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, whose structure is shown in the margin. Use Figure 7.7 to predict the lengths of the C—S, C—H, S—H and bonds in this molecule.

Solution

Analyze and Plan: We are given three bonds and the list of bonding atomic radii. We will assume that each bond length is the sum of the radii of the two atoms involved.

Solve: Using radii for C, S, and H from Figure 7.7, we predict

$$\text{C—S bond length} = \text{radius of C} + \text{radius of S}$$
$$= 0.77\ \text{Å} + 1.02\ \text{Å} = 1.79\ \text{Å}$$
$$\text{C—H bond length} = 0.77\ \text{Å} + 0.37\ \text{Å} = 1.14\ \text{Å}$$
$$\text{S—H bond length} = 1.02\ \text{Å} + 0.37\ \text{Å} = 1.39\ \text{Å}$$

Check: The experimentally determined bond lengths in methyl mercaptan (taken from the chemical literature) are C—S = 1.82 Å, C—H = 1.10 Å, and S—H = 1.33 Å. (In general, the lengths of bonds involving hydrogen show larger deviations from the values predicted by the sum of the atomic radii than do those bonds involving larger atoms.)

Comment: Notice that the estimated bond lengths using bonding atomic radii are close, but not exact matches, to the experimental bond lengths. Atomic radii must be used with some caution in estimating bond lengths. In Chapter 8 we will examine some of the average lengths of common types of bonds.

Practice Exercise

Using Figure 7.7, predict which will be greater, the P—Br bond length in PBr_3 or the As—Cl bond length in $AsCl_3$.

Answer: P—Br

Sample Exercise 7.2 Atomic Radii

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

Solution

Analyze and Plan: We are given the chemical symbols for four elements. We can use their relative positions in the periodic table and the two periodic trends just described to predict the relative order of their atomic radii.

Solve: Notice that P and S are in the same row of the periodic table, with S to the right of P. Therefore, we expect the radius of S to be smaller than that of P. (Radii decrease as we move from left to right.) Likewise, the radius of Se is expected to be smaller than that of As. We also notice that As is directly below P and that Se is directly below S. We expect, therefore, that the radius of As is greater than that of P and the radius of Se is greater than that of S. From these observations, we predict S < P, P < As, S < Se, and S < As. We can therefore conclude that S has the smallest radius of the four elements and that As has the largest radius. Using just the two trends described above, we cannot determine whether P or Se has the larger radius. To go from P to Se in the periodic table, we must move down (radius tends to increase) and to the right (radius tends to decrease). In Figure 7.7 we see that the radius of Se (1.16 Å) is greater than that of P (1.06 Å). 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.

Check: From Figure 7.7, we have S (1.02 Å) < P (1.06 Å) < Se (1.16 Å) < As (1.19 Å).

Comment: Note that the trends we have just discussed are for the *s*- and *p*-block elements. You will see in Figure 7.7 that the transition elements do not show a regular decrease upon moving from left to right across a row.

Sample Exercise 7.2 Atomic Radii

Practice Exercise

Arrange the following atoms in order of increasing atomic radius: ${}_{11}Na$, ${}_{4}Be$, ${}_{12}Mg$.
Answer: Be < Mg < Na

Sample Exercise 7.3 Atomic and Ionic Radii

Arrange these atoms and ions in order of decreasing size: Mg^{2+}, Ca^{2+}, and Ca.

Solution

Cations are smaller than their parent atoms, and so the Ca^{2+} ion is smaller than the Ca atom. Because Ca is below Mg in group 2A of the periodic table, Ca^{2+} is larger than $Mg2^{+}$. Consequently, Ca > Ca^{2+} > $Mg2^{+}$.

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

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

Practice Exercise

Which of the following ions is largest, Rb^+, Sr^{2+}, or Y^{3+}?
Answer: Rb^+

Sample Exercise 7.5 Trends in Ionization Energy

Three elements are indicated in the periodic table in the margin. Based on their locations, predict the one with 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 element in group 1A (Na), indicated by the red box, has only 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 box) and Ca (blue box), have two or more valence electrons. Thus, Na should have the largest second ionization energy.

Check: If we consult a chemistry handbook, we find the following values for the second ionization energies (I_2) of the respective elements: Ca (1,145 kJ/mol) < S (2,252 kJ/mol) < Na (4,562 kJ/mol).

Practice Exercise

Which will have 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 following atoms in order of increasing first ionization energy: Ne, Na, P, Ar, K.

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 Na < P < Ar.

Solve: Ionization energy increases as we move left to right across a row. It decreases as we move from the top of a group to the bottom. Because Na, P, and Ar are in the same row of the periodic table, we expect *I*1 to vary in the order Na < P < Ar.

Because Ne is above Ar in group 8A, we expect Ne to have the greater first ionization energy: Ar < Ne.

Similarly, K is the alkali metal directly below Na in group 1A, and so we expect I_1 for K to be less than that of Na: 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 7.12 confirm this prediction.

Practice Exercise

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

Answer: Al lowest, C highest

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 the parent atom. We then remove electrons to form cations or add electrons to form anions. 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

$$Ca: [Ar]4s^2$$

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

$$Co: [Ar]3d^7 4s^2$$

To form a 3+ ion, three electrons must be removed. As discussed in the text preceding this Sample Exercise, the 4*s* electrons are removed before the 3*d* electrons. Consequently, the electron configuration for Co^{3+} is

$$Co^{3+}: [Ar]3d^6$$

(c) Sulfur (atomic number 16) has the electron configuration

$$S: [Ne]3s^2\ 3p^4$$

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

$$S^{2-}: [Ne]3s^2\ 3p^6 = [Ar]$$

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)

Sample Exercise 7.7 Electron Configurations of Ions

Practice Exercise

Write the electron configuration for **(a)** Ga^{3+}, **(b)** Cr^{3+}, and **(c)** Br^{-}.
Answer: **(a)** $[Ar]3d^{10}$, **(b)** $[Ar]3d^{3}$, **(c)** $[Ar]3d^{10}4s^{2}4p^{6}$ = [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 would expect it to be an ionic solid. Indeed it is, with the very high melting point of 2485 °C.

(b) In its compounds, scandium has a 3+ charge, Sc^{3+}; 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, $Sc(NO_3)_3$. The balanced chemical equation is

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

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 equations for the reactions of solid selenium dioxide with **(a)** water, **(b)** aqueous sodium hydroxide.

Solution

Analyze and Plan: We first note that selenium (Se) is a nonmetal. We therefore need to write chemical equations for the reaction of a nonmetal oxide, first with water and then 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) Selenium dioxide is SeO_2. Its reaction with water is like that of carbon dioxide (Equation 7.14):

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

(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 summarized by Equation 7.16:

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

Practice Exercise

Write the balanced chemical equation for the reaction of solid tetraphosphorus hex-oxide 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 that predicts the reaction of cesium metal with **(a)** $Cl_2(g)$, **(b)** $H_2O(l)$, **(c)** $H_2(g)$.

Solution

Analyze and Plan: Cesium is an alkali metal (atomic number 55). We therefore expect that its chemistry will be dominated by oxidation of the metal to Cs^+ ions. Further, we recognize that Cs is far down the periodic table, which means it will be among the most active of all metals and will probably react with all three of the substances listed.

Solve: The reaction between Cs and Cl_2 is a simple combination reaction between two elements, one a metal and the other a nonmetal, forming the ionic compound CsCl:

$$2\,Cs(s) + Cl_2(g) \longrightarrow 2\,CsCl(s)$$

By analogy to Equations 7.19 and 7.17, respectively, we predict the reactions of cesium with water and hydrogen to proceed as follows:

$$2\,Cs(s) + 2\,H_2O(l) \longrightarrow 2\,CsOH(aq) + H_2(g)$$

$$2\,Cs(s) + H_2(g) \longrightarrow 2\,CsH(s)$$

All three of these reactions are redox reactions where cesium forms a Cs^+ ion in the product. The chloride (Cl^-), hydroxide (OH^-), and hydride (H^-) ions are all 1– ions, which means the final products have 1:1 stoichiometry with Cs^+.

Practice Exercise

Write a balanced equation for the reaction between potassium metal and elemental sulfur.
Answer: $2\,K(s) + S(s) \rightarrow K_2S(s)$

Sample Integrative Exercise Putting Concepts Together

The element bismuth (Bi, atomic number 83) is the heaviest member of group 5A. A salt of the element, bismuth subsalicylate, is the active ingredient in Pepto-Bismol®, an over-the-counter medication for gastric distress.

(a) The covalent atomic radii of thallium (Tl) and lead (Pb) are 1.48 Å and 1.47 Å, respectively. Using these values and those in Figure 7.7, predict the covalent atomic radius of the element bismuth (Bi). Explain your answer.

(b) What accounts for the general increase in atomic radius going down the group 5A elements?

(c) Another major use of bismuth has been as an ingredient in low-melting metal alloys, such as those used in fire sprinkler systems and in typesetting. The element itself is a brittle white crystalline solid. How do these characteristics fit with the fact that bismuth is in the same periodic group with such nonmetallic elements as nitrogen and phosphorus?

(d) Bi_2O_3 is a basic oxide. Write a balanced chemical equation for its reaction with dilute nitric acid. If 6.77 g of Bi_2O_3 is dissolved in dilute acidic solution to make 0.500 L of solution, what is the molarity of the solution of Bi^{3+} ion?

(e) ^{209}Bi is the heaviest stable isotope of any element. How many protons and neutrons are present in this nucleus?

(f) The density of Bi at 25 °C is 9.808 g/cm^3. How many Bi atoms are present in a cube of the element that is 5.00 cm on each edge? How many moles of the element are present?

Solution

(a) Note that there is a gradual decrease in radius of the elements in Groups 3A–5A as we proceed across the fifth period, that is, in the series In–Sn–Sb. Therefore, it is reasonable to expect a decrease of about 0.02 Å as we move from Pb to Bi, leading to an estimate of 1.45 Å. The tabulated value is 1.46 Å.

Sample Integrative Exercise Putting Concepts Together

Solution (continued)

(b) The general increase in radius with increasing atomic number in the group 5A elements occurs because additional shells of electrons are being added, with corresponding increases in nuclear charge. The core electrons in each case largely shield the outermost electrons from the nucleus, so the effective nuclear charge does not vary greatly as we go to higher atomic numbers. However, the principal quantum number, *n*, of the outermost electrons steadily increases, with a corresponding increase in orbital radius.

(c) The contrast between the properties of bismuth and those of nitrogen and phosphorus illustrates the general rule that there is a trend toward increased metallic character as we move down in a given group. Bismuth, in fact, is a metal. The increased metallic character occurs because the outermost electrons are more readily lost in bonding, a trend that is consistent with its lower ionization energy.

(d) Following the procedures described in Section 4.2 for writing molecular and net ionic equations, we have the following:

$$\textit{Molecular equation:}\quad Bi_2O_3(s) + 6\,HNO_3(aq) \longrightarrow 2\,Bi(NO_3)_3(aq) + 3\,H_2O(l)$$

$$\textit{Net ionic equation:}\quad Bi_2O_3(s) + 6\,H^+(aq) \longrightarrow 2\,Bi^{3+}(aq) + 3\,H_2O(l)$$

In the net ionic equation, nitric acid is a strong acid and $Bi(NO_3)_3$ is a soluble salt, so we need show only the reaction of the solid with the hydrogen ion forming the $Bi^{3+}(aq)$ ion and water.

To calculate the concentration of the solution, we proceed as follows (Section 4.5):

$$\frac{6.77\text{ g }Bi_2O_3}{0.500\text{ L soln}} \times \frac{1\text{ mol }Bi_2O_3}{466.0\text{ g }Bi_2O_3} \times \frac{2\text{ mol }Bi^{3+}}{1\text{ mol }Bi_2O_3} = \frac{0.0581\text{ mol }Bi^{3+}}{\text{L soln}} = 0.0581\ M$$

Sample Integrative Exercise Putting Concepts Together

Solution (continued)

(e) We can proceed as in Section 2.3. Bismuth is element 83; there are therefore 83 protons in the nucleus. Because the atomic mass number is 209, there are 209 – 83 = 126 neutrons in the nucleus.

(f) We proceed as in Sections 1.4 and 3.4: the volume of the cube is $(5.00)^3\ \text{cm}^3 = 125\ \text{cm}^3$. Then we have

$$125\ \text{cm}^3\ \text{Bi} \times \frac{9.808\ \text{g Bi}}{1\ \text{cm}^3} \times \frac{1\ \text{mol Bi}}{209.0\ \text{g Bi}} = 5.87\ \text{mol Bi}$$

$$5.87\ \text{mol Bi} \times \frac{6.022 \times 10^{23}\ \text{atom Bi}}{1\ \text{mol Bi}} = 3.54 \times 10^{24}\ \text{atoms Bi}$$