The previous chapter discussed two extreme forms of bonding—metallic and ionic. We noted that oxidation numbers in compounds of two nonmetals are not real oxidation states. This chapter will explain a third extreme form of bonding—covalent bonding—without even mentioning oxidation numbers. We can use this model of bonding to predict the characteristics of compounds formed from nonmetals. We can also use this model with compounds containing metals, but it is not well adapted for this use.

### Covalent Bonds

How do two hydrogen atoms bond to form a molecule? The electrons are not free to form the sea of electrons typical of metallic bonds. There is no difference in electrical charges to promote an ionic bond. The answer lies in the sharing of electrons. Each hydrogen atom could complete its 1s orbital if only it had another electron. Sharing an extra electron is almost as good as having one, so hydrogen atoms stay close enough to each other to permit effective sharing. This is shown in Figure 21.1, along with the electron-dot structure that helps to keep track of the number of valence electrons. Notice how sharing helps fluorine complete shell 2. The two electrons shared between atoms constitute a *covalent chemical bond*. Four electrons shared between the atoms constitute a double bond; six shared electrons constitute a triple bond (see the examples of O$_2$ and N$_2$ in Fig. 21.1). The positions of the outer electrons are arbitrary, but they are normally written as pairs. A line between symbols represents a bond, as in H – H. Two lines designate a double bond (O = O), and three designate a triple bond (N = N). Quadruple bonds between nonmetals are not energetically favorable and do not exist.

When atoms share electrons to fill their outermost shell or a subshell consisting of the s- and p-orbitals, it is a means of lowering the electron energy of the atoms and forming stable connecting bonds between them. Since the s- and p-orbitals together can hold eight electrons, most nonmetal atoms are trying to gain access to a total of eight valence electrons by sharing at least two. This tendency of nonmetal atoms to gain access to eight electrons is known as the *octet rule*. Hydrogen, of course, only requires two electrons to fill its outermost shell because shell 1 does not have p-orbitals. For fluorine, eight electrons are required to complete shell 2. Beyond neon, the atoms form covalent bonds by sharing to fill the subshell of s- and p-orbitals. In particular, the shared electrons form orbitals that overlap both of the atoms and act as an electron glue much like the valence orbitals in the metallic bond.

Only valence electrons (those that are outside filled shells) are used in electron-dot structures. Table 21.1 shows the valence electrons (as dots) for many of the common elements. Not surprisingly, the number of valence electrons corresponds to the Roman numeral at the head of each column of the Periodic Table.

Indeed, electron-dot structures provide a more sophisticated way to view the chemical bonding of nonmetals. A correct electron-dot structure must fulfill two requirements: (1) all of the valence electrons brought in by the atoms must show up in the structure, and (2) every atom must have access to eight electrons (its own bonding electrons will be counted once for one atom and then again for the adjacent bonded atom). However, hydrogen needs access to only two electrons.

Now that you can recognize correct electron-dot structures, you can write the structure for any compound, provided you are told which atom is bonded to which if more than two are involved. You may need several tries to get the structure right. Apply the following rules (SO$_2$ is used as the example):
For each atom, find the number of valence electrons available (Table 21.1 or calculated from the Roman numerals at the head of the appropriate column of the Periodic Table). Now add all of these valence electrons (sulfur has 6, and two oxygens have 12, giving a total of 18).

If each atom is to have access to 8 electrons (2 for hydrogen), how many electrons will be required (sulfur needs 8, and two oxygens need 16, requiring a total of 24)?

Notice that the number of electrons available (18 in the example) is not enough to satisfy all of the atoms (24 required in the example). Find how many electrons must be shared (24 minus 18 gives 6 in this example).

Place the atoms as symmetrically as possible (O:S:O). Note that a hydrogen atom cannot be bonded to more than one other atom.

Place the number of electrons to be shared between the atoms. First place one pair of electrons between each pair of atoms (O:S:O which uses up 4 electrons in this example). Now place remaining pairs in positions to form double or triple bonds until all the bonding electrons have been used (6 in this example).

Put the remainder of the available electrons in positions that give each atom access to 8 electrons. Electrons which are not shared are not placed between atoms. They are placed elsewhere around the periphery of the atoms.

If, as in this example, all of the available valence electrons are distributed in such a way that every atom has access to exactly eight electrons (two for hydrogen), and if there are no electrons left over, the structure is said to be a proper electron-dot structure. With few exceptions, these molecules will be stable compounds found in nature. If it is impossible to write a proper electron-dot structure for the proposed nonmetallic reactions product, it is unlikely that the reaction will proceed because the product—if it ever forms at all—will be too flimsy and will deteriorate quickly to a more stable compound. The most notable exceptions to this rule are NO and NO₂, which are stable molecules even though they have odd numbers of electrons and a proper electron-dot structure does not exist. However, exceptions are rare.

### Table 21.1. Valence electrons.

<table>
<thead>
<tr>
<th>GROUP</th>
<th>IA</th>
<th>IIA</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
<th>VIIIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of electrons in highest energy level</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8 (except He)</td>
</tr>
<tr>
<td>H⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H²⁻</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Be⁺:</td>
<td>B⁺:</td>
<td>C⁺:</td>
<td>N⁺:</td>
<td>O⁺:</td>
<td>F⁺:</td>
<td>Ne⁺:</td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>Mg⁺:</td>
<td>Al⁺:</td>
<td>Si⁺:</td>
<td>P⁺:</td>
<td>S⁺:</td>
<td>Cl⁺:</td>
<td>Ar⁺:</td>
<td></td>
</tr>
<tr>
<td>K⁺</td>
<td>Ca⁺:</td>
<td>Ga⁺:</td>
<td>Ge⁺:</td>
<td>As⁺:</td>
<td>Se⁺:</td>
<td>Br⁺:</td>
<td>Kr⁺:</td>
<td></td>
</tr>
<tr>
<td>Rb⁺</td>
<td>Sr⁺:</td>
<td>In⁺:</td>
<td>Sn⁺:</td>
<td>Sb⁺:</td>
<td>Te⁺:</td>
<td>I⁺:</td>
<td>Xe⁺:</td>
<td></td>
</tr>
<tr>
<td>Cs⁺</td>
<td>Ba⁺:</td>
<td>Tl⁺:</td>
<td>Pb⁺:</td>
<td>Bi⁺:</td>
<td>Po⁺:</td>
<td>At⁺:</td>
<td>Rn⁺:</td>
<td></td>
</tr>
<tr>
<td>Fr⁺</td>
<td>Ra⁺:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Electron-dot structures work well for ions as well as for neutral molecules. If the ion has a negative charge, it means the ion has one more electron than the total from Table 21.1. For instance, F\(^–\) has a total of 8 valence electrons, rather than the 7 shown in Table 21.1. The nitrite ion, NO\(_2^–\), has 18 valence electrons, rather than 17. If the ion has a double negative charge, add 2 electrons. The carbonate ion CO\(_3^{2–}\) has 24 valence electrons.

For positively charged ions, subtract. The lithium ion, Li\(^+\), has no valence electrons (its remaining electrons fill the 1s shell). The ammonium ion, NH\(_4^+\), has 8 available valence electrons.

Notice in the example of SO\(_2\) that one oxygen has a single bond (two electrons) and the other has a double bond (four electrons). This implies a difference between the two oxygens in OSO, but in reality they are identical. We think of the electrons of the extra bond as belonging part of the time to one of the oxygen atoms and part of the time to the other. This phenomenon is called “resonance.” Resonant double bonds also occur in benzene (Fig. 21.2).

**Properties of Covalent Molecules**

Covalent bonds usually lead to individual molecules, rather than to crystals with large networks of bonds. Like water, most covalently bonded substances melt and boil at easily accessible temperatures. Only a small percentage of covalent molecules are nontoxic. The nontoxic molecules include CO\(_2\) (carbon dioxide), H\(_2\)O (water), and foods and vitamins made of various combinations of C, H, O, and N. Other molecules with covalent bonds are mildly toxic in moderate amounts, for example, CH\(_2\)CH\(_2\)OH (ethanol or grain alcohol) and N\(_2\)O (nitrous oxide or laughing gas). Many are extremely toxic, including HCN (hydrogen cyanide, used in the gas chamber for executions), H\(_2\)S (hydrogen sulfide, the odor of rotten eggs), and NO\(_2\) (nitrogen dioxide, a component of smog).

**Molecular Ions**

Some ions are composed of more than one atom, such as the carbonate ion, CO\(_3^{2–}\). The carbon atom and its three oxygen atoms remain together in carbonate salts and in solution. These molecular (or polyatomic) ions are stable structures that satisfy the octet rule. Nevertheless, they are charged objects. The molecular ions get their charge by taking electrons from metal atoms, just as if they were single nonmetal atoms.

When negative molecular ions are combined with positive metal ions, they form crystalline salts with the same features as ionic bonds: white, crystalline, transparent, brittle, and so forth. Examples of this kind of compound are calcium carbonate (CaCO\(_3\), limestone) and sodium carbonate (Na\(_2\)CO\(_3\), washing soda).

Other important molecular ions are NH\(_4^+\), ammonium ion, found in many cleaning solutions; NO\(_3^–\), nitrate ion, found in many commercial fertilizers; and SO\(_4^{2–}\), sulfate ion, found in plaster of paris.

The NO\(_3^–\) and CO\(_3^{2–}\) ions are flat, so when these unsymmetrical ions are incorporated into crystals, they often distort the shape of the crystal. Calcium carbonate is not a cubic structure like sodium chloride; it is a skewed parallelepiped.

Electron-dot structures can be applied to ionic compounds between metals and nonmetals, but separate structures must be drawn for the metal ion and the nonmetal ion. The ionic bond between the two ions is the same as before (Chapter 20). The metallic ion gives its valence electrons to the nonmetallic partner.

**Minerals**

Silicon and oxygen constitute about 75 percent (by weight) of the earth’s crust and are important components of many minerals (see Table 21.2). Minerals are
inorganic crystalline solids. The crystals of a given mineral have a specific internal arrangement of atoms, which is reflected in the shapes of the crystals themselves. Minerals are rather unusual chemical compounds because the chemical composition can vary within certain limits for the same mineral. At least in some minerals different kinds of ions can be substituted for others. For example, olivine is a mineral to which we can assign a “chemical formula” \((\text{Mg, Fe})_2\text{SiO}_4\). The mineral can contain either magnesium (Mg) ions or iron (Fe) ions or both kinds in its structure. These two ions are almost exactly the same size, so they can freely substitute for one another. The total number of iron and magnesium atoms is constant, relative to the number of silicon and oxygen atoms in the olivine, but the ratio of iron to magnesium can be different in different samples. The common minerals feldspar, pyroxene, amphibole, and mica each constitute a family (group of related minerals) in which ionic substitution produces a range of chemical composition, physical appearance, and properties.

Although there are more than 2000 known minerals, more than 90 percent (by volume) of the earth’s crust consists of silicates. The basic building block is the complex ion \(\text{SiO}_4^{4-}\), which is tetrahedral in shape. The four oxygen atoms surround a smaller silicon atom at the center. Each oxygen atom of a given tetrahedron

<table>
<thead>
<tr>
<th>Element</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>46.60</td>
</tr>
<tr>
<td>Si</td>
<td>27.72</td>
</tr>
<tr>
<td>Al</td>
<td>8.13</td>
</tr>
<tr>
<td>Fe</td>
<td>5.00</td>
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<tr>
<td>Ca</td>
<td>3.63</td>
</tr>
<tr>
<td>Na</td>
<td>2.83</td>
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<tr>
<td>K</td>
<td>2.59</td>
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<tr>
<td>Mg</td>
<td>2.09</td>
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<tr>
<td>Ti</td>
<td>0.44</td>
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<td>H</td>
<td>0.14</td>
</tr>
<tr>
<td>P</td>
<td>0.12</td>
</tr>
<tr>
<td>Mn</td>
<td>0.10</td>
</tr>
<tr>
<td>S</td>
<td>0.05</td>
</tr>
<tr>
<td>C</td>
<td>0.03</td>
</tr>
<tr>
<td>Others</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Table 21.2. Concentration of the most abundant elements in the earth’s crust (by weight). (From Hamblin, *The Earth’s Dynamic Systems*, p. 65.)

Figure 21.3. Some examples of the arrangements of silica tetrahedra in silicate minerals. (After Hamblin, *The Earth’s Dynamic Systems*, p. 66).
can add a bond to a second silicon atom. Each oxygen atom that links two silicon atoms together is part of both tetrahedra. Many tetrahedra can be chained together with strong silicon-oxygen bonds. The resulting structures may be single chains, double chains, sheets, or complicated three-dimensional structures (see Fig. 21.3).

**Summary**

Nonmetal atoms form covalent bonds with one another. In covalent bonds, some of the valence electrons form orbitals around both of the atoms in such a way as to be shared by the two atoms. When two electrons are shared, the bond is referred to as a single covalent bond; when four are shared the bond is referred to as a double bond, and so on.

Covalent bonds among nonmetal atoms usually lead to individual molecules rather than to an extended structure like a crystal or a piece of metal. Most covalently bonded substances melt and boil at easily accessible temperatures; thus, they are usually liquids or gases rather than solids. Most covalent molecules are toxic to one degree or another. Carbon dioxide, water, and foods and vitamins made of combinations of carbon, hydrogen, oxygen, and nitrogen are exceptions.

In general, it is energetically favorable for atoms to bond by filling their valence shells or subshells. In particular, the subshell consisting of the s and p orbitals has room for 8 electrons. The tendency of atoms to try to gain access to 8 valence electrons by sharing with other atoms is called the octet rule.

Electron-dot structures are simple models of covalent molecules used to determine whether all of the atoms in the molecule have satisfied the octet rule. If all of the atoms in an electron-dot structure have access to eight valence electrons (two for hydrogen) with no electrons left over, the electron-dot structure is said to be proper. Molecules with proper electron-dot structure are very likely to be stable structures found in nature. If it is impossible to write a proper electron-dot structure for a proposed nonmetallic reaction product, it is unlikely that the reaction will proceed because the product—if it ever forms at all—will be too flimsy and will deteriorate quickly to a more stable compound.

Molecular ions are charged covalent structures, that is, the structures have become electrically charged by gaining or losing electrons. Molecular ions are stable structures which satisfy the octet rule if the gained or lost electrons are added or subtracted from the number of valence electrons. Molecular ions may form ionic bonds with metals or other molecular ions. The resulting compounds have the characteristics which we earlier associated with the ionic bond.

Minerals are crystalline solids which are unusual compounds because the chemical composition may vary within certain limits for the same mineral. Thus, a mineral may have a range of chemical composition, physical appearance, and properties.

**STUDY GUIDE**

**Chapter 21: Compounds of Nonmetals**

A. **FUNDAMENTAL PRINCIPLES**

B. **MODELS, IDEAS, QUESTIONS, OR APPLICATIONS**
1. What conditions are required for atoms to form covalent bonds?
2. What is the “octet” rule?
3. What are the properties of compounds held together in covalent bonds?
4. Can you describe a procedure that can be used to apply the octet rule to see if a compound is likely to be found in nature?
5. What are molecular ions?
6. What are minerals?

C. **GLOSSARY**
1. **Covalent Bond:** The chemical bond between nonmetals and nonmetals characterized by a sharing of valence electrons.
2. **Electron-Dot Structure:** A simple diagram of covalent bonding which explicitly shows how the octet rule is satisfied for each atom in a molecule.
3. **Mineral:** Inorganic crystalline solids having a specific internal arrangement of atoms, but which are unusual because the chemical composition may vary within certain limits for the same mineral.
4. **Molecular (or Polyatomic) Ion:** Ions composed of more than one atom in a stable structure that satisfies the octet rule.
5. **Octet Rule:** The tendency of atoms to lower the energy of electrons and thus form a chemical bond by gaining access to eight valence electrons by sharing or by exchange.
6. **Silicate:** A class of minerals containing silicon and oxygen. Ninety percent of the earth’s crust (by volume) consists of silicates.

D. **FOCUS QUESTIONS**
1. For the following proposed compounds or molecular ions:
   a. Outline a procedure for applying the “octet rule” to see if the compound is likely to exist in nature.
   b. Apply the procedure and sketch out the electron-dot structure for the compound.
c. Is the compound likely to occur? [You may assume in each case that the oxygens bond to the other nonmetal atoms and not to each other.]

(1) CO₂
(2) CO₃²⁻
(3) NO₃
(4) NO₃⁻
(5) SiO₄⁴⁻

E. EXERCISES

21.1. Is the correct total number of electrons shown for each of the following electron-dot structures?

(a) 
(b) 
(c) 
(d) 
(e) 

21.2. Mark the electron-dot structures which are incorrect.

(a) 
(b) 
(c) 
(d) 

21.3. Draw correct electron-dot structures for the following ions: Cl⁻, OH⁻, NH₄⁺, and H₂O⁺.

21.4. Draw the electron-dot structures for nitric acid, HNO₃,

21.5. Which of the following pairs of elements would you expect to be covalently bonded (no ionic or metallic bonds):

(a) ⁷⁷Co and ⁶⁵Ni
(b) ³⁹K and ³⁵F
(c) ¹⁵P and ³⁸O
(d) ¹¹Na and ⁵³I

21.6. When gasoline and other petroleum products are burned, they release oxides of sulfur into the air. We have discussed one of them, SO₂, in the instructions for drawing electron-dot structures. If correct electron-dot structures exist for others, such as those shown below,

they may also exist as air pollutants. For which—if any—of these can correct electron-dot structures be drawn?

21.7. Draw electron-dot structures for CH₄ and H₃CCH₃. Notice that these are the first two compounds in a series with a carbon chain as a backbone and enough hydrogens to make the dot structures come out correctly. Do you know of anything that prohibits the formation of chains hundreds or even thousands of carbons long?

21.8. Draw electron-dot structures for the following six molecules. Circle those which show resonance.

Br₂
H₂S
SCS
NO₃⁻ (three oxygens attached to nitrogen)
PH₃ (three hydrogens attached to phosphorus)
CF₄ (four fluorines attached to carbon)

21.9. What characteristics of CCl₄ make it different from metals and also from ionically bonded compounds?

21.10. Which of the following pairs of elements would you expect to be covalently bonded?

(a) ¹⁷Cl and ¹⁵³I
(b) ¹³⁵Cs and ¹²³Br
(c) ¹⁴Si and ¹⁹F

21.11. Explain why oxygen is drawn with six valence electrons and fluorine with seven. How do these facts explain the –2 oxidation number of oxygen and the –1 oxidation number of fluorine?

21.12. Many materials burn well in air, better in oxygen, and furiously in fluorine, F₂. It is impossible for water to put out a fluorine fire because fluorine burns water. If this is true, there must be a compound of hydrogen and fluorine and a compound of oxygen and fluorine (or oxygen and two fluorines). Draw the electron-dot structures of the proposed compounds. If no valid structures exist, then F₂ probably does not burn water.

21.13. Name the commercial fertilizer whose formula is NH₄NO₃.

21.14. Sulfuric acid is formed when H⁺ and SO₄²⁻ get together to form a neutral molecule. What is the correct formula for sulfuric acid (uncharged)?
21.15. Which of the following electron dot structures is incorrect?

(a) \( \cdot \cdot \cdot \cdot \) \( \cdot \cdot \cdot \cdot \) (b) \( \cdot \cdot \cdot \cdot \) \( \cdot \cdot \cdot \cdot \) (c) \( \cdot \cdot \cdot \cdot \) \( \cdot \cdot \cdot \cdot \) (d) \( \cdot \cdot \cdot \cdot \) \( \cdot \cdot \cdot \cdot \) (e) \( \cdot \cdot \cdot \cdot \) \( \cdot \cdot \cdot \cdot \)

21.16. A diatomic molecule consists of one F atom and one Cl atom. How many covalent bonds exist between the two atoms?

(a) single
(b) double
(c) triple
(d) quadruple
(e) none of the above

21.17. Determine the metal or nonmetal nature of C and O. If C and O form a compound, which of the following properties will it have?

(a) metallic alloy, conducting
(b) transparent gas
(c) metallic alloy, nonconducting
(d) brittle, transparent solid, nonconducting
(e) greenish liquid


<table>
<thead>
<tr>
<th>NAME</th>
<th>TYPE ELEMENTS</th>
<th>FORMULA</th>
<th>BONDING</th>
<th>PHYSICAL STATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>nonmetals</td>
<td>CO</td>
<td>covalent</td>
<td>transparent</td>
</tr>
<tr>
<td>Calcium bromide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon tetrachloride</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper-zinc alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>