Sample Exercise 7.1 Bond Lengths in a Molecule

Natural gas used in home heating and cooking is odorless. Because natural gas leaks pose the danger of explosion or suffocation, various smelly substances are added to the gas to allow detection of a leak. One such substance is methyl mercaptan, CH_3SH. Use Figure 7.6 to predict the lengths of the C—S, C—H, and S—H bonds in this molecule.

Solution

Analyze and Plan We are given three bonds and told to use Figure 7.6 for bonding atomic radii. We will assume that each bond length is the sum of the bonding atomic radii of the two atoms involved.

Solve

C—S bond length = bonding atomic radius of C + bonding atomic radius of S

= 0.77Å + 1.02Å = 1.79Å

C—H bond length = 0.77Å + 0.37Å = 1.14Å

S—H bond length = 1.02Å = 0.37Å = 1.39Å

Check The experimentally determined bond lengths are C—S = 1.82Å, C—H = 1.10Å and S—H = 1.33Å. (In general, the lengths of bonds involving hydrogen show larger deviations from the values predicted from bonding atomic radii than do bonds involving larger atoms.)

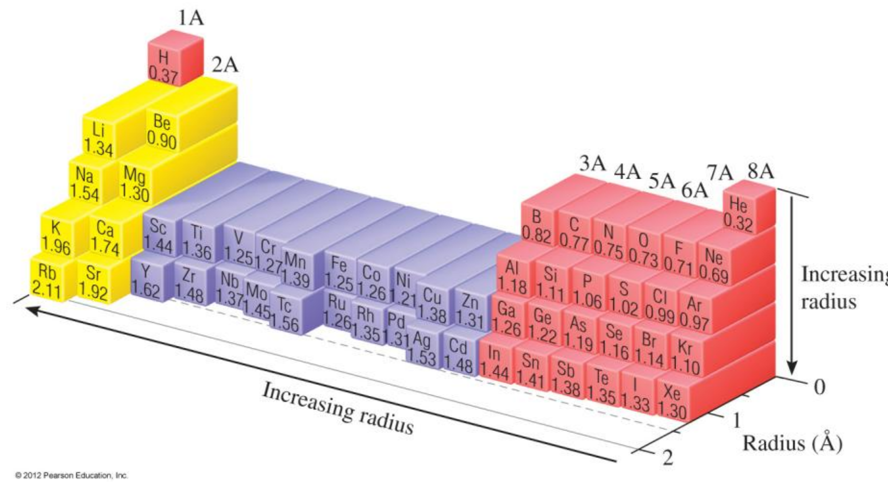

FIGURE 7.6 Trends in bonding atomic radii for periods 1 through 5.

Sample Exercise 7.1 Bond Lengths in a Molecule

Continued

Comment Notice that our estimated bond lengths are close but not exact matches to the measured bond lengths. Bonding atomic radii must be used with some caution in estimating bond lengths.

Practice Exercise

Using Figure 7.6, predict which is longer, the bond in PBr_3 or the As—Cl bond in $AsCl_3$.

Answer: P—Br

Sample Exercise 7.2 Atomic Radii

Referring to a periodic table, arrange (as much as possible) the atoms $_{15}P$, $_{16}S$, $_{33}As$, and $_{34}Se$ in order of increasing size. (Atomic numbers are given to help you locate the atoms quickly in the table.)

Solution

Analyze and Plan We are given the chemical symbols for four elements and told to use their relative positions in the periodic table to predict the relative size of their atomic radii. We can use the two periodic trends just described to help with this problem.

Solve P and S are in the same period, with S to the right of P. Therefore, we expect the radius of S to be smaller than that of P because radii decrease as we move across a period. Likewise, the radius of Se is expected to be smaller than that of As. As is directly below P, and Se is directly below S. We expect, therefore, the radius of P to be smaller than that of As and the radius of S to be smaller than that of Se. Thus, so far we can say S < P, P < As, S < Se, Se < As. We can therefore conclude that S has the smallest radius and As has the largest radius and so can write S < ? < ? < As.

Our two periodic trends for atomic size do not supply enough information to allow us to determine whether P or Se (represented by the two question marks) has the larger radius, however. Going from P to Se in the periodic table, we move down (radius tends to increase) and to the right (radius tends to decrease). In Figure 7.6 we see that the radius of Se is greater than that of P. If you examine the figure carefully, you will discover that for the s- and p-block elements the increase in radius moving down a column tends to be the greater effect. There are exceptions, however.

Sample Exercise 7.2 Atomic Radii

Continued

Solution

Check From Figure 7.6, we have S(1.02Å) < (1.06Å) < Se(1.16Å) < As(1.19Å).

Comment Note that the trends we have just discussed are for the *s*- and *p*-block elements. Figure 7.6 shows that the transition elements do not show a regular decrease moving across a period.

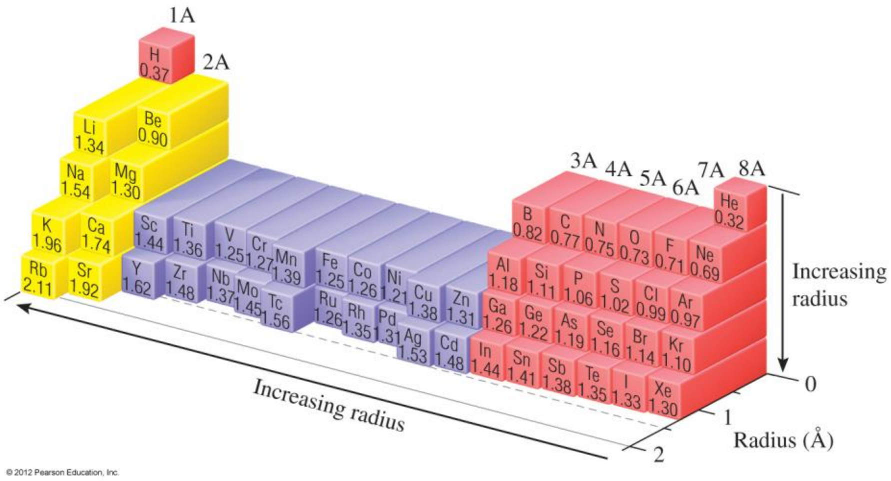

FIGURE 7.6 Trends in bonding atomic radii for periods 1 through 5.

Practice Exercise

Arrange $_{11}$Na, $_{4}$Be, and $_{12}$Mg in order of increasing atomic radius.

Answer: Be < Mg < Na

Sample Exercise 7.3 Atomic and Ionic Radii

Arrange Mg^{2+}, Ca^{2+}, and Ca in order of decreasing radius..

Solution

Cations are smaller than their parent atoms, and so Ca^{2+} < Ca. Because Ca is below Mg in group 2A, Ca^{2+} is larger than Mg^{2+}. Consequently, Ca > Ca^{2}+ > Mg^{2+}.

Practice Exercise

Which of the following atoms and ions is largest: S^{2-}, S, O^{2-}?

Answer: S^{2-}

Sample Exercise 7.4 Ionic Radii in an Isoelectronic Series

Arrange the ions K^+, Cl^-, Ca^{2+}, and S^{2-} in order of decreasing size.

Solution

This is an isoelectronic series, with all ions having 18 electrons. In such a series, size decreases as nuclear charge (atomic number) increases. The atomic numbers of the ions are S 16, Cl 17, K 19, Ca 20. Thus, the ions decrease in size in the order $S^{2-} > Cl^- > K^+ > Ca^{2+}$.

Practice Exercise

In the isoelectronic series Rb^+, Sr^{2+}, Y^{3+}, which ion is largest?

Answer: Rb^+

Sample Exercise 7.5 Trends in Ionization Energy

Three elements are indicated in the periodic table in the margin. Which one has the largest second ionization energy?

Solution

Analyze and Plan The locations of the elements in the periodic table allow us to predict the electron configurations. The greatest ionization energies involve removal of core electrons. Thus, we should look first for an element with only one electron in the outermost occupied shell.

Solve The red box represents Na, which has one valence electron. The second ionization energy of this element is associated, therefore, with the removal of a core electron. The other elements indicated, S (green) and Ca (blue), have two or more valence electrons. Thus, Na should have the largest second ionization energy.

Check A chemistry handbook gives these I_2 values: Ca 1145 kJ/mol, S 2252 kJ/mol, Na 4562 kJ/mol.

Practice Exercise

Which has the greater third ionization energy, Ca or S?

Answer: Ca

Sample Exercise 7.6 Periodic Trends in Ionization Energy

Referring to a periodic table, arrange the atoms Ne, Na, P, Ar, K in order of increasing first ionization energy.

Solution

Analyze and Plan We are given the chemical symbols for five elements. To rank them according to increasing first ionization energy, we need to locate each element in the periodic table. We can then use their relative positions and the trends in first ionization energies to predict their order.

Solve Ionization energy increases as we move left to right across a period and decreases as we move down a group. Because Na, P, and Ar are in the same period, we expect I_1 to vary in the order Na < P < Ar. Because Ne is above Ar in group 8A, we expect Ar < Ne. Similarly, K is directly below Na in group 1A, and so we expect K < Na.

From these observations, we conclude that the ionization energies follow the order

$$K < Na < P < Ar < Ne$$

Check The values shown in Figure 7.9 confirm this prediction.

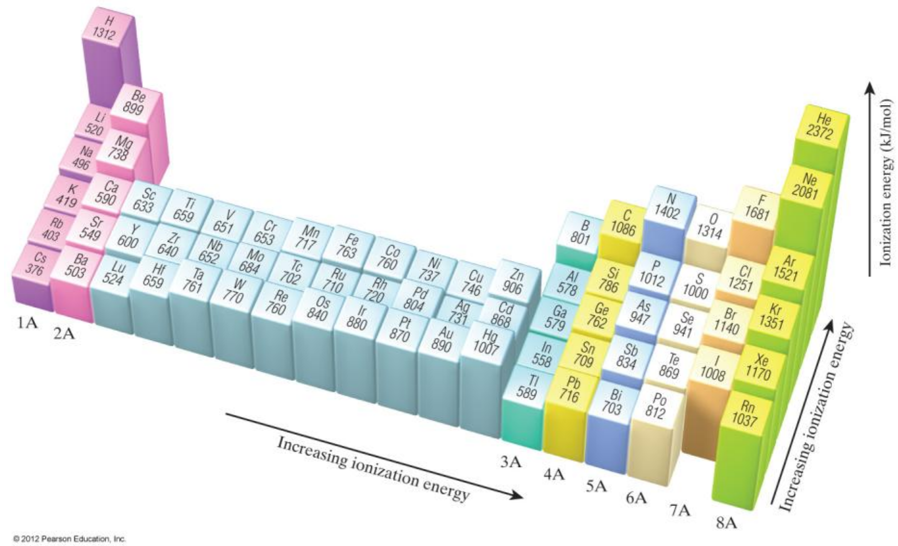

FIGURE 7.9 Trends in first ionization energies of the elements

Practice Exercise

Which has the lowest first ionization energy, B, Al, C, or Si? Which has the highest?

Answer: Al lowest, C highest

Chemistry, The Central Science, 12th Edition
Theodore L. Brown; H. Eugene LeMay, Jr.; Bruce E. Bursten; Catherine J. Murphy; and Patrick Woodward

Sample Exercise 7.7 Electron Configurations of Ions

Write the electron configuration for (**a**) Ca^{2+}, (**b**) Co^{3+}, and (**c**) S^{2-}.

Solution

Analyze and Plan We are asked to write electron configurations for three ions. To do so, we first write the electron configuration of each parent atom, then remove or add electrons to form the ions. Electrons are first removed from the orbitals having the highest value of *n*. They are added to the empty or partially filled orbitals having the lowest value of *n*.

Solve (**a**) Calcium (atomic number 20) has the electron configuration $[Ar]4s^2$. To form a 2+ ion, the two outer electrons must be removed, giving an ion that is isoelectronic with Ar: Ca^2:[Ar]

(**b**) Cobalt (atomic number 27) has the electron configuration $[Ar]3d^74s^2$. To form a 3+ ion, three electrons must be removed. As discussed in the text, the 4*s* electrons are removed before the 3*d* electrons. Consequently, the electron configuration for Co^{3+}:$[Ar]3d^6$

(**c**) Sulfur (atomic number 16) has the electron configuration $[Ne]3s^23p^4$. To form a 2– ion, two electrons must be added. There is room for two additional electrons in the 3*p* orbitals. Thus, the S^{2-} electron configuration is S^{2-}:$[Ne]3s^23p^6 = [Ar]$

Comment Remember that many of the common ions of the *s*- and *p*-block elements, such as Ca^{2+} and S^{2-}, have the same number of electrons as the closest noble gas. •(Section 2.7)

Practice Exercise

Write the electron configuration for (**a**) Ga^{3+}, (**b**) Cr^{3+}, and (**c**) Br^-.

Answers: (**a**) $[Ar]3d^{10}$, (**b**) $[Ar]3d^3$, (**c**) $[Ar]3d^{10}4s^24p^6 = [Kr]$

Sample Exercise 7.8 Metal Oxides

(**a**) Would you expect scandium oxide to be a solid, liquid, or gas at room temperature?
(**b**) Write the balanced chemical equation for the reaction of scandium oxide with nitric acid.

Solution

Analyze and Plan We are asked about one physical property of scandium oxide—its state at room temperature—and one chemical property—how it reacts with nitric acid.

Solve

(**a**) Because scandium oxide is the oxide of a metal, we expect it to be an ionic solid. Indeed it is, with the very high melting point of 2485ºC.

(b) In compounds, scandium has a 3+ charge, Sc^{3+}, and the oxide ion is O^{2-}. Consequently, the formula of scandium oxide is Sc_2O_3. Metal oxides tend to be basic and, therefore, to react with acids to form a salt plus water. In this case the salt is scandium nitrate, $Sc(NO_3)_3$:

$$Sc_2O_3(s) + 6\ HNO_3(aq) \rightarrow 2\ Sc(NO_3)_3(aq) + 3\ H_2O(l)$$

Practice Exercise

Write the balanced chemical equation for the reaction between copper(II) oxide and sulfuric acid.

Answer: $CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$

Sample Exercise 7.9 Nonmetal Oxides

Write the balanced chemical equation for the reaction of solid selenium dioxide, SeO2(s), with (**a**) water, (**b**) aqueous sodium hydroxide.

Solution

Analyze and Plan We note that selenium is a nonmetal. We therefore need to write chemical equations for the reaction of a nonmetal oxide with water and with a base, NaOH. Nonmetal oxides are acidic, reacting with water to form an acid and with bases to form a salt and water.

Solve (**a**) The reaction between selenium dioxide and water is like that between carbon dioxide and water (Equation 7.13):

$$SeO_2(s) + H_2O(l) \rightarrow H_2SeO_3(aq)$$

(It does not matter that SeO_2 is a solid and CO_2 is a gas under ambient conditions; the point is that both are water-soluble nonmetal oxides.)

(**b**) The reaction with sodium hydroxide is like the reaction in Equation 7.15:

$$SeO_2(s) + 2\ NaOH(aq) \rightarrow Na_2SeO_3(aq) + H_2O(l)$$

Practice Exercise

Write the balanced chemical equation for the reaction of solid tetraphosphorus hexoxide with water.

Answer: $P_4O_6(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_3(aq)$

Sample Exercise 7.10 Reactions of an Alkali Metal

Write a balanced equation for the reaction of cesium metal with (**a**) $Cl_2(g)$, (**b**) $H_2O(l)$, (**c**) $H_2(g)$.

Solution

Analyze and Plan Because cesium is an alkali metal, we expect its chemistry to be dominated by oxidation of the metal to Cs^+ ions. Further, we recognize that Cs is far down the periodic table, which means it is among the most active of all metals and probably reacts with all three substances.

Solve The reaction between Cs and Cl_2 is a simple combination reaction between a metal and a nonmetal, forming the ionic compound CsCl: $2\ Cs(s) + Cl_2(g) \rightarrow 2\ CsCl(s)$

From Equations 7.18 and 7.16, we predict the reactions of cesium with water and hydrogen to proceed as follows:

$$2Cs(s) + 2\ H_2O(l) \rightarrow 2\ CsOH(aq) + H_2(g)$$
$$2\ Cs(s) + H_2(g) \rightarrow 2\ CsH(s)$$

All three reactions are redox reactions where cesium forms a Cs^+ ion. The Cl^-, OH^-, and H^- are all ions, which means the products have 1:1 stoichiometry with Cs^+.

Practice Exercise

Write a balanced equation for the reaction between potassium metal and elemental sulfur.

Answer: $2\ K(s) + S(s) \rightarrow K_2S(s)$