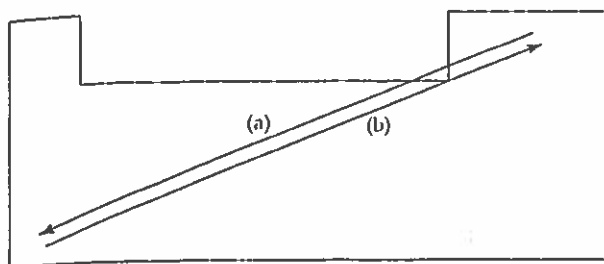


7 Periodic Properties of the Elements

Visualizing Concepts

- 7.1 (a) The light bulb itself represents the nucleus of the atom. The brighter the bulb, the more nuclear charge the electron "sees." A frosted glass lampshade between the bulb and our eyes reduces the brightness of the bulb. The shade is analogous to core electrons in the atom shielding outer electrons (our eyes) from the full nuclear charge (the bare light bulb).
- (b) Increasing the wattage of the light bulb mimics moving right along a row of the periodic table. The brighter bulb inside the same shade is analogous to having more protons in the nucleus while the core electron configuration doesn't change.
- (c) Moving down a family, both the nuclear charge and the core electron configuration change. To simulate the addition of core electrons farther from the nucleus, we would add larger frosted glass shades; to simulate the increase in Z , we would increase the wattage of the bulb. In our analogy, the brightness of the light should decrease, because the increased distance of the observer from the bulb and the additional frosted shades more than compensate for the increase in bulb wattage. This mimics the actual decrease in attraction of a valence electron for the nucleus as we move down a column. (Note that Z_{eff} does increase slightly going down a column, but this property is more than offset by the increased distance of valence electrons from the nucleus.)
- 7.2 The larger 1.80 \AA radius is the so-called *nonbonding* or *van der Waals* radius of a sulfur atom. This is the estimated radius of a sulfur atom involved in a nonbonding (elastic, billiard ball-like) collision with another atom. The smaller 1.02 \AA radius is the *bonding* atomic radius of a sulfur atom. A bonding radius is always smaller (shorter) than a nonbonding radius, because bonding is an attractive interaction that brings atoms closer together than they would be in a nonbonding interaction.
- 7.3 (a) The bonding atomic radius of A, r_A , is $d_1/2$. The distance d_2 is the sum of the bonding atomic radii of A and X, $r_A + r_X$. Since we know that $r_A = d_1/2$, $d_2 = r_X + d_1/2$, $r_X = d_2 - d_1/2$.
- (b) The length of the X-X bond is $2r_X$.
- $$2r_X = 2(d_2 - d_1/2) = 2d_2 - d_1.$$

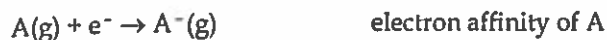
7.4



Lines (a) and (b) coincide, but their directions are opposite. Line (a) goes from upper right to lower left, and line (b) from lower left to upper right.

- (c) From the diagram, we observe that the trends in bonding atomic radius (size) and ionization energy are opposite each other. As bonding atomic radius increases, ionization energy decreases, and vice versa.

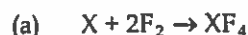
7.5



The energy change for the reaction is the ionization energy of A plus the electron affinity of A.

This process is endothermic for both nonmetals and metals. Considering data for Cl and Na from Figures 7.9 and 7.11, the endothermic ionization energy term dominates the exothermic electron affinity term, even for Cl which has the most exothermic electron affinity listed.

7.6



- (b) If X is a nonmetal, XF_4 is a molecular compound. If X is a metal, XF_4 is ionic. For an ionic compound with this formula, X would have a charge of 4+, and a much smaller bonding atomic radius than F^- . X in the diagram has about the same bonding radius as F, so it is likely to be a nonmetal.

Periodic Table; Effective Nuclear Charge (sections 7.1 and 7.2)

7.7

The number of columns in the various blocks of the periodic chart corresponds to the maximum number of electrons that can occupy the various kinds of atomic orbitals: 2 columns on the left for 2 electrons in s orbitals, 10 columns in the transition metals for 10 electrons in d orbitals, 6 columns on the right for 6 electrons in p orbitals, 14-member rows below for 14 electrons in f orbitals. The order of blocks corresponds to the filling order of atomic orbitals, and the row number corresponds to the principal quantum number of the valence electrons of elements in that row, $ns, np, (n-1)d, (n-2)f$.

7.8

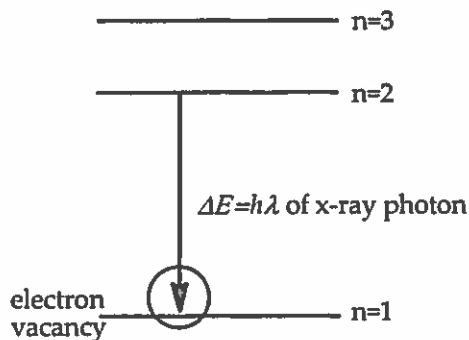
Assuming *eka-* means one place below or under, *eka-manganese* on Figure 7.1 is technetium, Tc.

7.9

According to Figure 7.1, the first elements to be discovered, those known since ancient times, were Fe, Cu, Ag, Au, Hg, Sn, Pb, C and S. These elements are present in nature in elemental form; they can be observed directly and their isolation does not require chemical processing. In general, elements are discovered according to their ease of isolation in elemental form. This depends on chemical properties rather than relative abundance.

7 Periodic Properties of the Elements Solutions to Exercises

- 7.10 (a) Moseley bombarded metal targets with high-energy electrons. These impinging electrons knock out core electrons from metal atoms in the target, creating an electron vacancy or hole. Outer, higher energy electrons in the metal atoms then "drop down" into the lower energy hole. Energy in the form of X-rays is emitted when atomic electrons move from a higher energy to a lower energy state.



- (b) The main determining factor of physical and especially chemical properties is electron configuration. For electrically neutral elements, the number of electrons equals the number of protons, which in turn is the atomic number of an element. Atomic weight is related to mass number, protons plus neutrons. The number of neutrons in its nucleus does influence the mass of an atom, but mass is a minor or non-factor in determining properties.
- 7.11 (a) *Effective nuclear charge, Z_{eff}* , is a representation of the average electrical field experienced by a single electron. It is the average environment created by the nucleus and the other electrons in the molecule, expressed as a net positive charge at the nucleus. It is approximately the nuclear charge, Z , minus the number of core electrons.
- (b) Going from left to right across a period, nuclear charge increases while the number of electrons in the core is constant. This results in an increase in Z_{eff} .
- 7.12 (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.
- 7.13 (a) *Analyze/Plan.* $Z_{\text{eff}} = Z - S$. Find the atomic number, Z , of Na and K. Write their electron configurations and count the number of core electrons. Assume S = number of core electrons.
- Solve.* Na: $Z = 11$; $[\text{Ne}]3s^1$. In the Ne core there are 10 electrons. $Z_{\text{eff}} = 11 - 10 = 1$.
 K: $Z = 19$; $[\text{Ar}]4s^1$. In the Ar core there are 18 electrons. $Z_{\text{eff}} = 19 - 18 = 1$.
- (b) *Analyze/Plan.* $Z_{\text{eff}} = Z - S$. Write the complete electron configuration for each element to show counting for Slater's rules. $S = 0.35$ (# of electrons with same n) + 0.85 (# of electrons with $(n-1)$) + 1 (# of electrons with $(n-2)$).

Solve. Na: $1s^2 2s^2 2p^6 3s^1$. $S = 0.35(0) + 0.85(8) + 1(2) = 8.8$. $Z_{\text{eff}} = 11 - 8.8 = 2.2$

K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. $S = 0.35(0) + 0.85(8) + 1(10) = 16.8$. $Z_{\text{eff}} = 19 - 16.8 = 2.2$

- (c) For both Na and K, the two values of Z_{eff} are 1.0 and 2.2. The Slater value of 2.2 is closer to the values of 2.51 (Na) and 3.49 (K) obtained from detailed calculations.
- (d) Both approximations, 'core electrons 100% effective' and Slater, yield the same value of Z_{eff} for Na and K. Neither approximation accounts for the gradual increase in Z_{eff} moving down a group.
- (e) Following the trend from detailed calculations, we predict a Z_{eff} value of approximately 4.5 for Rb.
- 7.14 Follow the method in the preceding question to calculate Z_{eff} values.
- (a) Si: $Z = 14$; $[\text{Ne}]3s^2 3p^2$. 10 electrons in the Ne core. $Z_{\text{eff}} = 14 - 10 = 4$
 Cl: $Z = 17$; $[\text{Ne}]3s^2 3p^5$. 10 electrons in the Ne core. $Z_{\text{eff}} = 17 - 10 = 7$
- (b) Si: $1s^2 2s^2 2p^6 3s^2 3p^2$. $S = 0.35(3) + 0.85(8) + 1(2) = 9.85$. $Z_{\text{eff}} = 14 - 9.85 = 4.15$
 Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$. $S = 0.35(6) + 0.85(8) + 1(2) = 10.90$. $Z_{\text{eff}} = 17 - 10.90 = 6.10$
- (c) The Slater values of 4.15 (Si) and 6.10 (Cl) are closer to the results of detailed calculations, 4.29 (Si) and 6.12 (Cl).
- (d) The Slater method of approximation more closely approximates the gradual increase in Z_{eff} moving across a row. The 'core 100%-effective' approximation underestimates Z_{eff} for Si but overestimates it for Cl. Slater values are closer to detailed calculations, and a better indication of the change in Z_{eff} moving from Si to Cl.
- (e) Relative to Si, P has one more proton ($Z + 1$) and one more 3p electron ($S + 0.35$), so it is reasonable to predict $Z_{\text{eff}} + 0.65$. That is, Z_{eff} for P will be $(4.15 + 0.65) = 4.80$.
- 7.15 Krypton has a larger nuclear charge ($Z = 36$) than argon ($Z = 18$). The shielding of electrons in the $n = 3$ shell by the 1s, 2s and 2p core electrons in the two atoms is approximately equal, so the $n = 3$ electrons in Kr experience a greater effective nuclear charge and are thus situated closer to the nucleus.
- 7.16 $\text{Mg} < \text{P} < \text{K} < \text{Ti} < \text{Rh}$. The shielding of electrons in the $n = 3$ shell by 1s, 2s and 2p core electrons in these elements is approximately equal, so the effective nuclear charge increases as Z increases.

Atomic and Ionic Radii (section 7.3)

- 7.17 (a) Atomic radii are determined by measuring distances between nuclei (interatomic distances) in various bonding and nonbonding situations.
- (b) Bonding radii are calculated from the internuclear separation of two atoms joined by a chemical bond. Nonbonding radii are calculated from the internuclear separation between two gaseous atoms that collide and move apart, but do not bond.
- (c) For a given element, the nonbonding radius is always larger than the bonding radius. When a chemical bond forms, electron clouds of the two atoms

7 Periodic Properties of the Elements Solutions to Exercises

interpenetrate, bringing the two nuclei closer together and resulting in a smaller bonding atomic radius (Figure 7.5).

- (d) If a free atom reacts to become part of a covalent molecule, the atom gets smaller; its radius changes from nonbonding to bonding.
- 7.18 (a) Since the quantum mechanical description of the atom does not specify the exact location of electrons, there is no specific distance from the nucleus where the last electron can be found. Rather, the electron density decreases gradually as the distance from the nucleus increases. There is no quantum mechanical "edge" of an atom.
- (b) When nonbonded atoms touch, it is their electron clouds that interact. These interactions are primarily repulsive because of the negative charges of electrons. Thus, the size of the electron clouds determines the nuclear approach distance of nonbonded atoms.
- 7.19 (a) The atomic (*metallic*) radius of W is the interatomic W-W distance divided by 2, $2.74 \text{ \AA} / 2 = 1.37 \text{ \AA}$.
- (b) Under high pressure, we expect atoms in a pure substance to move closer together. That is, the distance between W atoms will decrease.
- 7.20 The distance between Si atoms in solid silicon is two times the bonding atomic radius from Figure 7.6. The Si-Si distance is $2 \times 1.11 \text{ \AA} = 2.22 \text{ \AA}$.
- The C-C distance in diamond is 1.54 \AA (from Section 7.3; from Figure 7.6, $2 \times 0.77 \text{ \AA} = 1.54 \text{ \AA}$). We expect the Si-Si distance to be greater, because the bonding (valence) electrons in Si are in the $n=3$ shell, while those in C are in the $n=2$ shell.
- 7.21 From bonding atomic radii in Figure 7.6, $\text{As-I} = 1.19 \text{ \AA} + 1.33 \text{ \AA} = 2.52 \text{ \AA}$. This is very close to the experimental value of 2.55 \AA in AsI_3 .
- 7.22 $\text{Bi-I} = 2.81 \text{ \AA} = r_{\text{Bi}} + r_{\text{I}}$. From Figure 7.6, $r_{\text{I}} = 1.33 \text{ \AA}$.
- $$r_{\text{Bi}} = [\text{Bi-I}] - r_{\text{I}} = 2.81 \text{ \AA} - 1.33 \text{ \AA} = 1.48 \text{ \AA}$$
- 7.23 (a) Atomic radii decrease moving from left to right across a row and (b) increase from top to bottom within a group.
- (c) $\text{O} < \text{Si} < \text{Ge} < \text{I}$. The order for the first three atoms is unambiguous according to the trends of increasing atomic radius moving down a column and to the left in a row of the table. Moving from Ge to I, radius increases moving down but decreases moving right. It is usually true that a change in row number, which involves a change in principal quantum number of valence electrons, is a larger effect than a horizontal change across a row. This is verified by values for the atomic radii of Ge and I on Figure 7.6.
- 7.24 (a) The vertical difference in radius is due to a change in principal quantum number of the valence electrons. The horizontal difference in radius is due to the change in electrostatic attraction between an 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 principal quantum level to the next.

- (b) $\text{Si} < \text{Al} < \text{Ge} < \text{Ga}$. 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 Si to Ge is larger than the change from Si to Al. This order is confirmed by the values in Figure 7.6.
- 7.25 *Plan.* Locate each element on the periodic chart and use trends in radii to predict their order. *Solve.*
- (a) $\text{Cs} > \text{K} > \text{Li}$ (b) $\text{Pb} > \text{Sn} > \text{Si}$ (c) $\text{N} > \text{O} > \text{F}$
- 7.26 (a) $\text{Na} < \text{Ca} < \text{Ba}$ (b) $\text{As} < \text{Sb} < \text{Sn}$
- (c) $\text{Be} < \text{Si} < \text{Al}$. This order assumes the increase in radius from the second to the third row is greater than the decrease moving right in the third row. Radii in Figure 7.6 confirm this assumption.
- 7.27 (a) False. Cations are smaller than their corresponding neutral atoms. Electrostatic repulsions are reduced by removing an electron from a neutral atom, Z_{eff} increases, and the cation is smaller.
- (b) True. [See (a) above.]
- (c) False. I^- is bigger than Cl^- . Going down a column, the n value of the valence electrons increases and they are farther from the nucleus. Valence electrons also experience greater shielding by core electrons. The greater radial extent of the valence electrons outweighs the increase in Z , and the size of particles with like charge increases.
- 7.28 (a) As Z stays constant and the number of electrons increases, the electron-electron repulsions increase, the electrons spread apart, and the anion becomes larger. The reverse is true for the cation, which becomes smaller than the neutral atom.
- $\text{I}^- > \text{I} > \text{I}^+$
- (b) For cations with the same charge, ionic radii increase going down a column because there is an increase in the principle quantum number and the average distance from the nucleus of the outer electrons.
- $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Be}^{2+}$
- (c) Fe: $[\text{Ar}]4s^23d^6$; Fe^{2+} : $[\text{Ar}]3d^6$; Fe^{3+} : $[\text{Ar}]3d^5$. The 4s valence electrons in Fe are on average farther 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. $\text{Fe} > \text{Fe}^{2+} > \text{Fe}^{3+}$
- 7.29 The size of the red sphere decreases on reaction, so it loses one or more electrons and becomes a cation. Metals lose electrons when reacting with nonmetals, so the red sphere represents a metal. The size of the blue sphere increases on reaction, so it gains one or more electrons and becomes an anion. Nonmetals gain electrons when reacting with metals, so the blue sphere represents a nonmetal.
- 7.30 The order of radii is $\text{Br}^- > \text{Br} > \text{F}$, so the largest brown sphere is Br^- , the intermediate blue one is Br, and the smallest red one is F.

7 Periodic Properties of the Elements Solutions to Exercises

- 7.31 (a) An isoelectronic series is a group of atoms or ions that have the same number of electrons.
- (b) Ga^{3+} : Ni; Zr^{4+} : Kr; Mn^{7+} : Ar; I: Xe; Pb^{2+} : Hg
- 7.32 (a) Cl^- , K^+ (b) Mn^{2+} , Fe^{3+} (c) Sn^{2+} , Sb^{3+}
- 7.33 (a) Cl^- : Ar (b) Sc^{3+} : Ar
- (c) Fe^{2+} : $[\text{Ar}]3d^6$. Fe^{2+} has 24 electrons. Neutral Cr has 24 electrons, $[\text{Ar}]4s^13d^5$. Because transition metals fill the s subshell first but also lose s electrons first when they form ions, many transition metal ions do not have neutral atoms with the same electron configuration.
- (d) Zn^{2+} : $[\text{Ar}]3d^{10}$; no neutral atom with same configuration [same reason as (c)].
- (e) Sn^{4+} : $[\text{Kr}]4d^{10}$; no neutral atom with same electron configuration [same reason as (c)], but Sn^{4+} does have the same configuration as Cd^{2+} .
- 7.34 (a) *Analyze/Plan.* Follow the logic in Sample Exercise 7.4.
Solve. Na^+ is smaller. Since F^- and Na^+ are isoelectronic, the ion with the larger nuclear charge, Na^+ , has the smaller radius.
- (b) *Analyze/Plan.* The electron configuration of the ions is $[\text{Ne}]$ or $[\text{He}]2s^22p^6$. The ions have either 10 core electrons or 2 core electrons. Apply Equation 7.1 to both cases and check the result.
Solve. F^- : $Z = 9$. For 10 core electrons, $Z_{\text{eff}} = 9 - 10 = -1$. While we might be able to interpret a negative value for Z_{eff} , positive values will be easier to compare; we will assume a He core of 2 electrons.
 F^- , $Z = 9$. $Z_{\text{eff}} = 9 - 2 = 7$. Na^+ : $Z_{\text{eff}} = 11 - 2 = 9$
- (c) *Analyze/Plan.* The electron of interest has $n = 2$. There are 7 other $n = 2$ electrons, and two $n = 1$ electrons.
Solve. $S = 0.35(7) + 0.85(2) + 1(0) = 4.15$
 F^- : $Z_{\text{eff}} = 9 - 4.15 = 4.85$. Na^+ : $Z_{\text{eff}} = 11 - 4.15 = 6.85$
- (d) For isoelectronic ions (without d electrons), the electron configurations and therefore shielding values (S) are the same. Only the nuclear charge changes. So, as nuclear charge (Z) increases, effective nuclear charge (Z_{eff}) increases and ionic radius decreases.
- 7.35 (a) K^+ (larger Z) is smaller.
- (b) Cl^- and K^+ : $[\text{Ne}]3s^23p^6$. 10 core electrons
 Cl^- , $Z = 17$. $Z_{\text{eff}} = 17 - 10 = 7$
 K^+ , $Z = 19$. $Z_{\text{eff}} = 19 - 10 = 9$
- (c) Valence electron, $n = 3$; 7 other $n = 3$ electrons; eight $n = 2$ electrons; two $n = 1$ electrons. $S = 0.35(7) + 0.85(8) + 1(2) = 11.25$
 Cl^- : $Z_{\text{eff}} = 17 - 11.25 = 5.75$. K^+ : $Z_{\text{eff}} = 19 - 11.25 = 7.75$
- (d) For isoelectronic ions (without d electrons), the electron configurations and therefore shielding values (S) are the same. Only the nuclear charge changes. So, as nuclear charge (Z) increases, effective nuclear charge (Z_{eff}) increases and ionic radius decreases.

7 Periodic Properties of the Elements Solutions to Exercises

7.36 *Analyze/Plan.* Use relative location on periodic chart and trends in atomic and ionic radii to establish the order.



(c) Even though K has the largest Z value, the n -value of the outer electron is larger than the n -value of valence electrons in S and Cl so K atoms are largest. When the 4s electron is removed, K^+ is isoelectronic with Cl^- and S^{2-} . The larger Z value causes the 3p electrons in K^+ to experience the largest effective nuclear charge and K^+ is the smallest ion.

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

7.38 Make a table of $d(\text{measured})$, $d(\text{ionic radii})$, $d(\text{covalent radii})$, as well as differences between measured and estimated values. The estimated distances are just the sum of the various ionic radii from Figure 7.7 and covalent radii from Figure 7.6. All distances and differences are given in Å. Use these values to judge accuracy in parts (b) and (c).

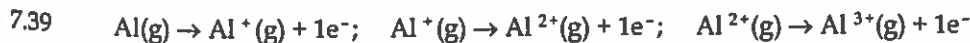
(a)

	$d(\text{meas})$	(a) $d(\text{ion})$	(b) $\Delta(\text{ion} - \text{meas})$	(c) $d(\text{cov})$	(c) $\Delta(\text{cov} - \text{meas})$
Li-F	2.01	2.09	0.08	2.05	0.04
Na-Cl	2.82	2.83	0.01	2.53	-0.29
K-Br	3.30	3.34	0.04	3.10	-0.20
Rb-I	3.67	3.72	0.05	3.44	-0.23

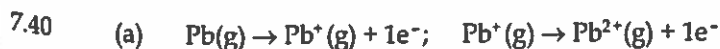
(b) The agreement between measured distances in specific ionic compounds and predicted distances based on ionic radii is not perfect. Differences for Na-Cl and K-Br are within the 0.04 Å experimental error, while those for Li-F and Rb-I are not. Ionic radii are averages compiled from distances in many ionic compounds containing the ion in question. The sum of these average radii may not give an exact match for the distance in any specific compound, but it will give good distance estimates for many ionic compounds. While ionic radii provide a good estimate of ion-ion distances, the estimates are not the same as experimental values.

(c) Distance estimates from bonding atomic radii are not as accurate as those from ionic radii, except for Li-F. This indicates that bonding in NaCl, KBr, and RbI is more accurately described as ionic, rather than covalent. The measured bond distance for LiF is midway between the two estimates, indicating that the bonding in LiF could have significant covalent character. The details of these two models will be discussed in Chapter 8.

Ionization Energies; Electron Affinities (sections 7.4 and 7.5)



The process for the first ionization energy requires the least amount of energy. When an electron is removed from an atom or ion, electrostatic repulsions are reduced, Z_{eff} increases, and the energy required to remove the next electron increases. This rationale is confirmed by the ionization energies listed in Table 7.2.



7 Periodic Properties of the Elements Solutions to Exercises

- (b) $\text{Zr}^{3+}(\text{g}) \rightarrow \text{Zr}^{4+}(\text{g}) + 1\text{e}^-$
- 7.41 (a) False. Ionization energies are always positive quantities.
- (b) False. F has a greater first ionization energy than O, because Z_{eff} for F is greater than Z_{eff} for O.
- (c) True.
- 7.42 (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: $[\text{Ar}] 4s^2 3d^1$; Ti: $[\text{Ar}] 4s^2 3d^2$. The fourth ionization of titanium involves removing a 3d valence electron, while the fourth ionization of Sc requires removing a 3p electron from the [Ar] core. The effective nuclear charges experienced by the two 3d electrons in Ti are much more similar than the effective nuclear charges of a 3d valence 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 $[\text{He}]2s^1$. 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 farther from the nucleus of Be^+ .
- 7.43 (a) In general, the smaller the atom, the larger its first ionization energy.
- (b) According to Figure 7.9, He has the largest and Cs the smallest first ionization energy of the nonradioactive elements.
- 7.44 (a) Moving from F to I in group 7A, first ionization energies decrease and atomic radii increase. The greater the atomic radius, the smaller the electrostatic attraction of an outer electron for the nucleus and the smaller the ionization energy of the element.
- (b) First ionization energies increase slightly going from K to Kr and atomic sizes decrease. As valence electrons are drawn closer to the nucleus (atom size decreases), it requires more energy to completely remove them from the atom (first ionization energy increases). Each trend has a discontinuity at Ga, owing to the increased shielding of the 4p electrons by the filled 3d subshell.
- 7.45 *Plan.* Use periodic trends in first ionization energy. *Solve.*
- (a) Cl (b) Ca (c) K (d) Ge (e) Sn
- 7.46 Greater distance of valence electrons from the nucleus predicts lower first ionization energy in all the pairs of elements below. Z_{eff} decreases moving left along a row, but increases slightly moving down column. These trends are not (solely) predictive of first ionization energy for the pairs of elements in this exercise.
- (a) Ba. Recall that transition metals like Ti lose *ns* electrons first when forming ions. The 6s valence electrons in Ba are farther from the nucleus and have a smaller first ionization energy than the 4s electrons of Ti.

- (b) Ag. Recall that transition elements lose *ns* electrons first when forming ions. The 5s valence electron of Ag is farther from the nucleus and has a lower first ionization energy than the 4s valence electron of Cu.
- (c) Ge. The 4p valence electrons in Ge have a smaller first ionization energy than the 3p valence electrons in Cl. Going from Cl to Ge, the decrease in Z_{eff} moving four places to the left may more than compensate for the small increase moving one place down. If so, the trends in Z_{eff} and distance of valence electrons from the nucleus cooperate to produce the (significantly) lower first ionization energy for Ge.
- (d) Pb. The 6p valence electrons in Pb are farther from the nucleus and have a smaller first ionization energy than the 5p valence electrons in Sb, despite the build-up in nuclear charge (Z) associated with filling the 4f subshell between Sb and Pb.
- 7.47 *Plan.* Follow the logic of Sample Exercise 7.7. *Solve.*
- (a) Fe^{2+} : $[\text{Ar}]3d^6$ (b) Hg^{2+} : $[\text{Xe}]4f^{14}5d^{10}$
- (c) Mn^{2+} : $[\text{Ar}]3d^5$ (d) Pt^{2+} : $[\text{Xe}]4f^{14}5d^8$
- (e) P^{3-} : $[\text{Ne}]3s^23p^6$
- 7.48 (a) Cr^{3+} : $[\text{Ar}]3d^3$
- (b) N^{3-} : $[\text{He}]2s^22p^6 = [\text{Ne}]$, noble-gas configuration
- (c) Sc^{3+} : $[\text{Ar}]$, noble-gas configuration (d) Cu^{2+} : $[\text{Ar}]3d^9$
- (e) Tl^+ : $[\text{Xe}]6s^24f^{14}5d^{10}$ (f) Au^+ : $[\text{Xe}]4f^{14}5d^{10}$
- 7.49 *Plan.* Focus on transition metals, which have d electrons in their outer shell. Use Figure 7.14 to find representative oxidation states for transition metals. Note that, by definition, metals lose electrons to form positive ions.
- Solve.* Elements in group 10 and beyond have at least 8 d electrons. Of these, the group 10 metals all form 2+ ions with the electron configuration nd^8 . Of the elements in groups 11 and 12, only Au adopts a sufficiently high positive charge to form an ion with the configuration nd^8 . (Other possibilities not listed on Figure 7.14 exist.)
- Ni^{2+} : $[\text{Ar}]3d^8$; Pd^{2+} : $[\text{Kr}]4d^8$; Pt^{2+} : $[\text{Xe}]4f^{14}5d^8$; Au^{3+} : $[\text{Xe}]4f^{14}5d^8$
- 7.50 The 2+ ions of group 8 metals and the 3+ ions of group 9 metals have the electrons configuration nd^6 . (Other possibilities not listed on Figure 7.14 exist.)
- Fe^{2+} : $[\text{Ar}]3d^6$; Ru^{2+} : $[\text{Kr}]4d^6$; Os^{2+} : $[\text{Xe}]6s^24f^{14}5d^6$
- Co^{3+} : $[\text{Ar}]3d^6$; Rh^{3+} : $[\text{Kr}]4d^6$; Ir^{3+} : $[\text{Xe}]6s^24f^{14}5d^6$
- 7.51 *Analyze/Plan.* Consider the definitions of ionization energy, electron affinity and the electron configuration of Ar. *Solve.*
- (a) Argon is a noble gas, with a very stable core electron configuration. This causes the element to resist chemical change. Positive, endothermic, values for ionization energy and electron affinity mean that energy is required to either remove or add electrons. Valence electrons in Ar experience the largest Z_{eff} of any

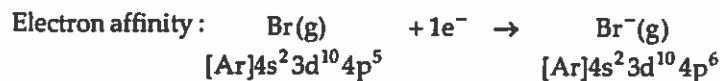
7 Periodic Properties of the Elements Solutions to Exercises

element in the third row, because the nuclear buildup is not accompanied by an increase in screening. This results in a large, positive ionization energy. When an electron is added to Ar, the $n = 3$ electrons become core electrons which screen the extra electrons so effectively that Ar^- has a higher energy than an Ar atom and a free electron. This results in a large positive electron affinity.

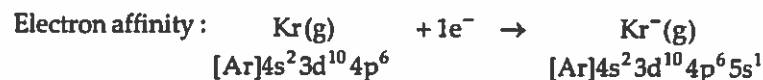
(b) The units of electron affinity are kJ/mol.

7.52 No. The process described by electron affinity can be written as: $\text{A} + 1e^- \rightarrow \text{A}^-$. If ΔE for this process is negative, it means that the energy of A^- is lower than the total energy of A plus the energy of a free electron. If electron affinity is negative, the entity that is lower in energy, or more stable, is the added electron. An electron in an atom or ion is stabilized by its attraction for the atomic nucleus and is lower in energy than a free electron.

7.53 *Analyze/Plan.* Consider the definitions of ionization energy and electron affinity, along with pertinent electron configurations. *Solve.*



When a Br atom gains an electron, the Br^- ion adopts the stable electron configuration of Kr. Since the electron is added to the same 4p subshell as other outer electrons, it experiences essentially the same attraction for the nucleus. Thus, the energy of the Br^- ion is lower than the total energy of a Br atom and an isolated electron, and electron affinity is negative.



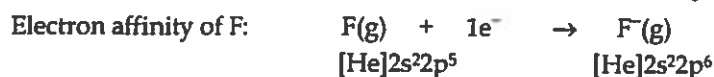
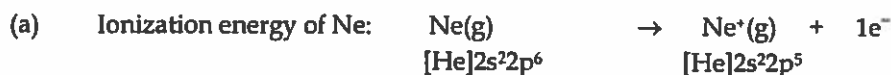
Energy is required to add an electron to a Kr atom; Kr^- has a higher energy than the isolated Kr atom and free electron. In Kr^- the added electron would have to occupy the higher energy 5s orbital; a 5s electron is farther from the nucleus and effectively shielded by the spherical Kr core and is not stabilized by the nucleus.

7.54 Ionization energy of F^- : $\text{F}^-(\text{g}) \rightarrow \text{F}(\text{g}) + 1e^-$

Electron affinity of F: $\text{F}(\text{g}) + 1e^- \rightarrow \text{F}^-(\text{g})$

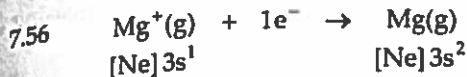
The two processes are the reverse of each other. The energies are equal in magnitude but opposite in sign. $I_1(\text{F}^-) = -E(\text{F})$

7.55 *Analyze/Plan.* Consider the definitions of ionization energy and electron affinity, along with the appropriate electron configurations. *Solve.*



(b) The I_1 of Ne is positive, while E_1 of F is negative. All ionization energies are positive.

- (c) One process is apparently the reverse of the other, with one important difference. The Z (and Z_{eff}) for Ne is greater than Z (and Z_{eff}) for F^- . So we expect $I_1(\text{Ne})$ to be somewhat greater in magnitude and opposite in sign to $E_1(F)$. [Repulsion effects approximately cancel; repulsion decrease upon I_1 causes smaller positive value; repulsion increase upon E_1 causes smaller negative value.]



This process is the reverse of the first ionization of Mg. The magnitude of the energy change for this process is the same as the magnitude of the first ionization energy of Mg, 738 kJ/mol.

Properties of Metals and Nonmetals (section 7.6)

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

7.58 The first ionization energies are: Ag, 731 kJ/mol; Mn, 717 kJ/mol. According to Figure 7.12, we define metallic character as showing the opposite trend as ionization energy. That is, the smaller the ionization energy, the greater the metallic character. Since Mn has the smaller ionization energy, it should have the greater metallic character. (It is difficult to predict the relative metallic character of these two elements from trends. Ag is one row lower but four columns further right than Mn; these are opposing trend directions.)

- 7.59 *Analyze/Plan.* Use Figure 7.12, "Metals, metalloids and nonmetals", and Figure 7.14, "Representative oxidation states of the elements", to inform our discussion.

Solve. Agree. An element that commonly forms a cation is a metal. The only exception to this statement shown on Figure 7.14 is antimony, Sb, a metalloid which commonly forms cations. Although Sb is a metalloid, it is far down (in the fifth row) on the chart and likely to have significant metallic character.

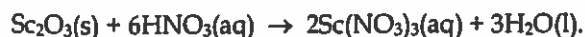
- 7.60 Disagree. According to Figure 7.14, both Sb and Te are metalloids and commonly form ions. Sb forms cations and Te forms anions.

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

Ionic: SnO_2 , Al_2O_3 , Li_2O , Fe_2O_3 ; molecular: CO_2 , H_2O

Sn, Al, Li and Fe are metals; C and H are nonmetals.

- 7.62 Follow the logic in Sample Exercise 7.8. Scandium is a metal, so we expect Sc_2O_3 to be ionic. Metal oxides are usually basic and react with acid to form a salt and water. We choose $\text{HNO}_3(\text{aq})$ as the acid for our equation.



The net ionic equation is:



7 Periodic Properties of the Elements Solutions to Exercises

- 7.63 (a) When dissolved in water, an "acidic oxide" produces an acidic ($\text{pH} < 7$) solution. A "basic oxide" dissolved in water produces a basic ($\text{pH} > 7$) solution.
- (b) Oxides of nonmetals are acidic. Example: $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$. Oxides of metals are basic. Example: CaO (quick lime). $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq})$.
- 7.64 The more nonmetallic the central atom, the more acidic the oxide. In order of increasing acidity: $\text{CaO} < \text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{CO}_2 < \text{P}_2\text{O}_5 < \text{SO}_3$
- 7.65 *Analyze/Plan.* Cl_2O_7 is a molecular compound formed by two nonmetallic elements. More specifically, it is a nonmetallic oxide and acidic. *Solve.*
- (a) Dichlorineheptoxide
- (b) Elemental chlorine and oxygen are diatomic gases.

$$2\text{Cl}_2(\text{g}) + 7\text{O}_2(\text{g}) \rightarrow 2\text{Cl}_2\text{O}_7(\text{l})$$
- (c) Most nonmetallic oxides we have seen, such as CO_2 and SO_3 , are gases. However, oxides with more atoms, such as $\text{P}_2\text{O}_3(\text{l})$ and $\text{P}_2\text{O}_5(\text{s})$, exist in other states. A boiling point of 81°C is not totally unexpected for a large molecule like Cl_2O_7 .
- (d) Cl_2O_7 is an acidic oxide, so it will be more reactive to base, OH^- .

$$\text{Cl}_2\text{O}_7(\text{l}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{ClO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
- (e) The oxidation state of Cl in Cl_2O_7 is +7. In this oxidation state, the electron configuration of Cl is $[\text{He}]2s^22p^6$ or $[\text{Ne}]$.
- 7.66 (a) $\text{XCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{XO}_2(\text{s}) + 4\text{HCl}(\text{g})$
 The second product is $\text{HCl}(\text{g})$.
- (b) If X were a metal, both the oxide and the chloride would be high melting solids. If X were a nonmetal, XO_2 would be a nonmetallic, molecular oxide and probably gaseous, like CO_2 , NO_2 , and SO_2 . Neither of these statements describes the properties of XO_2 and XCl_4 , so X is probably a metalloid.
- (c) Use the *Handbook of Chemistry* to find formulas and melting points of oxides, and formulas and boiling points of chlorides of selected metalloids.

metalloid	formula of oxide	m.p. of oxide	formula of chloride	b.p. of chloride
boron	B_2O_3	460°C	BCl_3	12°C
silicon	SiO_2	$\sim 1700^\circ\text{C}$	SiCl_4	58°C
germanium	GeO GeO_2	710°C $\sim 1100^\circ\text{C}$	GeCl_2 GeCl_4	decomposes 84°C
arsenic	As_2O_3 As_2O_5	315°C 315°C	AsCl_3	132°C

Boron, arsenic, and, by analogy, antimony, do not fit the description of X, because the formulas of their oxides and chlorides are wrong. Silicon and germanium, in the same family, have oxides and chlorides with appropriate formulas. Both SiO_2 and GeO_2 melt above 1000°C , but the boiling point of SiCl_4 is much closer to that of XCl_4 . Element X is silicon.

- 7.67 (a) $\text{BaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ba(OH)}_2\text{(aq)}$
 (b) $\text{FeO(s)} + 2\text{HClO}_4\text{(aq)} \rightarrow \text{Fe(ClO}_4)_2\text{(aq)} + \text{H}_2\text{O(l)}$
 (c) $\text{SO}_3\text{(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_4\text{(aq)}$
 (d) $\text{CO}_2\text{(g)} + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{CO}_3\text{(aq)} + \text{H}_2\text{O(l)}$
- 7.68 (a) $\text{K}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightarrow 2\text{KOH(aq)}$
 (b) $\text{P}_2\text{O}_3\text{(l)} + 3\text{H}_2\text{O(l)} \rightarrow 2\text{H}_3\text{PO}_3\text{(aq)}$
 (c) $\text{Cr}_2\text{O}_3\text{(s)} + 6\text{HCl(aq)} \rightarrow 2\text{CrCl}_3\text{(aq)} + 3\text{H}_2\text{O(l)}$
 (d) $\text{SeO}_2\text{(s)} + 2\text{KOH(aq)} \rightarrow \text{K}_2\text{SeO}_3\text{(aq)} + \text{H}_2\text{O(l)}$

Group Trends in Metals and Nonmetals (sections 7.7 and 7.8)

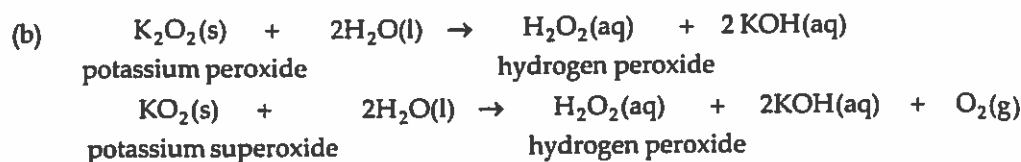
7.69 Yes, the reactivity of a metal correlates with its first ionization energy. Since metals lose electrons when they form ions, the less energy required for this process, the more reactive the metal. However, we usually observe reactivity of metals in the solid state and ionization energy is a gas phase property, so there are differences between the two properties.

7.70 Rb: $[\text{Kr}]5s^1$, $r = 2.11 \text{ \AA}$ Ag: $[\text{Kr}]5s^1 4d^{10}$, $r = 1.53 \text{ \AA}$

The electron configurations both have a [Kr] core and a single 5s electron; Ag has a completed 4d subshell as well. The smaller radius of Ag indicates that the 5s electron in Ag experiences a much greater effective nuclear charge than the 5s electron in Rb. 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. 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.

- 7.71 (a) Ca and Mg are both metals; they tend to lose electrons and form cations when they react. Ca is more reactive because it has a lower ionization energy than Mg. The Ca valence electrons in the 4s orbital are less tightly held because they are farther from the nucleus than the 3s valence electrons of Mg.
- (b) K and Ca are both metals; they tend to lose electrons and form cations when they react. K is more reactive because it has the lower first ionization energy. The 4s valence electron in K is less tightly held because it has the same n value as the valence electrons of Ca and experiences smaller Z and Z_{eff} .
- 7.72 (a) All alkali metals except Li form metal peroxides when they react with oxygen; the formation of a peroxide (or a superoxide) eliminates Li. The lilac-purple flame indicates that the metal is potassium (see Figure 7.21).

7 Periodic Properties of the Elements Solutions to Exercises



Both potassium peroxide and potassium superoxide react with water to form hydrogen peroxide. The white solid could be either potassium salt.

- 7.73 (a) $2\text{K}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{KCl}(\text{s})$
 (b) $\text{SrO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Sr}(\text{OH})_2(\text{aq})$
 (c) $4\text{Li}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Li}_2\text{O}(\text{s})$
 (d) $2\text{Na}(\text{s}) + \text{S}(\text{l}) \rightarrow \text{Na}_2\text{S}(\text{s})$
- 7.74 (a) $2\text{Cs}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{CsOH}(\text{aq}) + \text{H}_2(\text{g})$
 (b) $\text{Sr}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Sr}(\text{OH})_2(\text{aq}) + \text{H}_2(\text{g})$
 (c) $2\text{Na}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{Na}_2\text{O}_2(\text{s})$ (See Equation [7.20].)
 (d) $\text{Ca}(\text{s}) + \text{I}_2(\text{s}) \rightarrow \text{CaI}_2(\text{s})$
- 7.75 (a) The reactions of the alkali metals with hydrogen and with a halogen are redox reactions. In both classes of reaction, the alkali metal loses electrons and is oxidized. Both hydrogen and the halogen gain electrons and are reduced. The product is an ionic solid, where either hydride ion, H^- , or a halide ion, X^- , is the anion and the alkali metal is the cation.
- (b) $\text{Ca}(\text{s}) + \text{F}_2(\text{g}) \rightarrow \text{CaF}_2(\text{s})$ $\text{Ca}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{CaH}_2(\text{s})$
 Both products are ionic solids containing Ca^{2+} and the corresponding anion in a 1:2 ratio.
- 7.76 Metallic hydrogen, in the form of an extended solid, will be much more like the other alkali metals, which are also extended solids. "Normal" gaseous hydrogen has a smaller atomic radius and larger first ionization energy than trends would predict for the first member of the alkali metals. Metallic hydrogen would have a larger atomic radius and smaller first ionization energy than "normal" hydrogen. Owing to its smaller first ionization energy, metallic hydrogen will be more reactive than "normal" hydrogen.
- 7.77
- | <u>Br</u> | <u>Cl</u> |
|--|--|
| (a) $[\text{Ar}]4\text{s}^24\text{p}^5$ | (a) $[\text{Ne}]3\text{s}^23\text{p}^5$ |
| (b) -1 | (b) -1 |
| (c) 1140 kJ/mol | (c) 1251 kJ/mol |
| (d) reacts slowly to form $\text{HBr} + \text{HOBr}$ | (d) reacts slowly to form $\text{HCl} + \text{HOCl}$ |
| (e) -325 kJ/mol | (e) -349 kJ/mol |
| (f) 1.14 Å | (f) 0.99 Å |

The $n = 4$ valence electrons in Br are farther from the nucleus and less tightly held than the $n = 3$ valence electrons in Cl. Therefore, the ionization energy of Cl is greater, the electron affinity is more negative and the atomic radius is smaller.

7.78 *Plan.* Predict the physical and chemical properties of At based on the trends in properties in the halogen (7A) family. *Solve.*

- (a) F, at the top of the column, is a diatomic gas; I, immediately above At, is a diatomic solid; the melting points of the halogens increase going down the column. At is likely to be a diatomic solid at room temperature.
- (b) Like the other halogens, we expect it to be a nonmetal. According to Figure 7.12, there are no metalloids in row 6 of the periodic table, and At is a nonmetal. (Looking forward to Chapter 8, the most likely way for At to satisfy the octet rule is for it to gain an electron to form At^- , which makes it a nonmetal.)
- (c) All halogens form ionic compounds with Na; they have the generic formula NaX . The compound formed by At will have the formula NaAt .

7.79 (a) The term "inert" was dropped because it no longer described all the group 8A elements.

(b) In the 1960s, scientists discovered that Xe would react with substances such as F_2 and PtF_6 that have a strong tendency to remove electrons. Thus, Xe could not be categorized as an "inert" gas.

(c) The group is now called the noble gases.

7.80 (a) Xe has a lower ionization energy than Ne. The valence electrons in Xe are much farther from the nucleus than those of Ne ($n = 5$ vs $n = 2$) and much less tightly held by the nucleus; they are more "willing" to be shared than those in Ne. Also, Xe has empty 5d orbitals that can help to accommodate the bonding pairs of electrons, while Ne has all its valence orbitals filled.

(b) In the CRC Handbook of Chemistry and Physics, 79th Edition, Xe - F bond distances in gas phase molecules are listed as: XeF_2 , 1.977 Å; XeF_4 , 1.94 Å; XeF_6 , 1.89 Å. From Figure 7.6, the sum of atomic radii for Xe and F is $(1.30 \text{ Å} + 0.71 \text{ Å}) = 2.01 \text{ Å}$. Bond lengths in specific compounds are not exactly equal to the sum of estimated atomic radii. Physical state, electronic and steric factors affect bond lengths in specific compounds.

7.81 (a) $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$

(b) $\text{Xe}(\text{g}) + \text{F}_2(\text{g}) \rightarrow \text{XeF}_2(\text{g})$

$\text{Xe}(\text{g}) + 2\text{F}_2(\text{g}) \rightarrow \text{XeF}_4(\text{s})$

$\text{Xe}(\text{g}) + 3\text{F}_2(\text{g}) \rightarrow \text{XeF}_6(\text{s})$

(c) $\text{S}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{H}_2\text{S}(\text{g})$

(d) $2\text{F}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{HF}(\text{aq}) + \text{O}_2(\text{g})$

7.82 (a) $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl}(\text{aq}) + \text{HOCl}(\text{aq})$

(b) $\text{Ba}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{BaH}_2(\text{s})$

(c) $2\text{Li}(\text{s}) + \text{S}(\text{s}) \rightarrow \text{Li}_2\text{S}(\text{s})$

(d) $\text{Mg}(\text{s}) + \text{F}_2(\text{g}) \rightarrow \text{MgF}_2(\text{s})$

Additional Exercises

- 7.83 Up to $Z = 82$, there are three instances where atomic weights are reversed relative to atomic numbers: Ar and K; Co and Ni; Te and I.
- In each case, the most abundant isotope of the element with the larger atomic number (Z) has one more proton, but fewer neutrons than the element with the smaller atomic number. The smaller number of neutrons causes the element with the larger Z to have a smaller than expected atomic weight.
- 7.84 (a) $2s$
- (b) Slater's rules provide a method for calculating the shielding, S , and Z_{eff} experienced by a particular electron in an atom. Slater assigns a shielding value of 0.35 to electrons with the same n -value, assuming that s and p electrons shield each other to the same extent. However, since s electrons have a finite probability of being very close to the nucleus (Figure 7.3), they shield p electrons more than p electrons shield them. To account for this difference, assign a slightly larger shielding value to s electrons and a slightly smaller shielding value to the p electrons. This will produce a slightly greater S and smaller Z_{eff} for p electrons than for s electrons with the same n -value.
- 7.85 (a) P: $[\text{Ne}]3s^23p^3$. $Z_{\text{eff}} = Z - S = 15 - 10 = 5$.
- (b) Four other $n = 3$ electrons, eight $n = 2$ electrons, two $n = 1$ electron. $S = 0.35(4) + 0.85(8) + 1(2) = 10.2$. $Z_{\text{eff}} = Z - S = 15 - 10.2 = 4.8$. The approximation in (a) and Slater's rules give very similar values for Z_{eff} .
- (c) The $3s$ electrons penetrate the $[\text{Ne}]$ core electrons (by analogy to Figure 7.3) and experience less shielding than the $3p$ electrons. That is, S is greater for $3p$ electrons, owing to the penetration of the $3s$ electrons, so $Z - S$ ($3p$) is less than $Z - S$ ($3s$).
- (d) The $3p$ electrons are the outermost electrons; they experience a smaller Z_{eff} than $3s$ electrons and thus a smaller attraction for the nucleus, given equal n -values. The first electron lost is a $3p$ electron. Each $3p$ orbital holds one electron, so there is no preference as to which $3p$ electron will be lost.
- 7.86 If two protons were able to form a bond, they would have to overcome the electrostatic repulsion of like-charged particles. This situation occurs in atomic nuclei, where protons (and neutrons) are so close together that the strong nuclear force overcomes electrostatic repulsion. If two "bare" protons were able to bond, the bond length would be on the order of the size of atomic nuclei, 10^{-15} m.
- 7.87 Atomic size (bonding atomic radius) is strongly correlated to Z_{eff} , which is determined by Z and S . Moving across the representative elements, electrons added to ns or np valence orbitals do not effectively screen each other. The increase in Z is not accompanied by a similar increase in S ; Z_{eff} increases and atomic size decreases. Moving across the transition elements, electrons are added to $(n-1)d$ orbitals and become part of the core electrons, which do significantly screen the ns valence electrons. The increase in Z is accompanied by a larger increase in S for the ns valence electrons; Z_{eff} increases more slowly and atomic size decreases more slowly.

- 7.88 (a) The estimated distances in the table below are the sum of the radii of the group 5A elements and H from Figure 7.6.

<u>bonded atoms</u>	<u>estimated distance</u>	<u>measured distance</u>
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. (Recall that the radii in Figure 7.6 come from measuring many different molecules for each element, not just the bonds listed in this exercise.)

- (b) The principal 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.
- 7.89 (a) The most common oxidation state of the chalcogens is -2 , while that of the halogens is -1 . Adding one extra electron to a neutral halogen atom fills its valence p orbitals. Adding two extra electrons to a neutral chalcogen atom fills its valence p orbitals.
- (b) The family listed has the larger value of the stated property.
- atomic radii, chalcogens
ionic radii of the most common oxidation state, chalcogens
first ionization energy, halogens
second ionization energy, halogens

- 7.90 Y: $[\text{Kr}]5s^24d^1$, $Z = 39$ Zr: $[\text{Kr}]5s^24d^2$, $Z = 40$
La: $[\text{Xe}]6s^25d^1$, $Z = 57$ Hf: $[\text{Xe}]6s^24f^{14}5d^2$, $Z = 72$

The completed 4f subshell in Hf leads to a much larger change in Z going from Zr to Hf ($72 - 40 = 32$) than in going from Y to La ($57 - 39 = 18$). The 4f electrons in Hf do not completely shield the valence electrons, so there is also a larger increase in Z_{eff} . This larger increase in Z_{eff} going from Zr to Hf leads to a smaller increase in atomic radius than in going from Y to La.

- 7.91 (a) Co^{4+} is smaller.
- (b) Co^{4+} , $0.67 \text{ \AA} < \text{Co}^{3+}$, $0.75 \text{ \AA} < \text{Li}^+$, 0.90 \AA
Values from WebElements©, CN 6, high spin (for comparing equivalent ion environments)
- (c) As Li^+ ions are inserted, smaller Co^{4+} ions are reduced to larger Co^{3+} ions and the lithium cobalt electrode will expand.
- (d) "Sodium cobalt oxide" will probably not work as an electrode material, because Na^+ ions are much larger than Li^+ ions, which are larger than Co^{4+} and Co^{3+} ions. Na^+ ions would be too large to insert into the electrode without disrupting the structure of the material.

- (e) An alternative metal for a sodium version of the electrode would have redox-active ions with larger ionic radii than the Co^{4+} and Co^{3+} ions. Moving left along the fourth row of the periodic table, $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ ion couples are possibilities. Both have radii larger than $\text{Co}^{4+}/\text{Co}^{3+}$ ions. Mn^{3+} is more redox-active than Fe^{3+} and may be a more effective electrode material.



- (b) Assume that the corners of the cube are at the centers of the outermost O^{2-} ions, and that the edges each pass through the center of one Sr^{2+} ion. The length of an edge is then $r(\text{O}^{2-}) + 2r(\text{Sr}^{2+}) + r(\text{O}^{2-}) = 2r(\text{O}^{2-}) + 2r(\text{Sr}^{2+}) = 2(1.32 \text{ \AA}) + 2(1.26 \text{ \AA}) = 5.16 \text{ \AA}$.

- (c) Density is the ratio of mass to volume.

$$d = \frac{\text{mass SrO in cube}}{\text{vol cube}} = \frac{\# \text{ SrO units} \times \text{mass of SrO}}{\text{vol cube}}$$

Calculate the mass of 1 SrO unit in grams and the volume of the cube in cm^3 ; solve for number of SrO units.

$$\frac{103.62 \text{ g SrO}}{\text{mol}} \times \frac{1 \text{ mol SrO}}{6.022 \times 10^{23} \text{ SrO units}} = 1.7207 \times 10^{-22} = 1.721 \times 10^{-22} \text{ g/SrO unit}$$

$$V = (5.16)^3 \text{ \AA}^3 \times \frac{(1 \times 10^{-8})^3 \text{ cm}^3}{\text{ \AA}^3} = 1.3739 \times 10^{-22} = 1.37 \times 10^{-22} \text{ cm}^3$$

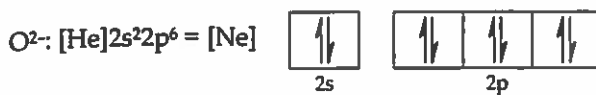
$$d = \frac{\# \text{ of SrO units} \times 1.7207 \times 10^{-22} \text{ g/SrO unit}}{1.3739 \times 10^{-22} \text{ cm}^3} = 5.10 \text{ g/cm}^3$$

$$\# \text{ of SrO units} = 5.10 \text{ g/cm}^3 \times \frac{1.3739 \times 10^{-22} \text{ cm}^3}{1.7207 \times 10^{-22} \text{ g/SrO unit}} = 4.07 \text{ units}$$

Since the number of formula units must be an integer, there are four SrO formula units in the cube. Using average values for ionic radii to estimate the edge length probably leads to the small discrepancy.

- 7.93 C: $1s^2 2s^2 2p^2$. I_1 through I_4 represent loss of the 2p and 2s electrons in the outer shell of the atom. The values of I_1 – I_4 increase as expected. The nuclear charge is constant, but removing each electron reduces repulsive interactions between the remaining electrons, so effective nuclear charge increases and ionization energy increases. I_5 and I_6 represent loss of the 1s core electrons. These 1s electrons are much closer to the nucleus and experience the full nuclear charge (they are not shielded), so the values of I_5 and I_6 are significantly greater than I_1 – I_4 . I_6 is larger than I_5 because all repulsive interactions have been eliminated.

- 7.94 Relative to elements in group 4A, Z_{eff} experienced by an electron added to a group 3A element is smaller, and electron affinity is less negative. Adding an electron to a neutral atom from group 5A requires pairing the electron in an already partially filled p orbital. The resulting electron-electron repulsion offsets some of the electrostatic attraction for the nucleus, and the electron affinity is not as negative as expected.



- (b) O^{3-} : $[\text{Ne}]3s^1$ The third electron would be added to the 3s orbital, which is farther from the nucleus and more strongly shielded by the $[\text{Ne}]$ core. The overall attraction of this 3s electron for the O nucleus is not large enough for O^{3-} to be a stable particle.

- 7.96 (a) P: $[\text{Ne}] 3s^23p^3$; S: $[\text{Ne}] 3s^23p^4$. In P, each 3p orbital contains a single electron, while in S one 3p orbital contains a pair of electrons. Removing an electron from S eliminates the need for electron pairing and reduces electrostatic repulsion, so the overall energy required to remove the electron is smaller than in P, even though Z is greater.

- (b) C: $[\text{He}] 2s^22p^2$; N: $[\text{He}] 2s^22p^3$; O: $[\text{He}] 2s^22p^4$. An electron added to a N atom must be paired in a relatively small 2p orbital, so the additional electron-electron repulsion more than compensates for the increase in Z and the electron affinity is smaller (less exothermic) than that of C. In an O atom, one 2p orbital already contains a pair of electrons, so the additional repulsion from an extra electron is offset by the increase in Z and the electron affinity is greater (more exothermic). Note from Figure 7.11 that the electron affinity of O is only slightly more exothermic than that of C, although the value of Z has increased by 2.

- (c) O^+ : $[\text{He}] 2s^22p^3$; O^{2+} : $[\text{He}] 2s^22p^2$; F: $[\text{He}] 2s^22p^5$; F^+ : $[\text{He}] 2s^22p^4$. Both 'core-only' [$Z_{\text{eff}}(\text{F}) = 7$; $Z_{\text{eff}}(\text{O}^+) = 6$] and Slater [$Z_{\text{eff}}(\text{F}) = 5.2$; $Z_{\text{eff}}(\text{O}^+) = 4.9$] predict that F has a greater Z_{eff} than O^+ . Variation in Z_{eff} does not offer a satisfactory explanation. The decrease in electron-electron repulsion going from F to F^+ energetically favors ionization and causes it to be less endothermic than the second ionization of O, where there is no significant decrease in repulsion.

- (d) Mn^{2+} : $[\text{Ar}]3d^5$; Mn^{3+} : $[\text{Ar}] 3d^4$; Cr^{2+} : $[\text{Ar}] 3d^4$; Cr^{3+} : $[\text{Ar}] 3d^3$; Fe^{2+} : $[\text{Ar}] 3d^6$; Fe^{3+} : $[\text{Ar}] 3d^5$. The third ionization energy of Mn is expected to be larger than that of Cr because of the larger Z value of Mn. The third ionization energy of Fe is less than that of Mn because going from $3d^6$ to $3d^5$ reduces electron repulsions, making the process less endothermic than predicted by nuclear charge arguments.

- 7.97 (a) The group 2B metals have complete $(n-1)d$ subshells. An additional electron would occupy an np subshell and be substantially shielded by both ns and $(n-1)d$ electrons. Overall this is not a lower energy state than the neutral atom and a free electron.

- (b) Valence electrons in Group 1B elements experience a relatively large effective nuclear charge due to the buildup in Z with the filling of the $(n-1)d$ subshell (and for Au, the 4f subshell.) Thus, the electron affinities are large and negative.

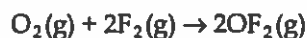
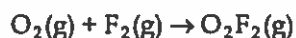
7 Periodic Properties of the Elements Solutions to Exercises

Group 1B elements are exceptions to the usual electron filling order and have the generic electron configuration $ns^1(n-1)d^{10}$. The additional electron would complete the ns subshell and experience repulsion with the other ns electron. Going down the group, size of the ns subshell increases and repulsion effects decrease. That is, effective nuclear charge is greater going down the group because it is less diminished by repulsion, and electron affinities become more negative.

- 7.98 (a) For both H and the alkali metals, the added electron will complete an ns subshell ($1s$ for H and ns for the alkali metals) so shielding and repulsion effects will be similar. For the halogens, the electron is added to an np subshell, so the energy change is likely to be quite different.
- (b) True. Only He has a smaller estimated "bonding" atomic radius, and no known compounds of He exist. The electron configuration of H is $1s^1$. The single $1s$ electron experiences no repulsion from other electrons and feels the full unshielded nuclear charge. It is held very close to the nucleus. The outer electrons of all other elements that form compounds are shielded by a spherical inner core of electrons and are less strongly attracted to the nucleus, resulting in larger bonding atomic radii.
- (c) Ionization is the process of removing an electron from an atom. For the alkali metals, the ns electron being removed is effectively shielded by the core electrons, so ionization energies are low. For the halogens, a significant increase in nuclear charge occurs as the np orbitals fill, and this is not offset by an increase in shielding. The relatively large effective nuclear charge experienced by np electrons of the halogens is similar to the unshielded nuclear charge experienced by the H $1s$ electron. Both H and the halogens have large ionization energies.
- (d) Ionization energy of hydride: $H^-(g) \rightarrow H(g) + 1e^-$
- (e) Electron affinity of hydrogen: $H(g) + 1e^- \rightarrow H^-(g)$

The two processes in parts (d) and (e) are the exact reverse of one another. The value for the ionization energy of hydride is equal in magnitude but opposite in sign to the electron affinity of hydrogen.

- 7.99 Since Xe reacts with F_2 , and O_2 has approximately the same ionization energy as Xe, O_2 will probably react with F_2 . Possible products would be O_2F_2 , analogous to XeF_2 , or OF_2 .



- 7.100 (a) $C > Si > Ge > Sn > Pb$. We know that Pb and Sn are metals, Ge and Si are metalloids and C is a nonmetal. For metals in the same family, such as the alkali metals, the lower the ionization energy, the more metallic and the lower melting. So, we guess that Pb has a lower melting point than Sn. For molecular nonmetals, such as the halogens, melting point usually increases as molecular weight increases. However, Ge, Si and C are not molecular nonmetals. (We will examine the details of bonding in these elements in Chapter 11.) By observation of physical properties, we know all three substances to be very hard solids,

considering C in the form of diamond. In fact, diamond is one of the hardest known substances. If melting point is related to hardness, then diamond will be the highest melting. Assume the melting points of the Si and Ge to decrease going down the family.

- (b) From WebElements©, the melting points in °C are:

C, 3500; Si, 1414; Ge, 938.3; Sn, 231.93; Pb, 327.46

We were correct that C is the highest melting, and that Si and Ge decrease going down the family. The melting points of the metals are indeed less than those of C and the metalloids. However, Sn is lowest melting, not Pb. Perhaps this has something to do with the increase in Z and Z_{eff} due to the filling of the f orbitals, which does not impact the properties of the alkali or alkaline earth metals. From Figure 7.9, we see that the ionization energy of Pb is greater than that of Sn, so its higher melting point is not too surprising.

- 7.101 (a) The pros are that Zn and Cd are in the same family, have the same electron configuration and thus similar chemical properties. The same can be said for Zn^{2+} and Cd^{2+} ions. Because of their chemical similarity, we expect Cd^{2+} to easily substitute for Zn^{2+} in flexible molecules. The main difference is that Zn^{2+} , with an ionic radius of 0.88 Å, is much smaller than Cd^{2+} , with an ionic radius of 1.09 Å. While Zn^{2+} is beneficial in living systems, Cd^{2+} is toxic. This difference in biological function could be related to the size difference, and is a definite con.

- (b) Cu^+ is isoelectronic with Zn^{2+} . That is, the two ions have the same number of electrons and the same electron configurations. The ionic radius of Cu^+ is 0.91 Å, very similar to that of Zn^{2+} . We expect Cu^+ to be a reasonable substitute for Zn^{2+} in terms of chemical properties and size. Electrostatic interactions may vary, because of the difference in charges of the two ions. (All ionic radii are taken from WebElements©.)

- 7.102 (a) *Plan.* Use qualitative physical (bulk) properties to narrow the range of choices, then match melting point and density to identify the specific element. *Solve.*

Hardness varies widely in metals and nonmetals, so this information is not too useful. The relatively high density, appearance, and ductility indicate that the element is probably less metallic than copper. Focus on the block of nine main group elements centered around Sn. Pb is not a possibility because it was used as a comparison standard. The melting point of the five elements closest to Pb are:

Tl, 303.5°C; In, 156.1°C; Sn, 232°C; Sb, 630.5°C; Bi, 271.3°C

The best match is In. To confirm this identification, the density of In is 7.3 g/cm³, also a good match to properties of the unknown element.

- (b) In order to write the correct balanced equation, determine the formula of the oxide product from the mass data, assuming the unknown is In.

5.08 g oxide - 4.20 g In = 0.88 g O

4.20 g In/114.82 g/mol = 0.0366 mol In; 0.0366/0.0366 = 1

0.88 g O/16.00 g/mol = 0.0550 mol O; 0.0550/0.0366 = 1.5

7 Periodic Properties of the Elements Solutions to Exercises

Multiplying by 2 produces an integer ratio of 2 In: 3 O and a formula of In_2O_3 .
The balanced equation is: $4 \text{In}(s) + 3\text{O}_2(g) \rightarrow 2 \text{In}_2\text{O}_3(s)$

- (c) According to Figure 7.1, the element In was discovered between 1843–1886. The investigator who first recorded this data in 1822 could have been the first to discover In.

7.103 *Plan.* According to the periodic table on the inside cover of your text, element 116 is in group 6A, so element 117 will be in group 7A, the halogens. Write the electron configuration and use information from Figures 7.6, 7.9, 7.11, 7.14 and Table 7.7 along with periodic trends to estimate values for properties. Remember that element 117 is two rows below iodine, and that the increase in Z and Z_{eff} that accompanies filling of the f orbitals will decrease the size of the changes in ionization energy, electron affinity and atomic size. *Solve.*

Electron configuration:	$[\text{Rn}]7s^25f^{14}6d^{10}7p^5$
First ionization energy:	805 kJ/mol
Electron affinity:	-235 kJ/mol
Atomic size:	1.65 Å
Common oxidation state:	-1

- 7.104 (a) Si and Ge are in group 4A and have 4 valence electrons. GaAs and GaP have their first element in group 3A with 3 valence electrons and their second element in group 5A with 5 valence electrons. Cd in CdS and CdSe is in group 2B and has 2 valence electrons, while S and Se are in group 6A with 6 valence electrons. In each case, the two elements in the compound semiconductor have an *average* of 4 valence electrons.
- (b) The roman numerals represent the number of valence electrons in the component elements of the compound semiconductor. CdS and CdSe are II-VI materials, while GaAs and GaP are III-V materials.
- (c) Replace Ga with In: InP, InAs, InSb; replace Se with Te: CdTe. It is problematic to replace Cd with Hg, because Hg is toxic. ZnS is ionic and an insulator, so Zn may not be a good substitute for Cd.

Integrative Exercises

- 7.105 (a) $v = c/\lambda$; $1 \text{ Hz} = 1 \text{ s}^{-1}$

$$\text{Ne: } v = \frac{2.998 \times 10^8 \text{ m/s}}{14.610 \text{ Å}} \times \frac{1 \text{ Å}}{1 \times 10^{-10} \text{ m}} = 2.052 \times 10^{17} \text{ s}^{-1} = 2.052 \times 10^{17} \text{ Hz}$$

$$\text{Ca: } v = \frac{2.998 \times 10^8 \text{ m/s}}{3.358 \times 10^{-10} \text{ m}} = 8.928 \times 10^{17} \text{ Hz}$$

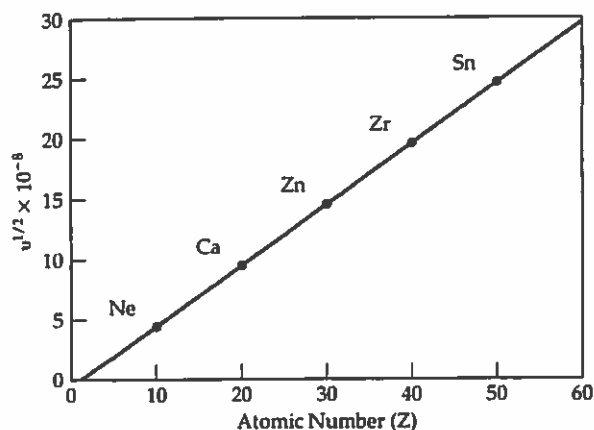
$$\text{Zn: } v = \frac{2.998 \times 10^8 \text{ m/s}}{1.435 \times 10^{-10} \text{ m}} = 20.89 \times 10^{17} \text{ Hz}$$

$$\text{Zr: } \nu = \frac{2.998 \times 10^8 \text{ m/s}}{0.786 \times 10^{-10} \text{ m}} = 38.14 \times 10^{17} = 38.1 \times 10^{17} \text{ Hz}$$

$$\text{Sn: } \nu = \frac{2.998 \times 10^8 \text{ m/s}}{0.491 \times 10^{-10} \text{ m}} = 61.06 \times 10^{17} = 61.1 \times 10^{17} \text{ Hz}$$

(b)

Element	Z	ν	$\nu^{1/2}$
Ne	10	2.052×10^{17}	4.530×10^8
Ca	20	8.928×10^{17}	9.449×10^8
Zn	30	20.89×10^{17}	14.45×10^8
Zr	40	38.14×10^{17}	19.5×10^8
Sn	50	61.06×10^{17}	24.7×10^8



- (c) The plot in part (b) indicates that there is a linear relationship between atomic number and the square root of the frequency of the X-rays emitted by an element. Thus, elements with each integer atomic number should exist. This relationship allowed Moseley to predict the existence of elements that filled "holes" or gaps in the periodic table.

- (d) For Fe, $Z = 26$. From the graph, $\nu^{1/2} = 12.5 \times 10^8$, $\nu = 1.56 \times 10^{18} \text{ Hz}$.

$$\lambda = c/\nu = \frac{2.998 \times 10^8 \text{ m/s}}{1.56 \times 10^{18} \text{ s}^{-1}} \times \frac{1 \text{ \AA}}{1 \times 10^{-10} \text{ m}} = 1.92 \text{ \AA}$$

- (e) $\lambda = 0.980 \text{ \AA} = 0.980 \times 10^{-10} \text{ m}$

$$\nu = c/\lambda = \frac{2.998 \times 10^8 \text{ m/s}}{0.980 \times 10^{-10} \text{ m}} = 30.6 \times 10^{17} \text{ Hz}; \nu^{1/2} = 17.5 \times 10^8$$

From the graph, $\nu^{1/2} = 17.5 \times 10^8$, $Z = 36$. The element is krypton, Kr.

- 7.106 (a) Li: $[\text{He}]2s^1$. Assume that the $[\text{He}]$ core is 100% effective at shielding the 2s valence electron $Z_{\text{eff}} = Z - S \approx 3 - 2 = 1+$.

7 Periodic Properties of the Elements Solutions to Exercises

- (b) The first ionization energy represents loss of the 2s electron.

$\Delta E = \text{energy of free electron } (n = \infty) - \text{energy of electron in ground state } (n = 2)$

$$\Delta E = I_1 = [-2.18 \times 10^{-18} \text{ J } (Z^2/\infty^2)] - [-2/18 \times 10^{-18} \text{ J } (Z^2/2^2)]$$

$$\Delta E = I_1 = 0 + 2.18 \times 10^{-18} \text{ J } (Z^2/2^2)$$

For Li, which is not a one-electron particle, let $Z = Z_{\text{eff}}$.

$$\Delta E \approx 2.18 \times 10^{-18} \text{ J } (+1^2/4) \approx 5.45 \times 10^{-19} \text{ J/atom}$$

- (c) Change the result from part (b) to kJ/mol so it can be compared to the value in

$$\text{Table 7.4. } 5.45 \times 10^{-19} \frac{\text{J}}{\text{atom}} \times \frac{6.022 \times 10^{23} \text{ atom}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 328 \text{ kJ/mol}$$

The value in Table 7.4 is 520 kJ/mol. This means that our estimate for Z_{eff} was a lower limit, that the [He] core electrons do not perfectly shield the 2s electron from the nuclear charge.

- (d) From Table 7.4, $I_1 = 520 \text{ kJ/mol}$.

$$\frac{520 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 8.6350 \times 10^{-19} \text{ J/atom}$$

Use the relationship for I_1 and Z_{eff} developed in part (b).

$$Z_{\text{eff}}^2 = \frac{4(8.6350 \times 10^{-19} \text{ J})}{2.18 \times 10^{-18} \text{ J}} = 1.5844 = 1.58; Z_{\text{eff}} = 1.26$$

This value, $Z_{\text{eff}} = 1.26$, based on the experimental ionization energy, is greater than our estimate from part (a), which is consistent with the explanation in part (c).

- 7.107 (a) $E = hc/\lambda$; $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$; $58.4 \text{ nm} = 58.4 \times 10^{-9} \text{ m}$;

$$1 \text{ eV} = 96.485 \text{ kJ/mol}, 1 \text{ eV} \cdot \text{mol} = 96.485 \text{ kJ}$$

$$E = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.998 \times 10^8 \text{ m/s}}{58.4 \times 10^{-9} \text{ m}} = 3.4015 \times 10^{-18} = 3.40 \times 10^{-18} \text{ J/photon}$$

$$\frac{3.4015 \times 10^{-18} \text{ J}}{\text{photon}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}} \times \frac{1 \text{ eV} \cdot \text{mol}}{96.485 \text{ kJ}} = 21.230 = 21.2 \text{ eV}$$

- (b) $\text{Hg}(g) \rightarrow \text{Hg}^+(g) + 1e^-$

- (c) $I_1 = E_{58.4} - E_K = 21.23 \text{ eV} - 10.75 \text{ eV} = 10.48 = 10.5 \text{ eV}$

$$10.48 \text{ eV} \times \frac{96.485 \text{ kJ}}{1 \text{ eV} \cdot \text{mol}} = 1.01 \times 10^3 \text{ kJ/mol}$$

- (d) From Figure 7.9, iodine (I) appears to have the ionization energy closest to that of Hg, approximately 1000 kJ/mol.

- 7.108 (a) The X-ray source had an energy of 1253.6 eV. Change eV to J/photon and use the relationship $\lambda = hc/E$ to find wavelength.

$$1253.6 \text{ eV} \times \frac{96.485 \text{ kJ}}{1 \text{ eV} \cdot \text{mol}} \times \frac{1 \text{ mol}}{6.0221 \times 10^{23} \text{ photons}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 2.0085 \times 10^{-16} \text{ J/photon}$$

$$\lambda = \frac{6.6261 \times 10^{-34} \text{ J} \cdot \text{s} \times 2.9979 \times 10^8 \text{ m/s}}{2.0085 \times 10^{-16} \text{ J}} = 9.8902 \times 10^{-10} \text{ m} = 0.98902 \text{ nm} = 9.8902 \text{ \AA}$$

- (b) Express energies of Hg 4f and O 1s electrons in terms of kJ/mol for comparison with data from Figure 7.9 of the text.

$$\text{Hg } 4f: 105 \text{ eV} \times \frac{96.485 \text{ kJ}}{1 \text{ eV} \cdot \text{mol}} = 10,131 = 1.01 \times 10^4 \text{ kJ/mol}$$

$$\text{O } 1s: 531 \text{ eV} \times \frac{96.485 \text{ kJ}}{1 \text{ eV} \cdot \text{mol}} = 51,234 = 5.12 \times 10^4 \text{ kJ/mol}$$

By definition, the first ionization energy is the minimum energy required to remove the first electron from an atom. This first electron is the highest energy valence electron in the neutral atom. We expect the energies of valence electrons to be higher than those of core electrons, and first ionization energies to be less than the energy required to remove a lower energy core electron.

For Hg, the first ionization energy is 1007 kJ/mol, while the XPS energy of the 4f electron is 10,100 kJ/mol. The energy required to remove a 4f core electron is 10 times the energy required to remove a 6s valence electron.

For O, the first ionization energy is 1314 kJ/mol, while the XPS energy of a 1s electron is 51,200 kJ/mol. The energy required to remove a 1s core electron is 50 times that required to remove a 2p valence electron.

- (c) Hg^{2+} : $[\text{Xe}]4f^{14}5d^{10}$; valence electrons are 5d
 O^{2-} : $[\text{He}]2s^22p^6$ or $[\text{Ne}]$; valence electrons are 2p
- (d) (Recall that Slater's rules are best applied to elements that do not contain d or f electrons.)

Hg^{2+} 5d valence: $n = 5$ ($5s+5p+5d$) has $18 e^-$; subtract one for the electron under consideration = $17 e^-$ with the same n value as the one under consideration.

$n = 4$ ($4s+4p+4d+4f$) has $32 e^-$ with $(n - 1)$; $n = 3, 2, 1$ have $(18+8+2) = 28 e^-$ with $(n - 2)$ or less.

$$S(5d) = 0.35(17) + 0.85(32) + 1.0(28) = 61.15. Z_{\text{eff}} = Z - S = 80 - 61.15 = 18.85$$

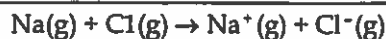
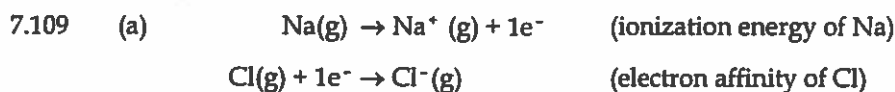
Hg^{2+} 4f: The 4f electrons are not shielded by electrons with $n > 4$. $n = 4$ has $(32 - 1) = 31 e^-$; $n = 3$ has $18 e^-$ with $(n - 1)$; $n = 2, 1$ have $10 e^-$ with $(n - 2)$ or less.

$$S(4f) = 0.35(31) + 0.85(18) + 1.0(10) = 36.15. Z_{\text{eff}} = Z - S = 80 - 36.15 = 43.85$$

O^{2-} 2p valence: $n = 2$ has $(8 - 1) = 7 e^-$; $n = 1$ has $2 e^-$.

$$S = 0.35(7) + 0.85(2) = 4.15; Z_{\text{eff}} = 8 - 4.15 = 3.85$$

7 Periodic Properties of the Elements Solutions to Exercises



(b) $\Delta H = I_1(\text{Na}) + E_1(\text{Cl}) = +496 \text{ kJ} - 349 \text{ kJ} = +147 \text{ kJ}$, endothermic

(c) The reaction $2\text{Na(s)} + \text{Cl}_2(\text{g}) \rightarrow 2\text{NaCl(s)}$ involves many more steps than the reaction in part (a). One important difference is the production of NaCl(s) versus NaCl(g) . The condensation $\text{NaCl(g)} \rightarrow \text{NaCl(s)}$ is very exothermic and is the step that causes the reaction of the elements in their standard states to be exothermic, while the gas phase reaction is endothermic.



The driving force is the production of $\text{NH}_3(\text{g})$.

(c) After the second heating, all the Mg is converted to MgO.

Calculate the initial mass Mg.

$$0.486 \text{ g MgO} \times \frac{24.305 \text{ g Mg}}{40.305 \text{ g MgO}} = 0.293 \text{ g Mg}$$

$$x = \text{g Mg converted to MgO}; y = \text{g Mg converted to Mg}_3\text{N}_2; x = 0.293 - y$$

$$\text{g MgO} = x \left(\frac{40.305 \text{ g MgO}}{24.305 \text{ g Mg}} \right); \text{g Mg}_3\text{N}_2 = y \left(\frac{100.929 \text{ g Mg}_3\text{N}_2}{72.915 \text{ g Mg}} \right)$$

$$\text{g MgO} + \text{g Mg}_3\text{N}_2 = 0.470$$

$$(0.293 - y) \left(\frac{40.305}{24.305} \right) + y \left(\frac{100.929}{72.915} \right) = 0.470$$

$$(0.293 - y)(1.6583) + y(1.3842) = 0.470$$

$$-1.6583 y + 1.3842 y = 0.470 - 0.48588$$

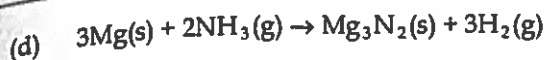
$$-0.2741 y = -0.01588 = -0.016$$

$$y = 0.05794 = 0.058 \text{ g Mg in Mg}_3\text{N}_2$$

$$\text{g Mg}_3\text{N}_2 = 0.05794 \text{ g Mg} \times \frac{100.929 \text{ g Mg}_3\text{N}_2}{72.915 \text{ g Mg}} = 0.0802 = 0.080 \text{ g Mg}_3\text{N}_2$$

$$\text{mass \% Mg}_3\text{N}_2 = \frac{0.0802 \text{ g Mg}_3\text{N}_2}{0.470 \text{ g (MgO} + \text{Mg}_3\text{N}_2)} \times 100 = 17\%$$

(The final mass % has two sig figs because the mass of Mg obtained from solving simultaneous equations has two sig figs.)



$$6.3 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.305 \text{ g Mg}} = 0.2592 = 0.26 \text{ mol Mg}$$

$$2.57 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.031 \text{ g NH}_3} = 0.1509 = 0.15 \text{ mol NH}_3$$

$$0.2592 \text{ mol Mg} \times \frac{2 \text{ mol NH}_3}{3 \text{ mol Mg}} = 0.1728 = 0.17 \text{ mol NH}_3$$

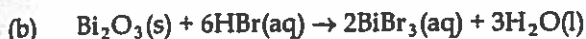
0.26 mol Mg requires more than the available NH₃, so NH₃ is the limiting reactant.

$$0.1509 \text{ mol NH}_3 \times \frac{3 \text{ mol H}_2}{2 \text{ mol NH}_3} \times \frac{2.016 \text{ g H}_2}{\text{mol H}_2} = 0.4563 = 0.46 \text{ g H}_2$$

$$(e) \quad \Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ \text{Mg}_3\text{N}_2(s) + 3\Delta H_f^\circ \text{H}_2(g) - 3\Delta H_f^\circ \text{Mg}(s) - 2\Delta H_f^\circ \text{NH}_3(g)$$

$$= -461.08 \text{ kJ} + 3(0) - 3(0) - 2(-46.19) = -368.70 \text{ kJ}$$

$$7.111 \quad (a) \quad r_{\text{Bi}} = r_{\text{BiBr}_3} - r_{\text{Br}} = 2.63 \text{ \AA} - 1.14 \text{ \AA} = 1.49 \text{ \AA}$$



(c) Bi₂O₃ is soluble in acid solutions because it acts as a base and undergoes acid-base reactions like the one in part (b). It is insoluble in base because it cannot act as an acid. Thus, Bi₂O₃ is a basic oxide, the oxide of a metal. Based on the properties of its oxide, Bi is characterized as a metal.

(d) Bi: [Xe]6s²4f¹⁴5d¹⁰6p³. Bi has five outer electrons in the 6p and 6s subshells. If all five electrons participate in bonding, compounds such as BiF₅ are possible. Also, Bi has a large enough atomic radius (1.49 Å) and low-energy orbitals available to accommodate more than four pairs of bonding electrons.

(e) The high ionization energy and relatively large negative electron affinity of F, coupled with its small atomic radius, make it the most electron withdrawing of the halogens. BiF₅ forms because F has the greatest tendency to attract electrons from Bi. Also, the small atomic radius of F reduces repulsions between neighboring bonded F atoms. The strong electron withdrawing properties of F are also the reason that only F compounds of Xe are known.



(b) K, +1; O, -1/2 (O₂⁻ is superoxide ion); C, +4; O, -2 → K, +1; C, +4; O, -2; O, 0
Oxygen (in the form of superoxide) is oxidized (to O₂) and reduced (to O²⁻).

$$(c) \quad 18.0 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{4 \text{ mol KO}_2}{2 \text{ mol CO}_2} \times \frac{71.10 \text{ g KO}_2}{1 \text{ mol KO}_2} = 58.2 \text{ g KO}_2$$

$$18.0 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{3 \text{ mol O}_2}{2 \text{ mol CO}_2} \times \frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} = 19.6 \text{ g O}_2$$