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.

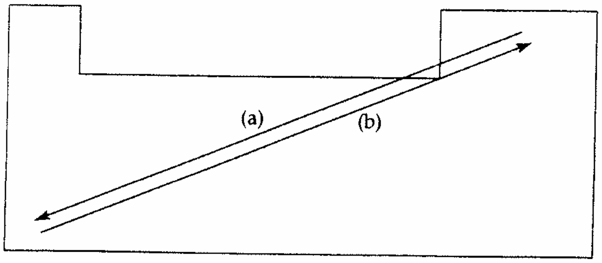
(c) Moving down a family, both the nuclear charge and the core electron configuration changes. To simulate the addition of core electrons farther from the nucleus, we would add larger frosted glass shades as well as increase the wattage of the bulb to show the increase in Z. The effect of the shade should dominate the increase in wattage, so that the brightness of the light decreases moving down a column.

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.

7.6 (a) $X + 2F_2 \rightarrow XF_4$

(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

7.8 (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 Mendeleev table (the positions of Ar and K or Te and I) are eliminated.

7.10 (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.

7.12 (a) $Z_{eff} = Z - S$; S: $[Ne]3s^2 3p^4$; $Z = 16$. If the 10 core electrons provide perfect shielding and the 6 valence electrons provide no shielding, $S = 10$.

$Z_{eff} = 16 - 10 = 6$.

(b) An estimate of Z_{eff} based on the assumption in part (a) will always be lower than the value based on detailed calculations. Because outer electrons have some probability of being in the core, the core electrons are never 100% effective at shielding; the number of core electrons represents an upper limit for S.

7.14 $Mg < P < K < Ti < Rh$. 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.

Atomic and Ionic Radii

7.16 (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.

7.18 The distance between Ge atoms in solid germanium is two times the bonding atomic radius from Figure 7.6. The Ge-Ge distance is 2×1.22 Å $= 2.44$ Å.

7.20 Bi – I = 2.81 Å $= r_{Bi} + r_I$. From Figure 7.6, $r_I = 1.33$ Å.

$r_{Bi} = [\text{Bi} - \text{I}] - r_I = 2.81$ Å $- 1.33$ Å $= 1.48$ Å.

7.22 (a) The vertical difference in radius is due to a change in principal 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 principal 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.

7.24 (a) K < Rb < Cs (b) Te < Sn < In (c) Cl < P < Sr

7.26 (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 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. $Fe > Fe^{2+} > Fe^{3+}$

7.28 The order of radii is $Ca > Ca^{2+} > Mg^{2+}$, so the largest sphere is Ca, the intermediate one is Ca^{2+}, and the smallest is Mg^{2+}.

(b) (i) N^{3-}: Ne (ii) Ba^{2+}: Xe (iii) Se^{2-}: Kr (iv) Bi^{3+}: Hg

7.30 (a) Sr^{2+}, Br^- (b) Y^{3+}, Br^-, Kr (c) P^{3-}, Ti^{4+} (d) Fe^{3+}, Mn^{2+}

7.32 (a) Cl < S < K (b) $K^+ < Cl^- < S^{2-}$

(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.

7.34 (a) Cl^- is larger than Cl because the increase in electron repulsions that accompany addition of an electron causes 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.

Ionization Energies; Electron Affinities

7.36 (a) $Sn(g) \rightarrow Sn^+(g) + 1e^-$; $Sn^+(g) \rightarrow Sn^{2+}(g) + 1e^-$

(b) $Ti^{3+}(g) \rightarrow Ti^{4+}(g) + 1e^-$

7.38 (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] $4s^23d^1$; Ti: [Ar] $4s^23d^2$. 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 farther from the nucleus of Be^+.

7.40 (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.

7.42 (a) Mo. As the effective nuclear charge increases in moving from left to right in the fifth row, the energy required to remove an electron increases.

(b) N. Valence electrons in N are closer to the nucleus ($n = 2$) and are shielded only by the [He] core, so they experience greater attraction for the nucleus and have a higher ionization energy.

(c) Cl. Effective nuclear charge increases moving both right across a row and up a family. Valence electrons in Cl, which is to the right and above Ga, experience the greater Z_{eff} and have the larger first ionization energy.

(d) Rn. Pb and Rn are in the same row, so Rn with the larger Z experiences a greater effective nuclear charge and a larger ionization energy.

7.44 (a) Mn^{3+}: $[Ar]3d^4$

(b) Se^{2-}: $[Ar]4s^23d^{10}4p^6$ = [Kr], noble-gas configuration

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

(e) Tl^+: $[Xe]6s^24f^{14}5d^{10}$ (f) Au^+: $[Xe]4f^{14}5d^{10}$

7.46 (a) Cu^{2+}, 1 unpaired electron (b) Tl^+, 0 unpaired electrons

7.48 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 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.

7.50 Electron affinity

$$\underset{[Ar]4s^2 3d^{10} 4p^5}{Br(g)} \quad + 1e^- \quad \rightarrow \quad \underset{[Ar]4s^2 3d^{10} 4p^6}{Br^-(g)}$$

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.

Electron affinity :

$$\underset{[Ar]4s^2 3d^{10} 4p^6}{Kr(g)} \quad + 1e^- \quad \rightarrow \quad \underset{[Ar]4s^2 3d^{10} 4p^6 5s^1}{Kr^-(g)}$$

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.

7.52 $Mg^+(g) + 1e^- \rightarrow Mg(g)$

$[Ne]\,3s^1$ $[Ne]\,3s^2$

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

7.54 S < Si < Ge < Ca. S is a nonmetal, Si and Ge are metalloids, and Ca 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.

7.56 (a) In general, ionization energy decreases as metallic character increases. According to Figure 7.11 the ionization energies of the group 5A elements decrease as atomic weight increases (going down the column). Therefore, metallic character of the group 5A elements increases with increasing atomic weight.

(b) Ag < Sn < Se < C < F. Nonmetallic character increases going up and to the right on the periodic chart. Vertical trends dominate the relationship between Se and C.

7.58 (a) metal oxides: $Li_2O(s) + H_2O(l) \rightarrow 2\,LiOH(aq)$

$BaO(s) + H_2O(l) \rightarrow Ba(OH)_2(aq)$

nonmetal oxides: $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

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

(b) Metals have lower ionization energies than nonmetals, so they tend to form ionic oxides, while nonmetals form molecular oxides. Ionic compounds, in this case oxides, dissociate into ions when they dissolve in water. The reactive oxide ion ends up as hydroxide, separated from the metal ion. Molecular oxides do not ionize upon dissolution, so the oxygen remains bound to the nonmetal.

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

7.62 (a) $XCl_4(l) + 2H_2O(l) \rightarrow XO_2(s) + 4HCl(g)$

The second product is HCl(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.