \\
&= +0.26 \text{ V} - 0.94 \text{ V} \\
&= -0.68 \text{ V}
\end{aligned}$$

The fact that the concentrations of  $\text{Ag}^+$  and  $\text{I}^-$  are limited in solution means that the redox potential for a spontaneous reaction is never achieved.

**15.87** The molecular orbital diagram for  $\text{NO}^+$  should have the oxygen orbitals slightly lower in energy than the nitrogen orbitals, because oxygen is more electronegative. This will cause the bonding to be more ionic than in either  $\text{N}_2$  or  $\text{O}_2$ . There is an ambiguity, however, in that the MO diagram could be similar to either that of  $\text{N}_2$  or that of  $\text{O}_2$ . Refer to Figures 3.34 and 3.35 where you will see that the  $\sigma_{2p}$  or the  $\pi_{2p}$  have different relative energies. There are consequently two possibilities for the orbital energy diagram:

(b) The two orbital diagrams predict the same bond order (3) and same magnetic properties (diamagnetic), so these properties cannot be used to determine which diagram is the correct one. That must be determined by more complex spectroscopic measurements.

**15.89** (a) Pyrite adopts a face-centered cubic unit cell. (b) The iron atoms lie at the corners and at the face centers of the unit cell. Eight sulfur atoms lie completely within the unit cell. (c) The coordination number of iron is six (octahedral). (d) Each sulfur atom is bonded to one other sulfur atom and three iron atoms. (e) The locations of the sulfur atoms can be considered in one of two ways. An examination of the structure shows that these are best thought of as  $\text{S}_2^{2-}$  ions. The locations of the midpoints of the S-S bonds are at the centers of half of the edges of the unit cell ( $6\text{S}_2^{2-} \times 1/2$ )



plus 1  $\text{S}_2^{2-}$  ion in the center of the unit cell (only half the ions have sulfur atoms within a given cell). This gives a total of 4  $\text{S}_2^{2-}$  ions in the unit cell. Alternatively, identify eight S atoms within the unit cell.

**15.91** (a) State A:  $94.72 \text{ kJ} \cdot \text{mol}^{-1}$ , State B:  $157.85 \text{ kJ} \cdot \text{mol}^{-1}$ . State B is the higher energy state because it requires more energy to pair electrons in the same orbital than it does to force the spins of two electrons in different orbitals to be antiparallel

(b)

$$\lambda = \frac{h \cdot c}{E} = \frac{(6.62608 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m} \cdot \text{s}^{-1})(6.02214 \times 10^{23} \text{ mol}^{-1})}{(94720 \text{ J} \cdot \text{mol}^{-1})}$$

$$= 1.263 \times 10^{-6} \text{ m} \text{ or } 1.263 \mu\text{m}$$

**15.93**

