6.88 $\Delta H^{\circ}_{rxn} = \Delta H^{\circ}_f \, O_2(g) + \Delta H^{\circ}_f \, O(g) - \Delta H^{\circ}_f \, O_3(g)$

$\Delta H^{\circ}_{rxn} = 0 + 247.5 \text{ kJ} - 142.3 \text{ kJ} = +105.2 \text{ kJ}$

$$\frac{105.2 \text{ kJ}}{\text{mol } O_3} \times \frac{1 \text{ mol } O_3}{6.022 \times 10^{23} \text{ molecules}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = \frac{1.747 \times 10^{-19} \text{ J}}{O_3 \text{ molecule}}$$

$$\Delta E = hc/\lambda; \; \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.998 \times 10^8 \text{ m/s}}{1.747 \times 10^{-19} \text{ J}} = 1.137 \times 10^{-6} \text{ m}$$

Radiation with this wavelength is in the infrared portion of the spectrum. (Clearly, processes other than simple photodissociation cause O_3 to absorb ultraviolet radiation.)

6.90   (a)   Each oxide ion, O^{2-}, carries a 2- charge. Each metal oxide is a neutral compound, so the metal ion or ions must adopt a total positive charge equal to the total negative charge of the oxide ions in the compound. The table below lists the electron configuration of the neutral metal atom, the positive charge of each metal ion in the oxide, and the corresponding electron configuration of the metal ion.

   i.   K: $[Ar] 4s^1$ 1+   [Ar]
   ii.   Ca: $[Ar] 4s^2$ 2+   [Ar]
   iii. Sc: $[Ar] 4s^2 3d^1$ 3+   [Ar]
   iv. Ti: $[Ar] 4s^2 3d^2$ 4+   [Ar]
   v.   V: $[Ar] 4s^2 3d^3$ 5+   [Ar]
   vi. Cr: $[Ar] 4s^1 3d^5$ 6+   [Ar]

Each metal atom loses all (valence) electrons beyond the Ar core configuration. In K_2O, Sc_2O_3 and V_2O_5, where the metal ions have odd charges, two metal ions are required to produce a neutral oxide.

(b)   i. potassium oxide   ii. calcium oxide   iii. scandium(III) oxide

iv. titanium (IV) oxide   v. vanadium (V) oxide   vi. chromium(VI) oxide

(Roman numerals are required to specify the charges on the transition metal ions, because more than one stable ion may exist.)

(c)   Recall that $\Delta H^{\circ}_f = 0$ for elements in their standard states. In these reactions, M(s) and $H_2(g)$ are elements in their standard states.
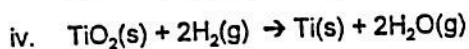
   i. $K_2O(s) + H_2(g) \rightarrow 2K(s) + H_2O(g)$
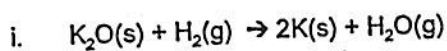
     $\Delta H^{\circ} = \Delta H^{\circ}_f \, H_2O(g) + 2\Delta H^{\circ}_f \cdot K(s) - \Delta H \, K_2O(s) - \Delta H^{\circ}_f \, H_2(g)$

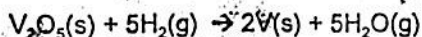 $\Delta H^{\circ} = -241.82 \text{ kJ} + 2(0) - (-363.2 \text{ kJ}) - 0 = 121.4 \text{ kJ}$

   ii. $CaO(s) + H_2(g) \rightarrow Ca(s) + H_2O(g)$
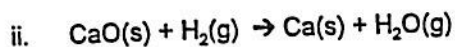
     $\Delta H^{\circ} = \Delta H^{\circ}_f \, H_2O(g) + \Delta H^{\circ}_f \, Ca(s) - \Delta H^{\circ}_f \, CaO(s) - \Delta H^{\circ}_f \, H_2(g)$

     $\Delta H^{\circ} = -241.82 \text{ kJ} + 0 - (-635.1 \text{ kJ}) - 0 = 393.3 \text{ kJ}$

   iv. $TiO_2(s) + 2H_2(g) \rightarrow Ti(s) + 2H_2O(g)$

     $\Delta H^{\circ} = 2\Delta H^{\circ}_f \, H_2O(g) + \Delta H^{\circ}_f \, Ti(s) - \Delta H^{\circ}_f \, TiO_2(s) - 2\Delta H^{\circ}_f \, H_2(g)$

     $= 2(-241.82) + 0 - (-938.7) - 2(0) = 455.1 \text{ kJ}$

$$V_2O_5(s) + 5H_2(g) \rightarrow 2V(s) + 5H_2O(g)$$

$$\Delta H^\circ = 5\Delta H_f^\circ \, H_2O(g) + 2\Delta H_f^\circ \, V(s) - \Delta H_f^\circ \, V_2O_5(s) - 5\Delta H_f^\circ \, H_2(g)$$

$$= 5(-241.82) + 2(0) - (-1550.6) - 5(0) = 341.5 \text{ kJ}$$

(d) ΔH_f° becomes more negative moving from left to right across this row of the periodic chart. Since Sc lies between Ca and Ti, the median of the two ΔH_f° values is approximately -785 kJ/mol. However, the trend is clearly not linear. Dividing the ΔH_f° values by the positive charge on the pertinent metal ion produces the values -363, -318, -235 and -310. The value between Ca^{2+} (-318) and Ti^{4+} (-235) is Sc^{3+} (-277). Multiplying (-277) by 3, a value of approximately -830 kJ results. A reasonable range of values for ΔH_f° of $Sc_2O_3(s)$ is then -785 to -830 kJ/mol.

7.1 Mendeleev insisted that elements with similar chemical and physical properties be placed within a family or column of the table. Since many elements were as yet undiscovered, Mendeleev left blanks. He predicted properties for the "blanks" based on properties of other elements in the family.

7.2 (a) The verification of the existence of many new elements by accurately measuring their atomic weights spurred interest in a classification scheme. Mendeleev (and Meyer) noted that certain chemical and physical properties recur periodically when the elements are arranged by increasing atomic weight. The accurate atomic weights provided a common property on which to base a classification scheme of the elements.

(b) Moseley realized that the characteristic X-ray frequencies emitted by each element were related to a unique integer that he assigned to each element. We now know this integer as the atomic number, the number of protons in the nucleus of an atom. In general, atomic weight increases as atomic number increases, but there are a few exceptions. If elements are arranged by increasing atomic number, a few seeming contradictions in the Mendelev table (the positions of Ar and K or Te and I) are eliminated.

7.4 (a) Electrostatic attraction for the nucleus lowers the energy of an electron, while electron-electron repulsions increase this energy. The concept of effective nuclear charge allows us to model this increase in the energy of an electron as a smaller net attraction to a nucleus with a smaller positive charge, Z_{eff}.

(b) In Be (or any element), the 1s electrons are not shielded by any core electrons, so they experience a much greater Z_{eff} than the 2s electrons.

7.5 *Analyze/Plan.* The problem states that shielding, S, is exactly equal to the number of electrons in the core. $Z_{eff} = Z - \#$ of core electrons. *Solve:*

(a) K: 19 - 18 = +1   (b) Br: 35 - 28 = +7

7.8 Mg < P < K < Ti < Rh. The shielding of electrons in the $n = 3$ shell by 1s and 2s core electrons in these elements is approximately equal, so the effective nuclear charge increases as Z increases.

7.14 (a) The estimated distances in the table below are the sum of the radii of the group 5A elements and H from Table 7.5.

bonded atoms	estimated distance	measured distance
P – H	1.43	1.419
As – H	1.56	1.519
Sb – H	1.75	1.707

In general, the estimated distances are a bit longer than the measured distances. This probably shows a systematic bias in either the estimated radii or in the method of obtaining the measured values.

(b) The principle quantum number of the outer electrons and thus the average distance of these electrons from the nucleus increases from P ($n = 3$) to As ($n = 4$) to Sb ($n = 5$). This causes the systematic increase in M–H distance.

7.16 (a) The vertical difference in radius is due to a change in principle quantum number of the outer electrons. The horizontal difference in radius is due to the change in electrostatic attraction between the outer electron and a nucleus with one more or one fewer proton. Adding or subtracting a proton has a much smaller radius effect than moving from one principle quantum level to the next.

(b) S < Si < Se < Ge. This order is predicted by the trends in increasing atomic radius moving to the left in a row and down a column of the periodic chart, assuming that changes moving down a column are larger [see part (a)]. That is, the order above assumes that the change from S to Se is larger than the change from S to Si. This order is confirmed by the values in Figure 7.5.

7.19 (a) Electrostatic repulsions are reduced by removing an electron from a neutral atom, Z_{eff} increases, and the cation is smaller.

(b) The additional electrostatic repulsion produced by adding an electron to a neutral atom causes the electron cloud to expand, so that the radius of the anion is larger than the radius of the neutral atom.

(c) Going down a column, the n value of the valence electrons increases and they are further from the nucleus. Thus, the size of particles with like charge increases.

7.20 (a) As Z stays constant and the number of electrons increases, the electron-electron repulsions increase, the electrons spread apart and the ions become larger. $I^- > I > I^+$

(b) Going down a column, the increasing average distance of the outer electrons from the nucleus causes the size of particles with like charge to increase. $Ca^{2+} > Mg^{2+} > Be^{2+}$

(c) Fe: $[Ar]4s^23d^6$; Fe^{2+}: $[Ar]3d^6$; Fe^{3+}: $[Ar]3d^5$. The 4s valence electrons in Fe are on average further from the nucleus than the 3d electrons, so Fe is larger than Fe^{2+}. Since there are five 3d orbitals, in Fe^{2+} at least one orbital must contain a pair of electrons. Removing one electron to form Fe^{3+} significantly reduces repulsion, increasing the nuclear charge experienced by each of the other d electrons and decreasing the size of the ion. $Fe > Fe^{2+} > Fe^{3+}$

7.23 (a) An isoelectronic series is a group of atoms or ions that have the same number of electrons, and thus the same electron configuration.

(b) (i) Cl^- : Ar (ii) Se^{2-} : Kr (iii) Mg^{2+} : Ne

7.27 *Plan.* Use relative location on periodic chart and trends in ionic radii to establish the order.

Solve: (a) $Se < Se^{2-} < Te^{2-}$ (b) $Co^{3+} < Fe^{3+} < Fe^{2+}$ (c) $Ti^{4+} < Sc^{3+} < Ca$ (d) $Be^{2+} < Na^+ < Ne$

7.28 (a) Cl^- is larger than Cl because the increase in electron repulsions that accompany addition of an electron cause the electron cloud to expand.

(b) S^{2-} is larger than O^{2-}, because for particles with like charges, size increases going down a family.

(c) K^+ is larger than Ca^{2+} because the two ions are isoelectronic and K^+ has the larger Z.

7.30 (a) $Ga(g) \rightarrow Ga^+(g) + 1e^-$; $Ga^+(g) \rightarrow Ga^{2+}(g) + 1e^-$ (b) $Rh^{3+}(g) \rightarrow Rh^{4+}(g) + 1e^-$

7.32 (a) The effective nuclear charges of Li and Na are similar, but the outer electron in Li has a smaller n-value and is closer to the nucleus than the outer electron in Na. More energy is needed to overcome the greater attraction of the Li electron for the nucleus.

(b) Sc: $[Ar] 4s^2 3d^1$; Ti: $[Ar] 4s^2 3d^2$. The fourth ionization of titanium involves removing a 4s outer electron, while the fourth ionization of Sc requires removing a 3p electron from the [Ar] core. The effective nuclear charges experienced by the two 4s electrons in Ti are much more similar than the effective nuclear charges of a 4s outer electron

and a 3p core electron in Sc. Thus, the difference between the third and fourth ionization energies of Sc is much larger.

(c) The electron configuration of Li^+ is $1s^2$ or [He] and that of Be^+ is $[He]2s^1$. Be^+ has one more valence electron to lose while Li^+ has the stable noble gas configuration of He. It requires much more energy to remove a 1s core electron close to the nucleus of Li^+ than a 2s valence electron further from the nucleus of Be^+.

7.33 (a) In general, the smaller the atom, the larger its first ionization energy.

(b) According to Figure 7.10, He has the largest and Cs the smallest first ionization energy of the nonradioactive elements.

7.37 *Plan.* Follow the logic of Sample Exercise 7.7. *Solve:*

(a) Sb^{3+}: $[Kr]5s^2 4d^{10}$ (b) Ga^+: $[Ar]4s^2 3d^{10}$ (c) P^{3-}: $[Ne]3s^2 3p^6$ or [Ar]

(d) Cr^{3+}: $[Ar]3d^3$ (e) Zn^{2+}: $[Ar]3d^{10}$ (f) Ag^+: $[Kr]4d^{10}$

7.38 (a) Mn^{3+} $[Ar]3d^4$ (b) Se^{2-} $[Ar]4s^2 3d^{10}4p^6 = [Kr]$, noble-gas configuration

(c) Sc^{3+}: [Ar], noble-gas configuration (d) Ru^{2+}: $[Kr]4d^6$

(e) Tl^+: $[Xe]6s^2 4f^{14} 5d^{10}$ (f) Au^+: $[Xe]4f^{14} 5d^{10}$

7.45 The smaller the first ionization energy of an element, the greater the metallic character of that element.

7.46 P < Sb < Ag. P is a nonmetal, Sb is a metalloid and Ag is a metal. We expect that electrical conductivity increases as metallic character increases. Since metallic character increases going down a column and to the left in a row, the order of increasing electrical conductivity is as shown above.

7.49 Analyze/Plan. Ionic compounds are formed by combining a metal and a nonmetal; molecular compounds are formed by two or more nonmetals. *Solve:*

Ionic: MgO, Li_2O, Y_2O_3; molecular: SO_2, P_2O_5, N_2O, XeO_3

7.52 The more **nonmetallic** the central atom, the more acidic the oxide. In order of increasing acidity: $CaO < Al_2O_3 < SiO_2 < CO_2 < P_2O_5 < SO_3$

7.54 (a) $K_2O(s) + H_2O(l) \rightarrow 2KOH(aq)$

(b) $P_2O_3(s) + 3H_2O(l) \rightarrow 2H_3PO_3(aq)$

(c) $Cr_2O_3(s) + 6HCl(aq) \rightarrow 2CrCl_3(aq) + 3H_2O(l)$

(d) $SeO_2(s) + 2KOH(aq) \rightarrow K_2SeO_3(aq) + H_2O(l)$

7.56 (a) Rb: [Kr] $5s^1$, r = 2.11 Å   Ag: [Kr] $5s^14d^{10}$, r = 1.53 Å

The electron configurations both have a [Kr] core and a single 5s electron; Ag has a completed 4d subshell as well. The radii are very different because the 5s electron in Ag experiences a much greater effective nuclear charge. Ag has a much larger Z (47 vs. 37), and although the 4d electrons in Ag shield the 5s electron somewhat, the increased shielding does not compensate for the large increase in Z.

(b) Ag is much less reactive (less likely to lose an electron) because its 5s electron experiences a much larger effective nuclear charge and is more difficult to remove.

7.58 (a) Cs is much more reactive than Li toward H_2O because its valence electron is less tightly held (greater n value), and Cs is more easily oxidized.

(b) The purple flame indicates that the metal is potassium (see Figure 7.22).

(c) $K_2O_2(s)$ + $H_2O(l)$ → $H_2O_2(aq)$ + $K_2O(aq)$
potassium peroxide   hydrogen peroxide

7.59 (a) $2K(s) + Cl_2(g)$ → $2KCl(s)$

(b) $SrO(s) + H_2O(l)$ → $Sr(OH)_2(aq)$

(c) $4Li(s) + O_2(g)$ → $2Li_2O(s)$

(d) $2Na(s) + S(l)$ → $Na_2S(s)$

7.60 (a) $2K(s) + 2H_2O(l)$ → $2KOH(aq) + H_2(g)$

(b) $Ba(s) + 2H_2O(l)$ → $Ba(OH)_2(aq) + H_2(g)$

(c) $6Li(s) + N_2(g)$ → $2Li_3N(s)$

(d) $2Mg(s) + O_2(g)$ → $2MgO(s)$

7.65 Under ambient conditions, the Group 8A elements are all gases that are extremely unreactive, owing to their stable core electron configurations. Thus, the name "inert gases" seemed appropriate.

In the 1960s, scientists discovered that Xe, which has the lowest ionization energy of the nonradioactive Noble gases, would react with substances having a strong tendency to remove electrons, such as PtF_6 or F_2. Thus, the term "inert" no longer described all the Group 8A elements. (Kr also reacts with F_2, but reactions of Ar, Ne and He are as yet unknown.)

7.70 (a) $S(s) + 2F_2(g)$ → $SF_4(g)$

(b) O_2, oxygen; O_3, ozone

(c) Fluorine can remove electrons from silica glass (SiO_2) according to the reaction $SiO_2(s) + 2F_2(g)$ → $SiF_4(g) + O_2(g)$. Thus, fluorine gas would "dissolve" the glass container. This process is also known as etching.