

CHEMISTRY

AN ATOMS FIRST APPROACH

THIRD EDITION

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Third Edition

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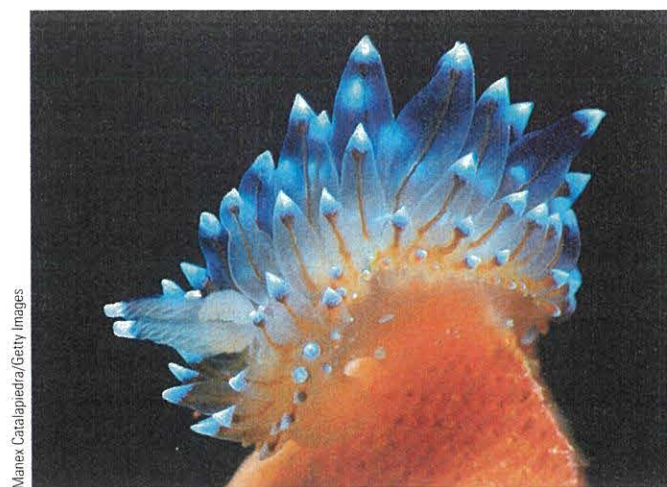
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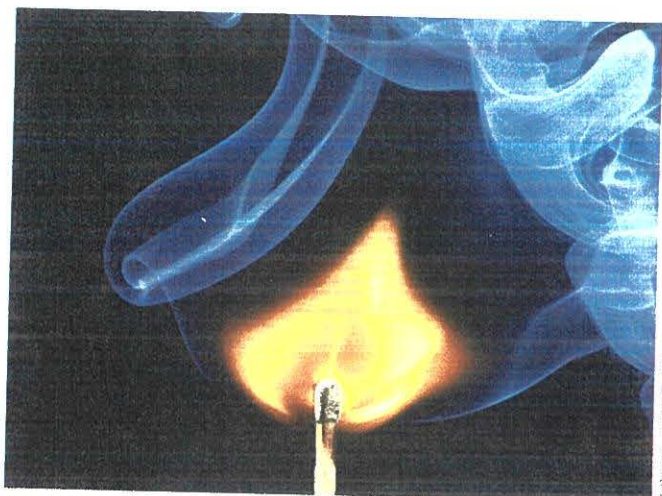
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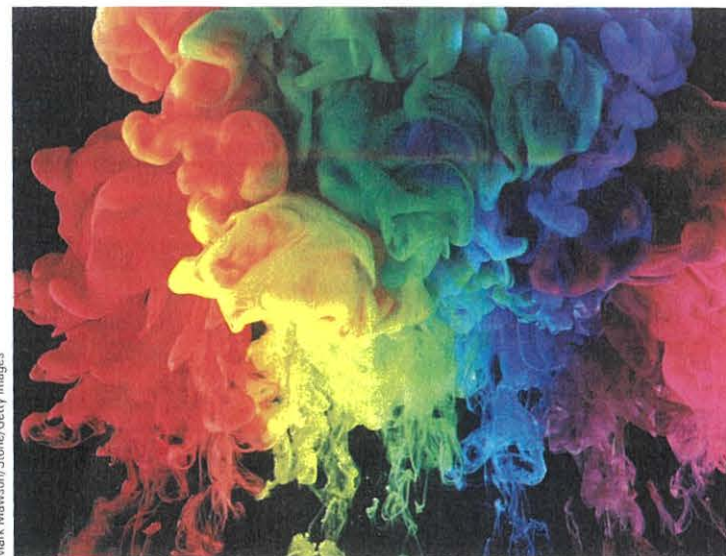
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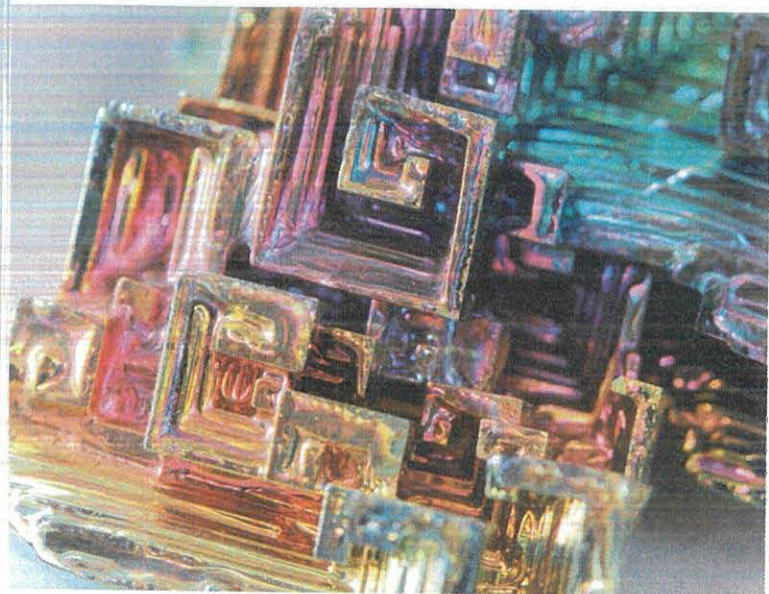
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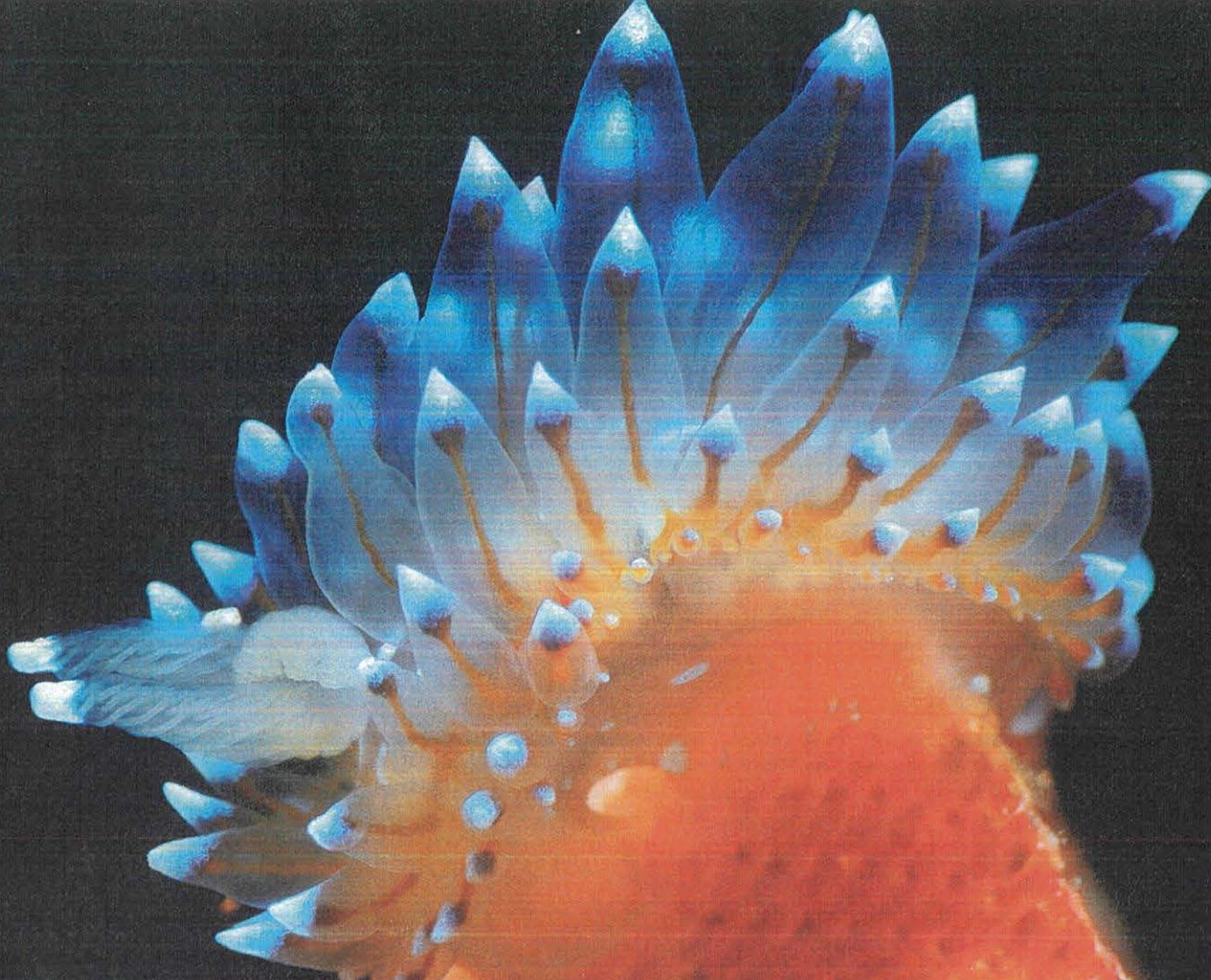
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CHAPTER 3

The nudibranch uses a particular molecule (called an allomone) to defend itself against predators. (Manex Catalapiedra/Getty Images)

Bonding: General Concepts

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Acids

As we examine the world around us, we find it to be composed almost entirely of compounds and mixtures of compounds: Rocks, coal, soil, petroleum, trees, and human bodies are all complex mixtures of chemical compounds in which different kinds of atoms are bound together. Substances composed of unbound atoms do exist in nature, but they are very rare. Examples are the argon in the atmosphere and the helium mixed with natural gas reserves.

The manner in which atoms are bound together has a profound effect on chemical and physical properties. For example, graphite is a soft, slippery material used as a lubricant in locks, and diamond is one of the hardest materials known, valuable both as a gemstone and in industrial cutting tools. Why do these materials, both composed solely of carbon atoms, have such different properties? The answer, as we will see, lies in the bonding in these substances.

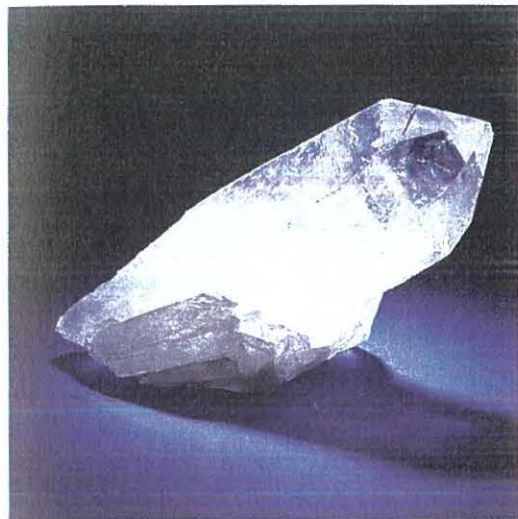
Silicon and carbon are next to each other in Group 4A of the periodic table. From our knowledge of periodic trends, we might expect SiO_2 and CO_2 to be very similar. But SiO_2 is the empirical formula of silica, which is found in sand and quartz, and carbon dioxide is a gas, a product of respiration. Why are they so different? We will be able to answer this question after we have developed models for bonding.

Molecular bonding and structure play the central role in determining the course of all chemical reactions, many of which are vital to our survival. Later in this book we will demonstrate their importance by showing how enzymes facilitate complex chemical reactions, how genetic characteristics are transferred, and how hemoglobin in the blood carries oxygen throughout the body. All of these fundamental biological reactions hinge on the geometric structures of molecules, sometimes depending on very subtle differences in molecular shape to channel the chemical reaction one way rather than another.

Many of the world's current problems require fundamentally chemical answers: disease and pollution control, the search for new energy sources, the development of new fertilizers to increase crop yields, the

improvement of the protein content in various staple grains, and many more. To understand the behavior of natural materials, we must understand the nature of chemical bonding and the factors that control the structures of compounds. In this chapter we will present various classes of compounds that illustrate the different types of bonds and then develop models to describe the structure and bonding that characterize materials found in nature. Later these models will be useful in understanding chemical reactions.

In Chapters 1 and 2, we were concerned with the structure and properties of atoms. But as we stated earlier, free atoms in nature are rare—natural substances are almost always atoms bonded together. Thus, we will now turn our attention to how the atoms combine to form molecules. Why is it that atoms bond together in a molecule? How do they do this? Once we understand this, we will be able to make sense of the structure of molecules (Chapter 4) and we will use this knowledge to better understand the forces that hold molecules together in liquids and solids (Chapter 9).



▲ Quartz grows in beautiful, regular crystals.

3.1 Types of Chemical Bonds

From a chemist's viewpoint, the most interesting characteristic of an atom is its ability to combine with other atoms to form compounds. It was John Dalton who first recognized that chemical compounds are collections of atoms, but he could not determine the structure of atoms or their means for binding to each other. During the twentieth century we learned that atoms have electrons and that these electrons participate in bonding one atom to another.

The forces that hold atoms together in compounds are called **chemical bonds**. One way that atoms can form bonds is by *sharing electrons*. These bonds are called **covalent bonds**, and the resulting collection of atoms is called a **molecule**. Molecules can be represented in several different ways. The simplest method is the **chemical formula**, in which the symbols for the elements are used to indicate the types of atoms present and subscripts are used to indicate the relative numbers of atoms. For example, the formula for carbon dioxide is CO_2 , meaning that each molecule contains 1 atom of carbon and 2 atoms of oxygen.

Examples of molecules that contain covalent bonds are hydrogen (H_2), water (H_2O), oxygen (O_2), ammonia (NH_3), and methane (CH_4). More information about a molecule is given by its **structural formula**, in which the individual bonds are shown (indicated by lines). Structural formulas may or may not indicate the actual shape of the molecule. For example, water might be represented as



The structure on the right shows the actual shape of the water molecule. Scientists know from experimental evidence that the molecule looks like this. (We will study the shapes of molecules further in Chapter 4.)

The structural formula for ammonia is



Ammonia.

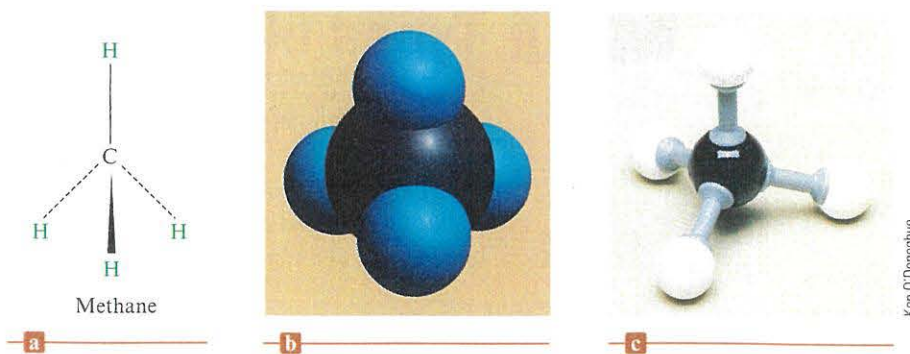
Note that atoms connected to the nitrogen atom by dashed lines are behind the plane of the paper, and atoms connected to the nitrogen atom by wedges are in front of the plane of the paper.

In a compound composed of molecules, the individual molecules move around as independent units. For example, a molecule of methane gas can be represented in several ways. The structural formula for methane (CH_4) is shown in Fig. 3.1(a). The **space-filling model** of methane, which shows the relative sizes of the atoms as well as their relative orientation in the molecule, is given in Fig. 3.1(b). **Ball-and-stick models** are also used to represent molecules. The ball-and-stick structure of methane is shown in Fig. 3.1(c).

What is a chemical bond? There is no simple and yet complete answer to this question. For our purposes we will define bonds as forces that hold groups of atoms together and make them function as a unit.

There are many types of experiments we can perform to determine the fundamental nature of materials. For example, we can study physical properties such as melting point, hardness, and electrical and thermal conductivity. We can also study solubility characteristics and the properties of the resulting solutions. To determine the charge distribution in a molecule, we can study its behavior in an electric field. We can obtain

FIGURE 3.1 (a) The structural formula for methane. (b) Space-filling model of methane. This type of model shows both the relative sizes of the atoms in the molecule and their spatial relationships. (c) Ball-and-stick model of methane.



Ken O'Donoghue

CHEMICAL CONNECTIONS 3.1

No Lead Pencils

Did you ever wonder why the part of a pencil that makes the mark is called the “lead”? Pencils have no lead in them now—and they never have. Apparently the association between writing and the element lead arose during the Roman Empire, when lead rods were used as writing utensils because they leave a gray mark on paper. Many centuries later, in 1564, a deposit of a black substance found to be very useful for writing was discovered in Borrowdale, England. This substance, originally called “black lead,” was shown in 1879 by Swedish chemist Carl Scheele to be a form of carbon and was subsequently named graphite (after the Greek *graphein*, meaning “to write”).

Originally, chunks of graphite from Borrowdale, called marking stones, were used as writing instruments. Later, sticks of graphite were used. Because graphite is brittle, the sticks needed reinforcement. At first they were wrapped in string, which was unwound as the core wore down. Eventually, graphite rods were tied between two wooden slats or inserted into hollowed-out wooden sticks to form the first crude pencils.

Although Borrowdale graphite was pure enough to use directly, most graphite must be mixed with other materials to be useful for writing instruments. In 1795, the French chemist Nicolas-Jaques Conté invented a process in which graphite is mixed with clay and water to produce pencil “lead,” a recipe that is still used today. In modern pencil manufacture, graphite and clay are mixed and crushed into a fine powder to which water is added. After the gray sludge is blended for several days, it is dried, ground up again, and mixed with more water to give a gray paste. The paste is extruded through a metal tube to form thin rods, which are then cut into pencil-length pieces called “leads.” These leads are heated in an oven to 1000°C until they are smooth and hard.

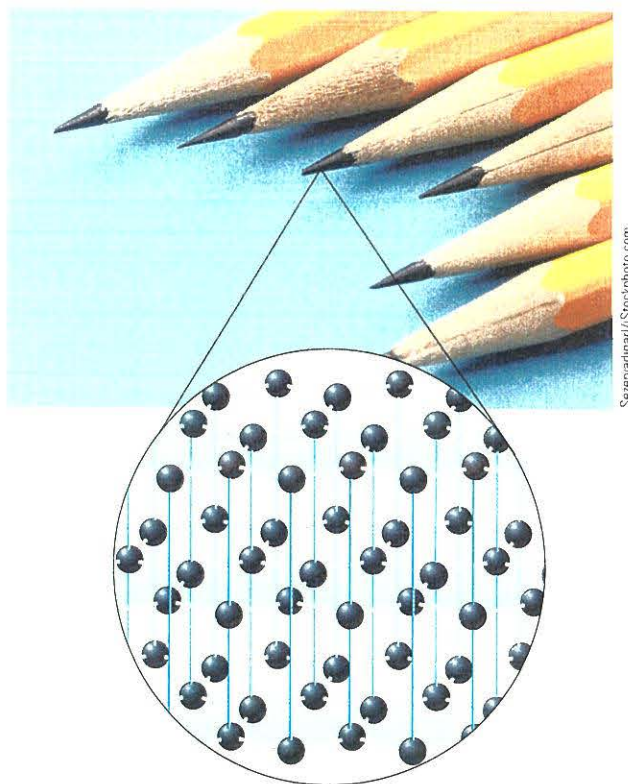
The ratio of clay to graphite is adjusted to vary the hardness of the lead—the more clay in the mix, the harder the lead and the lighter the line it makes.

Pencils are made from a slat of wood with several grooves cut in it to hold the leads. A similar grooved slat is then placed on top and glued to form a “sandwich” from which individual pencils are cut, sanded smooth, and painted. Although many types of wood have been used over the years to make pencils, the current favorite is incense cedar from the Sierra Nevada Mountains of California.

Modern pencils are simple but amazing instruments. The average pencil can write approximately 45,000 words, which is equivalent to a line 35 miles long. The graphite in a pencil is easily transferred to paper because graphite contains layers of carbon

atoms bound together in a “chicken-wire” structure. Although the bonding *within* each layer is very strong, the bonding *between* layers is weak, giving graphite its slippery, soft nature. In this way, graphite is much different from diamond, the other common elemental form of carbon. In diamond the carbon atoms are bound tightly in all three dimensions, making it extremely hard—the hardest natural substance.

Pencils are very useful—especially for doing chemistry problems—because we can erase our mistakes. Most pencils used in the United States have erasers (first attached to pencils in 1858), although most European pencils do not. Laid end to end, the number of pencils made in the United States each year would circle the earth about 15 times. Pencils illustrate how useful a simple substance like graphite can be.



Graphite

information about the strength of a bonding interaction by measuring the **bond energy**, which is the energy required to break the bond.

There are several ways in which atoms can interact with one another to form aggregates. We will consider several specific examples to illustrate the various types of chemical bonds.

We observe that when solid sodium chloride is dissolved in water, the resulting solution conducts electricity, a fact that helps to convince us that sodium chloride is composed of Na^+ and Cl^- ions. Therefore, when sodium and chlorine react to form sodium chloride, electrons are transferred from the sodium atoms to the chlorine atoms to form Na^+ and Cl^- ions, which then aggregate to form solid sodium chloride. Why does this happen? The best simple answer is that *the system can achieve the lowest possible energy by behaving in this way*. The attraction of a chlorine atom for the extra electron and the very strong mutual attractions of the oppositely charged ions provide the driving forces for the process. Note that in an ionic substance such as sodium chloride, there are no individual $\text{Na}^+\cdots\text{Cl}^-$ bonds but many simultaneous interactions among the ions. The resulting solid sodium chloride is a very sturdy material; it has a melting point of approximately 800°C . The bonding forces that produce this great thermal stability result from the electrostatic attractions of the closely packed, oppositely charged ions. This is an example of **ionic bonding**. Ionic substances are formed when an atom that loses electrons relatively easily reacts with an atom that has a high affinity for electrons. That is, an **ionic compound** results when a metal reacts with a nonmetal.

The energy of interaction between a pair of ions can be calculated using **Coulomb's law** in the form

$$E = (2.31 \times 10^{-19} \text{ J}\cdot\text{nm}) \left(\frac{Q_1 Q_2}{r} \right)$$

where E has units of joules, r is the distance between the ion centers in nanometers, and Q_1 and Q_2 are the numerical ion charges.

For example, in solid sodium chloride the distance between the centers of the Na^+ and Cl^- ions is $2.76 \text{ \AA}$ (0.276 nm), and the ionic energy per pair of ions is

$$E = (2.31 \times 10^{-19} \text{ J}\cdot\text{nm}) \left[\frac{(+1)(-1)}{0.276 \text{ nm}} \right] = -8.37 \times 10^{-19} \text{ J}$$

where the negative sign indicates an attractive force. That is, the *ion pair has lower energy than the separated ions*.

Coulomb's law also can be used to calculate the repulsive energy when two like-charged ions are brought together. In this case the calculated value of the energy will have a positive sign, indicating that the pair of like-charged ions have higher energy than when they are separated.

We have seen that a bonding force develops when two different types of atoms react to form oppositely charged ions. But how does a bonding force develop between two identical atoms? Let's explore this situation from a very simple point of view by considering the energy terms that result when two hydrogen atoms are brought close together, as shown in Fig. 3.2(a). When hydrogen atoms are brought close together, there are two unfavorable potential energy terms, proton-proton repulsion and electron-electron repulsion, and one favorable term, proton-electron attraction. Under what conditions will the H_2 molecule be favored over the separated hydrogen atoms? That is, what conditions will favor bond formation? The answer lies in the strong tendency in nature for any system to achieve the lowest possible energy. A bond will form (that is, the two hydrogen atoms will exist as a molecular unit) if the system can lower its total energy in the process.

In this case, then, the hydrogen atoms will position themselves so that the system will achieve the lowest possible energy; the system will act to minimize the sum of the



A bond will form if the energy of the aggregate is lower than that of the separated atoms.

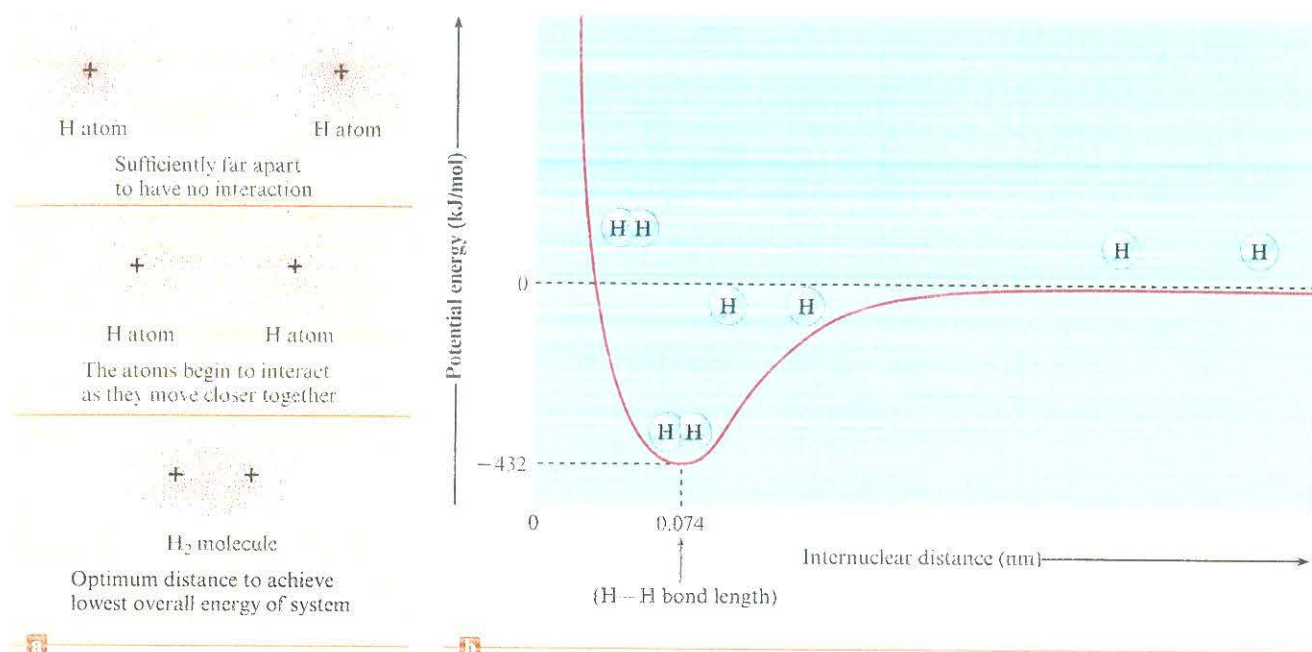


FIGURE 3.2 (a) The interaction of two hydrogen atoms (the red dots indicate electron density). Going from top to bottom, note that the electron density increases between the nuclei until the system reaches minimum energy. (b) Energy profile as a function of the distance between the nuclei of the hydrogen atoms. As the atoms approach each other (right side of graph), the energy decreases until the distance reaches 0.074 nm (74 pm) and then begins to increase again due to repulsions.

positive (repulsive) energy terms and the negative (attractive) energy term. The distance where the energy is minimal is called the **bond length**. The total energy of this system as a function of distance between the hydrogen nuclei is shown in Fig. 3.2(b). Note several important features of this diagram:

The energy terms involved are the net potential energy that results from the attractions and repulsions among the charged particles and the kinetic energy due to the motions of the electrons.

The zero point of energy is defined with the atoms at infinite separation.

At very short distances the energy rises steeply because of the importance of the repulsive forces when the atoms are very close together.

The bond length is the distance at which the system has minimum energy.

In the H₂ molecule, the electrons reside primarily in the space between the two nuclei, where they are attracted simultaneously by both protons. This positioning is precisely what leads to the stability of the H₂ molecule compared with two separated hydrogen atoms. The potential energy of each electron is lowered because of the increased attractive forces in this area. When we say that a bond is formed between the hydrogen atoms, we mean that the H₂ molecule is more stable than two separated hydrogen atoms by a certain quantity of energy (the bond energy). This is the energy that would be required to break apart the molecule into separate hydrogen atoms.

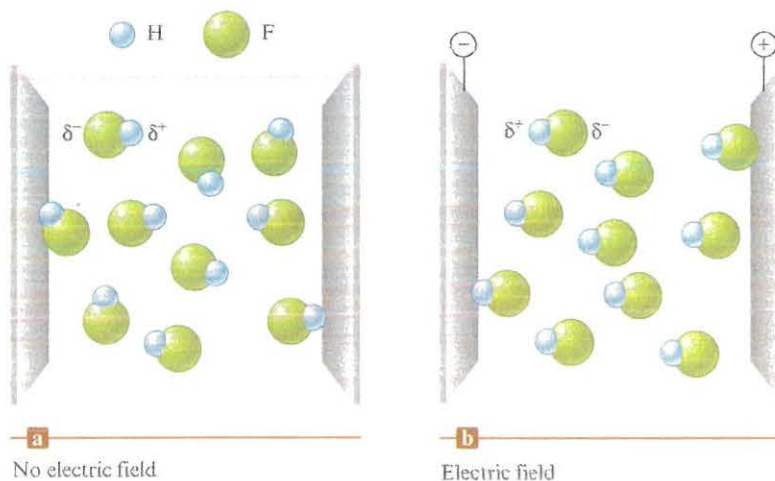
We can also think of a bond in terms of forces. The simultaneous attraction of each electron by the protons generates a force that pulls the protons toward each other and that just balances the proton-proton and electron-electron repulsive forces at the distance corresponding to the bond length.

Notice that to understand why a bond forms, we need to know the structure of the atoms.

FIGURE 3.3 The effect of an electric field on hydrogen fluoride molecules.

(a) When no electric field is present, the molecules are randomly oriented.

(b) When the field is turned on, the molecules tend to line up with their negative ends toward the positive pole and their positive ends toward the negative pole.



Ionic and covalent bonds are the extreme bond types.

The type of bonding we encounter in the hydrogen molecule and in many other molecules in which *electrons are shared by nuclei* is called **covalent bonding**.

So far we have considered two extreme types of bonding. In ionic bonding the participating atoms are so different that one or more electrons are transferred to form oppositely charged ions, which then attract each other. In covalent bonding between two identical atoms, the electrons are shared equally. The bonding results from the mutual attraction of the two nuclei for the shared electrons. Between these extremes are intermediate cases in which the atoms are not so different that electrons are completely transferred but are different enough that unequal sharing results, forming what is called a **polar covalent bond**. An example of this type of bond occurs in molecules of HF (hydrogen fluoride). When a sample of hydrogen fluoride gas is placed in an electric field, the molecules tend to orient themselves as shown in Fig. 3.3, with the fluoride end closest to the positive pole and the hydrogen end closest to the negative pole. This result implies that the HF molecule has the following charge distribution:



where δ (lowercase delta) is used to indicate a fractional charge.

The most logical explanation for the development of the partial positive and negative charges on the atoms (bond polarity) in molecules such as HF is that the electrons in the bonds are not shared equally. For example, we can account for the polarity of the HF molecule by assuming that the fluorine atom has a stronger attraction for the shared electrons than the hydrogen atom. Because bond polarity has important chemical implications, we find it useful to quantify the ability of an atom to attract shared electrons. In the next section we show how this is done.

3.2 Electronegativity

The different affinities of atoms for the electrons in a bond are described by a property called **electronegativity**: *the ability of an atom in a molecule to attract shared electrons to itself*.

The most widely accepted method for determining values of electronegativity is that of Linus Pauling (1901–1995), an American scientist who won the Nobel Prizes for both chemistry and peace. To understand Pauling's model, consider a hypothetical

molecule HX. The relative electronegativities of the H and X atoms are determined by comparing the measured H—X bond energy with the “expected” H—X bond energy. We will assume that the “expected” bond energy is an average of the H—H and X—X bond energies:

$$\text{Expected H—X bond energy} = \frac{\text{H—H bond energy} + \text{X—X bond energy}}{2}$$

The difference (Δ) between the actual (measured) and expected bond energies is

$$\Delta = (\text{H}-\text{X})_{\text{act}} - (\text{H}-\text{X})_{\text{exp}}$$

If H and X have identical electronegativities, $(\text{H}-\text{X})_{\text{act}}$ and $(\text{H}-\text{X})_{\text{exp}}$ are the same, and Δ is 0. On the other hand, if X has a greater electronegativity than H, the shared electron(s) will tend to be closer to the X atom. The molecule will be polar, with the following charge distribution:



Note that this bond can be viewed as having an ionic as well as a covalent component. The attraction between the partially (and oppositely) charged H and X atoms will lead to a greater bond strength. Thus $(H-X)_{act}$ will be larger than $(H-X)_{exp}$. The greater is the difference in the electronegativities of the atoms, the greater is the ionic component of the bond and the greater is the value of Δ . Thus the relative electronegativities of H and X can be assigned from the Δ values.

Electronegativity values have been determined by this process for virtually all the elements; the results are given in Fig. 3.4. Note that electronegativity generally increases going from left to right across a period and decreases going down a group for the representative elements. The range of electronegativity values is from 4.0 for fluorine to 0.7 for cesium.

The relationship between electronegativity and bond type is shown in Table 3.1. For identical atoms (an electronegativity difference of zero), the electrons in the bond are shared equally, and no polarity develops. When two atoms with very different electronegativities interact, electron transfer can occur to form the ions that make up an ionic substance. Intermediate cases give polar covalent bonds with unequal electron sharing.

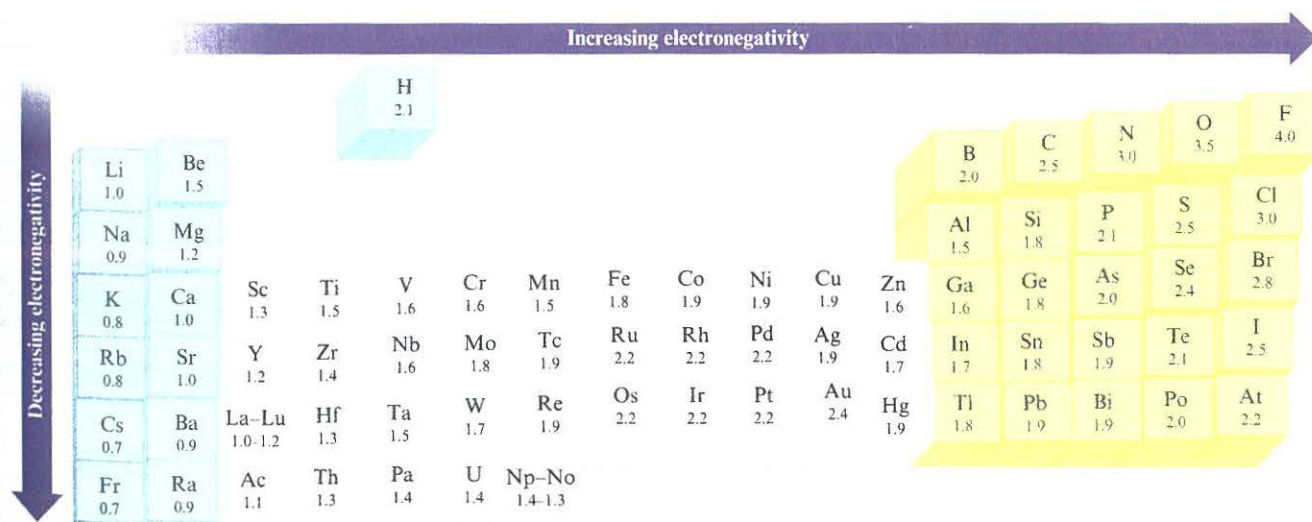


FIGURE 3.4 The Pauling electronegativity values. Electronegativity generally increases across a period and decreases down a group.

TABLE 3.1 | The Relationship Between Electronegativity and Bond Type

Electronegativity Difference in the Bonding Atoms	Bond Type	
Zero	Covalent	Covalent character
Intermediate	Polar covalent	
Large	Ionic	Ionic character

INTERACTIVE EXAMPLE 3.1**Relative Bond Polarities**

Order the following bonds according to polarity: H—H, O—H, Cl—H, S—H, and F—H.

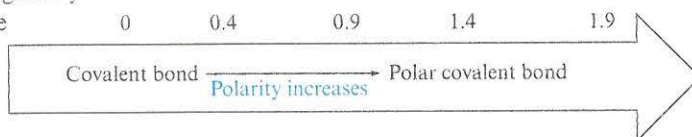
SOLUTION

Notice that the general trends are consistent with those of atomic radii. In general, smaller atoms across a row tend to have larger electronegativity values. This makes sense because the greater nuclear charge that causes the atom to be smaller will also have more attraction for a shared electron. As we move down a column, the atoms are larger and the shared electrons are further from the nucleus, thus they are not “held” as tightly. Note that electronegativity values generally decrease down a column.

The polarity of the bond increases as the difference in electronegativity increases. From the electronegativity values in Fig. 3.4, the following variation in bond polarity is expected (the electronegativity value appears in parentheses below each element):



Electronegativity difference



See Exercises 3.35 and 3.36

3.3**Ions: Electron Configurations and Sizes**

Atoms in stable compounds usually have a noble gas electron configuration.

The description of the electron arrangements in atoms that emerged from the quantum mechanical model has helped a great deal in our understanding of what constitutes a stable compound. In almost every case it has been observed that the atoms in a stable compound have a noble gas arrangement of electrons. Nonmetallic elements achieve a noble gas electron configuration either by sharing electrons with other nonmetals to form covalent bonds or by taking electrons from metals to form ions. In the second case, the nonmetals form anions, and the metals form cations. The generalizations that apply to electron configurations in stable compounds are as follows:

Electron Configuration of Compounds

- » When two *nonmetals* react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms. That is, both nonmetals attain noble gas electron configurations.

(Box continues on following page)

- » When a nonmetal and a representative-group metal react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal achieves the electron configuration of the next noble gas atom and the valence orbitals of the metal are emptied. In this way both ions achieve noble gas electron configurations.

These generalizations apply to the vast majority of compounds and are important to remember. We will deal with covalent bonds more thoroughly later, but now we will consider what implications these rules hold for ionic compounds.

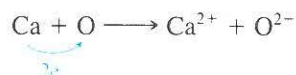
Predicting Formulas of Ionic Compounds

At the beginning of this discussion it should be emphasized that when chemists use the term *ionic compound*, they are usually referring to the solid state of that compound. In the solid state the ions are close together. That is, solid ionic compounds contain a large collection of positive and negative ions packed together in a way that minimizes the $\ominus \cdots \ominus$ and $\oplus \cdots \oplus$ repulsions and maximizes the $\oplus \cdots \ominus$ attractions. This situation stands in contrast to the gas phase of an ionic substance, where the ions are quite far apart on average. In the gas phase, a pair of ions may get close enough to interact, but large collections of ions do not exist. Thus, when we speak in this text of the stability of an ionic compound, we are referring to the solid state, where the large attractive forces present among oppositely charged ions tend to stabilize (favor the formation of) the ions. For example, as we mentioned in the preceding chapter, the O^{2-} ion is not stable as an isolated, gas-phase species but, of course, is very stable in many solid ionic compounds. That is, $\text{MgO}(s)$, which contains Mg^{2+} and O^{2-} ions, is very stable, but the isolated, gas-phase ion pair $\text{Mg}^{2+} \cdots \text{O}^{2-}$ is not energetically favorable in comparison with the separate neutral gaseous atoms. Thus you should keep in mind that in this section, and in most other cases where we are describing the nature of ionic compounds, the discussion usually refers to the solid state, where many ions are simultaneously interacting.

To illustrate the principles of electron configurations in stable, solid ionic compounds, we will consider the formation of an ionic compound from calcium and oxygen. We can predict what compound will form by considering the valence electron configurations of the two atoms:



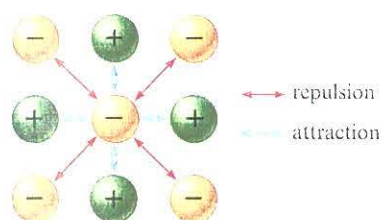
From Fig. 3.4 we see that the electronegativity of oxygen (3.5) is much greater than that of calcium (1.0). Because of this large difference, electrons will be transferred from calcium to oxygen to form oxygen anions and calcium cations in the compound. How many electrons are transferred? We can base our prediction on the observation that noble gas configurations are generally the most stable. Note that oxygen needs two electrons to fill its $2s$ and $2p$ valence orbitals and to achieve the configuration of neon ($1s^22s^22p^6$). And by losing two electrons, calcium can achieve the configuration of argon. Two electrons therefore transferred:



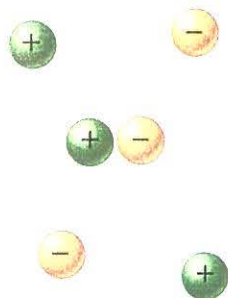
To predict the formula of the ionic compound, we simply recognize that chemical compounds are always electrically neutral—they have the same quantities of positive and negative charges. In this case we have equal numbers of Ca^{2+} and O^{2-} ions, and the empirical formula of the compound is CaO .

The same principles can be applied to many other cases. For example, consider the compound formed between aluminum and oxygen. Because aluminum has the configuration $[\text{Ne}]3s^23p^1$, it loses three electrons to form the Al^{3+} ion and thus achieves

In the solid state of an ionic compound the ions are relatively close together, and many ions are simultaneously interacting:



In the gas phase of an ionic substance the ions would be relatively far apart and would not contain large groups of ions:



While our observations lead us to see that ions in compounds generally have noble gas configurations, this does not mean that the isolated ion is more stable than the parent atom. We will discuss this in more detail at the end of Section 3.4.

TABLE 3.2 | Common Ions with Noble Gas Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^- , Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}		S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}		Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}		Te^{2-}	I^-	[Xe]



Courtesy: Aluminum Company of America

▲ A bauxite mine. Bauxite contains Al_2O_3 , the main source of aluminum.

the neon configuration. Therefore, the Al^{3+} and O^{2-} ions form in this case. Since the compound must be electrically neutral, there must be three O^{2-} ions for every two Al^{3+} ions, and the compound has the empirical formula Al_2O_3 .

Table 3.2 shows common elements that form ions with noble gas electron configurations in ionic compounds. In losing electrons to form cations, metals in Group 1A lose one electron, those in Group 2A lose two electrons, and those in Group 3A lose three electrons. In gaining electrons to form anions, nonmetals in Group 7A (the halogens) gain one electron, and those in Group 6A gain two electrons. Hydrogen typically behaves as a nonmetal when it forms ionic compounds and can gain one electron to form the hydride ion (H^-), which has the electron configuration of helium.

There are some important exceptions to the rules discussed here. For example, tin forms both Sn^{2+} and Sn^{4+} ions, and lead forms both Pb^{2+} and Pb^{4+} ions. Also, bismuth forms Bi^{3+} and Bi^{5+} ions, and thallium forms Tl^+ and Tl^{3+} ions. There are no simple explanations for the behavior of these elements when they form ions. For now, just note them as exceptions to the very useful rule that ions generally adopt noble gas electron configurations in ionic compounds. Our discussion here refers to representative metals. The transition metals exhibit more complicated behavior, forming a variety of ions.

Sizes of Ions

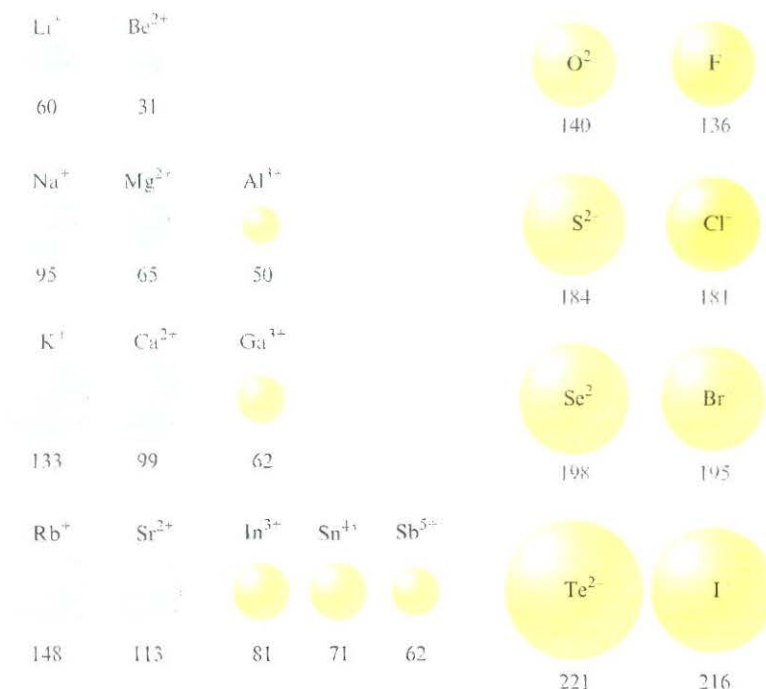
Ion size plays an important role in determining the structure and stability of ionic solids, the properties of ions in aqueous solution, and the biologic effects of ions. As with atoms, it is impossible to define precisely the sizes of ions. Most often, ionic radii are determined from the measured distances between ion centers in ionic compounds. This method, of course, involves an assumption about how the distance should be divided up between the two ions. Thus you will note considerable disagreement among ionic sizes given in various sources. Here we are mainly interested in trends and will be less concerned with absolute ion sizes.

Various factors influence ionic size. We will first consider the relative sizes of an ion and its parent atom. Since a positive ion is formed by removing one or more electrons from a neutral atom, the resulting cation is smaller than its parent atom. The opposite is true for negative ions; the addition of electrons to a neutral atom produces an anion significantly larger than its parent atom.

It is also important to know how the sizes of ions vary, depending on the positions of the parent elements in the periodic table. Fig. 3.5 shows the sizes of the most important ions (each with a noble gas configuration) and their positions in the periodic table. Note that ion size increases down a group. This is because the parent atoms increase in size going down a group. The changes that occur horizontally are complicated because of the change from predominantly metals on the left side of the periodic table to nonmetals on the right side. A given period thus contains both elements that give up electrons to form cations and ones that accept electrons to form anions.

One trend worth noting involves the relative sizes of a set of **isoelectronic ions**—ions containing the same number of electrons. Consider the ions O^{2-} , F^- , Na^+ , Mg^{2+} , and Al^{3+} . Each of these ions has the neon electron configuration. How do the sizes of

FIGURE 3.5 Sizes of ions related to positions of the elements on the periodic table. Note that size generally increases down a group. Also note that in a series of isoelectronic ions, size decreases with increasing atomic number. The ionic radii are given in units of picometers.



For isoelectronic ions, size decreases as Z increases.

these ions vary? In general, there are two important facts to consider in predicting the relative sizes of ions: the number of electrons and the number of protons. Since these ions are isoelectronic, the number of electrons is 10 in each case. Electron repulsions therefore should be about the same in all cases. However, the number of protons increases from 8 to 13 as we go from the O^{2-} ion to the Al^{3+} ion. Thus, in going from O^{2-} to Al^{3+} , the 10 electrons experience a greater attraction as the positive charge on the nucleus increases. This causes the ions to become smaller. You can confirm this by looking at Fig. 3.5. In general, for a series of isoelectronic ions, the size decreases as the nuclear charge Z increases.

Ions have different radii than their parent atoms. What if ions stayed the same size as their parent atoms? How would this affect ionic bonding in compounds?

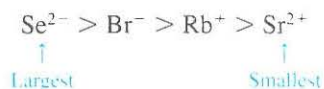
INTERACTIVE EXAMPLE 3.2

Relative Ion Size I

Arrange the ions Se^{2-} , Br^- , Rb^+ , and Sr^{2+} in order of decreasing size.

SOLUTION

This is an isoelectronic series of ions with the krypton electron configuration. Since these ions all have the same number of electrons, their sizes will depend on the nuclear charge. The Z values are 34 for Se^{2-} , 35 for Br^- , 37 for Rb^+ , and 38 for Sr^{2+} . Since the nuclear charge is greatest for Sr^{2+} , it is the smallest of these ions. The Se^{2-} ion is largest:



See Exercises 3.49 and 3.50

INTERACTIVE EXAMPLE 3.3

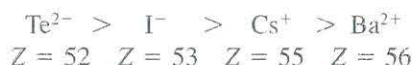
Relative Ion Size II

Choose the largest ion in each of the following groups.

- $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$
- $\text{Ba}^{2+}, \text{Cs}^+, \text{I}^-, \text{Te}^{2-}$

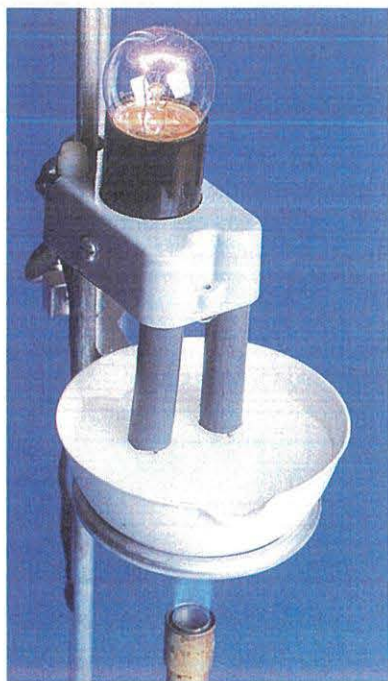
SOLUTION

- The ions are all from Group 1A elements. Since size increases down a group (the ion with the greatest number of electrons is largest), Cs^+ is the largest ion.
- This is an isoelectronic series of ions, all of which have the xenon electron configuration. The ion with the smallest nuclear charge is largest:



See Exercises 3.51 and 3.52

3.4 Partial Ionic Character of Covalent Bonds



▲ Molten NaCl conducts an electric current, indicating the presence of mobile Na^+ and Cl^- ions.

Recall that when atoms with different electronegativities react to form molecules, the electrons are not shared equally. The possible result is a polar covalent bond or, in the case of a large electronegativity difference, a complete transfer of one or more electrons to form ions. The cases are summarized in Fig. 3.6.

How well can we tell the difference between an ionic bond and a polar covalent bond? The only honest answer to this question is that there are probably no totally ionic bonds between *discrete pairs of atoms*. The evidence for this statement comes from calculations of the percent ionic character for the bonds of various binary compounds in the gas phase. These calculations are based on comparisons of the measured dipole moments for molecules of the type $\text{X}-\text{Y}$ with the calculated dipole moments for the completely ionic case, X^+Y^- . The percent ionic character of a bond can be defined as

$$\text{Percent ionic character of a bond} = \left(\frac{\text{measured dipole moment of } \text{X}-\text{Y}}{\text{calculated dipole moment of } \text{X}^+\text{Y}^-} \right) \times 100\%$$

Application of this definition to various compounds (in the gas phase) gives the results shown in Fig. 3.7, where percent ionic character is plotted versus the difference in the electronegativity values of X and Y. Note from this plot that ionic character increases with electronegativity difference, as expected. However, none of the bonds reaches 100% ionic character, even though compounds with the maximum possible electronegativity differences are considered. Thus, according to this definition, no individual bonds are completely ionic. This conclusion is in contrast to the usual classification of many of these compounds (as ionic solids). All the compounds shown in Fig. 3.7 with more than 50% ionic character are normally considered to be ionic solids. Recall, however, the results in Fig. 3.7 are for the gas phase, where individual XY molecules

FIGURE 3.6 The three possible types of bonds: (a) a covalent bond formed between identical F atoms; (b) the polar covalent bond of HF , with both ionic and covalent components; and (c) an ionic bond with no electron sharing.

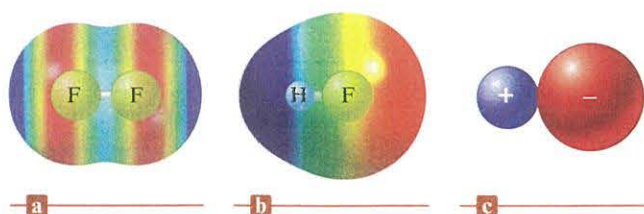
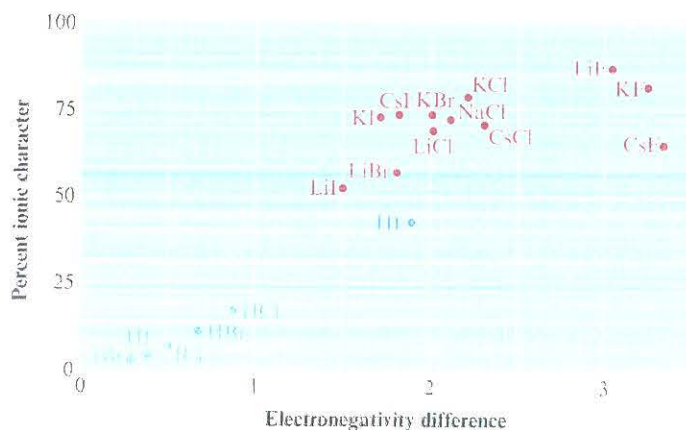


FIGURE 3.7 The relationship between the ionic character of a covalent bond and the electronegativity difference of the bonded atoms. Note that the compounds in red with ionic character greater than 50% are normally considered to be ionic compounds.



exist. These results cannot necessarily be assumed to apply to the solid state, where the existence of ions is favored by the multiple ion interactions.

Another complication in identifying ionic compounds is that many substances contain polyatomic ions. For example, NH_4Cl contains NH_4^+ and Cl^- ions, and Na_2SO_4 contains Na^+ and SO_4^{2-} ions. The bonds within the ammonium (NH_4^+) and sulfate (SO_4^{2-}) ions are covalent bonds.

We will avoid these problems by adopting an operational definition of ionic compounds: *Any compound that conducts an electric current when melted will be classified as ionic.*

3.5 The Covalent Chemical Bond: A Model

Before we develop specific models for covalent chemical bonding, it will be helpful to summarize some of the concepts introduced in this chapter. Also recall from your previous studies of chemistry that when we deal with atoms and molecules, the numbers involved are so large that we use the mole (6.022×10^{23} units) to describe quantities of atoms, molecules, or bonds. This concept was reviewed in Section R.10.

What is a chemical bond? Chemical bonds can be viewed as forces that cause a group of atoms to behave as a unit.

Why do chemical bonds occur? There is no principle of nature that states that bonds are favored or disfavored. Bonds are neither inherently “good” nor inherently “bad” as far as nature is concerned; *bonds result from the tendency of a system to seek its lowest possible energy.* From a simplistic point of view, bonds occur when collections of atoms are more stable (lower in energy) than the separate atoms. For example, approximately 1652 kJ of energy is required to break a mole of methane (CH_4) molecules into separate C and H atoms. Or, from the opposite view, 1652 kJ of energy is released when 1 mole of methane is formed from 1 mole of gaseous C atoms and 4 moles of gaseous H atoms. Thus we can say that 1 mole of CH_4 molecules in the gas phase is 1652 kJ lower in energy than 1 mole of carbon atoms plus 4 moles of hydrogen atoms. Methane is therefore a stable molecule relative to its separated atoms.

We find it useful to interpret molecular stability in terms of a model called a *chemical bond*. To understand why this model was invented, let’s continue with methane, which consists of four hydrogen atoms arranged at the corners of a tetrahedron around a carbon atom.

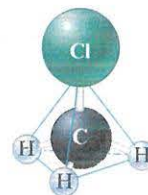


A tetrahedron has four equilateral triangular faces.

Given this structure, it is natural to envision four individual C—H interactions (we call them *bonds*). The energy of stabilization of CH₄ is divided equally among the four bonds to give an average C—H bond energy per mole of C—H bonds:

$$\frac{1652 \text{ kJ/mol}}{4} = 413 \text{ kJ/mol}$$

Next, consider methyl chloride, which consists of CH₃Cl molecules having the structure



Experiments have shown that approximately 1578 kJ of energy is required to break down 1 mole of gaseous CH₃Cl molecules into gaseous carbon, chlorine, and hydrogen atoms. The reverse process can be represented as



A mole of gaseous methyl chloride is lower in energy by 1578 kJ than its separate gaseous atoms. Thus a mole of methyl chloride is held together by 1578 kJ of energy. Again, it is very useful to divide this energy into individual bonds. Methyl chloride can be visualized as containing one C—Cl bond and three C—H bonds. If we assume arbitrarily that a C—H interaction represents the same quantity of energy in any situation (that is, that the strength of a C—H bond is independent of its molecular environment), we can do the following bookkeeping:

$$1 \text{ mol C—Cl bonds plus } 3 \text{ mol C—H bonds} = 1578 \text{ kJ}$$

$$\text{C—Cl bond energy} + 3(\text{average C—H bond energy}) = 1578 \text{ kJ}$$

$$\text{C—Cl bond energy} + 3(413 \text{ kJ/mol}) = 1578 \text{ kJ}$$

$$\text{C—Cl bond energy} = 1578 - 1239 = 339 \text{ kJ/mol}$$

These assumptions allow us to associate given quantities of energy with C—H and C—Cl bonds. So far we have considered bonds in which one pair of electrons is shared. This type of bond is called a **single bond**. As we will see in more detail later, atoms sometimes share two pairs of electrons, forming a **double bond**, or share three pairs of electrons, forming a **triple bond**.

It is important to note that the bond concept is a human invention. Bonds provide a method for dividing up the energy evolved when a stable molecule is formed from its component atoms. Thus in this context a bond represents a quantity of energy obtained from the overall molecular energy of stabilization in a rather arbitrary way. This is not to say that the concept of individual bonds is a bad idea. In fact, the modern concept of the chemical bond, conceived by the American chemists G. N. Lewis and Linus Pauling, is one of the most useful ideas chemists have ever developed.

Models: An Overview

The framework of chemistry, like that of any science, consists of *models*—attempts to explain how nature operates on the microscopic level, based on experiences in the macroscopic world. To understand chemistry, one must understand its models and how they are used. We will use the concept of bonding to reemphasize the important characteristics of models, including their origin, structure, and uses.

Bonding is a model proposed to explain molecular stability.

Models originate from our observations of the properties of nature. For example, the concept of bonds arose from the observations that most chemical processes involve collections of atoms and that chemical reactions involve rearrangements of the ways the atoms are grouped. Therefore, to understand reactions, we must understand the forces that bind atoms together.

In natural processes there is a tendency toward lower energy. Collections of atoms therefore occur because the aggregated state has lower energy than the separated atoms. Why? As we saw earlier in this chapter, the best explanations for the energy change involve atoms sharing electrons or atoms transferring electrons to become ions. In the case of electron sharing, we find it convenient to assume that individual bonds occur between pairs of atoms. Let's explore the validity of this assumption and see how it is useful.

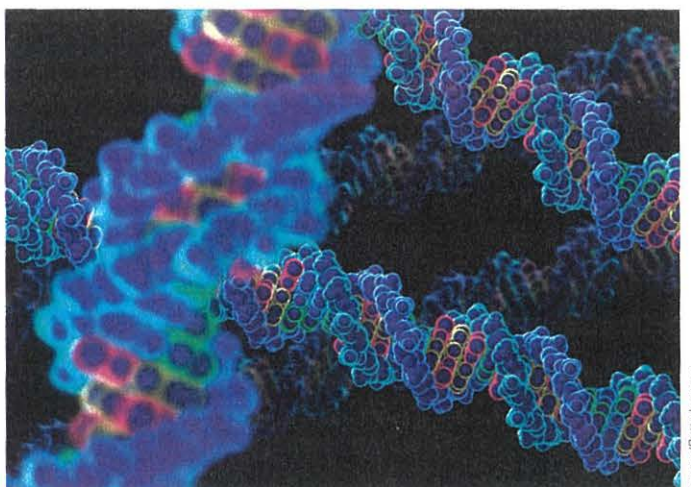
In a diatomic molecule such as H_2 , it is natural to assume that a bond exists between the atoms, holding them together. It is also useful to assume that individual bonds are present in polyatomic molecules such as CH_4 . Therefore, instead of thinking of CH_4 as a unit with a stabilization energy of 1652 kJ per mole, we choose to think of CH_4 as containing four C—H bonds, each worth 413 kJ of energy per mole of bonds. Without this concept of individual bonds in molecules, chemistry would be hopelessly complicated. There are millions of different chemical compounds, and if each of these compounds had to be considered as an entirely new entity, the task of understanding chemical behavior would be overwhelming.

The bonding model provides a framework to systematize chemical behavior by enabling us to think of molecules as collections of common fundamental components. For example, a typical biomolecule, such as a protein, contains hundreds of atoms and might seem discouragingly complex. However, if we think of a protein as constructed of individual bonds, C—C, C—H, C—N, C—O, N—H, and so on, it helps tremendously in predicting and understanding the protein's behavior. The essential idea is that we expect a given bond to behave about the same in any molecular environment. Used in this way, the model of the chemical bond has helped chemists to systematize the reactions of the millions of existing compounds.

In addition to being useful, the bonding model is physically sensible. It makes sense that atoms can form stable groups by sharing electrons; shared electrons give a lower energy state because they are simultaneously attracted by two nuclei.

Also, as we will see in Chapter 7, bond energy data support the existence of discrete bonds that are relatively independent of the molecular environment. It is very important to remember, however, that the chemical bond is only a model. Although our concept of discrete bonds in molecules agrees with many of our observations, some molecular properties require that we think of a molecule as a whole, with the electrons free to move through the entire molecule. This is called *delocalization* of the electrons, a concept that will be discussed more completely in the next chapter.

► The concept of individual bonds makes it much easier to deal with complex molecules such as DNA. A small segment of a DNA molecule is shown here.



LET'S REVIEW Fundamental Properties of Models

- » Models are human inventions, always based on an incomplete understanding of how nature works. *A model does not equal reality.*
- » Models are often wrong. This property derives from the previous property. Models are based on speculation and are always oversimplifications.
- » Models tend to become more complicated as they age. As flaws are discovered in our models, we “patch” them and thus add more detail.
- » It is very important to understand the assumptions inherent in a particular model before you use it to interpret observations or to make predictions. Simple models usually involve very restrictive assumptions and can be expected to yield only qualitative information. Asking for a sophisticated explanation from a simple model is like expecting to get an accurate mass for a diamond using a bathroom scale.

For a model to be used effectively, we must understand its strengths and weaknesses and ask only appropriate questions. An illustration of this point is the simple aufbau principle used to account for the electron configurations of the elements. Although this model correctly predicts the configuration for most atoms, chromium and copper, for example, do not agree with the predictions. Detailed studies show that the configurations of chromium and copper result from complex electron interactions that are not taken into account in the simple model. However, this does not mean that we should discard the simple model that is so useful for most atoms. Instead, we must apply it with caution and not expect it to be correct in every case.

- » When a model is wrong, we often learn much more than when it is right. If a model makes a wrong prediction, it usually means we do not understand some fundamental characteristics of nature. We often learn by making mistakes. (Try to remember this when you get back your next chemistry test.)

3.6 The Localized Electron Bonding Model

So far we have discussed the general characteristics of the chemical bonding model and have seen that properties such as bond strength and polarity can be assigned to individual bonds. In this section we introduce a specific model used to describe covalent bonds. We need a simple model that can be applied easily even to very complicated molecules and that can be used routinely by chemists to interpret and organize the wide variety of chemical phenomena. The model that serves this purpose is the **localized electron (LE) model**, which assumes that *a molecule is composed of atoms that are bound together by sharing pairs of electrons using the orbitals of the bound atoms*. Electron pairs in the molecule are assumed to be localized on a particular atom or in the space between two atoms. Those pairs of electrons localized on an individual atom are called **lone pairs**, and those found in the space between the atoms are called **bonding pairs**.

As we will apply it, the LE model has three parts:

1. Description of the valence electron arrangement in the molecule using Lewis structures (will be discussed in the next section).
2. Prediction of the geometry of the molecule using the valence shell electron-pair repulsion (VSEPR) model (will be discussed in Chapter 4).
3. Description of the type of orbitals used by the atoms to share electrons or hold lone pairs (will be discussed in Chapter 4).

As we discussed earlier, we use models that are as simple as possible. The quantum mechanical model discussed in Chapter 2 views electron distribution in terms of probability. We now will consider a simpler model in which the electrons exist between the atoms in a molecule.

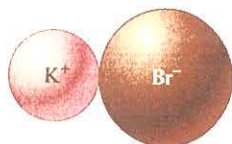
FIGURE 3.8 G. N. Lewis (1875–1946).



3.7 Lewis Structures

While the phrase “atoms want to be like a noble gas” is a way to remember charges for ions and to determine Lewis structures, it does not tell us why this occurs.

Lewis structures show only valence electrons.



The **Lewis structure** of a molecule shows how the valence electrons are arranged among the atoms in the molecule. These representations are named after G. N. Lewis (Fig. 3.8). The rules for writing Lewis structures are based on observations of thousands of molecules. From experiments, chemists have learned that the *most important guidelines for the formation of a stable compound is that the atoms achieve noble gas electron configurations*.

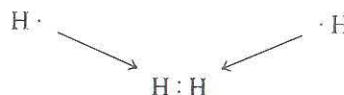
We have already seen that when metals and nonmetals react to form binary ionic compounds, electrons are transferred and the resulting ions typically have noble gas electron configurations. An example is the formation of KBr, where the K^+ ion has the [Ar] electron configuration and the Br^- ion has the [Kr] electron configuration. In writing Lewis structures, the rule is that *only the valence electrons are included*. Using dots to represent electrons, the Lewis structure for KBr is



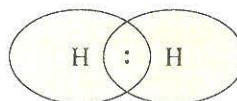
No dots are shown on the K^+ ion because it has no valence electrons. The Br^- ion is shown with eight electrons because it has a filled valence shell.

Next we will consider Lewis structures for molecules with covalent bonds, involving elements in the first and second periods. The principle of achieving a noble gas electron configuration applies to these elements as follows:

- Hydrogen forms stable molecules where it shares two electrons. That is, it follows a **duet rule**. For example, when two hydrogen atoms, each with one electron, combine to form the H_2 molecule, we have



By sharing electrons, each hydrogen in H_2 , in effect, has two electrons; that is, each hydrogen has a filled valence shell.

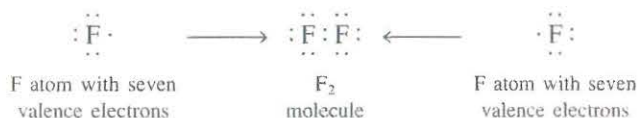


Carbon, nitrogen, oxygen, and fluorine always obey the octet rule in stable molecules.

- Helium does not form bonds because its valence orbital is already filled; it is a noble gas. Helium has the electron configuration $1s^2$ and can be represented by the Lewis structure



- The second-row nonmetals carbon through fluorine form stable molecules when they are surrounded by enough electrons to fill the valence orbitals, that is, the $2s$ and the three $2p$ orbitals. Since eight electrons are required to fill these orbitals, these elements typically obey the **octet rule**; they are surrounded by eight electrons. An example is the F_2 molecule, which has the following Lewis structure:



Note that each fluorine atom in F_2 is, in effect, surrounded by eight electrons, two of which are shared with the other atom. This is a *bonding pair* of electrons, as discussed earlier. Each fluorine atom also has three pairs of electrons not involved in bonding. These are the *lone pairs*.

- Neon does not form bonds because it already has an octet of valence electrons (it is a noble gas). The Lewis structure is



Note that only the valence electrons of the neon atom ($2s^2 2p^6$) are represented by the Lewis structure. The $1s^2$ electrons are core electrons and are not shown.

We can formulate the following rules for writing the Lewis structures of molecules containing atoms from the first two periods.

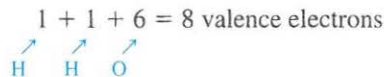
PROBLEM-SOLVING STRATEGY

Steps for Writing Lewis Structures

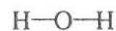
1. Sum the valence electrons from all the atoms. Do not worry about keeping track of which electrons come from which atoms. It is the *total* number of electrons that is important.
2. Use a pair of electrons to form a bond between each pair of bound atoms.
3. Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements.

To see how these steps are applied, we will draw the Lewis structures of a few molecules. We will first consider the water molecule and follow the previous steps.

1. We sum the *valence* electrons for H_2O as shown:



2. Using a pair of electrons per bond, we draw in the two O—H single bonds:



Note that a *line instead of a pair of dots* is used to indicate each pair of bonding electrons. This is the standard notation.

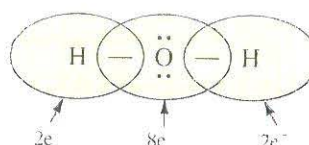
3. We distribute the remaining electrons to achieve a noble gas electron configuration for each atom. Since four electrons have been used in forming the two bonds, four electrons ($8 - 4$) remain to be distributed. Hydrogen is satisfied with two

H—O—H represents H₂O

electrons (duet rule), but oxygen needs eight electrons to have a noble gas configuration. Thus the remaining four electrons are added to oxygen as two lone pairs. Dots are used to represent the lone pairs:



This is the correct Lewis structure for the water molecule. Each hydrogen has two electrons and the oxygen has eight, as shown below:

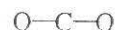


As a second example, let's write the Lewis structure for carbon dioxide (CO₂).

- Summing the valence electrons gives



- Pairs of electrons are used to form a bond between the carbon and each oxygen,



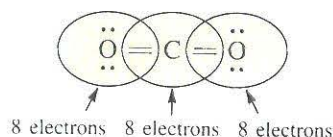
and the remaining electrons are distributed to achieve noble gas configurations on each atom. In this case we have 12 electrons (16 - 4) remaining after the bonds are drawn. The distribution of these electrons is determined by a trial-and-error process. We have 6 pairs of electrons to distribute. Suppose we try 3 pairs on each oxygen to give



- Is this correct? To answer this question, we need to check two things:

- The total number of electrons. There are 16 valence electrons in this structure, which is the correct number.
- The octet rule for each atom. Each oxygen has 8 electrons, but the carbon has only 4. This cannot be the correct Lewis structure.

How can we arrange the 16 available electrons to achieve an octet for each atom? Suppose there are 2 shared pairs between the carbon and each oxygen:



Now each atom is surrounded by 8 electrons, and the total number of electrons is 16, as required. This is the correct Lewis structure for carbon dioxide, which has two double bonds and four lone pairs.

Finally, let's consider the Lewis structure of the CN⁻ (cyanide) ion. Summing the valence electrons, we have



Note that the negative charge means an extra electron is present. After drawing a single bond (C—N), we distribute the remaining electrons to achieve a noble gas configuration for each atom. Eight electrons remain to be distributed. We can try various possibilities, for example:



This structure is incorrect because C and N have only six electrons each instead of eight. The correct arrangement is



(Satisfy yourself that both carbon and nitrogen have eight electrons.)

INTERACTIVE EXAMPLE 3.4

Writing Lewis Structures

Give the Lewis structure for each of the following.

- a. HF d. CH₄
b. N₂ e. CF₄
c. NH₃ f. NO⁺

SOLUTION

In each case we apply the three steps for writing Lewis structures. Recall that lines are used to indicate shared electron pairs and that dots are used to indicate nonbonding pairs (lone pairs). We have the following tabulated results:

	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations	Check Number of Electrons
a. HF	1 + 7 = 8	H—F	6	H—F:	H, 2 F, 8
b. N ₂	5 + 5 = 10	N—N	8	:N≡N:	N, 8
c. NH ₃	5 + 3(1) = 8	$\begin{array}{c} \text{H} - \text{N} - \text{H} \\ \\ \text{H} \end{array}$	2	$\begin{array}{c} \text{H} - \text{N} - \text{H} \\ \\ \text{H} \end{array}$	H, 2 N, 8
d. CH ₄	4 + 4(1) = 8	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	0	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	H, 2 C, 8
e. CF ₄	4 + 4(7) = 32	$\begin{array}{c} \text{F} \\ \\ \text{F} - \text{C} - \text{F} \\ \\ \text{F} \end{array}$	24	$\begin{array}{c} \text{:F:} \\ \\ \text{:F} - \text{C} - \text{F:} \\ \\ \text{:F:} \end{array}$	F, 8 C, 8
f. NO ⁺	5 + 6 - 1 = 10	N—O	8	[:N≡O:] ⁺	N, 8 O, 8

See Exercises 3.53 through 3.56

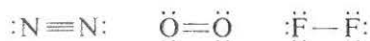
When writing Lewis structures, do not worry about which electrons come from which atoms in a molecule. The best way to look at a molecule is to regard it as a new entity that uses all the available valence electrons of the atoms to achieve the lowest

CONNECTING TO ATOMS 3.1

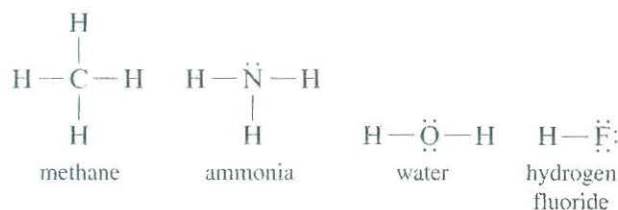
Lewis Structures and the Periodic Table

The periodic table was originally organized to represent patterns in chemical properties of the elements. We now see that there are patterns of valence electron arrangements in the table, which makes sense since the electrons are responsible for how elements react. We have already discussed trends of atomic radius, ionization energy, electron affinity, and electronegativity across rows and down columns of the periodic table.

We can also see periodic trends with respect to Lewis structures. For example, consider the diatomic molecules N_2 , O_2 , and F_2 as seen below:



Note that the nitrogen atoms (Group 5A) each have three bonds and one lone pair, the oxygen atoms (Group 6A) have two bonds and two lone pairs, and the fluorine atoms (Group 7A) have one bond and three lone pairs. We can also see a pattern in the compounds formed with hydrogen by the elements in the second row:



Note the pattern across the row in terms of number of bonds and number of lone pairs, including Group 4A (four bonds and no lone pairs). Of course, neon (Group 8A) does not form a compound with hydrogen, meaning there are 0 bonds.

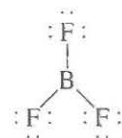
C	N	O	F	Ne
4 bonds 0 lone pairs	3 bonds 1 lone pair	2 bonds 2 lone pairs	1 bond 3 lone pairs	0 bonds

It is not the case that all Lewis structures with these elements will follow these patterns exactly, but these patterns give us a good starting point.

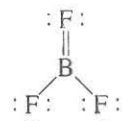
possible energy.* The valence electrons belong to the molecule, rather than to the individual atoms. Simply distribute all valence electrons so that the various rules are satisfied, without regard for the origin of each particular electron.

3.8 Exceptions to the Octet Rule

The localized electron model is a simple but very successful model, and the rules we have used for Lewis structures apply to most molecules. However, with such a simple model, some exceptions are inevitable. Boron, for example, tends to form compounds in which the boron atom has fewer than eight electrons around it—it does not have a complete octet. Boron trifluoride (BF_3), a gas at normal temperatures and pressures, reacts very energetically with molecules such as water and ammonia that have available electron pairs (lone pairs). The violent reactivity of BF_3 with electron-rich molecules arises because the boron atom is electron-deficient. Boron trifluoride has 24 valence electrons. The Lewis structure often drawn for BF_3 is

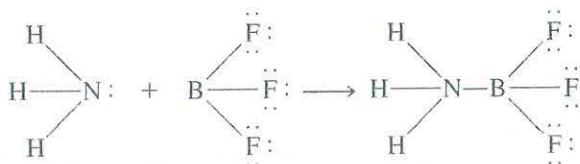


Note that in this structure boron has only 6 electrons around it. The octet rule for boron can be satisfied by drawing a structure with a double bond, such as



*In a sense this approach corrects for the fact that the localized electron model overemphasizes that a molecule is simply a sum of its parts—that is, that the atoms retain their individual identities in the molecule.

Recent studies indicate that double bonding may be important in BF_3 . However, the boron atom in BF_3 certainly behaves as if it is electron-deficient, as indicated by the reactivity of BF_3 toward electron-rich molecules, for example, toward NH_3 to form H_3NBF_3 :



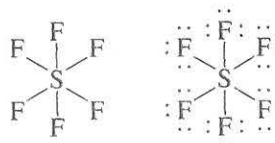
In this stable compound, boron has an octet of electrons.

It is characteristic of boron to form molecules in which the boron atom is electron-deficient. On the other hand, carbon, nitrogen, oxygen, and fluorine can be counted on to obey the octet rule.

Some atoms exceed the octet rule. This behavior is observed only for those elements in Period 3 of the periodic table and beyond. To see how this arises, we will consider the Lewis structure for sulfur hexafluoride (SF_6), a well-known and very stable molecule. The sum of the valence electrons is

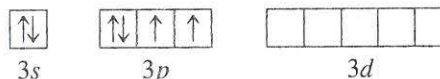
$$6 + 6(7) = 48 \text{ electrons}$$

Indicating the single bonds gives the structure on the left below:



We have used 12 electrons to form the $\text{S}-\text{F}$ bonds, which leaves 36 electrons. Since fluorine always follows the octet rule, we complete the six fluorine octets to give the structure on the right above. This structure uses all 48 valence electrons for SF_6 , but sulfur has 12 electrons around it; that is, sulfur *exceeds* the octet rule. How can this happen?

The answer to this question is very complicated. Originally, it was assumed that because the sulfur atom has empty d orbitals



Whether the atoms that exceed the octet rule actually place the extra electrons in their d orbitals is a matter of controversy among theoretical chemists. We will not consider this issue in this text.

that these orbitals would be used to hold the extra electrons. Recent evidence indicates that this reasoning is not correct. However, the new explanation is beyond the scope of this text.

INTERACTIVE EXAMPLE 3.5

Lewis Structures for Molecules That Violate the Octet Rule I

Write the Lewis structure for PCl_5 .

SOLUTION

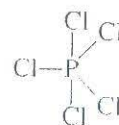
We can follow the same stepwise procedure we used previously for sulfur hexafluoride.

1. Sum the valence electrons.

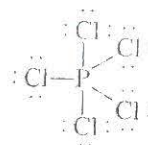
$$5 + 5(7) = 40 \text{ electrons}$$



2. Indicate single bonds between bound atoms.



3. Distribute the remaining electrons. In this case, 30 electrons ($40 - 10$) remain. These are used to satisfy the octet rule for each chlorine atom. The final Lewis structure is



Note that phosphorus, which is a third-row element, has exceeded the octet rule by two electrons.

See Exercises 3.59 and 3.60

LET'S REVIEW Lewis Structures: Comments About the Octet Rule

- » The second-row elements C, N, O, and F should always be assumed to obey the octet rule.
- » The second-row elements B and Be often have fewer than eight electrons around them in their compounds. These electron-deficient compounds are very reactive.
- » The second-row elements never exceed the octet rule, since their valence orbitals (2s and 2p) can accommodate only eight electrons.
- » Third-row and heavier elements often satisfy the octet rule but can exceed the octet rule.
- » When writing the Lewis structure for a molecule, satisfy the octet rule for the atoms first. If electrons remain after the octet rule has been satisfied, then place them on any element from Period 3 or beyond.

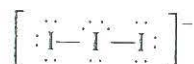
In the PCl_5 and SF_6 molecules, the central atoms (P and S, respectively) must have the extra electrons. However, in molecules having more than one atom that can exceed the octet rule, it is not always clear which atom should have the extra electrons. Consider the Lewis structure for the triiodide ion (I_3^-), which has

$$3(7) + 1 = 22 \text{ valence electrons}$$

Indicating the single bonds gives $\text{I}-\text{I}-\text{I}$. At this point, 18 electrons ($22 - 4$) remain. Trial and error will convince you that one of the iodine atoms must exceed the octet rule, but *which* one?

The rule we will follow is that *when it is necessary to exceed the octet rule for one of several third-row (or higher) elements, assume that the extra electrons should be placed on the central atom.*

Thus for I_3^- the Lewis structure is



where the central iodine exceeds the octet rule. This structure agrees with known properties of I_3^- .

INTERACTIVE EXAMPLE 3.6

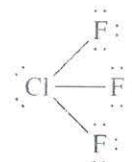
Lewis Structures for Molecules That Violate the Octet Rule II

Write the Lewis structure for each molecule or ion.

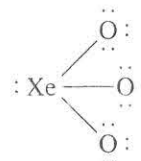
- a.
- ClF_3
- b.
- XeO_3
- c.
- RnCl_2
- d.
- BeCl_2
- e.
- ICl_4^-

SOLUTION

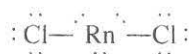
- a. The chlorine atom (third row) accepts the extra electrons.



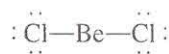
- b. All atoms obey the octet rule.



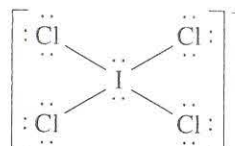
- c. Radon, a noble gas in Period 6, accepts the extra electrons.



- d. Beryllium is electron-deficient.



- e. Iodine exceeds the octet rule.



See Exercises 3.57, 3.59, and 3.60

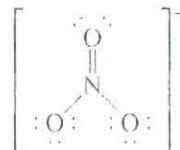
Odd-Electron Molecules

Relatively few molecules formed from nonmetals contain odd numbers of electrons. One common example is nitric oxide (NO), which is formed when nitrogen and oxygen gases react at high temperatures in automobile engines. Nitric oxide is emitted into the air, where it immediately reacts with oxygen to form gaseous nitrogen dioxide (NO_2), another odd-electron molecule.

Since the localized electron model is based on pairs of electrons, it does not handle odd-electron cases in a natural way. To treat odd-electron molecules, a more sophisticated model is needed.

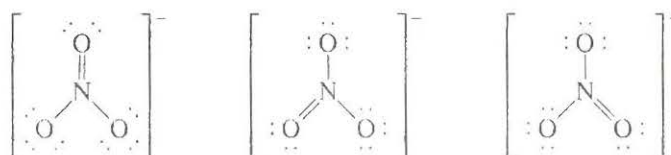
3.9 Resonance

Sometimes more than one valid Lewis structure (one that obeys the rules we have outlined) is possible for a given molecule. Consider the Lewis structure for the nitrate ion (NO_3^-), which has 24 valence electrons. To achieve an octet of electrons around each atom, a structure like this is required:



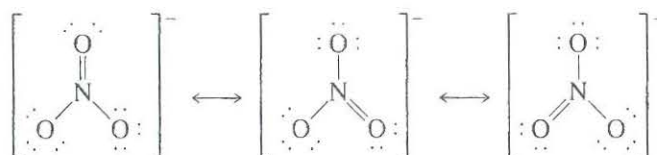
If this structure accurately represents the bonding in NO_3^- , there should be two types of N—O bonds observed in the molecule: one shorter bond (the double bond) and two identical longer ones (the two single bonds). However, experiments clearly show that NO_3^- exhibits only *one* type of N—O bond with a length and strength *between* those expected for a single bond and a double bond. Thus, although the structure we have shown above is a valid Lewis structure, it does *not* correctly represent the bonding in NO_3^- . This is a serious problem, and it means that the model must be modified.

Look again at the proposed Lewis structure for NO_3^- . There is no reason for choosing a particular oxygen atom to have the double bond. There are really three valid Lewis structures:



Is any of these structures a correct description of the bonding in NO_3^- ? No, because NO_3^- does not have one double and two single bonds—it has three equivalent bonds. We can solve this problem by making the following assumption: The correct description of NO_3^- is *not given by any one* of the three Lewis structures but is given only by the *superposition of all three*.

The nitrate ion does not exist as any of the three extreme structures but exists as an average of all three. **Resonance is the condition in which more than one valid Lewis structure can be written for a particular molecule (in which the atoms are connected in the same order). The resulting electron structure of the molecule is given by the average of these resonance structures.** This situation is usually represented by double-headed arrows as follows:



Note that in all these resonance structures the arrangement of the nuclei is the same. Only the placement of the electrons differs. The arrows do not mean that the molecule “flips” from one resonance form to another. They simply show that the *actual structure is an average of the three resonance structures*.

The concept of resonance is necessary because the localized electron model postulates that electrons are localized between a given pair of atoms. However, nature does not really operate this way. Electrons are really delocalized—they can move around the entire molecule. The valence electrons in the NO_3^- ion distribute themselves to provide equivalent N—O bonds. Resonance is necessary to compensate for the defective assumption of the localized electron model. However, this model is so useful that we retain the concept of localized electrons and add resonance to allow the model to treat species such as NO_3^- .

The concept of resonance serves as a reminder that all models are simplifications. Electrons are not localized within a molecule, and we will discuss more complex models in Chapter 4.

EXAMPLE 3.7

Resonance Structures

Describe the electron arrangement in the nitrite anion (NO_2^-), using the localized electron model.

SOLUTION

We will follow the usual procedure for obtaining the Lewis structure for the NO_2^- ion. In NO_2^- there are $5 + 2(6) + 1 = 18$ valence electrons. Indicating the single bonds gives the structure



The remaining 14 electrons ($18 - 4$) can be distributed to produce these structures:

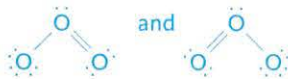


This is a resonance situation. Two equivalent Lewis structures can be drawn. *The electronic structure of the molecule is correctly represented not by either resonance structure but by the average of the two.* There are two equivalent N—O bonds, each one intermediate between a single and a double bond.

See Exercises 3.61 through 3.66

Formal Charge

Equivalent Lewis structures contain the same numbers of single and multiple bonds. For example, the resonance structures for O_3



are equivalent Lewis structures. These are equally important in describing the bonding in O_3 . Nonequivalent Lewis structures contain different numbers of single and multiple bonds.

Molecules or polyatomic ions containing atoms that can exceed the octet rule often have many nonequivalent Lewis structures, all of which obey the rules for writing Lewis structures. For example, as we will see in detail below, the sulfate ion (SO_4^{2-}) has a Lewis structure with all single bonds and several Lewis structures that contain double bonds. How do we decide which of the many possible Lewis structures best describes the actual bonding in sulfate? One method is to estimate the charge on each atom in the various possible Lewis structures and use these charges to select the most appropriate structure(s). We will see below how this is done, but first we must decide on a method to assign charges on the atoms within molecules.

We will now consider a concept called *formal charge* for estimating the charge of an individual atom in a molecule. We will use the formal charges of atoms to evaluate Lewis structures. As we will see below, the **formal charge** of an atom in a molecule is the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule.

Therefore, to determine the formal charge of a given atom in a molecule, we need to know two things:

1. The number of valence electrons on the free neutral atom (which has zero net charge because the number of electrons equals the number of protons)
2. The number of valence electrons “belonging” to the atom in a molecule

We then compare these numbers. If in the molecule the atom has the same number of valence electrons as it does in the free state, the positive and negative charges just balance, and it has a formal charge of zero. If the atom has one more valence electron in a molecule than it has as a free atom, it has a formal charge of -1 , and so on. Thus the formal charge on an atom in a molecule is defined as

$$\text{Formal charge} = (\text{number of valence electrons on free atom}) - (\text{number of valence electrons assigned to the atom in the molecule})$$

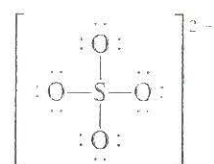
To compute the formal charge of an atom in a molecule, we assign the valence electrons in the molecule to the various atoms, making the following assumptions:

1. Lone pair electrons belong entirely to the atom in question.
2. Shared electrons are *divided equally* between the two sharing atoms.

Thus the number of valence electrons assigned to a given atom is calculated as follows:

$$(\text{Valence electrons})_{\text{assigned}} = (\text{number of lone pair electrons}) + \frac{1}{2} (\text{number of shared electrons})$$

We will illustrate the procedure for calculating formal charges by considering two of the possible Lewis structures for the sulfate ion, which has 32 valence electrons. For the Lewis structure



each oxygen atom has 6 lone pair electrons and shares 2 electrons with the sulfur atom. Thus, using the preceding assumptions, each oxygen is assigned 7 valence electrons.

$$\text{Valence electrons assigned to each oxygen} = 6 \text{ plus } \frac{1}{2}(2) = 7$$

↑ Lone pair electrons ↑ Shared electrons

$$\text{Formal charge on oxygen} = 6 \text{ minus } 7 = -1$$

↑ Valence electrons on a free O atom ↑ Valence electrons assigned to each O in SO_4^{2-}

The formal charge on each oxygen is -1 .

For the sulfur atom there are no lone pair electrons, and eight electrons are shared with the oxygen atoms. Thus, for sulfur,

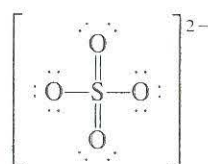
$$\text{Valence electrons assigned to sulfur} = 0 \text{ plus } \frac{1}{2}(8) = 4$$

↑ Lone pair electrons ↑ Shared electrons

$$\text{Formal charge on sulfur} = 6 \text{ minus } 4 = 2$$

↑ Valence electrons on a free S atom ↑ Valence electrons assigned to S in SO_4^{2-}

A second possible Lewis structure is



In this case the formal charges are as follows:

For oxygen atoms with single bonds:

$$\text{Valence electrons assigned} = 6 + \frac{1}{2}(2) = 7$$

$$\text{Formal charge} = 6 - 7 = -1$$

For oxygen atoms with double bonds:

$$\text{Valence electrons assigned} = 4 + \frac{1}{2}(4) = 6$$

↑
Each double
bond has 4
electrons

$$\text{Formal charge} = 6 - 6 = 0$$

For the sulfur atom:

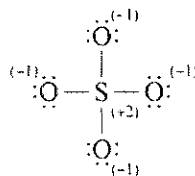
$$\text{Valence electrons assigned} = 0 + \frac{1}{2}(12) = 6$$

$$\text{Formal charge} = 6 - 6 = 0$$

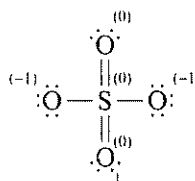
We will use two fundamental assumptions about formal charges to evaluate Lewis structures:

1. Atoms in molecules try to achieve formal charges as close to zero as possible.
2. Any negative formal charges are expected to reside on the most electronegative atoms.

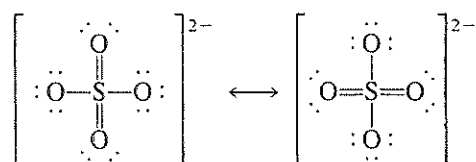
We can use these principles to evaluate the two nonequivalent Lewis structures for sulfate given previously. Notice that in the structure with only single bonds, each oxygen has a formal charge of -1 , while the sulfur has a formal charge of $+2$.



In contrast, in the structure with two double bonds and two single bonds, the sulfur and two oxygen atoms have a formal charge of 0, while two oxygens have a formal charge of -1 .



Based on the assumptions given previously, the structure with two double bonds is preferred—it has lower formal charges and the -1 formal charges are on electronegative oxygen atoms. Thus, for the sulfate ion, we might expect resonance structures such as



to more closely describe the bonding than the Lewis structure with only single bonds.

Rules Governing Formal Charge

- » To calculate the formal charge on an atom:
 1. Take the sum of the lone pair electrons and one-half the shared electrons. This is the number of valence electrons assigned to the atom in the molecule.
 2. Subtract the number of assigned electrons from the number of valence electrons on the free, neutral atom to obtain the formal charge.
- » The sum of the formal charges of all atoms in a given molecule or ion must equal the overall charge on that species.
- » If nonequivalent Lewis structures exist for a species, those with formal charges closest to zero and with any negative formal charges on the most electronegative atoms are considered to best describe the bonding in the molecule or ion.

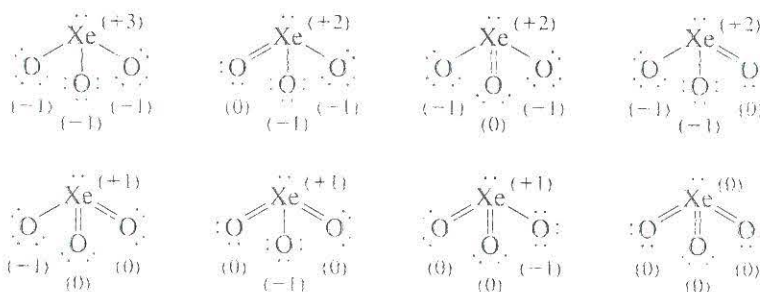
EXAMPLE 3.8

Formal Charges

Give possible Lewis structures for XeO_3 , an explosive compound of xenon. Which Lewis structure or structures are most appropriate according to the formal charges?

SOLUTION

For XeO_3 (26 valence electrons) we can draw the following possible Lewis structures (formal charges are indicated in parentheses):



Based on the ideas of formal charge, we would predict that the Lewis structures with the lower values of formal charge would be most appropriate for describing the bonding in XeO_3 .

See Exercises 3.73 and 3.74

As a final note, there are a couple of cautions about formal charge to keep in mind. Recognize that formal charges provide only *estimates* of charge—they should not be taken as actual atomic charges. Second, the evaluation of Lewis structures using formal charge ideas can lead to erroneous predictions. Tests based on experiments must be used to make the final decisions on the correct description of the bonding in a molecule or polyatomic ion.

3.10 Naming Simple Compounds

When chemistry was an infant science, there was no system for naming compounds. Names such as sugar of lead, blue vitrol, quicklime, Epsom salts, milk of magnesia, gypsum, and laughing gas were coined by early chemists. Such names are called *common names*. As chemistry grew, it became clear that using common names for compounds would lead to unacceptable chaos. Nearly 5 million chemical compounds are currently known. Memorizing common names for these compounds would be an impossible task.

The solution, of course, is to adopt a *system* for naming compounds in which the name tells something about the composition of the compound. After learning the system, a chemist given a formula should be able to name the compound or, given a name, should be able to construct the compound's formula. In this section we will specify the most important rules for naming compounds other than organic compounds (those based on chains of carbon atoms).

We will begin with the systems for naming inorganic **binary compounds**—compounds composed of two elements—which we classify into various types for easier recognition. We will consider both ionic and covalent compounds.

Binary Ionic Compounds (Type I)

Binary ionic compounds contain a positive ion (cation) always written first in the formula and a negative ion (anion). In naming these compounds, the following rules apply.

Naming Type I Binary Compounds

1. The cation is always named first and the anion second.
2. A monatomic (meaning "one-atom") cation takes its name from the name of the element. For example, Na^+ is called sodium in the names of compounds containing this ion.
3. A monatomic anion is named by taking the root of the element name and adding *-ide*. Thus the Cl^- ion is called chloride.

In formulas of ionic compounds, simple ions are represented by the element symbol: Cl means Cl^- , Na means Na^+ , and so on.

Some common monatomic cations and anions and their names are given in Table 3.3.

The rules for naming binary ionic compounds are illustrated by the following examples:

Compound	Ions Present	Name
NaCl	Na^+ , Cl^-	Sodium chloride
KI	K^+ , I^-	Potassium iodide
CaS	Ca^{2+} , S^{2-}	Calcium sulfide
Li_3N	Li^+ , N^{3-}	Lithium nitride
CsBr	Cs^+ , Br^-	Cesium bromide
MgO	Mg^{2+} , O^{2-}	Magnesium oxide

TABLE 3.3 | Common Monatomic Cations and Anions

Cation	Name	Anion	Name
H^+	Hydrogen	H^-	Hydride
Li^+	Lithium	F^-	Fluoride
Na^+	Sodium	Cl^-	Chloride
K^+	Potassium	Br^-	Bromide
Cs^+	Cesium	I^-	Iodide
Be^{2+}	Beryllium	O^{2-}	Oxide
Mg^{2+}	Magnesium	S^{2-}	Sulfide
Ca^{2+}	Calcium	N^{3-}	Nitride
Ba^{2+}	Barium	P^{3-}	Phosphide
Al^{3+}	Aluminum		

INTERACTIVE EXAMPLE 3.9

Naming Type I Binary Compounds

Name each binary compound.

- a. CsF b. AlCl_3 c. LiH

SOLUTION

- a. CsF is cesium fluoride.
 b. AlCl_3 is aluminum chloride.
 c. LiH is lithium hydride.

Notice that, in each case, the cation is named first, and then the anion is named.

See Exercise 3.79

Formulas from Names

So far we have started with the chemical formula of a compound and decided on its systematic name. The reverse process is also important. For example, given the name calcium chloride, we can write the formula as CaCl_2 because we know that calcium forms only Ca^{2+} ions and that, since chloride is Cl^- , two of these anions will be required to give a neutral compound.

INTERACTIVE EXAMPLE 3.10

Formulas from Names for Type I Binary Compounds

Given the following systematic names, write the formula for each compound:

- a. potassium iodide
 b. calcium oxide
 c. gallium bromide

SOLUTION

Name	Formula	Comments
a. potassium iodide	KI	Contains K^+ and I^- .
b. calcium oxide	CaO	Contains Ca^{2+} and O^{2-} .
c. gallium bromide	GaBr_3	Contains Ga^{3+} and Br^- . Must have 3Br^- to balance charge of Ga^{3+} .

See Exercise 3.79

Binary Ionic Compounds (Type II)

In the binary ionic compounds considered earlier (Type I), the metal present forms only a single type of cation. That is, sodium forms only Na^+ , calcium forms only Ca^{2+} , and so on. However, as we will see in more detail later in the text, there are many metals that form more than one type of positive ion and thus form more than one type of ionic compound with a given anion. For example, the compound FeCl_2 contains Fe^{2+} ions, and the compound FeCl_3 contains Fe^{3+} ions. In a case such as this, the *charge on the metal ion must be specified*. The systematic names for these two iron compounds are iron(II) chloride and iron(III) chloride, respectively, where the *Roman numeral indicates the charge of the cation*.

Another system for naming these ionic compounds that is seen in the older literature was used for metals that form only two ions. *The ion with the higher charge has a name ending in -ic, and the one with the lower charge has a name ending in -ous.* In this system, for example, Fe^{3+} is called the ferric ion, and Fe^{2+} is called the ferrous ion. The names for FeCl_3 and FeCl_2 are then ferric chloride and ferrous chloride, respectively. In this text we will use the system that employs Roman numerals. Table 3.4 lists the systematic names for many common Type II cations.

INTERACTIVE EXAMPLE 3.11

Type II binary ionic compounds contain a metal that can form more than one type of cation.

A compound must be electrically neutral.

Naming Type II Binary Compounds

1. Give the systematic name for each of the following compounds:
 - a. CuCl
 - b. HgO
 - c. Fe_2O_3
2. Given the following systematic names, write the formula for each compound:
 - a. Manganese(IV) oxide
 - b. Lead(II) chloride

SOLUTION

All of these compounds include a metal that can form more than one type of cation. Thus we must first determine the charge on each cation. This can be done by recognizing that a compound must be electrically neutral; that is, the positive and negative charges must exactly balance.

1.

Formula	Name	Comments
a. CuCl	Copper(I) chloride	Because the anion is Cl^- , the cation must be Cu^+ (for charge balance), which requires a Roman numeral I.
b. HgO	Mercury(II) oxide	Because the anion is O^{2-} , the cation must be Hg^{2+} [mercury(II)].
c. Fe_2O_3	Iron(III) oxide	The three O^{2-} ions carry a total charge of $6-$, so two Fe^{3+} ions [iron(III)] are needed to give a $6+$ charge.

2.

Name	Formula	Comments
a. Manganese(IV) oxide	MnO_2	Two O^{2-} ions (total charge $4-$) are required by the Mn^{4+} ion [manganese(IV)].
b. Lead(II) chloride	PbCl_2	Two Cl^- ions are required by the Pb^{2+} ion [lead(II)] for charge balance.

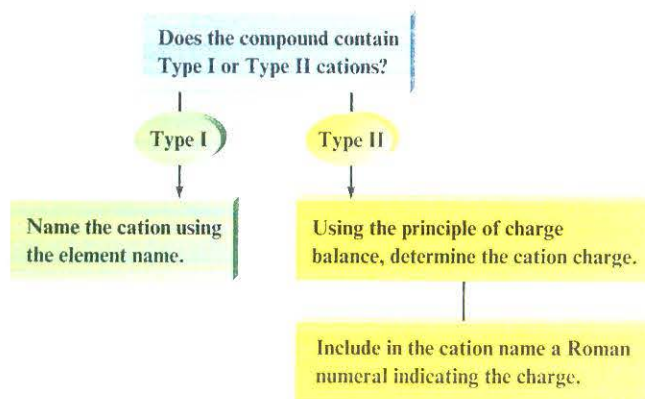


▲ Mercury(II) oxide.

A compound containing a transition metal usually requires a Roman numeral in its name.

See Exercise 3.80

Note that the use of a Roman numeral in a systematic name is required only in cases where more than one ionic compound forms between a given pair of elements. This case most commonly occurs for compounds containing transition metals, which often form more than one cation. **Elements that form only one cation do not need to be identified by a Roman numeral.** Common metals that do not require Roman numerals are the Group 1A (1) elements, which form only $1+$ ions; the Group 2A (2) elements, which form only $2+$ ions; and aluminum, which forms only Al^{3+} . The element silver deserves special mention at this point. In virtually all its compounds silver is found as the Ag^+ ion. Therefore, although silver is a transition metal (and can potentially form ions other than Ag^+), silver compounds are usually named without a

FIGURE 3.9 Flowchart for naming the cation in binary ionic compounds:**TABLE 3.4** | Common Type II Cations

Fe^{3+}	Iron(III)
Fe^{2+}	Iron(II)
Cu^{2+}	Copper(II)
Cu^{+}	Copper(I)
Co^{3+}	Cobalt(III)
Co^{2+}	Cobalt(II)
Sn^{4+}	Tin(IV)
Sn^{2+}	Tin(II)
Pb^{4+}	Lead(IV)
Pb^{2+}	Lead(II)
Hg_2^{2+}	Mercury(II)
Hg_2^{2+}	Mercury(I)
Ag^{+}	Silver [†]
Zn^{2+}	Zinc [†]
Cd^{2+}	Cadmium [†]

*Note that mercury(I) ions always occur bound together to form Hg_2^{2+} ions.

[†]Although these are transition metals, they form only one type of ion, and a Roman numeral is not used.

Roman numeral. Thus AgCl is typically called silver chloride rather than silver(I) chloride, although the latter name is technically correct. Also, a Roman numeral is not used for zinc compounds, since zinc forms only the Zn^{2+} ion.

As shown in Example 3.11, when a metal ion is present that forms more than one type of cation, the charge on the metal ion must be determined by balancing the positive and negative charges of the compound. To do this you must be able to recognize the common cations and anions and know their charges (see Tables 3.3 and 3.5). The procedure for naming binary ionic compounds is summarized in Fig. 3.9.

We can use the periodic table to tell us something about the stable ions formed by many atoms. For example, the atoms in column 1 always form $1+$ ions. The transition metals, however, can form more than one type of stable ion. What if each transition metal ion had only one possible charge? How would the naming of compounds be different?

TABLE 3.5 | Common Polyatomic Ions

Hg_2^{2+}	Mercury(I)	NCS^- or SCN^-	Thiocyanate
NH_4^+	Ammonium	CO_3^{2-}	Carbonate
NO_2^-	Nitrite	HCO_3^-	Hydrogen carbonate (bicarbonate is a widely used common name)
NO_3^-	Nitrate		
SO_3^{2-}	Sulfite		
SO_4^{2-}	Sulfate	ClO^- or OCl^-	Hypochlorite
HSO_4^-	Hydrogen sulfate (bisulfate is a widely used common name)	ClO_2^-	Chlorite
		ClO_3^-	Chlorate
		ClO_4^-	Perchlorate
OH^-	Hydroxide	$\text{C}_2\text{H}_3\text{O}_2^-$ or CH_3COO^-	Acetate
CN^-	Cyanide	MnO_4^-	Permanganate
PO_4^{3-}	Phosphate	$\text{Cr}_2\text{O}_7^{2-}$	Dichromate
HPO_4^{2-}	Hydrogen phosphate	CrO_4^{2-}	Chromate
H_2PO_4^-	Dihydrogen phosphate	O_2^{2-}	Peroxide
		$\text{C}_2\text{O}_4^{2-}$	Oxalate
		$\text{S}_2\text{O}_3^{2-}$	Thiosulfate

INTERACTIVE EXAMPLE 3.12

Naming Binary Compounds

- Give the systematic name for each of the following compounds:
 - CoBr_2
 - CaCl_2
 - Al_2O_3
- Given the following systematic names, write the formula for each compound:
 - Chromium(III) chloride
 - Gallium iodide

SOLUTION

1.

Formula	Name	Comments
a. CoBr_2	Cobalt(II) bromide	Cobalt is a transition metal; the compound name must have a Roman numeral. The two Br^- ions must be balanced by a Co^{2+} ion.
b. CaCl_2	Calcium chloride	Calcium, an alkaline earth metal, forms only the Ca^{2+} ion. A Roman numeral is not necessary.
c. Al_2O_3	Aluminum oxide	Aluminum forms only the Al^{3+} ion. A Roman numeral is not necessary.

2.

Name	Formula	Comments
a. Chromium(III) chloride	CrCl_3	Chromium(III) indicates that Cr^{3+} is present, so 3 Cl^- ions are needed for charge balance.
b. Gallium iodide	GaI_3	Gallium always forms 3+ ions, so 3 I^- ions are required for charge balance.



Richard Megna/Fundamental Photographs

▲ Various chromium compounds dissolved in water. From left to right: CrCl_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Cr}(\text{NO}_3)_3$, CrCl_3 , K_2CrO_4 .

See Exercises 3.81 and 3.82

The common Type I and Type II ions are summarized in Fig. 3.10. Also shown in Fig. 3.10 are the common monatomic ions.

1 1A	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
Li^+														N^{3-}	O^{2-}	F^-	
Na^+	Mg^{2+}	3	4	5	6 Cr^{2+} Cr^{3+}	7 Mn^{2+} Mn^{3+}	8 Fe^{2+} Fe^{3+}	9 Co^{2+} Co^{3+}	10	11 Cu^+ Cu^{2+}	12 Zn^{2+}	Al^{3+}			S^{2-}	Cl^-	
K^+	Ca^{2+}											Ga^{3+}				Br^-	
Rb^+	Sr^{2+}									Ag^+	Cd^{2+}		Sn^{2+} Sn^{4+}			I^-	
Cs^+	Ba^{2+}										Hg^{2+} Hg^{+}		Pb^{2+} Pb^{4+}				

FIGURE 3.10 The common cations and anions.

Common Type I cations Common Type II cations Common monatomic anions

Ionic Compounds with Polyatomic Ions

We have not yet considered ionic compounds that contain polyatomic ions. For example, the compound ammonium nitrate, NH_4NO_3 , contains the polyatomic ions NH_4^+ and NO_3^- . Polyatomic ions are assigned special names that *must be memorized* to name the compounds containing them. The most important polyatomic ions and their names are listed in Table 3.5.

Note in Table 3.5 that several series of anions contain an atom of a given element and different numbers of oxygen atoms. These anions are called **oxyanions**. When there are two members in such a series, the name of the one with the smaller number of oxygen atoms ends in *-ite* and the name of the one with the larger number ends in *-ate*—for example, sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}). When more than two oxyanions make up a series, *hypo-* (less than) and *per-* (more than) are used as prefixes to name the members of the series with the fewest and the most oxygen atoms, respectively. The best example involves the oxyanions containing chlorine, as shown in Table 3.5.

INTERACTIVE EXAMPLE 3.13

Naming Compounds Containing Polyatomic Ions

- Give the systematic name for each of the following compounds:
 - Na_2SO_4
 - KH_2PO_4
 - $\text{Fe}(\text{NO}_3)_3$
 - $\text{Mn}(\text{OH})_2$
 - Na_2SO_3
 - Na_2CO_3
- Given the following systematic names, write the formula for each compound:
 - Sodium hydrogen carbonate
 - Cesium perchlorate
 - Sodium hypochlorite
 - Sodium selenate
 - Potassium bromate

SOLUTION

1.	Formula	Name	Comments
a.	Na_2SO_4	Sodium sulfate	
b.	KH_2PO_4	Potassium dihydrogen phosphate	
c.	$\text{Fe}(\text{NO}_3)_3$	Iron(III) nitrate	Transition metal—name must contain a Roman numeral. The Fe^{3+} ion balances three NO_3^- ions.
d.	$\text{Mn}(\text{OH})_2$	Manganese(II) hydroxide	Transition metal—name must contain a Roman numeral. The Mn^{2+} ion balances three OH^- ions.
e.	Na_2SO_3	Sodium sulfite	
f.	Na_2CO_3	Sodium carbonate	

2.

	Name	Formula	Comments
a.	Sodium hydrogen carbonate	NaHCO_3	Often called sodium bicarbonate.
b.	Cesium perchlorate	CsClO_4	
c.	Sodium hypochlorite	NaOCl	
d.	Sodium selenate	Na_2SeO_4	Atoms in the same group, like sulfur and selenium, often form similar ions that are named similarly. Thus SeO_4^{2-} is selenate, like SO_4^{2-} (sulfate).
e.	Potassium bromate	KBrO_3	As above, BrO_3^- is bromate, like ClO_3^- (chlorate).

See Exercises 3.83 and 3.84

Binary Covalent Compounds (Type III)

Binary covalent compounds are formed between *two nonmetals*. Although these compounds do not contain ions, they are named very similarly to binary ionic compounds.

TABLE 3.6 | Prefixes Used to Indicate Number in Chemical Names

Prefix	Number Indicated
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

Naming Binary Covalent Compounds

1. The first element in the formula is named first, using the full element name.
2. The second element is named as if it were an anion.
3. Prefixes are used to denote the numbers of atoms present. These prefixes are given in Table 3.6.
4. The prefix *mono-* is never used for naming the first element. For example, CO is called carbon monoxide, *not* monocarbon monoxide.

To see how these rules apply, we will now consider the names of the several covalent compounds formed by nitrogen and oxygen:

Compound	Systematic Name	Common Name
N_2O	Dinitrogen monoxide	Nitrous oxide
NO	Nitrogen monoxide	Nitric oxide
NO_2	Nitrogen dioxide	
N_2O_3	Dinitrogen trioxide	
N_2O_4	Dinitrogen tetroxide	
N_2O_5	Dinitrogen pentoxide	

Notice from the preceding examples that to avoid awkward pronunciations, we often drop the final *o* or *a* of the prefix when the element begins with a vowel. For example, N_2O_4 is called dinitrogen tetroxide, *not* dinitrogen tetraoxide, and CO is called carbon monoxide, *not* carbon monooxide.

Some compounds are always referred to by their common names. Three examples are water, ammonia, and hydrogen peroxide. The systematic names for H_2O , NH_3 , and H_2O_2 are never used.

INTERACTIVE EXAMPLE 3.14

Naming Type III Binary Compounds

- Name each of the following compounds:
 - PCl_5
 - PCl_3
 - SO_2
- From the following systematic names, write the formula for each compound:
 - Sulfur hexafluoride
 - Sulfur trioxide
 - Carbon dioxide

SOLUTION

1.

Formula	Name
a. PCl_5	Phosphorus pentachloride
b. PCl_3	Phosphorus trichloride
c. SO_2	Sulfur dioxide

2.

Name	Formula
a. Sulfur hexafluoride	SF_6
b. Sulfur trioxide	SO_3
c. Carbon dioxide	CO_2

See Exercises 3.85 and 3.86

The rules for naming binary compounds are summarized in Fig. 3.11. Prefixes to indicate the number of atoms are used only in Type III binary compounds (those containing two nonmetals). An overall strategy for naming compounds is given in Fig. 3.12.

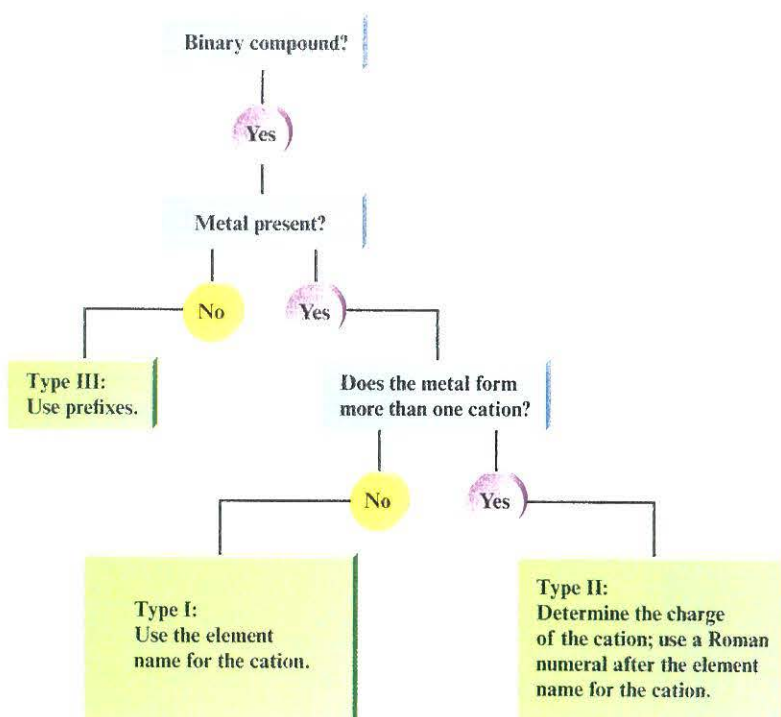
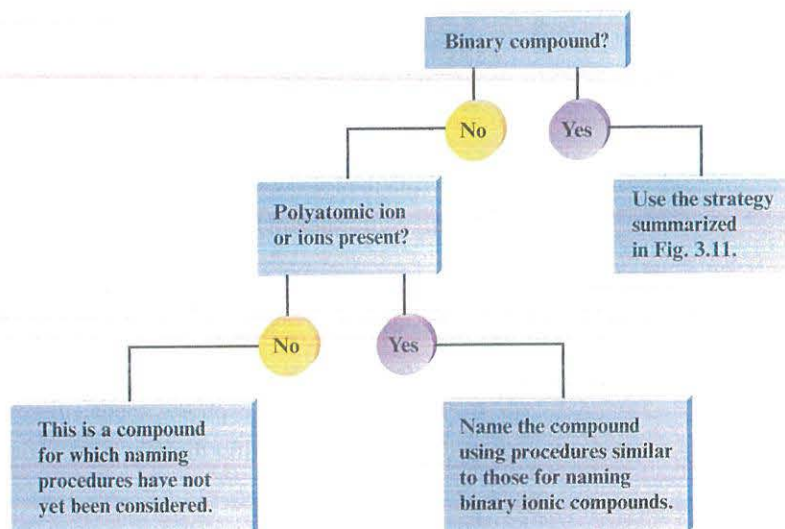


FIGURE 3.11 A flowchart for naming binary compounds.

FIGURE 3.12 Overall strategy for naming chemical compounds.



INTERACTIVE EXAMPLE 3.15

Naming Various Types of Compounds

- Give the systematic name for each of the following compounds:
 - P_4O_{10}
 - Nb_2O_5
 - Li_2O_2
 - $\text{Ti}(\text{NO}_3)_4$
- Given the following systematic names, write the formula for each compound:
 - Vanadium(V) fluoride
 - Dioxygen difluoride
 - Rubidium peroxide
 - Gallium oxide

SOLUTION

1.

Compound	Name	Comment
a. P_4O_{10}	Tetraphosphorus decaoxide	Binary covalent compound (Type III), so prefixes are used. The <i>a</i> in <i>deca-</i> is sometimes dropped.
b. Nb_2O_5	Niobium(V) oxide	Type II binary compound containing Nb^{5+} and O^{2-} ions. Niobium is a transition metal and requires a Roman numeral.
c. Li_2O_2	Lithium peroxide	Type I binary compound containing the Li^+ and O_2^{2-} (peroxide) ions.
d. $\text{Ti}(\text{NO}_3)_4$	Titanium(IV) nitrate	Not a binary compound. Contains the Ti^{4+} and NO_3^- ions. Titanium is a transition metal and requires a Roman numeral.

2.

Name	Chemical Formula	Comment
a. Vanadium(V) fluoride	VF_5	The compound contains V^{5+} ions and requires five F^- ions for charge balance.
b. Dioxygen difluoride	O_2F_2	The prefix <i>di-</i> indicates two of each atom.

- c. Rubidium peroxide Rb_2O_2 Because rubidium is in Group 1A, it forms only $1+$ ions. Thus two Rb^+ ions are needed to balance the $2-$ charge on the peroxide ion (O_2^{2-}).
- d. Gallium oxide Ga_2O_3 Because gallium is in Group 3A, like aluminum, it forms only $3+$ ions. Two Ga^{3+} ions are required to balance the charge on three O^{2-} ions.

Exercises 3.87, 3.91, and 3.92

Acids can be recognized by the hydrogen that appears first in the formula.

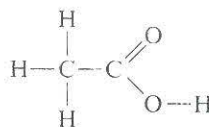
Acids

When dissolved in water, certain molecules produce a solution containing free H^+ ions (protons). These substances, **acids**, will be discussed in detail later in the text. Here we will simply present the rules for naming acids.

An acid is a molecule in which one or more H^+ ions are attached to an anion. The rules for naming acids depend on whether the anion contains oxygen. If the name of the *anion ends in -ide*, the acid is named with the prefix *hydro-* and the suffix *-ic*. For example, when gaseous HCl is dissolved in water, it forms *hydrochloric acid*. Similarly, HCN and H_2S dissolved in water are called hydrocyanic and hydrosulfuric acids, respectively.

When the *anion contains oxygen*, the acidic name is formed from the root name of the anion with a suffix of *-ic* or *-ous*, depending on the name of the anion.

1. If the anion name ends in *-ate*, the suffix *-ic* is added to the root name. For example, H_2SO_4 contains the sulfate anion (SO_4^{2-}) and is called sulfuric acid; H_3PO_4 contains the phosphate anion (PO_4^{3-}) and is called phosphoric acid; and $\text{HC}_2\text{H}_3\text{O}_2$ contains the acetate ion ($\text{C}_2\text{H}_3\text{O}_2^-$) and is called acetic acid. Note that acetic acid has the actual structure:



The formula is often written as CH_3COOH . Thus the formula of acetate ion would be CH_3COO^- . This structure does not conform to the rule that the acidic hydrogen is written first.

2. If the anion has an *-ite* ending, the *-ite* is replaced by *-ous*. For example, H_2SO_3 , which contains sulfite (SO_3^{2-}), is named sulfurous acid; and HNO_2 , which contains nitrite (NO_2^-), is named nitrous acid.

The application of these rules can be seen in the names of the acids of the oxyanions of chlorine:

Acid	Anion	Name
HClO_4	Perchlorate	Perchloric acid
HClO_3	Chlorate	Chloric acid
HClO_2	Chlorite	Chlorous acid
HClO	Hypochlorite	Hypochlorous acid

The names of the most important acids are given in Tables 3.7 and 3.8. An overall strategy for naming acids is shown in Fig. 3.13.

TABLE 3.7 | Names of Acids* That Do Not Contain Oxygen

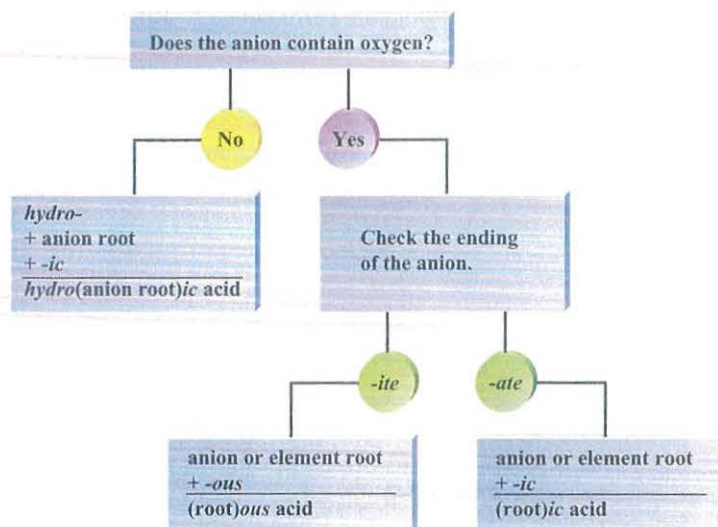
Formula	Name
HF	Hydrofluoric acid
HCl	Hydrochloric acid
HBr	Hydrobromic acid
HI	Hydroiodic acid
HCN	Hydrocyanic acid
H_2S	Hydrosulfuric acid

*Note that these acids are aqueous solutions containing these substances.

TABLE 3.8 | Names of Some Oxygen-Containing Acids

Acid	Name
HNO_3	Nitric acid
HNO_2	Nitrous acid
H_2SO_4	Sulfuric acid
H_2SO_3	Sulfurous acid
H_3PO_4	Phosphoric acid
$\text{HC}_2\text{H}_3\text{O}_2$	Acetic acid

FIGURE 3.13 A flowchart for naming acids. An acid is best considered as one or more H^+ ions attached to an anion.



CRITICAL THINKING In this chapter, you have learned a systematic way to name chemical compounds. What if all compounds had only common names? What problems would this cause?

For Review

Key Terms

Section 3.1

chemical bonds
covalent bonds
molecule
chemical formula
structural formula
space-filling model
ball-and-stick models
bond energy
ionic bonding
ionic compound
Coulomb's law
bond length
covalent bonding
polar covalent bond

Section 3.2

electronegativity

Section 3.3

isoelectronic ions

Chemical Bonds

- › Hold groups of atoms together
- › Occur when a group of atoms can lower its total energy by aggregating
- › Types of chemical bonds
 - › Ionic: electrons are transferred to form ions
 - › Covalent: equal sharing of electrons
 - › Polar covalent: unequal electron sharing
- › Percent ionic character of a bond $\text{X}-\text{Y}$

$$\frac{\text{Measured dipole moment of } \text{X}-\text{Y}}{\text{Calculated dipole moment for } \text{X}^+ \text{Y}^-} \times 100\%$$

- › Electronegativity: the relative ability of an atom to attract shared electrons
 - › The polarity of a bond depends on the electronegativity difference of the bonded atoms
 - › The spatial arrangement of polar bonds in a molecule determines whether the molecule has a dipole moment

Key Terms

Section 3.6

localized electron (LE) model

lone pairs

bonding pairs

Section 3.7

Lewis structure

duet rule

octet rule

Section 3.9

resonance

resonance structures

formal charge

Section 3.10

binary compounds

binary ionic compounds

oxyanions

binary covalent compounds

acids

Ionic Bonding

- › An ion has a different size than its parent atom
- › An anion is larger than its parent ion
- › A cation is smaller than its parent atom

Bond Energy

- › The energy necessary to break a covalent bond
- › Increases as the number of shared pairs increases
- › Can be used to estimate the energy change for a chemical reaction

Lewis Structures

- › Show how the valence electron pairs are arranged among the atoms in a molecule or polyatomic ion
- › Stable molecules usually contain atoms that have their valence orbitals filled
 - › Leads to a duet rule for hydrogen
 - › Leads to an octet rule for second-row elements
 - › The atoms of elements in the third row and beyond can exceed the octet rule
- › Several equivalent Lewis structures can be drawn for some molecules, a concept called resonance
- › When several nonequivalent Lewis structures can be drawn for a molecule, formal charge is often used to choose the most appropriate structure(s)

Compounds Are Named Using a System of Rules Depending on the Type of Compound.

- › Binary compounds
 - › Type I—contain a metal that always forms the same cation
 - › Type II—contain a metal that can form more than one cation
 - › Type III—contain two nonmetals
- › Compounds containing a polyatomic ion

Review Questions

Answers to the Review Questions can be found on the Student Web site.

1. Distinguish between the terms *covalent bond* versus *ionic bond* and *pure covalent bond* versus *polar covalent bond*. Characterize the types of bonds in terms of electronegativity difference. Energetically, why do ionic and covalent bonds form?
2. When metals react with nonmetals, an ionic compound generally results. What is the predicted general formula for the compound formed between an alkali metal and sulfur? Between an alkaline earth metal and nitrogen? Between aluminum and a halogen?
3. When an element forms an anion, what happens to the radius? When an element forms a cation, what happens to the radius? Why? Define the term *isoelectronic*. When comparing sizes of ions, which ion has the largest radius and which ion has the smallest radius in an isoelectronic series? Why?
4. Give a rationale for the octet rule and the duet rule for H in terms of orbitals. Give the steps for drawing a Lewis structure for a molecule or ion.
5. In general, molecules and ions always follow the octet rule unless it is impossible. The three types of exceptions are molecules/ions with too few electrons, molecules/ions with an odd number of electrons, and molecules/ions with too many electrons. Which atoms sometimes have fewer than 8 electrons around them? Give an example. Which atoms sometimes have more than 8 electrons around them? Give some examples. Why are odd-electron species generally very reactive and uncommon? Give an example of an odd-electron molecule.
6. Explain the terms *resonance* and *delocalized electrons*. When a substance exhibits resonance, we say that none of the individual Lewis structures accurately portrays

the bonding in the substance. Why do we draw resonance structures?

- Define formal charge and explain how to calculate it. What is the purpose of the formal charge? Organic compounds are composed mostly of carbon and hydrogen but also may have oxygen, nitrogen, and/or halogens in the formula. Formal charge arguments work very well for organic compounds when drawing the best Lewis structure. How do C, H, N, O, and Cl satisfy the

Active Learning Questions

These questions are designed to be used by groups of students in class.

- Explain the electronegativity trends across a row and down a column of the periodic table. Compare these trends with those of ionization energies and atomic radii. How are they related?
- Using only the periodic table, predict the most stable ion for Na, Mg, Al, S, Cl, K, Ca, and Ga. Arrange these from largest to smallest radius, and explain why the radius varies as it does. Compare your predictions with Fig. 3.5.
- Which has the greater bond lengths: NO_2^- or NO_3^- ? Explain.
- The following ions are best described with resonance structures. Draw the resonance structures, and using formal charge arguments, predict the best Lewis structure for each ion.
 - NCO^-
 - CNO^-
- What is meant by a chemical bond? Why do atoms form bonds with each other? Why do some elements exist as molecules in nature instead of as free atoms?
- Why are some bonds ionic and some covalent?
- How does a bond between Na and Cl differ from a bond between C and O? What about a bond between N and N?
- Does a Lewis structure tell which electrons come from which atoms? Explain.
- Evaluate each of the following as an acceptable name for water:
 - dihydrogen oxide
 - hydroxide hydride
 - hydrogen hydroxide
 - oxygen dihydride
- Why do we call $\text{Ba}(\text{NO}_3)_2$ barium nitrate, but we call $\text{Fe}(\text{NO}_3)_2$ iron(II) nitrate?
- Why is calcium dichloride not the correct systematic name for CaCl_2 ?
- The common name for NH_3 is ammonia. What would be the systematic name for NH_3 ? Support your answer.

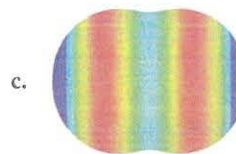
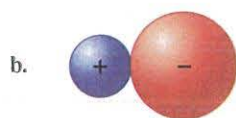
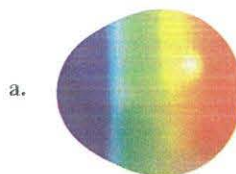
A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Student Solutions Manual*.

Questions

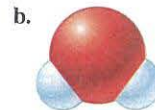
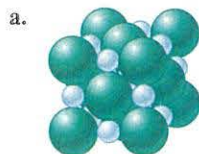
- Compare and contrast the bonding found in the $\text{H}_2(\text{g})$ and $\text{HF}(\text{g})$ molecules with that found in $\text{NaF}(\text{s})$.

octet rule in organic compounds so as to have a formula charge of zero?

- The compounds AlCl_3 , CrCl_3 , and ICl_3 have similar formulas, yet each follows a different set of rules to name it. Name these compounds, and then compare and contrast the nomenclature rules used in each case.
- How would you name HBrO_4 , KIO_3 , NaBrO_2 , and HIO ? Refer to Table 3.5 and the acid nomenclature discussion in the text.
- The following electrostatic potential diagrams represent H_2 , HCl , or NaCl . Label each and explain your choices.



- Describe the type of bonding that exists in the $\text{Cl}_2(\text{g})$ molecule. How does this type of bonding differ from that found in the $\text{HCl}(\text{g})$ molecule? How is it similar?
- Some of the important properties of ionic compounds are as follows:
 - low electrical conductivity as solids and high conductivity in solution or when molten
 - relatively high melting and boiling points
 - brittleness
 - solubility in polar solvents
 How does the concept of ionic bonding discussed in this chapter account for these properties?
- Label the type of bonding for each of the following.



- Distinguish between the following terms.
 - molecule versus ion
 - covalent bonding versus ionic bonding
 - molecule versus compound
 - anion versus cation

19. What is the electronegativity trend? Where does hydrogen fit into the electronegativity trend for the other elements in the periodic table?
20. When comparing the size of different ions, the general radii trend discussed in Chapter 2 is usually not very useful. What do you concentrate on when comparing sizes of ions to each other or when comparing the size of an ion to its neutral atom?
21. Which of the following statements is/are true? Correct the false statements.
 - a. It is impossible to satisfy the octet rule for all atoms in XeF_2 .
 - b. Because SF_2 exists, OF_2 should also exist, because oxygen is in the same family as sulfur.
 - c. The bond in NO^+ should be stronger than the bond in NO^- .
 - d. As predicted from the two Lewis structures for ozone, one oxygen–oxygen bond is stronger than the other oxygen–oxygen bond.
22. Three resonance structures can be drawn for CO_2 . Which resonance structure is best from a formal charge standpoint?
23. By analogy with phosphorus compounds, name the following: Na_3AsO_4 , H_3AsO_4 , $\text{Mg}_3(\text{SbO}_4)_2$.
24. Each of the following compounds has three possible names listed for it. For each compound, what is the correct name and why aren't the other names used?
 - a. N_2O : nitrogen oxide, nitrogen(I) oxide, dinitrogen monoxide
 - b. Cu_2O : copper oxide, copper(I) oxide, dicopper monoxide
 - c. Li_2O : lithium oxide, lithium(I) oxide, dilithium monoxide
29. Repeat Exercises 25 and 27, this time using the values for the electronegativities of the elements given in Fig. 3.4. Are there differences in your answers?
30. Repeat Exercises 26 and 28, this time using the values for the electronegativities of the elements given in Fig. 3.4. Are there differences in your answers?
31. Which of the following incorrectly shows the bond polarity? Show the correct bond polarity for those that are incorrect.
 - a. $^{\delta+}\text{H}-\text{F}^{\delta-}$
 - b. $^{\delta-}\text{Cl}-\text{I}^{\delta}$
 - c. $^{\delta-}\text{Si}-\text{S}^{\delta}$
 - d. $^{\delta+}\text{Br}-\text{Br}^{\delta-}$
 - e. $^{\delta+}\text{O}-\text{P}^{\delta-}$
32. Indicate the bond polarity (show the partial positive and partial negative ends) in the following bonds.
 - a. $\text{C}-\text{O}$
 - b. $\text{P}-\text{H}$
 - c. $\text{H}-\text{Cl}$
 - d. $\text{Br}-\text{Te}$
 - e. $\text{Se}-\text{S}$
33. Predict the type of bond (ionic, covalent, or polar covalent) one would expect to form between the following pairs of elements.
 - a. Rb and Cl
 - b. S and S
 - c. C and F
 - d. Ba and S
 - e. N and P
 - f. B and H
34. List all the possible bonds that can occur between the elements P, Cs, O, and H. Predict the type of bond (ionic, covalent, or polar covalent) one would expect to form for each bond.
35. Hydrogen has an electronegativity value between boron and carbon and identical to phosphorus. With this in mind, rank the following bonds in order of decreasing polarity: $\text{P}-\text{H}$, $\text{O}-\text{H}$, $\text{N}-\text{H}$, $\text{F}-\text{H}$, $\text{C}-\text{H}$.
36. Rank the following bonds in order of increasing ionic character: $\text{N}-\text{O}$, $\text{Ca}-\text{O}$, $\text{C}-\text{F}$, $\text{Br}-\text{Br}$, $\text{K}-\text{F}$.

Exercises

In this section, similar exercises are paired.

Chemical Bonds and Electronegativity

25. Without using Fig. 3.4, predict the order of increasing electronegativity in each of the following groups of elements.
 - a. C, N, O
 - b. S, Se, Cl
 - c. Si, Ge, Sn
 - d. Tl, S, Ge
26. Without using Fig. 3.4, predict the order of increasing electronegativity in each of the following groups of elements.
 - a. Na, K, Rb
 - b. B, O, Ga
 - c. F, Cl, Br
 - d. S, O, F
27. Without using Fig. 3.4, predict which bond in each of the following groups will be the most polar.
 - a. $\text{C}-\text{F}$, $\text{Si}-\text{F}$, $\text{Ge}-\text{F}$
 - b. $\text{P}-\text{Cl}$ or $\text{S}-\text{Cl}$
 - c. $\text{S}-\text{F}$, $\text{S}-\text{Cl}$, $\text{S}-\text{Br}$
 - d. $\text{Ti}-\text{Cl}$, $\text{Si}-\text{Cl}$, $\text{Ge}-\text{Cl}$
28. Without using Fig. 3.4, predict which bond in each of the following groups will be the most polar.
 - a. $\text{C}-\text{H}$, $\text{Si}-\text{H}$, $\text{Sn}-\text{H}$
 - b. $\text{Al}-\text{Br}$, $\text{Ga}-\text{Br}$, $\text{In}-\text{Br}$, $\text{Tl}-\text{Br}$
 - c. $\text{C}-\text{O}$ or $\text{Si}-\text{O}$
 - d. $\text{O}-\text{F}$ or $\text{O}-\text{Cl}$
37. Would you expect each of the following atoms to gain or lose electrons when forming ions? What ion is the most likely in each case?
 - a. Ra
 - b. In
 - c. P
 - d. Te
 - e. Br
 - f. Rb
38. For each of the following atomic numbers, use the periodic table to write the formula (including the charge) for the simple ion that the element is most likely to form in ionic compounds.
 - a. 13
 - b. 34
 - c. 56
 - d. 7
 - e. 87
 - f. 35
39. Write electron configurations for the most stable ion formed by each of the elements Al, Ba, Se, and I (when in stable ionic compounds).
40. Write electron configurations for the most stable ion formed by each of the elements Te, Cl, Sr, and Li (when in stable ionic compounds).
41. Predict the empirical formulas of the ionic compounds formed from the following pairs of elements. Name each compound.
 - a. Li and N
 - b. Ga and O
 - c. Rb and Cl
 - d. Ba and S
42. Predict the empirical formulas of the ionic compounds formed from the following pairs of elements. Name each compound.
 - a. Al and Cl
 - b. Na and O
 - c. Sr and F
 - d. Ca and Se

43. Write electron configurations for
 a. the cations Mg^{2+} , K^+ , and Al^{3+} .
 b. the anions N^{3-} , O^{2-} , F^- , and Te^{2-} .
44. Write electron configurations for
 a. the cations Sr^{2+} , Cs^+ , In^+ , and Pb^{2+} .
 b. the anions P^{3-} , S^{2-} , and Br^- .
45. Which of the following ions have noble gas electron configurations?
 a. Fe^{2+} , Fe^{3+} , Sc^{3+} , Co^{3+}
 b. Ti^+ , Te^{2-} , Cr^{3+}
 c. Pu^{4+} , Ce^{4+} , Ti^{4+}
 d. Ba^{2+} , Pt^{2+} , Mn^{2+}
46. What noble gas has the same electron configuration as each of the ions in the following compounds?
 a. cesium sulfide
 b. strontium fluoride
 c. calcium nitride
 d. aluminum bromide
47. Give the formula of a *negative* ion that would have the same number of electrons as each of the following *positive* ions.
 a. Na^+ c. Al^{3+}
 b. Ca^{2+} d. Rb^+
48. Give an example of an ionic compound where both the anion and the cation are isoelectronic with each of the following noble gases.
 a. Ne c. Kr
 b. Ar d. Xe
49. Give three ions that are isoelectronic with neon. Place these ions in order of increasing size.
50. Consider the ions Sc^{3+} , Cl^- , K^+ , Ca^{2+} , and S^{2-} . Match these ions to the following pictures that represent the relative sizes of the ions.

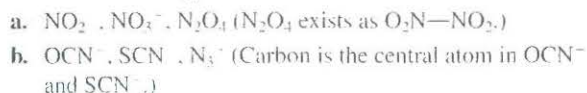


51. For each of the following groups, place the atoms and/or ions in order of decreasing size.
 a. Cu , Cu^+ , Cu^{2+}
 b. Ni^{2+} , Pd^{2+} , Pt^{2+}
 c. O , O^- , O^{2-}
 d. La^{3+} , Eu^{3+} , Gd^{3+} , Yb^{3+}
 e. Te^{2-} , I^- , Cs^+ , Ba^{2+} , La^{3+}
52. For each of the following groups, place the atoms and/or ions in order of decreasing size.
 a. V , V^{2+} , V^{3+} , V^{5+}
 b. Na^+ , K^+ , Rb^+ , Cs^+
 c. Te^{2-} , I^- , Cs^+ , Ba^{2+}
 d. P , P^- , P^{2-} , P^{3-}
 e. O^{2-} , S^{2-} , Se^{2-} , Te^{2-}

Lewis Structures and Resonance

53. Write Lewis structures that obey the octet rule (duet rule for H) for each of the following molecules. Carbon is the central atom in CH_4 , nitrogen is the central atom in NH_3 , and oxygen is the central atom in H_2O .
 a. F_2 e. NH_3
 b. O_2 f. H_2O
 c. CO g. HF
 d. CH_4
54. Write Lewis structures that obey the octet rule (duet rule for H) for each of the following molecules.
 a. H_2CO
 b. CO_2
 c. HCN
 Carbon is the central atom in all of these molecules.
55. Write Lewis structures that obey the octet rule for each of the following molecules.
 a. CCl_4 c. SeCl_2
 b. NCl_3 d. ICl
 In each case, the atom listed first is the central atom.
56. Write Lewis structures that obey the octet rule for each of the following molecules and ions. (In each case the first atom listed is the central atom.)
 a. POCl_3 , SO_4^{2-} , XeO_4 , PO_4^{3-} , ClO_4^-
 b. NF_3 , SO_3^{2-} , PO_3^{3-} , ClO_3^-
 c. ClO_2^- , SCl_2 , PCl_2^-
 d. Considering your answers to parts a, b, and c, what conclusions can you draw concerning the structures of species containing the same number of atoms and the same number of valence electrons?
57. One type of exception to the octet rule are compounds with central atoms having fewer than eight electrons around them. BeH_2 and BH_3 are examples of this type of exception. Draw the Lewis structures for BeH_2 and BH_3 .
58. Lewis structures can be used to understand why some molecules react in certain ways. Write the Lewis structures for the reactants and products in the reactions described below.
 a. Nitrogen dioxide dimerizes to produce dinitrogen tetroxide.
 b. Boron trihydride accepts a pair of electrons from ammonia, forming BH_3NH_3 .
 Give a possible explanation for why these two reactions occur.
59. The most common exceptions to the octet rule are compounds or ions with central atoms having more than eight electrons around them. PF_5 , SF_4 , ClF_3 , and Br_3^- are examples of this type of exception. Draw the Lewis structure for these compounds or ions. Which elements, when they have to, can have more than eight electrons around them? How is this rationalized?
60. SF_6 , ClF_5 , and XeF_4 are three compounds whose central atoms do not follow the octet rule. Draw Lewis structures for these compounds.

61. Write Lewis structures for the following. Show all resonance structures where applicable.



62. Some of the important pollutants in the atmosphere are ozone (O_3), sulfur dioxide, and sulfur trioxide. Write Lewis structures for these three molecules. Show all resonance structures where applicable.

63. Benzene (C_6H_6) consists of a six-membered ring of carbon atoms with one hydrogen bonded to each carbon. Write Lewis structures for benzene, including resonance structures.

64. Borazine ($\text{B}_3\text{N}_3\text{H}_6$) has often been called "inorganic" benzene. Write Lewis structures for borazine. Borazine contains a six-membered ring of alternating boron and nitrogen atoms with one hydrogen bonded to each boron and nitrogen.

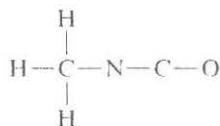
65. An important observation supporting the concept of resonance in the localized electron model was that there are only three different structures of dichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$). How does this fact support the concept of resonance (see Exercise 63)?

66. Consider the following bond lengths:

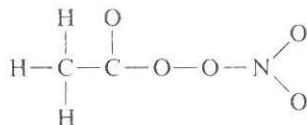


In the CO_3^{2-} ion, all three $\text{C}-\text{O}$ bonds have identical bond lengths of 136 pm. Why?

67. A toxic cloud covered Bhopal, India, in December 1984 when water leaked into a tank of methyl isocyanate, and the product escaped into the atmosphere. Methyl isocyanate is used in the production of many pesticides. Draw the Lewis structures for methyl isocyanate, CH_3NCO , including resonance forms. The skeletal structure is



68. Peroxyacetyl nitrate, or PAN, is present in photochemical smog. Draw the Lewis structures (including resonance forms) for PAN. The skeletal structure is



69. Order the following species with respect to carbon-oxygen bond length (longest to shortest).



What is the order from the weakest to the strongest carbon-oxygen bond? (CH_3OH exists as $\text{H}_3\text{C}-\text{OH}$.)

70. Place the species below in order of the shortest to the longest nitrogen-oxygen bond.



(H_2NOH exists as $\text{H}_2\text{N}-\text{OH}$.)

Formal Charge

71. Use the formal charge arguments to rationalize why BF_3 would not follow the octet rule.

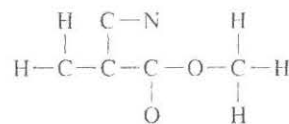
72. Use formal charge arguments to explain why CO has a less polar bond than expected on the basis of electronegativity.

73. Write Lewis structures that obey the octet rule for the following species. Assign the formal charge for each central atom.



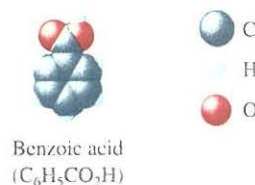
74. Write Lewis structures for the species in Exercise 73 that involve minimum formal charges.

75. A common trait of simple organic compounds is to have Lewis structures where all atoms have a formal charge of zero. Consider the following incomplete Lewis structure for an organic compound called *methyl cyanoacrylate*, the main ingredient in Super Glue.



Draw a complete Lewis structure for methyl cyanoacrylate in which all atoms have a formal charge of zero.

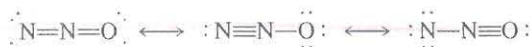
76. Benzoic acid is a food preservative. The space-filling model for benzoic acid is shown below.



Draw the Lewis structure for benzoic acid, including all resonance structures in which all atoms have a formal charge of zero.

77. Oxidation of the cyanide ion produces the stable cyanate ion, OCN^- . The fulminate ion, CNO^- , on the other hand, is very unstable. Fulminate salts explode when struck; $\text{Hg}(\text{CNO})_2$ is used in blasting caps. Write the Lewis structures and assign formal charges for the cyanate and fulminate ions. Why is the fulminate ion so unstable? (C is the central atom in OCN^- and N is the central atom in CNO^- .)

78. Nitrous oxide (
- N_2O
-) has three possible Lewis structures:

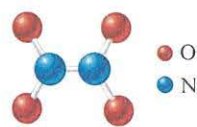


Given the following bond lengths,

N—N	167 pm	N=O	115 pm
N=N	120 pm	N—O	147 pm
N≡N	110 pm		

rationalize the observations that the N—N bond length in N_2O is 112 pm and that the N—O bond length is 119 pm. Assign formal charges to the resonance structures for N_2O . Can you eliminate any of the resonance structures on the basis of formal charges? Is this consistent with observation?

Nomenclature

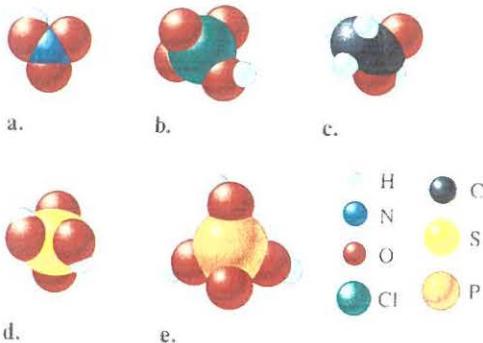
79. Name the compounds in parts a–d and write the formulas for the compounds in parts e–h.
- NaBr
 - Rb_2O
 - CaS
 - AlI_3
 - strontium fluoride
 - aluminum selenide
 - potassium nitride
 - magnesium phosphide
80. Name the compounds in parts a–d and write the formulas for the compounds in parts e–h.
- Hg_2O
 - FeBr_3
 - CoS
 - TiCl_4
 - tin(II) nitride
 - cobalt(III) iodide
 - mercury(II) oxide
 - chromium(VI) sulfide
81. Name each of the following compounds:
- CsF
 - Li_3N
 - Ag_2S
 - MnO_2
 - TiO_2
 - Sr_3P_2
82. Write the formula for each of the following compounds:
- zinc chloride
 - tin(IV) fluoride
 - calcium nitride
 - aluminum sulfide
 - mercury(I) selenide
 - silver iodide
83. Name each of the following compounds:
- BaSO_3
 - NaNO_2
 - KMnO_4
 - $\text{K}_2\text{Cr}_2\text{O}_7$
84. Write the formula for each of the following compounds:
- chromium(III) hydroxide
 - magnesium cyanide
 - lead(IV) carbonate
 - ammonium acetate
85. Name each of the following compounds:
- 
 - 
 - SO_2
 - P_2S_5
86. Write the formula for each of the following compounds:
- diboron trioxide
 - arsenic pentafluoride
 - dinitrogen monoxide
 - sulfur hexachloride
87. Name each of the following compounds:
- CuI
 - CuI_2
 - CoI_2
 - Na_2CO_3
 - NaHCO_3
 - S_4N_4
 - SF_4
 - NaOCl
 - BaCrO_4
 - NH_4NO_3
88. Name each of the following compounds. Assume the acids are dissolved in water.
- $\text{HC}_2\text{H}_3\text{O}_2$
 - NH_4NO_2
 - Co_2S_3
 - ICl
 - $\text{Pb}_3(\text{PO}_4)_2$
 - KClO_3
 - H_2SO_4
 - Sr_3N_2
 - $\text{Al}_2(\text{SO}_3)_3$
 - SnO_2
 - Na_2CrO_4
 - HClO
89. Elements in the same family often form oxyanions of the same general formula. The anions are named in a similar fashion. Give the names of the oxyanions of selenium and tellurium: SeO_4^{2-} , SeO_3^{2-} , TeO_4^{2-} , TeO_3^{2-} .
90. Knowing the names of similar chlorine oxyanions and acids, deduce the names of the following: IO^- , IO_2^- , IO_3^- , IO_4^- , HIO, HIO_2 , HIO_3 , HIO_4 .
91. Write the formula for each of the following compounds:
- sulfur difluoride
 - sulfur hexafluoride
 - sodium dihydrogen phosphate
 - lithium nitride
 - chromium(III) carbonate
 - tin(II) fluoride
 - ammonium acetate
 - ammonium hydrogen sulfate
 - cobalt(III) nitrate
 - mercury(I) chloride
 - potassium chlorate
 - sodium hydride
92. Write the formula for each of the following compounds:
- chromium(VI) oxide
 - disulfur dichloride
 - nickel(II) fluoride
 - potassium hydrogen phosphate
 - aluminum nitride
 - ammonia
 - manganese(IV) sulfide
 - sodium dichromate
 - ammonium sulfite
 - carbon tetraiodide

93. Write the formula for each of the following compounds:
- | | |
|--------------------------|---------------------------|
| a. sodium oxide | h. copper(I) chloride |
| b. sodium peroxide | i. gallium arsenide |
| c. potassium cyanide | j. cadmium selenide |
| d. copper(II) nitrate | k. zinc sulfide |
| e. selenium tetrabromide | l. nitrous acid |
| f. iodic acid | m. diphosphorus pentoxide |
| g. lead(IV) sulfide | |

94. Write the formula for each of the following compounds:

- ammonium hydrogen phosphate
- mercury(I) sulfide
- silicon dioxide
- sodium sulfite
- aluminum hydrogen sulfate
- nitrogen trichloride
- hydrobromic acid
- bromous acid
- perbromic acid
- potassium hydrogen sulfide
- calcium iodide
- cesium perchlorate

95. Name the acids illustrated below.



96. Each of the following compounds is incorrectly named. What is wrong with each name, and what is the correct name for each compound?

- FeCl_3 , iron chloride
- NO_2 , nitrogen(IV) oxide
- CaO , calcium(II) monoxide
- Al_2S_3 , dialuminum trisulfide
- $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$, manganese diacetate
- FePO_4 , iron(II) phosphide
- P_2S_5 , phosphorus sulfide
- Na_2O_2 , sodium oxide
- HNO_3 , nitrate acid
- H_2S , sulfuric acid

ChemWork Problems

These multiconcept problems (and additional ones) are found interactively online with the same type of assistance a student would get from an instructor.

- Identify the following elements based on their electron configurations and rank them in order of increasing electronegativity: $[\text{Ar}]4s^13d^5$; $[\text{Ne}]3s^23p^3$; $[\text{Ar}]4s^23d^{10}4p^3$; $[\text{Ne}]3s^23p^5$.
- Classify the bonding in each of the following molecules as ionic, polar covalent, or nonpolar covalent.

a. H_2	e. HF
b. K_3P	f. CCl_4
c. NaI	g. CF_4
d. SO_2	h. K_2S
- List the bonds $\text{P}-\text{Cl}$, $\text{P}-\text{F}$, $\text{O}-\text{F}$, and $\text{Si}-\text{F}$ from least polar to most polar.
- Arrange the atoms and/or ions in the following groups in order of decreasing size.
 - O , O^- , O^{2-}
 - Fe^{2+} , Ni^{2+} , Zn^{2+}
 - Ca^{2+} , K^+ , Cl^-
- Arrange the following in order of increasing radius and increasing ionization energy.
 - N^+ , N , N^-
 - Se , Se^- , Cl , Cl^-
 - Br^- , Rb^+ , Sr^{2+}
- Which member of the following pairs would you expect to be more energetically stable? Justify each choice.
 - NaBr or NaBr_2
 - ClO_4 or ClO_4^-
 - SO_4 or XeO_4
 - OF_4 or SeF_4
- What do each of the following sets of compounds/ions have in common?
 - SO_3 , NO_3^- , CO_3^{2-}
 - O_3 , SO_2 , NO_2^-
- Which of the following compounds or ions exhibit resonance?
 - O_3
 - CNO^-
 - AsI_3
 - CO_3^{2-}
 - AsF_3
- Although both Br_3^- and I_3^- ions are known, the F_3^- ion has not been observed. Explain.
- Complete the following table to predict whether the given atom will gain or lose electrons in forming the ion most likely to form when in ionic compounds.

Element	Group	Period	Ion Formed
K			
Cs			
Br			
S			
Se			

107. The formulas and common names for several substances are given below. Give the systematic names for these substances.

a. sugar of lead	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
b. blue vitrol	CuSO_4
c. quicklime	CaO
d. Epsom salts	MgSO_4
e. milk of magnesia	$\text{Mg}(\text{OH})_2$
f. gypsum	CaSO_4
g. laughing gas	N_2O

108. What are the formulas of the compounds that correspond to the names given in the following table?

Compound Name	Formula
Carbon tetrabromide	
Cobalt(II) phosphate	
Magnesium chloride	
Nickel(II) acetate	
Calcium nitrate	

109. What are the names of the compounds that correspond to the formulas given in the following table?

Formula	Compound Name
$\text{Co}(\text{NO}_2)_2$	
AsF_5	
LiCN	
K_2SO_3	
Li_3N	
PbCrO_4	

110. Which of the following statements is(are) correct?
- The symbols for the elements magnesium, aluminum, and xenon are Mn, Al, and Xe, respectively.
 - The elements P, As, and Bi are in the same family on the periodic table.
 - All of the following elements are expected to gain electrons to form ions in ionic compounds: Ga, Se, and Br.
 - The elements Co, Ni, and Hg are all transition elements.
 - The correct name for TiO_2 is titanium dioxide.
111. Identify each of the following elements:
- a member of the same family as oxygen whose most stable ion contains 54 electrons
 - a member of the alkali metal family whose most stable ion contains 36 electrons
 - a noble gas with 18 protons in the nucleus
 - a halogen with 85 protons and 85 electrons
112. A certain element has only two naturally occurring isotopes: one with 18 neutrons and the other with 20 neutrons. The element forms $1-$ charged ions when in ionic compounds. Predict the identity of the element. What number of electrons does the $1-$ charged ion have?

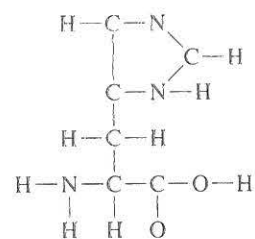
113. The designations 1A through 8A used for certain families of the periodic table are helpful for predicting the charges on ions in binary ionic compounds. In these compounds, the metals generally take on a positive charge equal to the family number, while the nonmetals take on a negative charge equal to the family number minus 8. Thus the compound between sodium and chlorine contains Na^+ ions and Cl^- ions and has the formula NaCl . Predict the formula and the name of the binary compound formed from the following pairs of elements.

a. Ca and N	e. Ba and I
b. K and O	f. Al and Se
c. Rb and F	g. Cs and P
d. Mg and S	h. In and Br

114. For each of the following ions, indicate the total number of protons and electrons in the ion. For the positive ions in the list, predict the formula of the simplest compound formed between each positive ion and the oxide ion. Name the compounds. For the negative ions in the list, predict the formula of the simplest compound formed between each negative ion and the aluminum ion. Name the compounds.

a. Fe^{2+}	e. S^{2-}
b. Fe^{3+}	f. P^{3-}
c. Ba^{2+}	g. Br^-
d. Cs^+	h. N^{3-}

115. The study of carbon-containing compounds and their properties is called *organic chemistry*. Besides carbon atoms, organic compounds also can contain hydrogen, oxygen, and nitrogen atoms (as well as other types of atoms). A common trait of simple organic compounds is to have Lewis structures where all atoms have a formal charge of zero. Consider the following incomplete Lewis structure for an organic compound called *histidine* (an amino acid), which is one of the building blocks of proteins found in our bodies:



Draw a complete Lewis structure for histidine in which all atoms have a formal charge of zero.

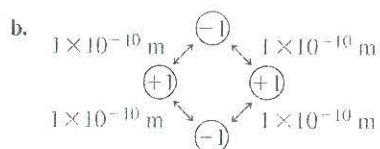
116. A polyatomic ion is composed of C, N, and an unknown element X. The skeletal Lewis structure of this polyatomic ion is $[\text{X}-\text{C}-\text{N}]^-$. The ion X^{2-} has an electron configuration of $[\text{Ar}]4s^23d^{10}4p^6$. What is element X? Knowing the identity of X, complete the Lewis structure of the polyatomic ion, including all important resonance structures.

Challenge Problems

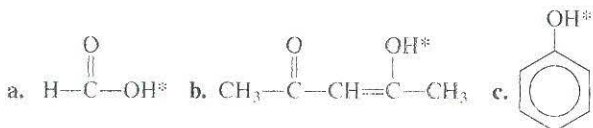
117. Use Coulomb's law.

$$V = \frac{Q_1 Q_2}{4\pi\epsilon_0 r} = 2.31 \times 10^{-19} \text{ J} \cdot \text{nm} \left(\frac{Q_1 Q_2}{r} \right)$$

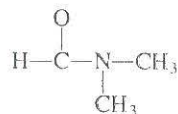
to calculate the energy of interaction, V , for the following two arrangements of charges, each having a magnitude equal to the electron charge.



118. Many times extra stability is characteristic of a molecule or ion in which resonance is possible. How could this be used to explain the acidities of the following compounds? (The acidic hydrogen is marked by an asterisk.) Part c shows resonance in the C_6H_5 ring.

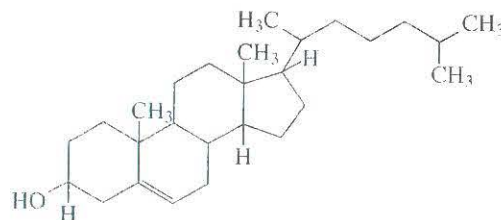


119. Draw a Lewis structure for the *N,N*-dimethylformamide molecule. The skeletal structure is



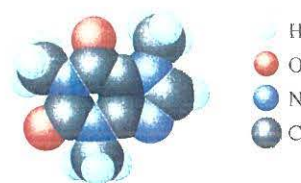
Various types of evidence lead to the conclusion that there is some double bond character to the C—N bond. Draw one or more resonance structures that support this observation.

120. Cholesterol ($C_{27}H_{46}O$) has the following structure:



In such shorthand structures, each point where lines meet represents a carbon atom, and most H atoms are not shown. Draw the complete structure showing all carbon and hydrogen atoms. (There will be four bonds to each carbon atom.)

121. Consider the following computer-generated model of caffeine.



Draw a Lewis structure for caffeine in which all atoms have a formal charge of zero.