CHAPTER 15

THE ELEMENTS: THE LAST FOUR MAIN GROUPS

15.2 (a) 0; (b) 0; (c)
$$-3$$
; (d) -2 ; (e) $+3$; (f) $+5$; (g) $+5$; (h) $+3$

15.4 (a)
$$HNO_2 + H_2NNH_2 \longrightarrow 2 H_2O + HN_3$$

$$(15.0 \text{ g H}_2\text{NNH}_2) \left(\frac{1 \text{ mol H}_2\text{NNH}_2}{32.05 \text{ g H}_2\text{NNH}_2} \right) \left(\frac{1 \text{ mol HN}_3}{1 \text{ mol H}_2\text{NNH}_2} \right)$$

$$\left(\frac{43.04 \text{ g HN}_3}{1 \text{ mol HN}_3}\right) = 20.1 \text{ g HN}_3$$

(b)
$$N_2O(g) + 2 \text{ NaNH}_2(l) \xrightarrow{175^{\circ}C} \text{NaN}_3(l) + \text{NaOH}(l) + \text{NH}_3(g)$$

(c) The oxidation number of nitrogen in hydrazine is -2, while in hydrazoic acid it is nominally -1/3. This process corresponds to an oxidation of the hydrazine.

15.6
$$2 \text{ NaN}_3 \longrightarrow 2 \text{ Na} + 3 \text{ N}_2$$

number of moles of N₂(g) =
$$n \frac{PV}{RT} = \frac{(1.5 \text{ atm})(100 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(293 \text{ K})}$$

= 6.24 mol

mass of NaN₃ needed =
$$(6.24 \text{ mol N}_2) \left(\frac{2 \text{ mol NaN}_3}{3 \text{ mol N}_2} \right) \left(\frac{65.02 \text{ g NaN}_3}{1 \text{ mol NaN}_3} \right)$$

= 270 g NaN_3

15.8
$$P_4O_6 - H_3PO_3$$
; $P_4O_6(s) + 6 H_2O(l) \longrightarrow 4 H_3PO_3(aq)$

$$P_4O_{10} - H_3PO_4$$
; $P_4O_{10}(s) + 6 H_2O(l) \longrightarrow 4 H_3PO_4(aq)$

- (b) Yes. Each oxygen atom has two bonds to phosphorus atoms and two lone pairs. Each phosphorus atom has three bonds to oxygen atoms and one lone pair.
- (c) The phosphorus atoms can be replaced by CH fragments and the oxygen atoms by CH₂ groups.
- (d) The molecule would be $C_{10}H_{16}$. This compound is known as adamantane.

$$\begin{array}{c|c} H & H & H \\ \hline H & C & H \\ \hline C & C & C \\ \hline H & C & H \\ \hline H & H & H \\ \hline H & H & H \\ \end{array}$$

15.12 First we balance the equation:

$$PCl_{5}(g) + 4 H_{2}O(l) \longrightarrow 5 HCl(aq) + H_{3}PO_{4}(aq)$$

$$\Delta G^{\circ}_{r} = 5(-131.23 \text{ kJ} \cdot \text{mol}^{-1}) + (-1142.54 \text{ kJ} \cdot \text{mol}^{-1})$$

$$- [(-305.0 \text{ kJ} \cdot \text{mol}^{-1}) + 4(-237.13 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$= -545.17 \text{ kJ} \cdot \text{mol}^{-1}$$

The reaction is spontaneous.

15.14 (a)
$$Na_2O(s) + H_2O(l) \longrightarrow 2 NaOH(aq)$$

(b)
$$Na_2O_2(s) + 2 H_2O(l) \longrightarrow 2 NaOH(aq) + H_2O_2(aq)$$

(c)
$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$

(d)
$$2 SO_2(g) + O_2(g) \xrightarrow{500^{\circ}C, V_2O_5} 2 SO_3(g)$$

15.16 (a)
$$FeS(s) + 2 HCl(aq) \longrightarrow FeCl_2(aq) + H_2S(g)$$

(b)
$$H_2(g) + S(s) \xrightarrow{\Delta} H_2S(g)$$

(c)
$$S_2Cl_2(l) + Cl_2(g) \xrightarrow{FeCl_3} 2 SCl_2(l)$$

15.18 (a) The Lewis structure of oleum is

- (a) The formal charges are 0 on all S and O atoms.
- (b) +6

15.20 The system is
$$HS^{-}(aq) + H_2O(1) \rightleftharpoons H_2S(aq) + OH^{-}(aq)$$

Concentration (mo	$l \cdot L^{-1}$) HS ⁻ +	$H_2O \rightleftharpoons H_2S + OH^-$		
initial	0.050		0	0
change	-x		+x	+x
equilibrium	0.050 - x	_	x	\boldsymbol{x}

$$K_{\rm b} = \frac{K_{\rm w}}{K_{\rm a}} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-7}} = 7.7 \times 10^{-8}$$

$$K_{\rm b} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050} = 7.7 \times 10^{-8}$$

$$x = 6.2 \times 10^{-5} = [OH^{-}]$$

$$pOH = 4.21$$

$$pH = 14.00 - 4.21 = 9.79$$

15.22 (a)
$$PbS(s) + 2 O_2(g) \longrightarrow PbSO_4(s)$$
 (1)

$$PbS(s) + 4 O_2(g) \longrightarrow PbO_2(s) + SO_2(g)$$
 (2)

(b) We do not have available the free energy of formation of PbS(s), so we need to discover a different method of determining this instead of

simply comparing the signs and relative magnitudes of the free energies of the two reactions. The appropriate reaction is

$$PbSO_4(s) \longrightarrow PbO_2(s) + SO_2(g)$$

Calculate ΔG°_{r}

$$\Delta G_{\rm r}^{\circ} = \Delta G_{\rm f}^{\circ}(\text{PbO}_{2}, s) + \Delta G_{\rm f}^{\circ}(\text{SO}_{2}, g) - \Delta G_{\rm f}^{\circ}(\text{PbSO}_{4}, s)$$

$$= [-217.33 + (-300.19) - (-813.14)] \text{ kJ} \cdot \text{mol}^{-1} = +295.62 \text{ kJ} \cdot \text{mol}^{-1}$$

The positive $\Delta G_{\rm r}^{\circ}$ is unfavorable to the formation of PbO₂. Thus, PbSO₄ is favored as a product over PbO₂ + SO₂.

15.24 (a)
$$H_2O_2 + 2 H^+ + 2 e^- \longrightarrow 2 H_2O$$
 $E^\circ = +1.78 V$

$$\frac{2(Fe^{2+} \longrightarrow Fe^{3+} + e^-)}{H_2O_2 + 2 Fe^{2+} + 2 H^+ \longrightarrow 2 Fe^{3+} + 2 H_2O} \qquad E^\circ = +1.01 V$$

The potential is positive so this process will be spontaneous.

- (b) The potential must be obtained from the Nernst equation. From part
- (a), the standard potential that will be appropriate for $1.00 \,\mathrm{M\,H^{+}}(\mathrm{aq})$ is
- 1.01 V. The Nernst equation expression for this reaction will be

$$E = +1.101 \text{ V} - \left(\frac{0.025 \text{ 693}}{2}\right) \ln \frac{[\text{Fe}^{3+}]^2}{[\text{H}_2\text{O}_2][\text{Fe}^{2+}]^2[\text{H}^+]^2}$$

To find the standard potential in neutral solution, the only parameter that changes is the concentration of H⁺. All other concentrations in the quotient will remain equal to 1.

$$E = +1.01 \text{ V} - \left(\frac{0.025 \text{ 693}}{2}\right) \ln \frac{1}{[\text{H}^+]^2}$$

$$E = +1.01 \text{ V} - \left(\frac{0.025 \text{ 693}}{2}\right) \ln \frac{1}{(1.0 \times 10^{-7})^2}$$

$$E = +0.60 \text{ V}$$

The reaction is still spontaneous in neutral solution; however, the reaction becomes less favorable as the pH increases.

- (c) Raising the pH above 7 would be complicated by the precipitation of insoluble iron hydroxide complexes.
- **15.26** (a) CaOCl; (b) It is an effective but mild oxidizing agent.
- **15.28** (a) IF_7 : F = -1; therefore I = +7
 - (b) NaIO₄: Na = +1, O = -2; therefore I = +7
 - (c) HBrO(aq): H = +1, O = -2; therefore Br = +1
 - (d) NaClO₂: Na = +1, O = -2; therefore Cl = +3
- 15.30 (a) $Cl_2(g) + H_2O(l) \longrightarrow HClO(aq) + HCl(aq)$
 - (b) $Cl_2(g) + 2 OH^-(aq) \longrightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$
 - (c) $3 \text{ Cl}_2(g) + 6 \text{ OH}^-(aq) \xrightarrow{\Delta} \text{ClO}_3^-(aq) + 5 \text{ Cl}^-(aq) + 3 \text{ H}_2\text{O}(l)$
 - (d) In part (a), Cl goes from $N_{ox} = 0$ to $N_{ox} = +1$ (in HClO) and from $N_{ox} = 0$ to $N_{ox} = -1$ (in HCl). In part (b), Cl goes from $N_{ox} = 0$ to $N_{ox} = +1$

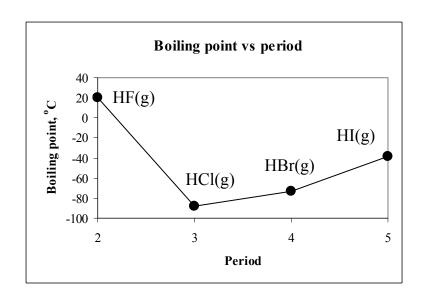
(in ClO⁻) and from $N_{ox} = 0$ to $N_{ox} = -1$ (in Cl⁻). In part (c), Cl goes from

 $N_{\rm ox} = 0$ to $N_{\rm ox} = +5$ (in ${\rm ClO_3}^-$) and from $N_{\rm ox} = 0$ to $N_{\rm ox} = -1$ (in ${\rm Cl}^-$). So

in each case, Cl is both oxidized and reduced.

- 15.32 (a) HIO < HBrO < HClO (Fluorine does not form oxoacids.)
 - (b) The electronegativity of the halogens increases in the order I to Cl; therefore, there is a greater electron-withdrawing effect upon the HO bond in this order, resulting in a greater tendency to release H and thus greater acid strength.

15.36



HF is anomalous, due to the hydrogen bonding that exists between HF molecules in the liquid state. The upward trend from HCl to HI is normal and parallels the increase in molecular weight and London forces.

15.38 (a) The following two half-cell reactions involving O₃ can occur:

$$O_3 + 2 H^+ + 2 e^- \longrightarrow O_2 + H_2O$$
 $E^{\circ} = +2.07 V$

$$O_3 + H_2O + 2 e^- \longrightarrow O_2 + 2 OH^- \quad E^\circ = +1.24 \text{ V}$$

These may be compared to

$$F_2 + 2 e^- \longrightarrow 2 F^ E^\circ = +2.87 V$$

Therefore, fluorine is a stronger oxidizing agent than ozone.

(b) No. While the reduction potential of ozone is considerably different in acidic (+2.07 V) versus basic (+1.24 V) solution, fluorine is still a much stronger oxidant (+2.87 V).

15.40
$$[I_2] = (0.028 \ 45 \ L) \left(\frac{0.025 \ \text{mol } S_2 O_3^{\ 2^-}}{1 \ L} \right) \left(\frac{1 \ \text{mol } I_2}{2 \ \text{mol } S_2 O_3^{\ 2^-}} \right) \left(\frac{1}{0.025 \ 00 \ L} \right)$$

$$= 0.014 \ \text{mol} \cdot L^{-1}$$

15.42 Because there is no data available for the free energy of formation of HClO, we must turn to the electrochemical data in Appendix 2B. The appropriate half-reactions are

$$\text{Cl}_2 + 2 \text{ e}^- \longrightarrow 2 \text{ Cl}^ E^\circ = +1.36 \text{ V}$$

$$\frac{\text{Cl}_2 + 2 \text{ H}_2\text{O} \longrightarrow 2 \text{ HClO} + 2 \text{ H}^+ + 2 \text{ e}^-}{2 \text{ Cl}_2 + 2 \text{ H}_2\text{O} \longrightarrow 2 \text{ HClO} + 2 \text{ H}^+ + 2 \text{ Cl}^-} \qquad E^\circ = -0.27 \text{ V}$$

$$2 \text{ Cl}_2 + 2 \text{ H}_2\text{O} \longrightarrow 2 \text{ HClO} + 2 \text{ H}^+ + 2 \text{ Cl}^ E^{\circ} = -0.27 \text{ V}$$

The E° will be the same for the reaction balanced as

$$Cl_2 + H_2O \longrightarrow HClO + H^+ + Cl^ E^{\circ} = -0.27 \text{ V}$$

but n will be $1 e^-$ rather than $2 e^-$ as in the previous equation.

 ΔG°_{r} can now be calculated from $\Delta G^{\circ}_{r} = -nFE^{\circ}$

$$\Delta G_{r}^{\circ} = -(1)(96 \ 485 \ \text{J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1})(-0.27 \ \text{V}) = +26 \ \text{kJ} \cdot \text{mol}^{-1}$$

(b) The equilibrium constant can be calculated from $\Delta G^{\circ}_{r} = -RT \ln K$

$$K = e^{-\frac{\Delta G_{r}^{\circ}}{RT}} = e^{-\frac{26\ 000\ J\cdot mol^{-1}}{(8.314\ J\cdot K^{-1}\cdot mol^{-1})(298\ K)}} \cong 2.8 \times 10^{-5}$$

- **15.44** Krypton and xenon are obtained by the distillation of liquid air.
- **15.46** (a) $XeO_3:O = -2$; therefore Xe = +6
 - (b) $XeO_6^{4-}:O = -2$; therefore Xe = +8
 - (c) XeF_2 : F = -1; therefore Xe = +2
 - (d) $HXeO_4^-: H = +1, O = -2;$ therefore Xe = +6
- **15.48** (a) $XeF_6(s) + 3H_2O(1) \longrightarrow XeO_3(s) + 6HF(aq)$
 - (b) $Pt(s) + XeF_4(s) \longrightarrow Xe(g) + PtF_4(s)$
 - (c) $Kr(g) + F_2(g) \xrightarrow{\text{electric discharge}} KrF_2(s)$

- **15.50** H₄XeO₆, in which Xe has an oxidation number of +8, is expected to be a stronger oxidizing agent than H₂XeO₄, in which the oxidation number is lower, +6.
- 15.52 Both these names refer to types of colloids, but the nature of what is suspended in what changes. An emulsion is a suspension of small particles of one liquid in another liquid. An example of this is a mixture of oil and vinegar. A gel is a type of solid emulsion in which a liquid or solid phase is suspended in a solid. Gels are characterized by being soft but holding their shape. Gelatin desserts are a type of gel. Gels are also formed when some water-sensitive metal complexes are hydrolyzed. These gels are industrially important as precursors to metal oxide materials.
- **15.54** (a) hydrogen bonds (b) hydrogen bonds (c) hydrogen bonds, dipoledipole forces, and London forces
- **15.56** The energy of the emitted radiation is always lower than that of the exciting radiation.
- 15.58 In a neon light, the emission of the radiation, which is seen as light, is occurring directly from the gas when it is excited by a voltage. In a fluorescent light, the gas that is excited by the voltage emits its energy as radiation, which then excites a fluorescent material that coats the walls of the fluorescent light bulb. The radiation observed is therefore not the radiation of the gas being excited.
- **15.60** As discussed in Chapter 6, the enthalpy of the reaction:

$$P_4(g) \rightarrow 2 P_2(g)$$

May be estimated by summing the energy needed to break the bonds of $P_4(g)$ and subtracting the energy released upon formation of the 2 P-P

bonds. This sum is given to us as 217 kJ mol^{-1} . Therefore, the bond enthalpy of P_2 is:

Bond enthalpy of
$$P_2 = \frac{6(200 \text{ kJ} \cdot \text{mol}^{-1}) - 217 \text{ kJ} \cdot \text{mol}^{-1}}{2} = 492 \text{ kJ} \cdot \text{mol}^{-1}$$

This bond enthalpy is significantly less than the bond enthalpy of N_2 , an isoelectronic compound, because in P_2 bonding involves electrons in a valence shell which is further from the nuclei, resulting in a weaker bond.

15.62 S + 2 e⁻
$$\longrightarrow$$
 S²⁻(aq) $E^{\circ} = -0.48 \text{ V}$

$$O_{2} + 4 \text{ H}^{+} + 4 \text{ e}^{-} \longrightarrow 2 \text{ H}_{2}\text{O} \qquad E^{\circ} = +1.23 \text{ V}$$

$$Cl_{2} + 2\text{ e}^{-} \longrightarrow 2 \text{ Cl}^{-} \qquad E^{\circ} = +1.36 \text{ V}$$

$$H_{2}O_{2} + 2 \text{ H}^{+} + 2 \text{ e}^{-} \longrightarrow 2 \text{ H}_{2}\text{O} \qquad E^{\circ} = +1.78 \text{ V}$$

Because a larger value of E° corresponds to greater oxidizing power, the order is

$$S < O_2 < Cl_2 < H_2O_2$$

15.64 Stage 1: 4 NH₃(g) + 5 O₂(g)
$$\longrightarrow$$
 4 NO(g) + 6 H₂O(g)

$$\Delta H^{\circ}_{r} = \Delta H^{\circ}_{f} \text{ (products)} - \Delta H^{\circ}_{f} \text{ (reactants)}$$

$$\Delta H^{\circ}_{r} = [(4)(90.25 \text{ kJ} \cdot \text{mol}^{-1}) + (6)(-241.82 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$-[(4)(-46.11 \text{ kJ} \cdot \text{mol}^{-1}]$$

$$\Delta H^{\circ}_{r} = -905.48 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S^{\circ}_{r} = S^{\circ} \text{ (products)} - S^{\circ} \text{ (reactants)}$$

$$H_{2}O_{2} + OH^{-} \longrightarrow O_{2} + H_{2}O + H^{+} + 2 \text{ e}^{-}$$

$$\Delta S^{\circ}_{r} = +180.52 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta G^{\circ}_{r} = \Delta H^{\circ}_{r} - T\Delta S^{\circ}_{r}$$

The reaction is spontaneous at all temperatures because ΔH° is negative and ΔS° is positive.

Stage 2:
$$2 \text{ NO(g)} + O_2(g) \longrightarrow 2 \text{ NO_2(g)}$$

$$\Delta H^{\circ}_{r} = \Delta H^{\circ}_{f} (products) - \Delta H^{\circ}_{f} (reactants)$$

$$\Delta H^{\circ}_{r} = [(2)(33.18 \text{ kJ} \cdot \text{mol}^{-1})] - [(2)(90.25 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$\Delta H^{\circ}_{r} = -114.14 \text{ kJ} \cdot \text{mol}^{-1}$$

$$H_{2}O_{2} \longrightarrow H^{+} + HO_{2}^{-}$$

$$\Delta S^{\circ}_{r} = \{[(2)(240.06)] - [(2)(210.76) + (205.14)]\} \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta S^{\circ}_{r} = -146.54 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Because both ΔH°_{r} and ΔS°_{r} are negative, the reaction is spontaneous at relatively low temperatures (up to 779 K), but above this temperature it is nonspontaneous.

Stage 3: 3 NO₂(g) + H₂O(l)
$$\longrightarrow$$
 2 HNO₃(aq) +NO(g)
 $\Delta H^{\circ}_{r} = \Delta H^{\circ}_{f}$ (products) $-\Delta H^{\circ}_{f}$ (reactants)
 $\Delta H^{\circ}_{r} = [(2)(-207.36 \text{ kJ} \cdot \text{mol}^{-1}) + (90.25 \text{ kJ} \cdot \text{mol}^{-1})] -$

$$[(3)(33.18 \text{ kJ} \cdot \text{mol}^{-1}) + (-285.83 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$\Delta H^{\circ}_{r} = -138.18 \text{ kJ} \cdot \text{mol}^{-1}$$

$$H_{2}O_{2} + 2 H^{+} + 2 e^{-} \longrightarrow 2 H_{2}O$$

$$\Delta S^{\circ}_{r} = [(2)(146.4) + (210.76)] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$-[(3)(240.06) + (69.91)] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta S^{\circ}_{r} = -286.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The reaction is spontaneous up to 482 K; above this temperature it is nonspontaneous.

15.66 (a)
$$2 \text{ KClO}_3(s) \xrightarrow{\text{MnO}_2, 70^\circ - 100^\circ \text{C}} 2 \text{ KCl}(s) + 3 \text{ O}_2(g)$$

This is a redox reaction that is used for the laboratory preparation of $O_2(g)$. It illustrates the mild instability of chlorates at higher temperatures. Cl is reduced and O is oxidized.

(b)
$$CaF_2(s) + 2 H_2SO_4(conc) \longrightarrow Ca(HSO_4)_2(aq) + 2 HF(g)$$

This is a Brønsted acid-base reaction. H⁺ is the acid and F⁻ is the base.

(c) $OF_2(g) + 2 OH^-(aq) \longrightarrow O_2(g) + 2 F^-(aq) + H_2O(l)$ This is a redox reaction. O in $OF_2(N_{ox} = +2)$ is reduced, O in $OH^-(N_{ox} = -2)$ is oxidized.

(d)
$$2 H_2S(g) + 3 O_2(g) \longrightarrow 2 SO_2(g) + 2 H_2O(l)$$

This is a redox reaction that illustrates the reducing ability of H_2S . This reaction is one of the principal sources of SO_2 in the atmosphere. S(-2) is oxidized and O (zero) is reduced.

15.68 (a)
$$SCl_2(l) + 2 C_2H_4 \rightarrow S(C_2H_4Cl)_2$$

(b) The S atom in mustard gas is sp^3 hybridized.

(c) Step 1:
$$SCl_2 + C_2H_4 \rightarrow Cl-S-CH_2CH_2Cl$$

Step 2: Cl–S–CH₂CH₂Cl + C₂H₄ \Rightarrow ClCH₂CH₂–S–CH₂CH₂Cl One plausible scenario is that a lone pair of electrons on the sulfur atom adds into the π^* orbital on ethene. This will leave a vacant p-orbital on the adjacent carbon atom, which can then act as an acceptor toward a chlorine atom. As the C—Cl bond is formed, the S—Cl bond would be broken. This process could then be repeated for the other lone pair on sulfur with another molecule of ethene.

(b)
$$I_2O_5$$
 $O = I = O$

15.72 (a)
$$[Cl^{-}] = \left(\frac{2.798 \text{ g AgCl}}{0.05000 \text{ L}}\right) \left(\frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}}\right) \left(\frac{1 \text{ mol Cl}^{-}}{1 \text{ mol AgCl}}\right)$$

= 0.3904 mol·L⁻¹

(b) AgF is soluble; therefore this method cannot be used for the determination of F⁻ ions in solution.

AX₅E, square pyramidal

15.76 The method of organization is determined by whether one wishes to emphasize similarities or differences. It seems easier and more logical to emphasize similarities rather than differences. Trends within groups from top to bottom tend to be quantitative (small numerical differences), rather than qualitative (large numerical differences leading to distinctly different behavior), as are observed from left to right within a period. Trends from metallic to nonmetallic behavior across a period would be more apparent in the organization by period, as would the related trends in ionization energy and electron affinity. One could also more readily see changes in valence as represented, say, by the formulas of common compounds, such as the oxides and chlorides. Trends in melting points and boiling points of the elements and their compounds would also be more apparent, as well as many other physical properties. So, there are advantages and disadvantages to both methods of organization. Organization by group still seems preferable, as organization by period would not permit the

generalizations and summaries that are useful features of the present arrangement.

15.78 (a) (1)
$$4 \operatorname{Zn}(s) + 6 \operatorname{H}_2O(1) + \operatorname{NO}_3(aq) \rightarrow$$

$$NH_3(aq) + 9 OH^-(aq) + 4 Zn^{2+}(aq)$$

(2)
$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$$

(3)
$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

(b) number of moles of unreacted HCl =
$$0.028\ 22\ L \times 0.00150\ mol \cdot L^{-1}$$

= $4.23\ \times 10^{-5}\ mol$

total number of moles of

$$HC1 = 0.050\ 00\ L \times 0.00250\ mol \cdot L^{-1} = 1.25 \times 10^{-4}\ mol$$

moles of HCl reacted = moles of NH
$$_3$$

= $(1.25 \times 10^{-4} \text{mol} - 4.23 \times 10^{-5} \text{mol})$

$$= 8.3 \times 10^{-5} \text{ mol NH}_3$$

$$[NO_3^-] = \frac{\left(8.3 \times 10^{-5} \,\text{mol NH}_3\right) \left(\frac{1 \,\text{mol NO}_3^-}{1 \,\text{mol NH}_3}\right)}{0.025 \,00 \,L} = 0.33 \times 10^{-3} \,\text{mol} \cdot L^{-1}$$

15.80 (a) The system is:

Concentration $(mol \cdot L^{-1})$	$I_2(s) +$	$I^{-}(aq) \rightleftharpoons$	$I_3^-(aq)$
initial		0.50	0
change		-x	+ x
equilibrium		0.50 - x	x

The equilibrium constant is given by:

$$K = 698 = \frac{x}{0.50 - x} \text{ and}$$
$$x = 0.50$$

The concentration of I₃ (aq) at equilibrium is, therefore, 0.50 M

(b) The mass of I₂(s) consumed during the reaction is:

$$(0.50 \text{ M})(0.250 \text{ L})(126.90 \text{ g} \cdot \text{mol}^{-1}) = 16 \text{ g}$$

The amount of $I_2(s)$ remaining after equilibrium is reached is:
 $35.0 \text{ g} - 16 \text{ g} = 19 \text{ g}$

- 15.82 The ionic radii of the halide ions increase down the group. The smaller the ion, the greater the lattice enthalpy of the compounds of the ion due to the greater concentration of the charge in the ion. Increased lattice enthalpy results in higher melting and boiling points; the ions cannot as easily break free from each other. Thus, melting and boiling points decrease from fluoride to iodide for ionic halides. The predominant forces between covalent halogen compounds are London forces, which are greater for larger atoms. Thus, the melting and boiling points increase from fluoride to iodide for molecular halides.
- **15.84** The balanced chemical equation is:

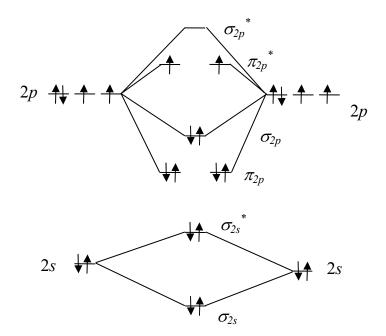
$$2 K_2MnF_6 + 4 SbF_5 \rightarrow 4 KSbF_6 + 2 MnF_3 + F_2$$

The amount, in moles, of F_2 produced is found by:

$$\frac{125 \text{ g K}_2 \text{MnF}_6}{247.14 \text{ g} \cdot \text{mol}^{-1}} \left(\frac{1 \text{ mol } F_2}{2 \text{ mol K}_2 \text{MnF}_6} \right) = 0.253 \text{ mol } F_2$$

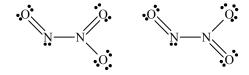
The volume of this amount of fluorine gas is:

$$V = \frac{nRT}{P} = \frac{(0.253 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{1 \text{ atm}}$$
$$= 6.18 \text{ L}$$



The O—O bond order is 2 (eight electrons in bonding orbitals and four electrons in antibonding orbitals). O_2 is paramagnetic with two unpaired electrons.

- (b) The paramagnetism of O_2 is not explained by its Lewis structure, although the Lewis structure does predict the correct bond order.
- (c) The highest occupied molecular orbital is antibonding.
- (d) The superoxide ion has one more electron than $\rm O_2$. This electron will populate an antibonding orbital, reducing the bond order to 1.5. The ion will remain paramagnetic but will have only one unpaired electron. The peroxide ion places another electron in an antibonding orbital. The bond order will be 1 and the ion will diamagnetic.
- **15.88** (a) The Lewis structure of N_2O_3 has two resonance forms:



- (b) The N—N bond order is 1.
- (c) Because of its small size, N can readily form multiple bonds to other atoms. This is not as easy for P and consequently it prefers a structure with only single bonds.
- **15.90** (a) The unit cell is hexagonal.
 - (b) There are ten Ca^{2+} ions and six PO_4^{3-} ions in the unit cell.
 - (c) Two Ca²⁺ ions lie completely within the unit cell plus 16 Ca²⁺ ions lying on the cell faces (1/2 is in the cell for a total of eight ions in the cell). The six phosphate ions lie completely within the unit cell.
 - (d) The X⁻ ions are not shown.
- 15.92 Ion-ion forces are among the strongest intermolecular interactions.

 Therefore, the interactions in (a) are the strongest shown. Hydrogen bonding is stronger than a dipole-dipole interaction indicating that the interactions in (c) are stronger than those shown in (d).