

# CHAPTER 11: CHEMICAL BONDING

## Enhanced Introductory College Chemistry

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### In this chapter, you will learn about

- The types of bonds that can occur when elements interact
- Application of electron configurations to predict chemical bonding

- Molecular structures and bond strengths

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Periodic Table
- Electron valence configuration of elements



**Figure 11a:** Nicknamed “buckyballs,” buckminsterfullerene molecules ( $C_{60}$ ) contain only carbon atoms. Here they are shown in a ball-and-stick model (left). These molecules have single and double carbon-carbon bonds arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (centre). This unconventional molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit left: *Chemistry (OpenStax)*, CC BY 4.0; credit middle: modification of work by “Petey21”, CC0; credit right: modification of work by Bill Morrow, CC BY 2.0)

It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene, commonly known as a “buckyball.” This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula,  $C_{60}$ , and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.

**Watch How atoms bond – George Zaidan and Charles Morton (4 mins)**

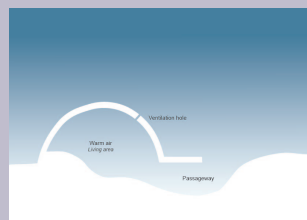
([https://www.youtube.com/watch?v=NgD9yHSJ29I&feature=emb\\_imp\\_woyt](https://www.youtube.com/watch?v=NgD9yHSJ29I&feature=emb_imp_woyt))

## Indigenous Perspective: Iglu

Igluit are built over the depression from where the blocks are cut. The entryway for the iglu is below ground level. The thermal properties ensures that the inside of the iglu is sufficiently warm even when the temperature outside is very low. (Anderson & Rayner-Canham, para. 11)

“As a result of the unique open crystal structure, snowflakes do not pack well together. This phenomenon results in one of the most important attributes of snow: its thermal insulation properties.” “When the Inuit transitioned from building igluit to using cabins and houses, we used the snow instead to pack tightly against the walls to insulate our homes.”

**Source:** Andersen, C.C., & Rayner-Canham, G. (2019, December). Snow: Making life possible in the Arctic: Chemistry Inuit Life and Culture (<https://uwaterloo.ca/chem13-news-magazine/december-2019/feature/snow-making-life-possible-arctic>). *Chem 13 News Magazine*.



**Figure 11.b:** Cross section of an iglu (credit: graphic by Revathi Mahadevan, CC BY 4.0)

## Attribution & References

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# 11.1 IONIC BONDING

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## Learning Objectives

By the end of this section, you will be able to:

- Explain the formation of cations, anions, and ionic compounds
- Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by **ionic bonds**: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas,  $\text{Cl}_2$ , a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure 11.1a). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.





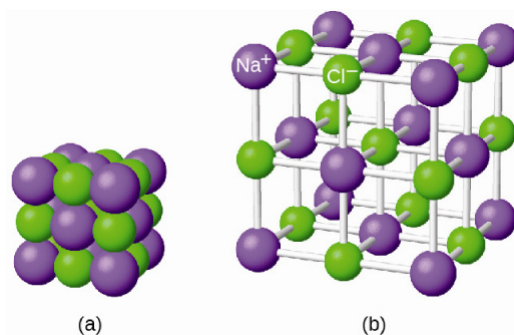
**Figure 11.1a:** (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by Jurii, CC BY 3.0; b: work by Greenhorn1, PD; c: work by Chemicalinterest, PD)

## The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

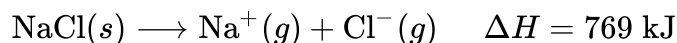
As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide,  $\text{Al}_2\text{O}_3$ , indicates that this ionic compound contains two aluminum cations,  $\text{Al}^{3+}$ , for every three oxide anions,  $\text{O}^{2-}$  [thus,  $(2 \times +3) + (3 \times -2) = 0$ ].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) “molecule” because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of  $\text{Na}^+$  cations and  $\text{Cl}^-$  anions (Figure 11.1b).

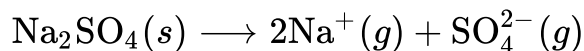


**Figure 11.1b:** The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is “bonded” to all of the surrounding ions—six in this case (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The strong electrostatic attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions holds them tightly together in solid  $\text{NaCl}$ . It requires 769 kJ of energy to dissociate one mole of solid  $\text{NaCl}$  into separate gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions:



Similarly, ionic compounds can be formed from polyatomic ions. As in the above example, energy would be required to dissociate the  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  ions of sodium sulfate because of the strong attraction between the ions. When dissociation occurs, any polyatomic ions retain their formula and charge.



## Electronic Structures of Simple Cations

When forming a cation, an atom of the main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground-state electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ . When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6$ . The  $\text{Ca}^{2+}$  ion is therefore isoelectronic with the noble gas Ar.

For groups 12–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full  $d$  subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions ( $\text{Al}^{3+}$ ).

Exceptions to the expected behaviour involve elements toward the bottom of the groups. In addition to the expected ions  $\text{Tl}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Pb}^{4+}$ , and  $\text{Bi}^{5+}$ , a partial loss of these atoms' valence shell electrons can also lead to the formation of  $\text{Tl}^{1+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Bi}^{3+}$  ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the **inert pair effect**, which reflects the relatively low energy of the valence  $s$ -electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behaviour: it forms a diatomic ion,  $\text{Hg}_2^{2+}$  (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion  $\text{Hg}^{2+}$  (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost  $s$  electron(s) first, sometimes followed by the loss of one or two  $d$  electrons from the next-to-outermost shell. For example, iron ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ ) forms the ion  $\text{Fe}^{2+}$  ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ ) by the loss of the  $4s$  electron and the ion  $\text{Fe}^{3+}$  ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ ) by the loss of the  $4s$  electron and one of the  $3d$  electrons. Although the  $d$  orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost  $s$  electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost  $s$  electrons and a  $d$  or  $f$  electron.

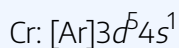
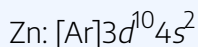
### Example 11.1a

#### Determining the Electronic Structures of Cations

There are at least 14 elements categorized as “essential trace elements” for the human body. They are called “essential” because they are required for healthy bodily functions, “trace” because they are required only in small amounts, and “elements” in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$ . Write the electron configurations of these cations.

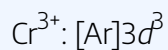
#### Solution

First, write the electron configuration for the neutral atoms:



Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the  $s$  orbital first and then from the  $d$  orbital. For the  $p$ -block elements, electrons are removed from the  $p$  orbitals and then from the  $s$  orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its  $s$  orbital. Chromium is a transition

element and should lose its  $s$  electrons and then its  $d$  electrons when forming a cation. Thus, we find the following electron configurations of the ions:



### Exercise 11.1a

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

**Check Your Answer<sup>1</sup>**

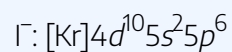
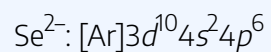
## Electronic Structures of Simple Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer  $s$  and  $p$  orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the  $s$  and  $p$  orbitals of the parent atom. Oxygen, for example, has the electron configuration  $1s^2 2s^2 2p^4$ , whereas the oxygen anion has the electron configuration of the noble gas neon (Ne),  $1s^2 2s^2 2p^6$ . The two additional electrons required to fill the valence orbitals give the oxide ion the charge of  $2-$  ( $\text{O}^{2-}$ ).

### Example 11.1b

#### Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

**Solution****Exercise 11.1b**

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

**Check Your Answer<sup>2</sup>****Exercise 11.1c**

Check Your Learning Exercise (Text Version)

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions:

- P
- I
- Mg
- Cl
- In
- Cs
- O
- Pb
- Co

## Check Your Answer<sup>3</sup>

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## Links to Interactive Learning Tools

Explore Ionic Bonding (<https://www.physicsclassroom.com/Concept-Builders/Chemistry/Ionic-Bonding>) from the Physics Classroom. (<https://www.physicsclassroom.com/>)

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## Notes

1.  $\text{K}^+$ : [Ar],  $\text{Mg}^{2+}$ : [Ne]
2. P:  $[\text{Ne}]3s^23p^3$ ;  $\text{P}^{3-}$ :  $[\text{Ne}]3s^23p^6$
3. P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

## 11.2 COVALENT BONDING

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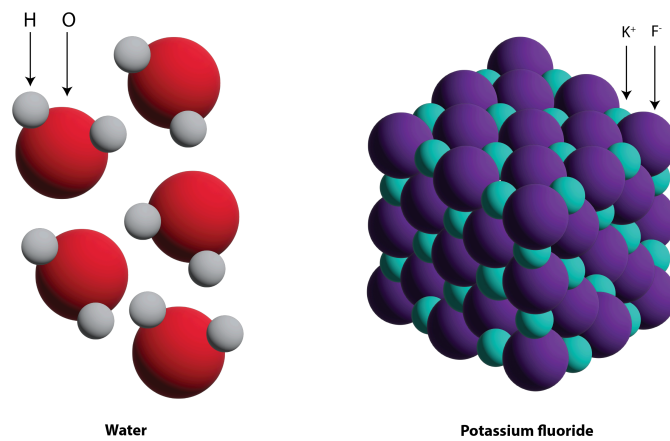
### Learning Objectives

By the end of this section, you will be able to:

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons equally between each other. Such bonds are called **covalent bonds**. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an  $\text{H}_2$  molecule; each hydrogen atom in the  $\text{H}_2$  molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

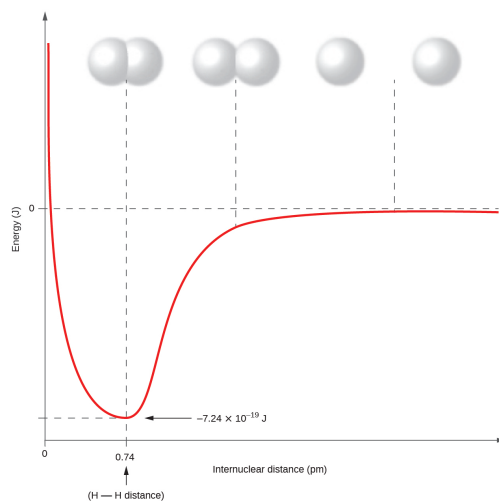


**Figure 11.2a:** The figure shows the structure of a water molecule and potassium fluoride. (credit: graphic by Revathi Mahadevan, CC BY 4.0.)

## Formation of Covalent Bonds

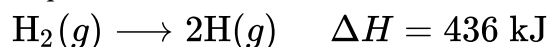
Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H<sub>2</sub>, contains a covalent bond between its two hydrogen atoms. Figure 11.2a illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the  $x$ -axis is the distance between the two atoms. As the two atoms approach each other (moving left along the  $x$ -axis), their valence orbitals ( $1s$ ) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The **bond length** is determined by the distance at which the lowest potential energy is achieved.



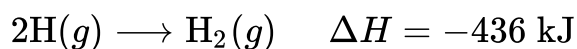


**Figure 11.2b:** The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved (credit: *Chemistry (OpenStax)*, CC BY 4.0).

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of  $\text{H}_2$ , the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:



Conversely, the same amount of energy is released when one mole of  $\text{H}_2$  molecules forms from two moles of H atoms:



## Exercise 11.2a

Check Your Learning Exercise (Text Version)

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

- $\text{Cl}_2\text{CO}$
- $\text{MnO}$
- $\text{NCl}_3$

- d.  $\text{CoBr}_2$
  - e.  $\text{K}_2\text{S}$
  - f.  $\text{CO}$
- a.  $\text{CaF}_2$
  - b.  $\text{HI}$
  - c.  $\text{CaO}$
  - d.  $\text{IBr}$
  - e.  $\text{CO}_2$

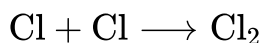
### Check Your Answer<sup>1</sup>

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## Non-Polar vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in  $\text{H}_2$ ,  $\text{Cl}_2$ , and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a **non-polar covalent bond**. Electrons shared in non-polar (or pure) covalent bonds have an equal probability of being near each nucleus.

In the case of  $\text{Cl}_2$ , each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

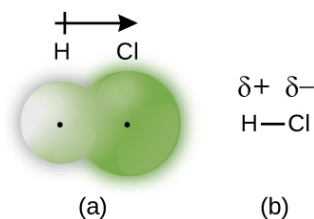


The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical,  $\text{Cl}_2$  also features a non-polar covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a **polar covalent bond**, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the  $\text{H}-\text{Cl}$  bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an  $\text{HCl}$  molecule, the chlorine atom carries a partial negative charge

and the hydrogen atom has a partial positive charge. Figure 11.2b shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,”  $\delta$ , with a plus sign or minus sign to indicate whether the atom has a partial positive charge ( $\delta+$ ) or a partial negative charge ( $\delta-$ ). This symbolism is shown for the H–Cl molecule in Figure 11.2c.



**Figure 11.2c:** (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols  $\delta+$  and  $\delta-$  indicate the polarity of the H–Cl bond (credit: *Chemistry (OpenStax)*, CC BY 4.0).

## Exercise 11.2b

Check Your Learning Exercise (Text version)

Why is it incorrect to speak of a molecule of solid NaCl?

### Check Your Answer<sup>2</sup>

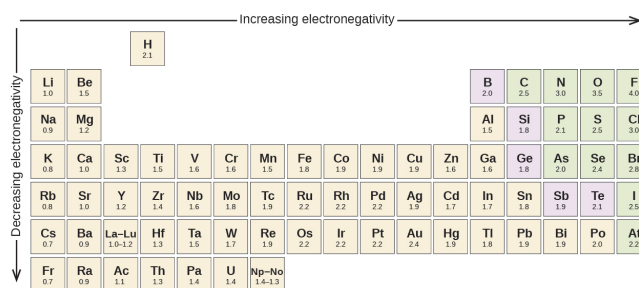
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## Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called **electronegativity**. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) toward itself. It determines how the shared electrons are distributed between the two atoms in a

bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 11.2d shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 11.2e). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as  $\text{XeO}_2$  do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)



**Figure 11.2d:** The electronegativity values derived by Pauling follow predictable periodic trends with higher electronegativities toward the upper right of the periodic table. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

## Electronegativity versus Electron Affinity

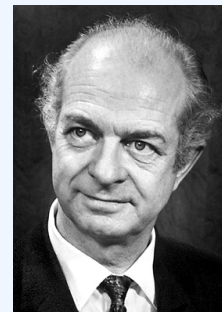
We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

## Linus Pauling

Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Linus Pauling, shown in Figure 11.2e, is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.

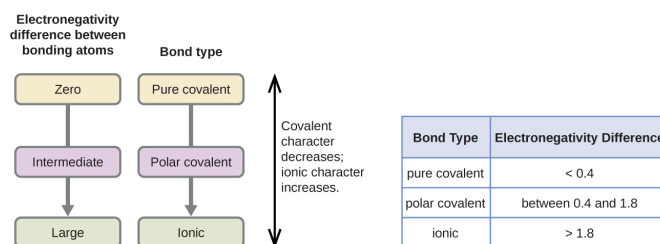
Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.



**Figure 11.2e:** Linus Pauling (1901–1994). (credit: work by unknown, courtesy of Nobel Foundation, PD)

## Electronegativity and Bond Type

The absolute value of the difference in electronegativity ( $\Delta EN$ ) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent, or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 11.2f shows the relationship between electronegativity difference and bond type.



**Figure 11.2f:** As the electronegativity difference increases between two atoms, the bond becomes more ionic (credit: Chemistry (OpenStax), CC BY 4.0).

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 11.2f. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in  $\text{NH}_3$  a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in  $\text{MnI}_2$  have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as  $\text{OH}^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ , are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate,  $\text{KNO}_3$ , contains the  $\text{K}^+$  cation and the polyatomic  $\text{NO}_3^-$  anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions  $\text{K}^+$  and  $\text{NO}_3^-$ , as well as covalent between the nitrogen and oxygen atoms in  $\text{NO}_3^-$ .

### Example 11.2a

#### Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure 11.2f, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols  $\delta^+$  and  $\delta^-$ :

C–H, C–N, C–O, N–H, O–H, S–H

#### Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the  $\delta^-$  designation is the more electronegative of the two. Table 11.a shows these bonds in order of increasing polarity.

Table 11.2a: Bond Polarity and Electronegativity Difference

Bond	$\Delta EN$	Polarity
C-H	0.4	$\delta^- \text{ C} - \text{ H } \delta^+$
S-H	0.4	$\delta^- \text{ S} - \text{ H } \delta^+$
C-N	0.5	$\delta^+ \text{ C} - \text{ N } \delta^-$
N-H	0.9	$\delta^- \text{ N} - \text{ H } \delta^+$
C-O	1.0	$\delta^+ \text{ C} - \text{ O } \delta^-$
O-H	1.4	$\delta^- \text{ O} - \text{ H } \delta^+$

## Exercise 11.2c

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si-O, Si-C, C-H, and C-C. Using the electronegativity values in Figure 11.2f, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols  $\delta^+$  and  $\delta^-$ .

**Check Your Answer<sup>3</sup>**

## Attribution & References

Except where otherwise noted, this page is adapted JR van Haarlem and Samantha Sullivan Sauer from “4.2 Covalent Bonding (<https://boisestate.pressbooks.pub/chemistry/chapter/4-2-covalent-bonding/>)” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>)

## Notes

1.
  1. ionic: b, d, e, g, i
  2. covalent: a, c, f, h, j, k
2. NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

3. **Solutions to Exercise 11.2c**

<b>Bond</b>	<b>Electronegativity Difference</b>	<b>Polarity</b>
C–C	0.0	nonpolar
C–H	0.4	$\delta^-$ $\delta^+$ C – H
Si–C	0.7	$\delta^+$ $\delta^-$ Si – C
Si–O	1.7	$\delta^+$ $\delta^-$ Si – O



## 11.3 LEWIS SYMBOLS AND STRUCTURES

### Learning Objectives

By the end of this section, you will be able to:

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

### Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A **Lewis symbol** consists of an elemental symbol surrounded by one dot for each of its valence electrons as shown in Figure 11.3a.



**Figure 11.3a:** Lewis structure of calcium atom  
(credit: *Chemistry (OpenStax)*, CC BY 4.0).

Lewis symbols illustrate the number of valence electrons for each element in the third period of the periodic table as shown in Figure 11.3b. Figure 11.3c shows the Lewis symbols for the first twenty elements of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	[Ne]3s <sup>1</sup>	Na ·
magnesium	[Ne]3s <sup>2</sup>	·Mg·
aluminum	[Ne]3s <sup>2</sup> 3p <sup>1</sup>	·Al·
silicon	[Ne]3s <sup>2</sup> 3p <sup>2</sup>	·Si·
phosphorus	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	·P·
sulfur	[Ne]3s <sup>2</sup> 3p <sup>4</sup>	:S·
chlorine	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	:Cl·
argon	[Ne]3s <sup>2</sup> 3p <sup>6</sup>	:Ar:

**Figure 11.3b:** Lewis symbols illustrate the number of valence electrons for each element in the third period of the periodic table (credit: *Chemistry (OpenStax)*, CC BY 4.0).

1A	2A	3A	4A	5A	6A	7A	Noble Gases
H·							He:
Li·	:Be	B·	·C·	·N·	·O·	·F·	:Ne:
Na·	:Mg	Al·	·Si·	·P·	·S·	·Cl·	:Ar:
K·	:Ca						

**Figure 11.3c:** Lewis symbols for elements of the periodic table. Review the Periodic Table of the Elements in other formats in Appendix A. (credit: graphic by Revathi Mahadevan, CC BY 4.0)

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



**Figure 11.3d:** Formation of sodium and calcium cations shown as Lewis structures (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



**Figure 11.3e:** Formation of chloride and sulfide anions shown as Lewis structures (credit: *Chemistry (OpenStax)*, CC BY 4.0).

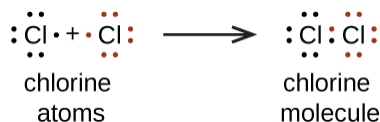
Figure 11.3f demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
$\text{Na}\cdot$ sodium atom	+	$\text{:Cl}\cdot$ chlorine atom	$\longrightarrow$	$\text{Na}^+ \left[ \text{:Cl:} \right]^-$ sodium chloride (sodium ion and chloride ion)
$\cdot\text{Mg}\cdot$ magnesium atom	+	$\text{:O}\cdot$ oxygen atom	$\longrightarrow$	$\text{Mg}^{2+} \left[ \text{:O:} \right]^{2-}$ magnesium oxide (magnesium ion and oxide ion)
$\cdot\text{Ca}\cdot$ calcium atom	+	$2 \cdot\text{F}\cdot$ fluorine atoms	$\longrightarrow$	$\text{Ca}^{2+} \left[ \text{:F:} \right]_2^-$ calcium fluoride (calcium ion and two fluoride ions)

**Figure 11.3f:** Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change (credit: *Chemistry (OpenStax)*, CC BY 4.0).

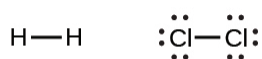
## Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in **Lewis structures**, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



**Figure 11.3g:** Two chlorine atoms bonding for form chlorine diatomic molecule,  $\text{Cl}_2$ , shown as Lewis structures (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called **lone pairs**) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:



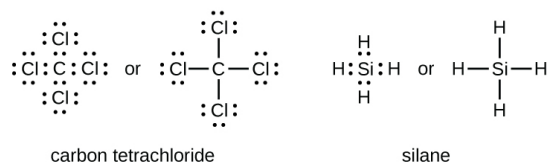
**Figure 11.3h:** Lewis structure of hydrogen diatomic molecule,  $\text{H}_2$ , and chlorine diatomic molecule,  $\text{Cl}_2$ , (with lone pairs) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

## The Octet Rule

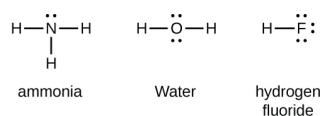
The other halogen molecules ( $\text{F}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ , and  $\text{At}_2$ ) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the **octet rule**.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in  $\text{CCl}_4$  (carbon tetrachloride) and silicon in  $\text{SiH}_4$  (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:



**Figure 11.3i:** Lewis structures of carbon tetrachloride,  $\text{CCl}_4$ , and silane,  $\text{SiH}_4$ . Bonding pairs of electrons can be as a dash or bond between atoms (credit: *Chemistry (OpenStax)*, CC BY 4.0).

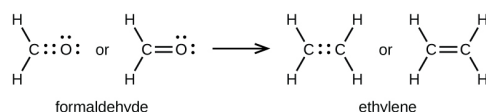
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in  $\text{NH}_3$  (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



**Figure 11.3j:** Lewis structures of ammonia, NH<sub>3</sub>, water, H<sub>2</sub>O, and hydrogen fluoride, HF (credit: *Chemistry (OpenStax)*, CC BY 4.0).

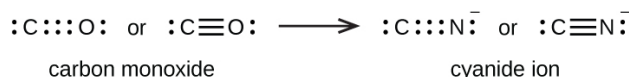
## Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A **double bond** forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH<sub>2</sub>O (formaldehyde) and between the two carbon atoms in C<sub>2</sub>H<sub>4</sub> (ethylene):



**Figure 11.3k:** Lewis structures of formaldehyde, CH<sub>2</sub>O, and ethylene, C<sub>2</sub>H<sub>4</sub>, showing double bonds (two shared pairs of electrons) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

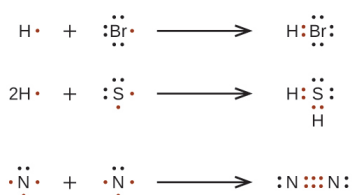
A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN<sup>-</sup>):



**Figure 11.3l:** Lewis structures of carbon monoxide, CO, and cyanide ion, CN<sup>-</sup>, showing triple bonds (three shared pairs of electrons) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

## Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms (Figure 11.3m):



**Figure 11.3m:** Lewis structures of the formation of hydrogen bromide, HBr, hydrogen sulfide, H<sub>2</sub>S, and nitrogen, N<sub>2</sub> (credit: *Chemistry (OpenStax)*, CC BY 4.0).

For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the centre.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH<sub>4</sub>, CHO<sub>2</sub><sup>-</sup>, NO<sup>+</sup>, and OF<sub>2</sub> as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
  - For a molecule, we add the number of valence electrons on each atom in the molecule:
 
$$\begin{array}{r}
 \text{SiH}_4 \\
 \text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 \\
 + \text{ H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4 \\
 \hline
 = 8 \text{ valence electrons}
 \end{array}$$
  - For a *negative ion*, such as CHO<sub>2</sub><sup>-</sup>, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{array}{r} \text{CHO}_2^- \\ \text{C: 4 valence electrons/atom} \times 1 \text{ atom} = 4 \\ \text{H: 1 valence electron/atom} \times 1 \text{ atom} = 1 \\ \text{O: 6 valence electrons/atom} \times 2 \text{ atoms} = 12 \\ + \text{ 1 additional electron} = 1 \\ \hline = 18 \text{ valence electrons} \end{array}$$

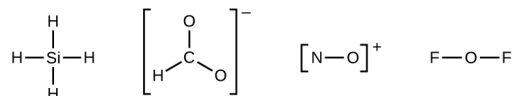
- For a *positive ion*, such as  $\text{NO}^+$ , we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{array}{r} \text{NO}^+ \\ \text{N: 5 valence electrons/atom} \times 1 \text{ atom} = 5 \\ \text{O: 6 valence electrons/atom} \times 1 \text{ atom} = 6 \\ + \text{ -1 electron (positive charge)} = -1 \\ \hline = 10 \text{ valence electrons} \end{array}$$

- Since  $\text{OF}_2$  is a neutral molecule, we simply add the number of valence electrons:

$$\begin{array}{r} \text{OF}_2 \\ \text{O: 6 valence electrons/atom} \times 1 \text{ atom} = 6 \\ + \text{ F: 7 valence electrons/atom} \times 2 \text{ atoms} = 14 \\ \hline = 20 \text{ valence electrons} \end{array}$$

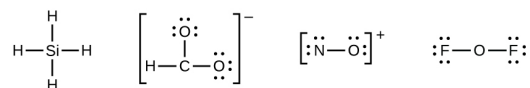
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



**Figure 11.3n:** Skeletal structures (incomplete Lewis structures) of  $\text{SiH}_4$ ,  $\text{CHO}_2^-$ ,  $\text{NO}^+$ , and  $\text{OF}_2$ . Step 2 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When several arrangements of atoms are possible, as for  $\text{CHO}_2^-$ , we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In  $\text{CHO}_2^-$ , the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in  $\text{POCl}_3$ , S in  $\text{SO}_2$ , and Cl in  $\text{ClO}_4^-$ . An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

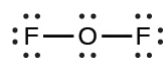
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
  - There are no remaining electrons on  $\text{SiH}_4$ , so it is unchanged:



**Figure 11.3o:** Lewis structure of  $\text{SiH}_4$ . Skeletal structures (incomplete Lewis structures) of  $\text{CHO}_2^-$ ,  $\text{NO}^+$ , and  $\text{OF}_2$ . Step 3 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

4. Place all remaining electrons on the central atom.

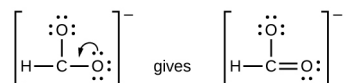
- For  $\text{SiH}_4$ ,  $\text{CHO}_2^-$ , and  $\text{NO}^+$ , there are no remaining electrons; we already placed all of the electrons determined in Step 1.
- For  $\text{OF}_2$ , we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



**Figure 11.3p:** Lewis structure of  $\text{OF}_2$ . Step 4 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

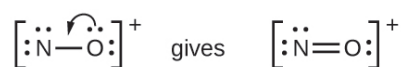
- $\text{SiH}_4$ : Si already has an octet, so nothing needs to be done.
- $\text{CHO}_2^-$ : We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



**Figure 11.3q:** Lewis structure of  $\text{CHO}_2^-$ . Step 5 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

- $\text{NO}^+$ : For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:





**Figure 11.3r:** Incomplete Lewis structure  $\text{NO}^+$ . Step 5 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

- This still does not produce an octet, so we must move another pair, forming a triple bond:



**Figure 11.3s:** Lewis structure of  $\text{NO}^+$ . Step 5 of process to draw Lewis structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

- In  $\text{OF}_2$ , each atom has an octet as drawn, so nothing changes.

## Example 11.3a

### Writing Lewis Structures

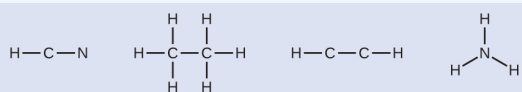
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide ( $\text{HCN}$ ) on Titan, one of Saturn's moons. Titan also contains ethane ( $\text{H}_3\text{CCH}_3$ ), acetylene ( $\text{HCCH}$ ), and ammonia ( $\text{NH}_3$ ). What are the Lewis structures of these molecules?

### Solution

1. Calculate the number of valence electrons.

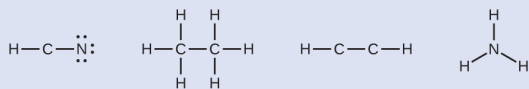
1.  $\text{HCN}$ :  $(1 \times 1) + (4 \times 1) + (5 \times 1) = 10$
2.  $\text{H}_3\text{CCH}_3$ :  $(1 \times 3) + (2 \times 4) + (1 \times 3) = 14$
3.  $\text{HCCH}$ :  $(1 \times 1) + (2 \times 4) + (1 \times 1) = 10$
4.  $\text{NH}_3$ :  $(5 \times 1) + (3 \times 1) = 8$

2. Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:



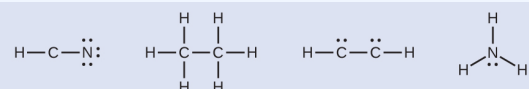
atom:

3. Where needed, distribute electrons to the terminal atoms:



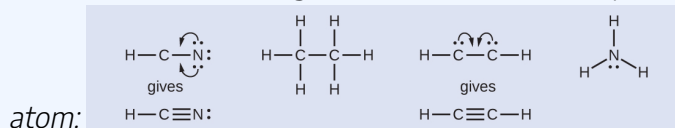
1. HCN: six electrons placed on N.
2. H<sub>3</sub>CCH<sub>3</sub>: no electrons remain.
3. HCCH: no terminal atoms capable of accepting electrons.
4. NH<sub>3</sub>: no terminal atoms capable of accepting electrons.

4. *Where needed, place remaining electrons on the central atom:*



1. HCN: no electrons remain.
2. H<sub>3</sub>CCH<sub>3</sub>: no electrons remain.
3. HCCH: four electrons placed on carbon.
4. NH<sub>3</sub>: two electrons placed on nitrogen.

5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each*



1. HCN: form two more C–N bonds.
2. H<sub>3</sub>CCH<sub>3</sub>: all atoms have the correct number of electrons.
3. HCCH: form a triple bond between the two carbon atoms.
4. NH<sub>3</sub>: all atoms have the correct number of electrons.

## Exercise 11.3a

Both carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO<sub>2</sub> has been implicated in global climate change. What are the Lewis structures of these two molecules?

## Check Your Answer<sup>1</sup>

### Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure 11.3t), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C<sub>60</sub> buckminsterfullerene

molecule (Figure 11.a in Chapter 11 Introduction). An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C<sub>60</sub>. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honoured him as the “Father of Nanotechnology.”

Learn more about Dr. Smalley by reading the article [Richard E. Smalley – Facts \[New Tab\]](https://www.nobelprize.org/prizes/chemistry/1996/smalley/facts/) (<https://www.nobelprize.org/prizes/chemistry/1996/smalley/facts/>) on the Nobel Prize website.

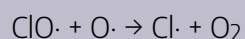
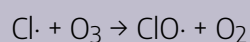


**Figure 11.3t:** This model shows the arrangement of carbon atoms in a fullerene (or ‘buckyball’) a large molecule made up of 60 carbon atoms. (credit: work by UCL Mathematical and Physical Science (<https://www.flickr.com/people/93636241@N07>), CC BY 2.0)

## Scientists in Action: Dr. Mario J. Molina

Dr. Mario J. Molina is a Mexican chemist who is best known for his role in the discovery of the impact that CFC's (chlorofluorocarbons) have on the ozone layer. He was a co-recipient of the Nobel Prize in Chemistry in 1995.

Part of his work included the hypothesis that CFCs in the upper atmosphere could produce a chlorine radical that would catalyze the destruction of ozone.



After data was collected that confirmed this hypothesis, steps were taken by countries across the world to discontinue the use of ozone-damaging compounds. The most significant actions were included in the Montreal Protocol [New Tab] ([https://en.wikipedia.org/wiki/Montreal\\_Protocol](https://en.wikipedia.org/wiki/Montreal_Protocol)).

Dr. Molina is currently a faculty member at UC San Diego and is involved in science outreach.

Watch Dr. Molina address students about his inspiration to become a scientist in this Nobel Prize video on YouTube [New Tab] (<https://www.youtube.com/watch?v=hm1ZncCkjgE>).



**Figure 11.3u:** Dr. Mario J. Molina (credit: work by <http://science.in2pic.com>, CC BY-SA 3.0)

## Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

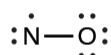
- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

## Odd-electron Molecules

We call molecules that contain an odd number of electrons **free radicals**. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

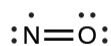
1. *Determine the total number of valence (outer shell) electrons.* The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule.* We can easily draw a skeleton with an N–O single bond: N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms.* In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:



**Figure 11.3v:**

Lewis structure of NO where oxygen has been assigned the eight electrons as it is more electronegative compared to nitrogen (credit: Chemistry (OpenStax), CC BY 4.0).

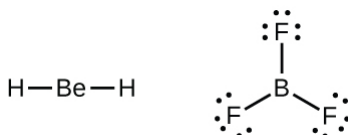
4. *Place all remaining electrons on the central atom.* Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

**Figure 11.3w:**

The Lewis structure of NO double bond where the electrons are rearranged to obtain octets where a double bond is formed so that nitrogen can move closer to an octet (credit: Chemistry (OpenStax), CC BY 4.0).

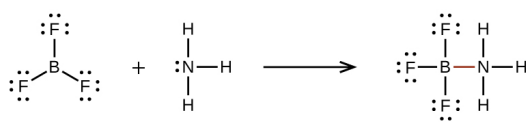
## Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 12, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride,  $\text{BeH}_2$ , and boron trifluoride,  $\text{BF}_3$ , the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in  $\text{BF}_3$ , satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



**Figure 11.3x:** The Lewis structures for beryllium dihydride,  $\text{BeH}_2$  (left), and boron trifluoride,  $\text{BF}_3$  (right) (credit: Chemistry (OpenStax), CC BY 4.0).

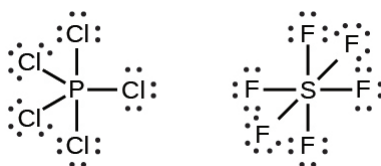
An atom like the boron atom in  $\text{BF}_3$ , which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example,  $\text{NH}_3$  reacts with  $\text{BF}_3$  because the lone pair on nitrogen can be shared with the boron atom (Figure 11.3y).



**Figure 11.3y:** The reaction between  $\text{BF}_3$  and  $\text{NH}_3$  come together to form a single bond between boron and nitrogen because boron requires the lone pair of electrons from nitrogen to fulfill its octet (credit: *Chemistry (OpenStax)*, CC BY 4.0).

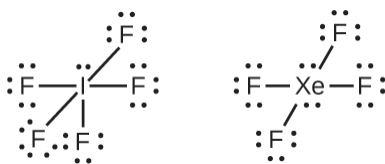
## Hypervalent Molecules

Elements in the second period of the periodic table ( $n = 2$ ) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one  $2s$  and three  $2p$  orbitals). Elements in the third and higher periods ( $n \geq 3$ ) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty  $d$  orbitals in the same shell. Molecules formed from these elements are sometimes called **hypervalent molecules**. Figure 11.3z shows the Lewis structures for two hypervalent molecules,  $\text{PCl}_5$  and  $\text{SF}_6$ .



**Figure 11.3z:** The Lewis structures for two hypervalent molecules,  $\text{PCl}_5$  and  $\text{SF}_6$  (credit: *Chemistry (OpenStax)*, CC BY 4.0).

In some hypervalent molecules, such as  $\text{IF}_5$  and  $\text{XeF}_4$ , some of the electrons in the outer shell of the central atom are lone pairs (Figure 11.3aa).



**Figure 11.3aa:** The Lewis structures for hypervalent molecules,  $\text{IF}_5$  and  $\text{XeF}_4$  (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

## Example 11.3b

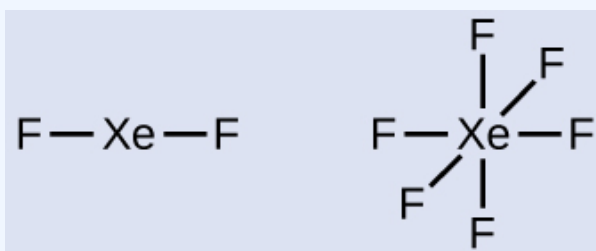
### Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined  $\text{XeF}_4$  earlier. What are the Lewis structures of  $\text{XeF}_2$  and  $\text{XeF}_6$ ?

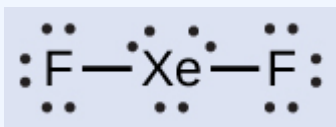
### Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

1. Calculate the number of valence electrons:  $\text{XeF}_2$ :  $8 + (2 \times 7) = 22$ ;  $\text{XeF}_6$ :  $8 + (6 \times 7) = 50$
2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:

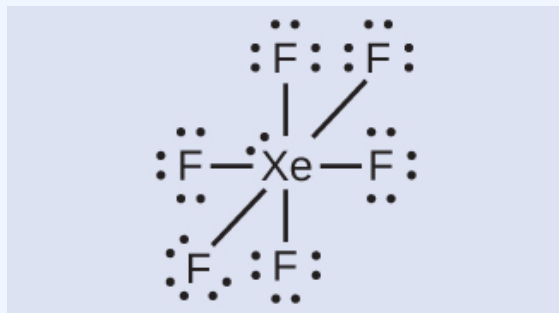


3. Distribute the remaining electrons.
  1.  $\text{XeF}_2$ : We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of  $\text{XeF}_2$  shows two bonding pairs and three lone pairs of electrons around the Xe atom:



2.  $\text{XeF}_6$ : We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:





### Exercise 11.3b

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens BrCl<sub>3</sub> and ICl<sub>4</sub><sup>-</sup>.

**Check Your Answer<sup>2</sup>**

### Links to Interactive Learning Tools

Explore Lewis Electron Dot Structures (<https://www.physicsclassroom.com/Concept-Builders/Chemistry/Lewis-Structures>) from the Physics Classroom (<https://www.physicsclassroom.com/>).

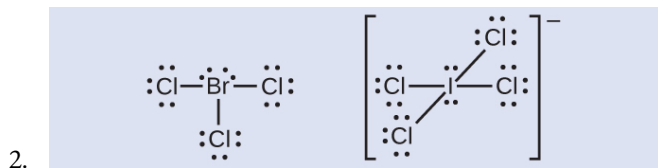
Explore Drawing Lewis Structures from Alchemie.

## Attribution & References

Except where otherwise noted, this page is adapted JR van Haarlem from “4.4 Lewis Symbols and Structures (<https://boisestate.pressbooks.pub/chemistry/chapter/4-4-lewis-symbols-and-structures/>)” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold,

Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>)

## Notes



## 11.4 FORMAL CHARGES AND RESONANCE

### Learning Objectives

By the end of this section, you will be able to:

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

### Calculating Formal Charge

The **formal charge** of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\text{formal charge} = \# \text{ valence shell electrons (free atom)} - \# \text{ lone pair electrons} - \frac{1}{2} \# \text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in

the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

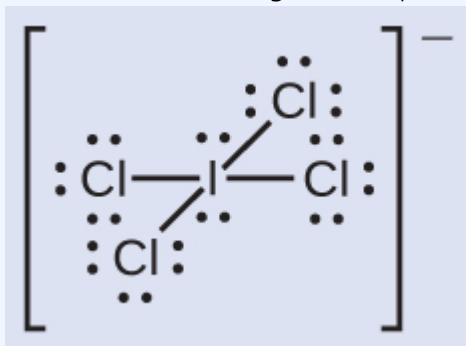
### Example 11.4a

#### Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion  $\text{ICl}_4^-$ .

#### Solution

1. We divide the bonding electron pairs equally for all I-Cl bonds:



2. We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.
3. Subtract this number from the number of valence electrons for the neutral atom: I:  $7 - 8 = -1$  Cl:  $7 - 7 = 0$  The sum of the formal charges of all the atoms equals  $-1$ , which is identical to the charge of the ion ( $-1$ ).

## Exercise 11.4a

Calculate the formal charge for each atom in the carbon monoxide molecule:

Check Your Answer<sup>1</sup>

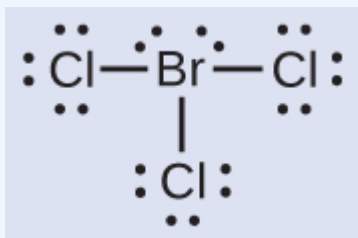
## Example 11.4b

## Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule  $\text{BrCl}_3$ .

## Solution

1. Assign one of the electrons in each  $\text{Br}-\text{Cl}$  bond to the  $\text{Br}$  atom and one to the  $\text{Cl}$  atom in that bond:



2. Assign the lone pairs to their atom. Now each  $\text{Cl}$  atom has seven electrons and the  $\text{Br}$  atom has seven electrons.
3. Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:  $\text{Br}: 7 - 7 = 0$   $\text{Cl}: 7 - 7 = 0$  All atoms in  $\text{BrCl}_3$  have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

## Exercise 11.4b

Determine the formal charge for each atom in  $\text{NCl}_3$ .

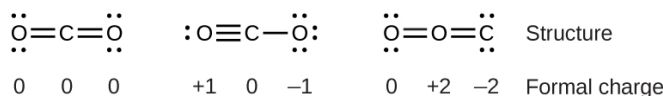
**Check Your Answer<sup>2</sup>**

## Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

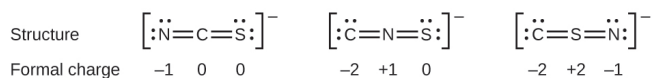
To see how these guidelines apply, let us consider some possible structures for carbon dioxide,  $\text{CO}_2$ . We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds (Figure 11.4a).



**Figure 11.4a:** Three possible structures for carbon dioxide,  $\text{CO}_2$  (credit: Chemistry (OpenStax), CC BY 4.0).

Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures:  $\text{CNS}^-$ ,  $\text{NCS}^-$ , or  $\text{CSN}^-$ . The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown in Figure 11.4b.



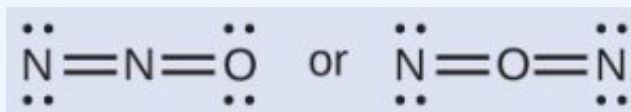
**Figure 11.4b:** Three possible structures for the thiocyanate ion (credit: Chemistry (OpenStax), CC BY 4.0).

Note that the sum of the formal charges in each case is equal to the charge of the ion ( $-1$ ). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

### Example 11.4c

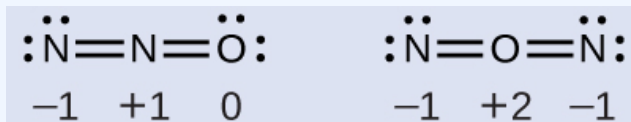
#### Using Formal Charge to Determine Molecular Structure

Nitrous oxide,  $\text{N}_2\text{O}$ , commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?

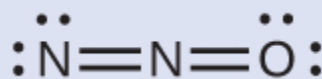


#### Solution

Determining formal charge yields the following:



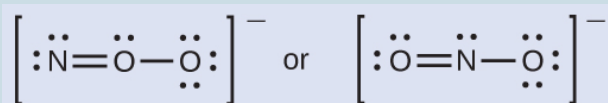
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

## Exercise 11.4c

Which is the most likely molecular structure for the nitrite ( $\text{NO}_2^-$ ) ion?



Check Your Answer<sup>3</sup>

## Resonance

You may have noticed that the nitrite anion in Example 3 above can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions as demonstrated in Figure 11.4c.

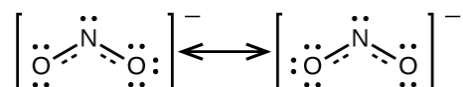


**Figure 11.4c:** The molecular structures for the nitrite anion,  $\text{NO}_2^-$  (credit: Chemistry (OpenStax), CC BY 4.0).

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in  $\text{NO}_2^-$  have the same strength and length, and are identical in all other properties.



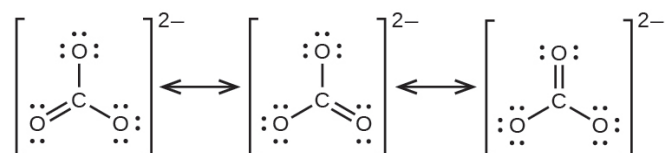
It is not possible to write a single Lewis structure for  $\text{NO}_2^-$  in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in  $\text{NO}_2^-$  is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the  $\text{NO}_2^-$  ion is shown in Figure 11.4d.



**Figure 11.4d:** The resonance structures of the nitrite anion,  $\text{NO}_2^-$  (credit: Chemistry (OpenStax), CC BY 4.0).

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion,  $\text{CO}_3^{2-}$ , provides a second example of resonance as shown in Figure 11.4e.



**Figure 11.4e:** The resonance structures for the carbonate anion,  $\text{CO}_3^{2-}$  (credit: Chemistry (OpenStax), CC BY 4.0).

One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures,

we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

## Key Equations

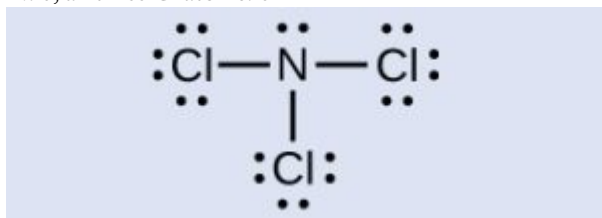
- formal charge = # valence shell electrons (free atom) – # lone pair electrons –  $\frac{1}{2}$ # bonding electrons

## Attribution & References

Except where otherwise noted, this page is adapted JR van Haarlem from “4.5 Formal Charges and Resonance (<https://boisestate.pressbooks.pub/chemistry/chapter/4-5-formal-charges-and-resonance/>)” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>)

## Notes

- C –1, O +1
- N: 0; all three Cl atoms: 0



- ONO<sup>–</sup>

# 11.5 STRENGTHS OF IONIC AND COVALENT BONDS

## Learning Objectives

By the end of this section, you will be able to:

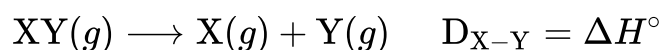
- Describe the energetics of covalent and ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds
- Use average covalent bond energies to estimate enthalpies of the reaction

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

## Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy (see Figure 11.2b in Chapter 11.2 Covalent Bonding). The stronger a bond, the greater the energy required to break it.

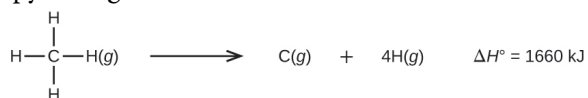
The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule,  $D_{X-Y}$ , is defined as the standard enthalpy change for the endothermic reaction:



For example, the bond energy of the (non-polar) covalent H–H bond,  $D_{H-H}$ , is 436 kJ per mole of H–H bonds broken:



Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH<sub>4</sub>, 1660 kJ, is equal to the standard enthalpy change of the reaction:



The average C–H bond energy,  $D_{\text{C-H}}$ , is  $1660/4 = 415$  kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 11.5a, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 11.5b. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

**Table 11.5a: Bond Energies (kJ/mol)**

<b>Bond</b>	<b>Type of Bond</b>	<b>Bond Energy</b>
H-H	single	436
H-C	single	415
H-N	single	390
H-O	single	464
H-F	single	569
H-Si	single	395
H-P	single	320
H-S	single	340
H-Cl	single	432
H-Br	single	370
H-I	single	295
C-C	single	345
C=C	double	611
C≡C	triple	837
C-N	single	290
C=N	double	615
C≡N	triple	891
C-O	single	350
C=O	double	741
C≡O	triple	1080
C-F	single	439
C-Si	single	360
C-P	single	265
C-S	single	260
C-Cl	single	330
C-Br	single	275
C-I	single	240
N-N	single	160
N=N	double	418

$\text{N}\equiv\text{N}$	triple	946
$\text{N}-\text{O}$	single	200
$\text{N}-\text{F}$	single	270
$\text{N}-\text{P}$	single	210
$\text{N}-\text{Cl}$	single	200
$\text{N}-\text{Br}$	single	245
$\text{O}-\text{O}$	single	140
$\text{O}=\text{O}$	double	498
$\text{O}-\text{F}$	single	160
$\text{O}-\text{Si}$	single	370
$\text{O}-\text{P}$	single	350
$\text{O}-\text{Cl}$	single	205
$\text{O}-\text{I}$	single	200
$\text{F}-\text{F}$	single	160
$\text{F}-\text{Si}$	single	540
$\text{F}-\text{P}$	single	489
$\text{F}-\text{S}$	single	285
$\text{F}-\text{Cl}$	single	255
$\text{F}-\text{Br}$	single	235
$\text{Si}-\text{Si}$	single	230
$\text{Si}-\text{P}$	single	215
$\text{Si}-\text{S}$	single	225
$\text{Si}-\text{Cl}$	single	359
$\text{Si}-\text{Br}$	single	290
$\text{Si}-\text{I}$	single	215
$\text{P}-\text{P}$	single	215
$\text{P}-\text{S}$	single	230
$\text{P}-\text{Cl}$	single	330
$\text{P}-\text{Br}$	single	270
$\text{P}-\text{I}$	single	215
$\text{S}-\text{S}$	single	215

S–Cl	single	250
S–Br	single	215
Cl–Cl	single	243
Cl–Br	single	220
Cl–I	single	210
Br–Br	single	190
Br–I	single	180
I–I	single	150

**Table 11.5b: Average Bond Lengths and Bond Energies for Some Common Bonds**

Bond	Bond type	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	single	1.54	345
C=C	double	1.34	611
C≡C	triple	1.20	837
C–N	single	1.43	290
C=N	double	1.38	615
C≡N	triple	1.16	891
C–O	single	1.43	350
C=O	double	1.23	741
C≡O	triple	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic. An exothermic reaction ( $\Delta H$  negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants. An endothermic reaction ( $\Delta H$  positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

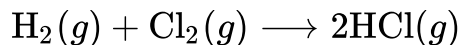
The enthalpy change,  $\Delta H$ , for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy “in”, positive sign) plus the energy released when all bonds are formed in the products (energy “out,” negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$

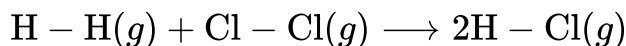
In this expression, the symbol  $\Sigma$  means “the sum of” and  $D$  represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table (like Table 11.5b) and will

depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because  $D$  values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:



or



To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing  $2 \times 432$  kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$

$$\Delta H = [D_{\text{H-H}} + D_{\text{Cl-Cl}}] - 2D_{\text{H-Cl}}$$

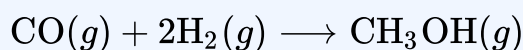
$$= [436 + 243] - 2(432) = -185 \text{ kJ}$$

This excess energy is released as heat, so the reaction is exothermic. Appendix H gives a value for the standard molar enthalpy of formation of HCl(g),  $\Delta H_f^\circ$ , of  $-92.307$  kJ/mol. Twice that value is  $-184.6$  kJ, which agrees well with the answer obtained earlier for the formation of two moles of HCl.

### Example 11.5a

#### Using Bond Energies to Calculate Approximate Enthalpy Changes

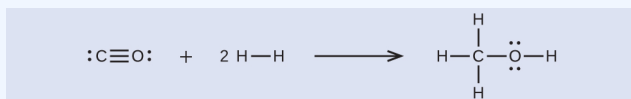
Methanol, CH<sub>3</sub>OH, may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen, H<sub>2</sub>, from which methanol can be produced. Using the bond energies in Table 11.5b, calculate the approximate enthalpy change,  $\Delta H$ , for the reaction here:





## Solution

First, we need to write the Lewis structures of the reactants and the products:



From this, we see that  $\Delta H$  for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$

$$\Delta H = [D_{\text{C}\equiv\text{O}} + 2(D_{\text{H}-\text{H}})] - [3(D_{\text{C}-\text{H}}) + D_{\text{C}-\text{O}} + D_{\text{O}-\text{H}}]$$

Using the bond energy values in Table 11.5b, we obtain:

$$\begin{aligned} \Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107 \text{ kJ} \end{aligned}$$

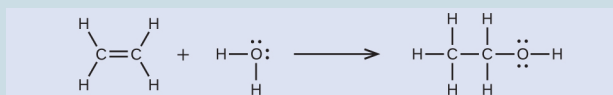
We can compare this value to the value calculated based on  $\Delta H_f^\circ$  data from Appendix H:

$$\begin{aligned} \Delta H &= [\Delta H_f^\circ \text{CH}_3\text{OH}(g)] - [\Delta H_f^\circ \text{CO}(g) + 2 \times \Delta H_f^\circ \text{H}_2] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5 \text{ kJ} \end{aligned}$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

## Exercise 11.5a

Ethyl alcohol,  $\text{CH}_3\text{CH}_2\text{OH}$ , was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:

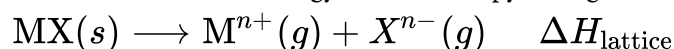


Using the bond energies in Table 11.5b, calculate an approximate enthalpy change,  $\Delta H$ , for this reaction.

### Check Your Answer<sup>1</sup>

## Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The **lattice energy** ( $\Delta H_{\text{lattice}}$ ) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:



Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be *endothermic* (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride,  $\Delta H_{\text{lattice}} = 769 \text{ kJ}$ . Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions. When one mole each of gaseous  $\text{Na}^+$  and  $\text{Cl}^-$  ions form solid NaCl, 769 kJ of heat is released.

The lattice energy  $\Delta H_{\text{lattice}}$  of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\text{lattice}} = \frac{C(Z^+)(Z^-)}{R_0}$$

in which C is a constant that depends on the type of crystal structure;  $Z^+$  and  $Z^-$  are the charges on the ions; and  $R_0$  is the interionic distance (the sum of the radii of the positive and negative ions). Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF ( $Z^+$  and  $Z^- = 1$ ) is 1023 kJ/mol, whereas that of MgO ( $Z^+$  and  $Z^- = 2$ ) is 3900 kJ/mol ( $R_0$  is nearly the same – about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of  $\text{MgF}_2$  (2957 kJ/mol) to that of  $\text{MgI}_2$  (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of  $\text{F}^-$  as compared to  $\text{I}^-$ .

## Example 11.5b

### Lattice Energy Comparisons

The precious gem ruby is aluminum oxide,  $\text{Al}_2\text{O}_3$ , containing traces of  $\text{Cr}^{3+}$ . The compound  $\text{Al}_2\text{Se}_3$  is used in the fabrication of some semiconductor devices. Which has the larger lattice energy,  $\text{Al}_2\text{O}_3$  or  $\text{Al}_2\text{Se}_3$ ?

### Solution

In these two ionic compounds, the charges  $Z^+$  and  $Z^-$  are the same, so the difference in lattice energy will depend upon  $R_0$ . The  $\text{O}^{2-}$  ion is smaller than the  $\text{Se}^{2-}$  ion. Thus,  $\text{Al}_2\text{O}_3$  would have a shorter interionic distance than  $\text{Al}_2\text{Se}_3$ , and  $\text{Al}_2\text{O}_3$  would have the larger lattice energy.

## Exercise 11.5b

Zinc oxide,  $\text{ZnO}$ , is a very effective sunscreen. How would the lattice energy of  $\text{ZnO}$  compare to that of  $\text{NaCl}$ ?

### Check Your Answer<sup>2</sup>

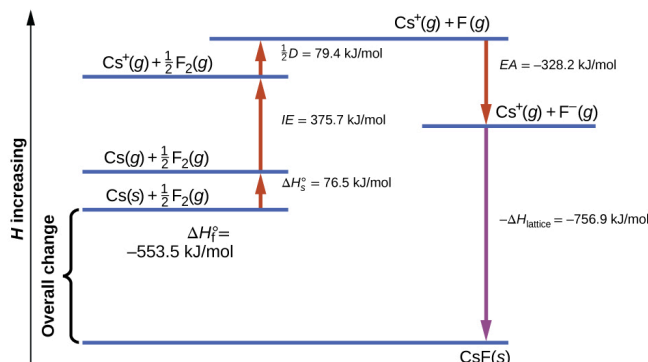
## The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The **Born-Haber cycle** is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- $\Delta H_f^\circ$ , the standard enthalpy of formation of the compound
- $IE$ , the ionization energy of the metal
- $EA$ , the electron affinity of the nonmetal
- $\Delta H_s^\circ$ , the enthalpy of sublimation of the metal
- $D$ , the bond dissociation energy of the nonmetal

- $\Delta H_{\text{lattice}}$ , the lattice energy of the compound

Figure 11.5a diagrams the Born-Haber cycle for the formation of solid cesium fluoride.



**Figure 11.5a:** The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states (credit: *Chemistry (OpenStax)*, CC BY 4.0).

We begin with the elements in their most common states,  $\text{Cs}(s)$  and  $\text{F}_2(g)$ . The  $\Delta H_{\text{f}}^{\circ}$  represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the  $y$ -axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation,  $\Delta H_{\text{f}}^{\circ}$ , of the compound from its elements. In this case, the overall change is exothermic.

Hess's law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table 11.5c shows this for cesium chloride,  $\text{CsCl}_2$ .

**Table 11.5c: Enthalpies and enthalpy formation for cesium chloride, CsCl<sub>2</sub>**

Steps in Formation Process	Enthalpy Equations
Enthalpy of sublimation of Cs(s)	$\text{Cs}(s) \longrightarrow \text{Cs}(g) \quad \Delta H = \Delta H_s^\circ = 76.5\text{kJ}$
One-half of the bond energy of Cl <sub>2</sub>	$\frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{Cl}(g) \quad \Delta H = \frac{1}{2} D = 122\text{kJ}$
Ionization energy of Na(g)	$\text{Na}(g) \longrightarrow \text{Na}^+(g) + e^- \quad \Delta H = IE = 496\text{kJ}$
Negative of the electron affinity of Cl	$\text{Cl}(g) + e^- \longrightarrow \text{Cl}^-(g) \quad \Delta H = -EA = -368\text{kJ}$
Negative of the lattice energy of NaCl(s)	$\text{Na}^+(g) + \text{Cl}^-(g) \longrightarrow \text{NaCl}(s) \quad \Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of NaCl(s), add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{NaCl}(s) = -411 \text{ kJ}$

Thus, the lattice energy can be calculated from other values. For cesium chloride, using this data, the lattice energy is:

$$\Delta H_{\text{lattice}} = (411 + 109 + 122 + 496 + 368) \text{ kJ} = 770 \text{ kJ}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation  $\Delta H_s^\circ$ , ionization energy (IE), bond dissociation enthalpy (D), lattice energy  $\Delta H_{\text{lattice}}$ , and standard enthalpy of formation  $\Delta H_f^\circ$  are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much higher than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extensive lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

## Key Equations

- Bond energy for a diatomic molecule:  $\text{XY}(g) \longrightarrow \text{X}(g) + \text{Y}(g) \quad D_{\text{X-Y}} = \Delta H^\circ$
- Enthalpy change:  $\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$
- Lattice energy for a solid MX:  $\text{MX}(s) \longrightarrow \text{M}^{n+}(g) + \text{X}^{n-}(g) \quad \Delta H_{\text{lattice}}$
- Lattice energy for an ionic crystal:  $\Delta H_{\text{lattice}} = \frac{C(\text{Z}^+)(\text{Z}^-)}{R_0}$

## Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from “4.6 Strengths of Ionic and Covalent Bonds” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>)

## Notes

1.  $-35 \text{ kJ}$
2. ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

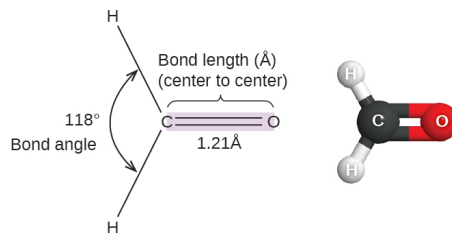
# 11.6 MOLECULAR STRUCTURE AND POLARITY

## Learning Objectives

By the end of this section, you will be able to:

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, the molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 11.6a). A **bond angle** is the angle between any two bonds that include a common atom, usually measured in degrees. A **bond distance** (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ) or picometers ( $1 \text{ pm} = 10^{-12} \text{ m}$ ,  $100 \text{ pm} = 1 \text{ \AA}$ ).



**Figure 11.6a:** Bond distances (lengths) and angles are shown for the formaldehyde (methanal) molecule,  $\text{H}_2\text{CO}$  (credit: *Chemistry (OpenStax)*, CC BY 4.0).

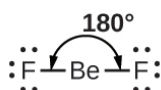
## VSEPR Theory

**Watch** What is the shape of a molecule? (3:47 min) ([https://www.youtube.com/watch?v=Jq\\_Ca-HKh1g](https://www.youtube.com/watch?v=Jq_Ca-HKh1g))

**Valence shell electron-pair repulsion theory (VSEPR theory)** enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.



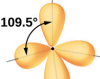






As a simple example of VSEPR theory, let us predict the structure of a gaseous  $\text{BeF}_2$  molecule. The Lewis structure of  $\text{BeF}_2$  (Figure 11.6b) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is  $180^\circ$  (Figure 11.6b).



**Figure 11.6b:** The  $\text{BeF}_2$  molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom (credit: Chemistry (OpenStax), CC BY 4.0).

Figure 11.6c illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a **linear** geometry; three regions form a **trigonal planar** geometry; four regions form a **tetrahedral** geometry; five regions form a **trigonal bipyramidal** geometry; and six regions form an **octahedral** geometry.



<b>Number of regions</b>	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
<b>Spatial arrangement</b>					
<b>Line-dash-wedge notation</b>	$\text{H}-\text{Be}-\text{H}$				
<b>Electron pair geometry</b>	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

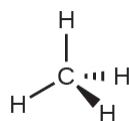
**Figure 11.6c:** The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

## Electron-pair Geometry versus Molecular Structure

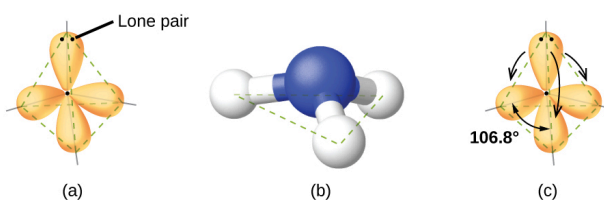
It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 11.6c describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron-pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure**. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

For example, the methane molecule,  $\text{CH}_4$ , which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 11.6d). On the other hand, the ammonia molecule,  $\text{NH}_3$ , also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 11.6e).

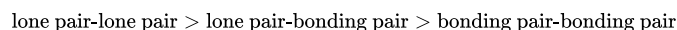


**Figure 11.6d:**  
Tetrahedral structure  
of methane,  $\text{CH}_4$   
(credit: *Chemistry*  
(*OpenStax*), CC BY  
4.0).

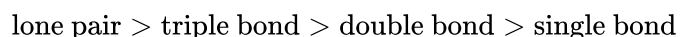


**Figure 11.6e:** (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than  $109.5^\circ$  (credit: *Chemistry* (*OpenStax*), CC BY 4.0).

As seen in Figure 11.6e, small distortions from the ideal angles in Figure 11.6c can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:


















This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:



Consider formaldehyde (methanal),  $\text{H}_2\text{CO}$ , which is used as a preservative for biological and anatomical specimens (Figure 11.6a). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with  $120^\circ$  bond angles, but we see that the double bond causes slightly larger angles ( $121^\circ$ ), and the angle between the single bonds is slightly smaller ( $118^\circ$ ).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 11.6e) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a

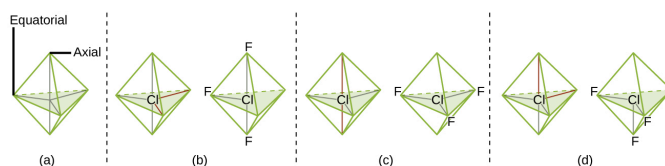
trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in  $\text{NH}_3$  are slightly smaller than the  $109.5^\circ$  angle in a regular tetrahedron (Figure 11.6c) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure 11.6e). Figure 11.6f illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

**Figure 11.6f:** The molecular structures are identical to the electron-pair geometries when there is no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry (credit: *Chemistry (OpenStax)*, CC BY 4.0).

According to VSEPR theory, the terminal atom locations (Xs in Figure 11.6f) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in Figure 11.6g: an **axial position** (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an **equatorial position** (three positions form an equator around the middle of the molecule). As shown in Figure 11.6f, the axial position is surrounded by bond angles of  $90^\circ$ , whereas the equatorial position has more space available because of the  $120^\circ$  bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the  $\text{ClF}_3$  molecule (Figure 11.6g). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.



**Figure 11.6g:** (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in  $\text{ClF}_3$  have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron ( $180^\circ$  apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure 11.6f).

## Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 11.6f, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 11.6f). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

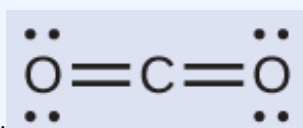
## Example 11.6a

Predicting Electron-pair Geometry and Molecular Structure:  $\text{CO}_2$  and  $\text{BCl}_3$ 

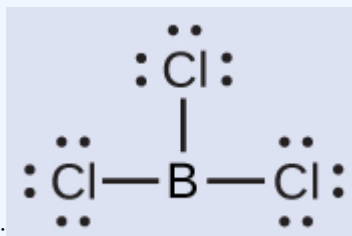
Predict the electron-pair geometry and molecular structure for each of the following:

- carbon dioxide,  $\text{CO}_2$ , a molecule produced by the combustion of fossil fuels
- boron trichloride,  $\text{BCl}_3$ , an important industrial chemical

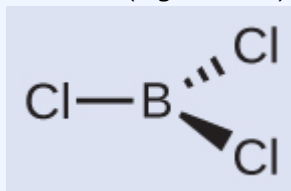
## Solution



- a. We write the Lewis structure of  $\text{CO}_2$  as: This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of  $180^\circ$ . The electron-pair geometry and molecular structure are identical, and  $\text{CO}_2$  molecules are linear.



- b. We write the Lewis structure of  $\text{BCl}_3$  as: Thus we see that  $\text{BCl}_3$  contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with  $120^\circ$  angles between them.  $\text{BCl}_3$  also has a trigonal planar molecular structure (Figure 11.6h).



**Figure 11.6h:** Trigonal planar molecule  $\text{BCl}_3$

The electron-pair geometry and molecular structure of  $\text{BCl}_3$  are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles ( $120^\circ$ ), unlike the Lewis structure shown above.

## Exercise 11.6a

Carbonate,  $\text{CO}_3^{2-}$ , is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

### Check Your Answer<sup>1</sup>

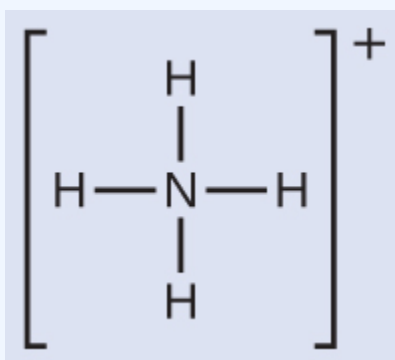
## Example 11.6b

### Predicting Electron-pair Geometry and Molecular Structure: Ammonium

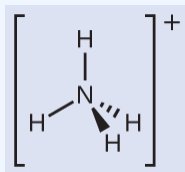
Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the  $\text{NH}_4^+$  cation.

### Solution

We write the Lewis structure of  $\text{NH}_4^+$  as:



We can see that  $\text{NH}_4^+$  contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (Figure 11.6i). Therefore, the electron pair geometry of  $\text{NH}_4^+$  is tetrahedral, and the molecular structure is also tetrahedral (Figure 11.6i).



**Figure 11.6i:** The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

## Exercise 11.6b

Identify a molecule with a trigonal bipyramidal molecular structure.

### Check Your Answer<sup>2</sup>

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

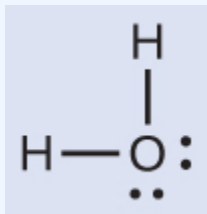
## Example 11.6c

### Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

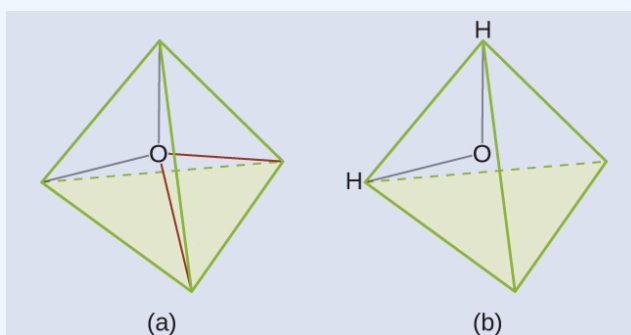
Predict the electron-pair geometry and molecular structure of a water molecule.

#### Solution

The Lewis structure of  $\text{H}_2\text{O}$  indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion (Figure 11.6j), as indicated in Figure 11.6e. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than  $109.5^\circ$ . In fact, the bond angle is  $104.5^\circ$ .



**Figure 11.6j:** (a)  $\text{H}_2\text{O}$  has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent (credit: Chemistry (OpenStax), CC BY 4.0).



## Exercise 11.6c

The hydronium ion,  $\text{H}_3\text{O}^+$ , forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

### Check Your Answer<sup>3</sup>

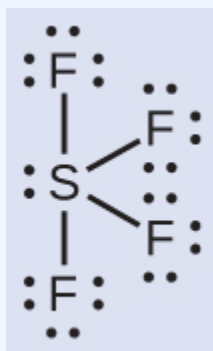
## Example 11.6d

### Predicting Electron-pair Geometry and Molecular Structure: $\text{SF}_4$

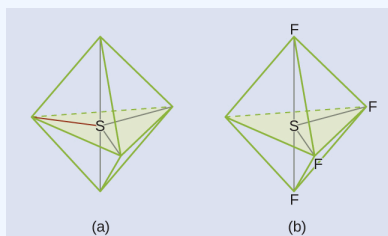
Sulfur tetrafluoride,  $\text{SF}_4$ , is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e.,  $\text{SF}_4$  is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of an  $\text{SF}_4$  molecule.

### Solution

The Lewis structure of  $\text{SF}_4$  indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (Figure 11.6k) is that of a seesaw (Figure 11.6k).



**Figure 11.6k:** (a) SF<sub>4</sub> has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure (credit: Chemistry (OpenStax), CC BY 4.0).

## Exercise 11.6d

Predict the electron pair geometry and molecular structure for molecules of XeF<sub>2</sub>.

**Check Your Answer<sup>4</sup>**

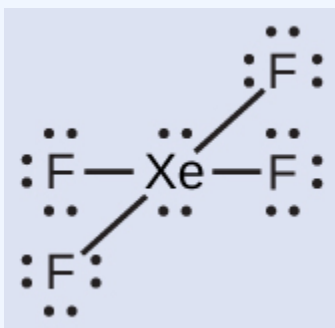
## Example 11.6e

### Predicting Electron-pair Geometry and Molecular Structure: XeF<sub>4</sub>

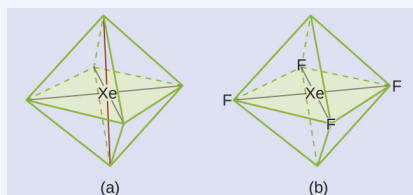
Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF<sub>4</sub> molecule.

#### Solution

The Lewis structure of XeF<sub>4</sub> indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement (Figure 11.6I), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure 11.6I). The five atoms are all in the same plane and have a square planar molecular structure.



**Figure 11.6I:** (a)  $\text{XeF}_4$  adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another (credit: *Chemistry (OpenStax)*, CC BY 4.0).

## Exercise 11.6e

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

**Check Your Answer<sup>5</sup>**

## Molecular Structure for Multicentre Molecules

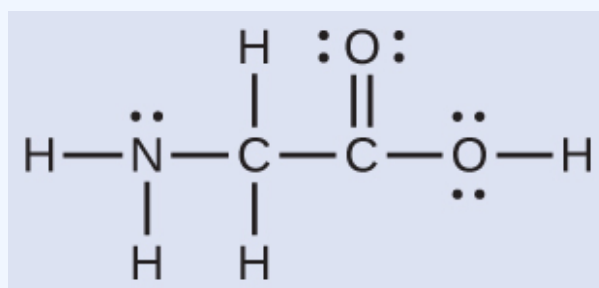
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of

interior atoms that each possess a “local” geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

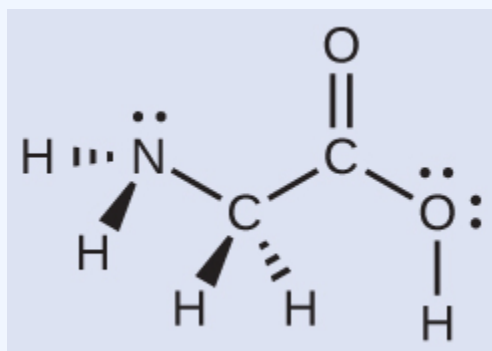
### Example 11.6f

#### Predicting Structure in Multicentre Molecules

The Lewis structure for the simplest amino acid, glycine,  $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ , is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



#### Solution



Consider each central atom independently. The electron-pair geometries:

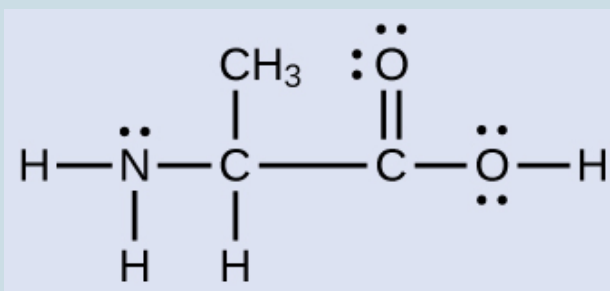
- nitrogen — four regions of electron density; tetrahedral
- carbon in the  $\text{CH}_2$  group — four regions of electron density; tetrahedral
- carbon in the  $\text{CO}_2$  group — three regions of electron density; trigonal planar
- oxygen in the  $\text{OH}$  group — four regions of electron density; tetrahedral

The local structures:

- nitrogen — three bonds, one lone pair; trigonal pyramidal
- carbon in the CH<sub>2</sub> group — four bonds, no lone pairs; tetrahedral
- carbon in the CO<sub>2</sub> group — three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen in the OH group — two bonds, two lone pairs; bent (109°)

### Exercise 11.6f

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Check Your Answer<sup>6</sup>

### Exercise 11.6g

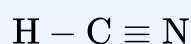
**Practice using the following PhET simulation Molecular Shapes**  
 ([https://phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes\\_en.html](https://phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes_en.html)):

## Example 11.6g

### Molecular Simulation

Use the molecular shape simulator in Exercise 11.6g. It allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:



Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

### Solution

The molecular structure is linear.

## Exercise 11.6h

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

**Check Your Answer**<sup>7</sup>

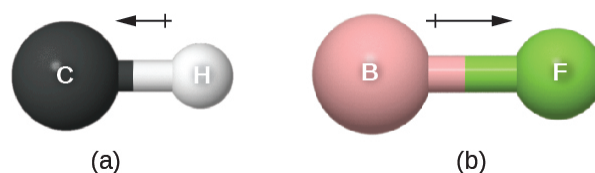
## Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge ( $\delta+$ ) and the other atom with a partial negative charge ( $\delta-$ ), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a **bond**

**dipole moment.** The magnitude of a bond dipole moment is represented by the Greek letter mu ( $\mu$ ) and is given by the formula shown here, where  $Q$  is the magnitude of the partial charges (determined by the electronegativity difference) and  $r$  is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a **vector**, a quantity having both direction and magnitude (Figure 11.6m). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

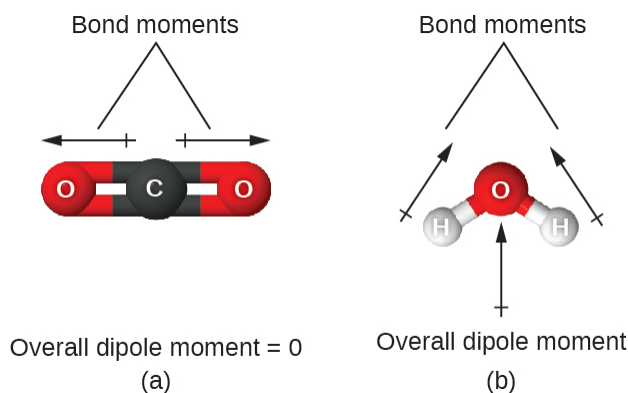


**Figure 11.6m:** (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a **polar molecule** (or dipole); otherwise the molecule is said to be nonpolar. The **dipole moment** measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

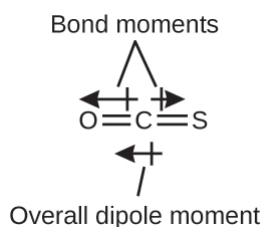
For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as  $\text{Br}_2$  and  $\text{N}_2$  have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as  $\text{CO}$ , there is a small dipole moment. For  $\text{HF}$ , there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in  $\text{CO}_2$  (Figure 11.6n). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the  $\text{CO}_2$  molecule is linear with polar  $\text{C}=\text{O}$  bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 11.6n), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).



**Figure 11.6n:** The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO<sub>2</sub> molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The OCS molecule (Figure 11.6o) has a structure similar to CO<sub>2</sub>, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

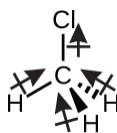


**Figure 11.6o:** The OCS molecule is shown to have a linear structure (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

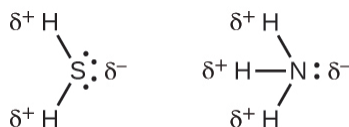
Chloromethane, CH<sub>3</sub>Cl (Figure 11.6p), is another example of a polar molecule. Although the polar C-Cl and C-H bonds are arranged in a tetrahedral geometry, the C-Cl bonds have a larger bond moment than the C-H bond, and the bond moments do not completely cancel each other. All of the dipoles have a downward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:





**Figure 11.6p:** The  $\text{CH}_3\text{Cl}$  structure has a tetrahedral shape and represents a polar molecule (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When we examine the highly symmetrical molecules  $\text{BF}_3$  (trigonal planar),  $\text{CH}_4$  (tetrahedral),  $\text{PF}_5$  (trigonal bipyramidal), and  $\text{SF}_6$  (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include  $\text{H}_2\text{S}$  and  $\text{NH}_3$  (Figure 11.6q). A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:



**Figure 11.6q**  $\text{H}_2\text{S}$  and  $\text{NH}_3$  represent structures where the dipoles do not cancel due to the lone pair of electrons (credit: *Chemistry (OpenStax)*, CC BY 4.0).

To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

## Exercise 11.6i

Check Your Learning Exercise (Text Version)

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

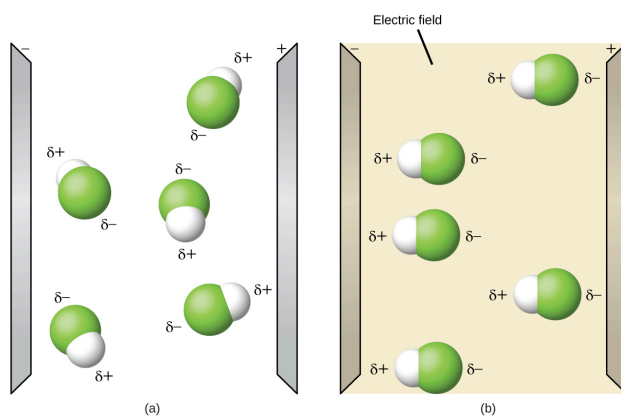
- C, F, H, N, O
- Br, Cl, F, H, I
- F, H, O, P, S
- Al, H, Na, O, P
- Ba, H, N, O, As

### Check Your Answer<sup>8</sup>

**Source:** “Exercise 11.6i” is adapted from “Exercise 4.2-7” in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

## Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate. We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.



**Figure 11.6r:** (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction (credit: *Chemistry (OpenStax)*, CC BY 4.0).

## Exercise 11.6J

**Practice using the following PhET simulation: Molecule Polarity.**

([https://phet.colorado.edu/sims/html/molecule-polarity/latest/molecule-polarity\\_en.html](https://phet.colorado.edu/sims/html/molecule-polarity/latest/molecule-polarity_en.html))

## Example 11.6h

### Polarity Simulations

Open the molecule polarity simulation and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjusters. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure 11.6r.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

- A and C are very electronegative and B is in the middle of the range.
- A is very electronegative, and B and C are not.

## Solution

- Molecular dipole moment points immediately between A and C.
- Molecular dipole moment points along the A–B bond, toward A.

## Exercise 11.6K

Determine the partial charges that will give the largest possible bond dipoles.

### Check Your Answer<sup>9</sup>

## Links to Interactive Learning Tools

Explore VSEPR Theory (<https://www.physicsclassroom.com/Concept-Builders/Chemistry/WODB-VSEPR>) from the Physics Classroom (<https://www.physicsclassroom.com/>).

Explore Drawing VSEPR Structures from Alchemie.

## Attribution & References

Except where otherwise noted, this page is adapted JR van Haarlem from “4.7 Molecular Structure and Polarity (<https://boisestate.pressbooks.pub/chemistry/chapter/4-7-molecular-structure-and-polarity/>)” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>)

## Notes

1. The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.
2. Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF<sub>5</sub> is a common example.
3. electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal
4. The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.
5. electron pair geometry: trigonal bipyramidal; molecular structure: linear
6. electron-pair geometries: nitrogen—tetrahedral; carbon (CH)—tetrahedral; carbon (CH<sub>3</sub>)—tetrahedral; carbon (CO<sub>2</sub>)—trigonal planar; oxygen (OH)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon (CH)—tetrahedral; carbon (CH<sub>3</sub>)—tetrahedral; carbon (CO<sub>2</sub>)—trigonal planar; oxygen (OH)—bent (109°)
7. Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. XeOF<sub>4</sub> is a molecule that adopts this structure.
8. (a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O
9. The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

# CHAPTER 11 - SUMMARY

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## 11.1 Ionic Bonding

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

## 11.2 Covalent Bonding

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

## 11.3 Lewis Symbols and Structures

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

## 11.4 Formal Charges and Resonance

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the

electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

## 11.5 Molecular Structure and Polarity

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

## 11.6 Molecular Structure and Polarity

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

### Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from “4.1 Ionic Bonding (<https://boisestate.pressbooks.pub/chemistry/chapter/4-1-ionic-bonding/>)”, “4.2 Covalent Bonding (<https://boisestate.pressbooks.pub/chemistry/chapter/4-2-covalent-bonding/>)”, “4.3 Lewis Symbols and Structures (<https://boisestate.pressbooks.pub/chemistry/chapter/4-3-chemical-nomenclature/>)”, “4.4 Lewis

Symbols and Structures (<https://boisestate.pressbooks.pub/chemistry/chapter/4-4-lewis-symbols-and-structures/>), “4.5 Formal Charges and Resonance (<https://boisestate.pressbooks.pub/chemistry/chapter/4-5-formal-charges-and-resonance/>)”, “4.6 Strengths of Ionic and Covalent Bonds (<https://boisestate.pressbooks.pub/chemistry/chapter/4-6-strengths-of-ionic-and-covalent-bonds/>)” and “4.7 Molecular Structure and Polarity” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>). / Extracted and used summary/key-takeaway content from each section for this page.



# CHAPTER 11 - REVIEW

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## 11.1 Ionic Bonding

1. Does a cation gain protons to form a positive charge or does it lose electrons? **Check Answer:** <sup>1</sup>
2. Iron(III) sulfate  $[\text{Fe}_2(\text{SO}_4)_3]$  is composed of  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  ions. Explain why a sample of iron(III) sulfate is uncharged.
3. Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co? **Check Answer:** <sup>2</sup>
4. Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?
5. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
  - a. P
  - b. Mg
  - c. Al
  - d. O
  - e. Cl
  - f. Cs**Check Answer:** <sup>3</sup>
6. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:
  - a. I
  - b. Sr
  - c. K
  - d. N
  - e. S
  - f. In
7. Write the electron configuration for each of the following ions:
  - a.  $\text{As}^{3-}$
  - b.  $\text{I}^-$
  - c.  $\text{Be}^{2+}$
  - d.  $\text{Cd}^{2+}$
  - e.  $\text{O}^{2-}$
  - f.  $\text{Ga}^{3+}$
  - g.  $\text{Li}^+$

- h.  $\text{N}^{3-}$
- i.  $\text{Sn}^{2+}$
- j.  $\text{Co}^{2+}$
- k.  $\text{Fe}^{2+}$
- l.  $\text{As}^{3+}$

**Check Answer:** <sup>4</sup>

8. Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):
- a. Cl
  - b. Na
  - c. Mg
  - d. Ca
  - e. K
  - f. Br
  - g. Sr
  - h. F
9. Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:
- a. Al
  - b. Br
  - c. Sr
  - d. Li
  - e. As
  - f. S

**Check Answer:** <sup>5</sup>

10. From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

## 11.2 Covalent Bonding

1. Why is it incorrect to speak of a molecule of solid NaCl? **Check Answer:** <sup>6</sup>
2. What information can you use to predict whether a bond between two atoms is covalent or ionic?
3. Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:
  - a.  $\text{Cl}_2\text{CO}$
  - b.  $\text{MnO}$

- c.  $\text{NCl}_3$
- d.  $\text{CoBr}_2$
- e.  $\text{K}_2\text{S}$
- f.  $\text{CO}$
- g.  $\text{CaF}_2$
- h.  $\text{HI}$
- i.  $\text{CaO}$
- j.  $\text{IBr}$
- k.  $\text{CO}_2$

**Check Answer:** <sup>7</sup>

- 4. Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.
- 5. From its position in the periodic table, determine which atom in each pair is more electronegative:
  - a. Br or Cl
  - b. N or O
  - c. S or O
  - d. P or S
  - e. Si or N
  - f. Ba or P
  - g. N or K

**Check Answer:** <sup>8</sup>

- 6. From its position in the periodic table, determine which atom in each pair is more electronegative:
  - a. N or P
  - b. N or Ge
  - c. S or F
  - d. Cl or S
  - e. H or C
  - f. Se or P
  - g. C or Si
- 7. From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:
  - a. C, F, H, N, O
  - b. Br, Cl, F, H, I
  - c. F, H, O, P, S
  - d. Al, H, Na, O, P
  - e. Ba, H, N, O, As

**Check Answer:** <sup>9</sup>

- 8. From their positions in the periodic table, arrange the atoms in each of the following series in order of

increasing electronegativity:

- As, H, N, P, Sb
  - Cl, H, P, S, Si
  - Br, Cl, Ge, H, Sr
  - Ca, H, K, N, Si
  - Cl, Cs, Ge, H, Sr
9. Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom? **Check Answer:**<sup>10</sup>
10. Which is the most polar bond?
- C–C
  - C–H
  - N–H
  - O–H
  - Se–H
11. Identify the more polar bond in each of the following pairs of bonds:
- HF or HCl
  - NO or CO
  - SH or OH
  - PCl or SCl
  - CH or NH
  - SO or PO
  - CN or NN
- Check Answer:**<sup>11</sup>
12. Which of the following molecules or ions contain polar bonds?
- O<sub>3</sub>
  - S<sub>8</sub>
  - O<sub>2</sub><sup>2-</sup>–O<sub>2</sub><sup>2-</sup>
  - NO<sub>3</sub><sup>-</sup>–NO<sub>3</sub><sup>-</sup>
  - CO<sub>2</sub>
  - H<sub>2</sub>S
  - BH<sub>4</sub><sup>-</sup>–BH<sub>4</sub><sup>-</sup>

## 11.3 Lewis Symbols and Structures

- Write the Lewis symbols for each of the following ions:
  - As<sup>3-</sup>
  - I<sup>-</sup>

- c.  $\text{Be}^{2+}$
- d.  $\text{O}^{2-}$
- e.  $\text{Ga}^{3+}$
- f.  $\text{Li}^+$
- g.  $\text{N}^{3-}$

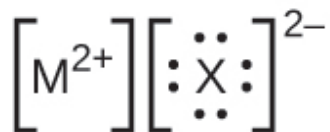
**Check Answer:** <sup>12</sup>

2. Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:
- a. Cl
  - b. Na
  - c. Mg
  - d. Ca
  - e. K
  - f. Br
  - g. Sr
  - h. F
3. Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:
- a.  $\text{MgS}$
  - b.  $\text{Al}_2\text{O}_3$
  - c.  $\text{GaCl}_3$
  - d.  $\text{K}_2\text{O}$
  - e.  $\text{Li}_3\text{N}$
  - f.  $\text{KF}$

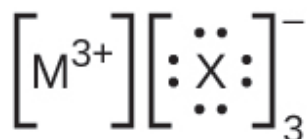
**Check Answer:** <sup>13</sup>

4. In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

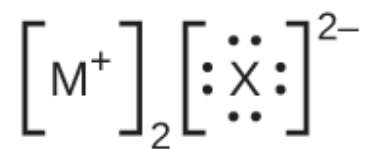
(a)



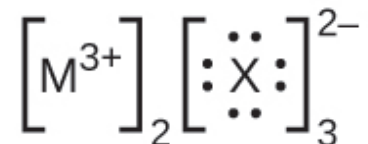
(b)



(c)



(d)



5. Write the Lewis structure for the diatomic molecule  $\text{P}_2$ , an unstable form of phosphorus found in high-temperature phosphorus vapor. **Check Answer:** <sup>14</sup>
6. Write Lewis structures for the following:
- $\text{H}_2$
  - $\text{HBr}$
  - $\text{PCl}_3$
  - $\text{SF}_2$
  - $\text{H}_2\text{CCH}_2$
  - $\text{HNNH}$
  - $\text{H}_2\text{CNH}$
  - $\text{NO}^-$
  - $\text{N}_2$
  - $\text{CO}$
  - $\text{CN}^-$
7. Write Lewis structures for the following:
- $\text{O}_2$
  - $\text{H}_2\text{CO}$
  - $\text{AsF}_3$
  - $\text{ClNO}$
  - $\text{SiCl}_4$
  - $\text{H}_3\text{O}^+$
  - $\text{NH}_4^+$
  - $\text{BF}_4^-$
  - $\text{HCCH}$
  - $\text{ClCN}$
  - $\text{C}_2^{2+}$
- Check Answer:** <sup>15</sup>
8. Write Lewis structures for the following:
- $\text{ClF}_3$

- b.  $\text{PCl}_5$
- c.  $\text{BF}_3$
- d.  $\text{PF}_6^-$

9. Write Lewis structures for the following:

- a.  $\text{SeF}_6$
- b.  $\text{XeF}_4$
- c.  $\text{SeCl}_3^+$
- d.  $\text{Cl}_2\text{BBCl}_2$  (contains a B–B bond)

**Check Answer:** <sup>16</sup>

10. Write Lewis structures for:

- a.  $\text{PO}_4^{3-}$
- b.  $\text{ICl}_4^-$
- c.  $\text{SO}_3^{2-}$
- d. HONO

11. Correct the following statement: “The bonds in solid  $\text{PbCl}_2$  are ionic; the bond in a  $\text{HCl}$  molecule is covalent. Thus, all of the valence electrons in  $\text{PbCl}_2$  are located on the  $\text{Cl}^-$  ions, and all of the valence electrons in a  $\text{HCl}$  molecule are shared between the H and Cl atoms.”

**Check Answer:** <sup>17</sup>

12. Write Lewis structures for the following molecules or ions:

- a.  $\text{SbH}_3$
- b.  $\text{XeF}_2$
- c.  $\text{Se}_8$  (a cyclic molecule with a ring of eight Se atoms)

13. Methanol,  $\text{H}_3\text{COH}$ , is used as the fuel in some race cars. Ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , is used extensively as motor fuel in Brazil. Both methanol and ethanol produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$  when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

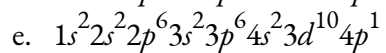
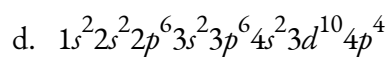
**Check Answer:** <sup>18</sup>

14. Many planets in our solar system contain organic chemicals including methane ( $\text{CH}_4$ ) and traces of ethylene ( $\text{C}_2\text{H}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), propyne ( $\text{H}_3\text{CCCH}$ ), and diacetylene ( $\text{HCCCCH}$ ). Write the Lewis structures for each of these molecules.

15. Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene,  $\text{Cl}_2\text{CO}$ . Write the Lewis structures for carbon tetrachloride and phosgene. **Check Answer:** <sup>19</sup>

16. Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

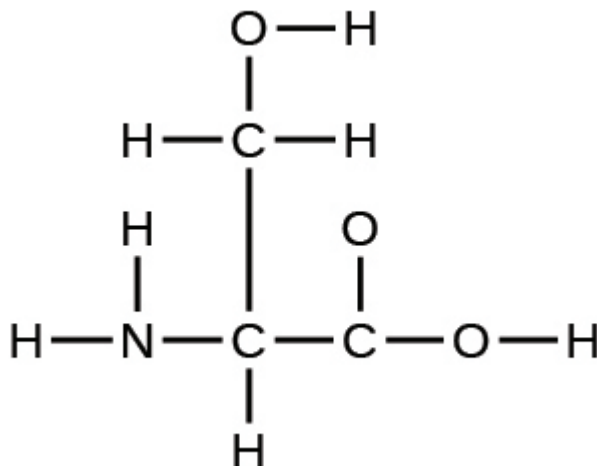
- a.  $1s^2 2s^2 2p^5$
- b.  $1s^2 2s^2 2p^6 3s^2$
- c.  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$



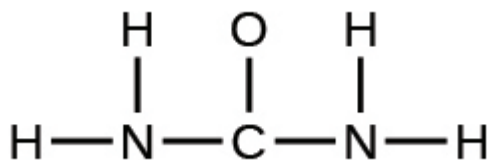
17. The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

**Check Answer:**<sup>20</sup>

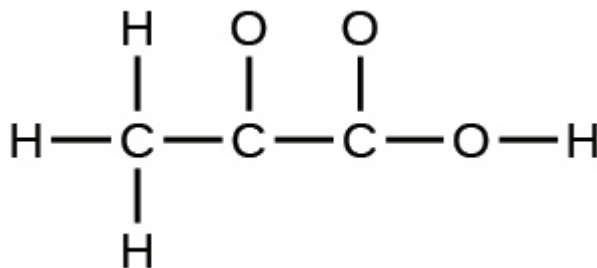
(a) the amino acid serine:



(b) urea:

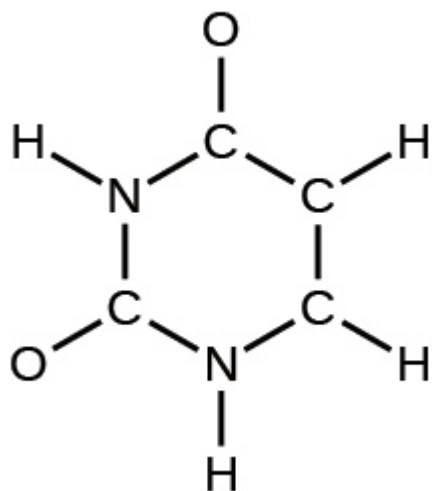


(c) pyruvic acid:

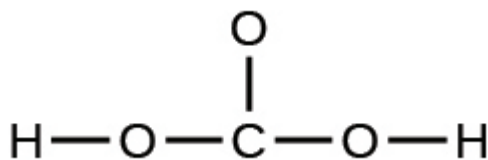


(d) uracil:





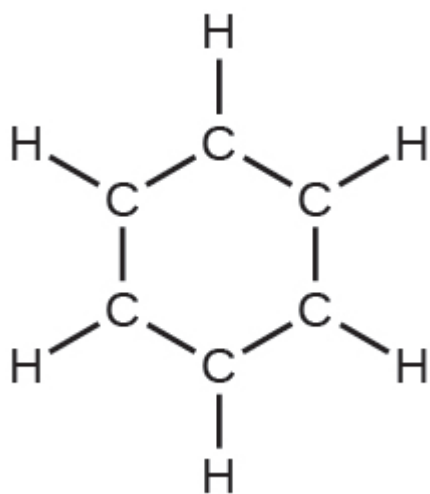
(e) carbonic acid:



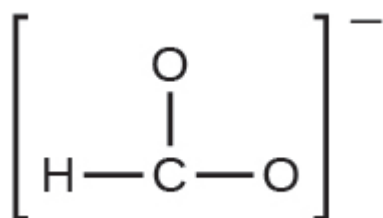
18. A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.
19. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound. **Check Answer:**<sup>21</sup>
20. Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.
21. How are single, double, and triple bonds similar? How do they differ? **Check Answer:**<sup>22</sup>

## 11.4 Formal Charges and Resonance

1. Write resonance forms that describe the distribution of electrons in each of these molecules or ions.
  - a. selenium dioxide, OSeO
  - b. nitrate ion, NO<sub>3</sub><sup>-</sup>
  - c. nitric acid, HNO<sub>3</sub> (N is bonded to an OH group and two O atoms)
  - d. benzene, C<sub>6</sub>H<sub>6</sub>:



e. the formate ion:

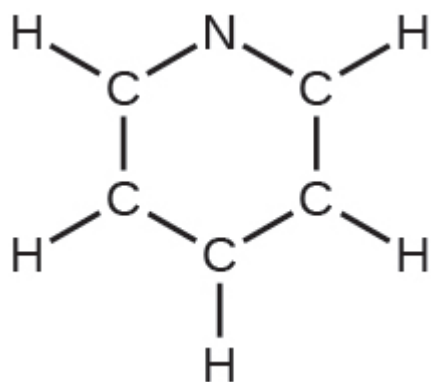


2. Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

a. sulfur dioxide, SO<sub>2</sub>

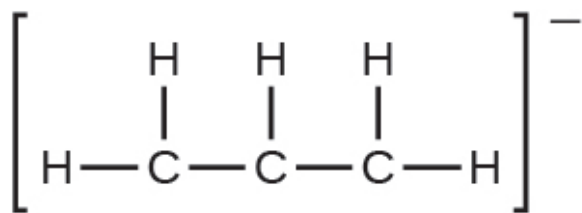
b. carbonate ion, CO<sub>3</sub><sup>2-</sup>

c. hydrogen carbonate ion, HCO<sub>3</sub><sup>-</sup> (C is bonded to an OH group and two O atoms)



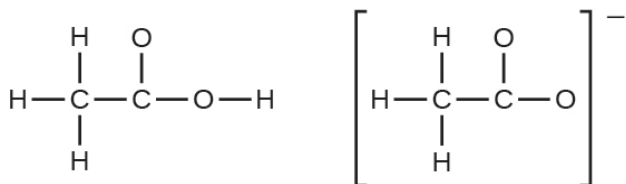
d. pyridine:

e. the allyl ion:



**Check Answer:** <sup>23</sup>

- Write the resonance forms of ozone,  $\text{O}_3$ , the component of the upper atmosphere that protects the Earth from ultraviolet radiation.
- Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion,  $\text{NO}_2^-$ . **Check Answer:** <sup>24</sup>
- In terms of the bonds present, explain why acetic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:



- Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.
  - $\text{CO}_2$
  - $\text{CO}$

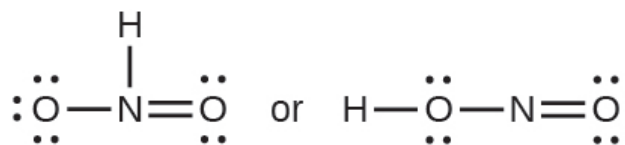
**Check Answer:** <sup>25</sup>

- Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.
- Determine the formal charge of each element in the following:
  - $\text{HCl}$
  - $\text{CF}_4$
  - $\text{PCl}_3$
  - $\text{PF}_5$

**Check Answer:** <sup>26</sup>

- Determine the formal charge of each element in the following:
  - $\text{H}_3\text{O}^+$
  - $\text{SO}_4^{2-}$
  - $\text{NH}_3$
  - $\text{O}_2^{2-}$
  - $\text{H}_2\text{O}_2$

10. Calculate the formal charge of chlorine in the molecules  $\text{Cl}_2$ ,  $\text{BeCl}_2$ , and  $\text{ClF}_5$ . **Check Answer:**<sup>27</sup>
11. Calculate the formal charge of each element in the following compounds and ions:
- $\text{F}_2\text{CO}$
  - $\text{NO}^-$
  - $\text{BF}_4^-$
  - $\text{SnCl}_3^-$
  - $\text{H}_2\text{CCH}_2$
  - $\text{ClF}_3$
  - $\text{SeF}_6$
  - $\text{PO}_4^{3-}$
12. Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:
- $\text{O}_3$
  - $\text{SO}_2$
  - $\text{NO}_2^-$
  - $\text{NO}_3^-$
- Check Answer:**<sup>28</sup>
13. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride:  $\text{ClNO}$  or  $\text{ClON}$ ?
14. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid:  $\text{HOCl}$  or  $\text{OClH}$ ? **Check Answer:**<sup>29</sup>
15. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide:  $\text{OSO}$  or  $\text{SOO}$ ?
16. Draw the structure of hydroxylamine,  $\text{H}_3\text{NO}$ , and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges? **Check Answer:**<sup>30</sup>
17. Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:
- $\text{IF}$
  - $\text{IF}_3$
  - $\text{IF}_5$
  - $\text{IF}_7$
18. Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound. **Check Answer:**<sup>31</sup>
19. Which of the following structures would we expect for nitrous acid? Determine the formal charges:



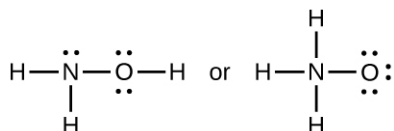
20. Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid,  $\text{H}_2\text{SO}_4$ , which has two oxygen atoms and two OH groups bonded to the sulfur. **Check Answer:**<sup>32</sup>

## 11.5 Strengths of Ionic and Covalent Bonds

- Which bond in each of the following pairs of bonds is the strongest?
  - C–C or C=C
  - C–N or C≡N
  - C≡O or C=O
  - H–F or H–Cl
  - C–H or O–H
  - C–N or C–O
- Using the bond energies in Table 11.5a, determine the approximate enthalpy change for each of the following reactions:
  - $\text{H}_2(g) + \text{Br}_2(g) \longrightarrow 2\text{HBr}(g)$
  - $\text{CH}_4(g) + \text{I}_2(g) \longrightarrow \text{CH}_3\text{I}(g) + \text{HI}(g)$
  - $\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(g)$

**Check Answer:**<sup>33</sup>

- Using the bond energies in Table 11.5a, determine the approximate enthalpy change for each of the following reactions:
  - $\text{Cl}_2(g) + 3\text{F}_2(g) \longrightarrow 2\text{ClF}_3(g)$
  - $\text{H}_2\text{C}=\text{CH}_2(g) + \text{H}_2(g) \longrightarrow \text{H}_3\text{CCH}_3(g)$
  - $2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(g)$
- When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:



**Check Answer:**<sup>34</sup>

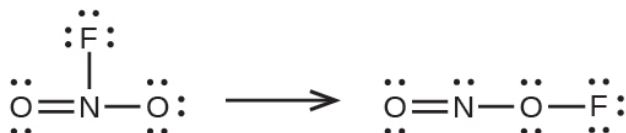
- How does the bond energy of  $\text{HCl}(g)$  differ from the standard enthalpy of formation of  $\text{HCl}(g)$ ?
- Using the standard enthalpy of formation data in Appendix H, show how the standard enthalpy of formation of  $\text{HCl}(g)$  can be used to determine the bond energy. **Check Answer:**<sup>35</sup>

7. Using the standard enthalpy of formation data in Appendix H, calculate the bond energy of the carbon-sulfur double bond in CS<sub>2</sub>.
8. Using the standard enthalpy of formation data in Appendix H, determine which bond is stronger: the S–F bond in SF<sub>4</sub>(g) or in SF<sub>6</sub>(g)? **Check Answer:**<sup>36</sup>
9. Using the standard enthalpy of formation data in Appendix H, determine which bond is stronger: the P–Cl bond in PCl<sub>3</sub>(g) or in PCl<sub>5</sub>(g)?
10. Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:



**Check Answer:**<sup>37</sup>

11. Use the bond energy to calculate an approximate value of  $\Delta H$  for the following reaction. Which is the more stable form of FNO<sub>2</sub>?



12. Use principles of atomic structure to answer each of the following:<sup>38</sup>
- The radius of the Ca atom is 197 pm; the radius of the Ca<sup>2+</sup> ion is 99 pm. Account for the difference.
  - The lattice energy of CaO(s) is –3460 kJ/mol; the lattice energy of K<sub>2</sub>O is –2240 kJ/mol. Account for the difference.
  - Given these ionization values in the data table below, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

- The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

**Check Answer:**<sup>39</sup>

13. The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values most closely

approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol? Explain your choice.

14. For which of the following substances is the least energy required to convert one mole of the solid into separate ions?
- MgO
  - SrO
  - KF
  - CsF
  - MgF<sub>2</sub>

**Check Answer:** <sup>40</sup>

15. The reaction of a metal, M, with a halogen, X<sub>2</sub>, proceeds by an exothermic reaction as indicated by this equation:  $M(s) + X_2(g) \longrightarrow MX_2(s)$ . For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.
- a large radius vs. a small radius for M<sup>+2</sup>
  - a high ionization energy vs. a low ionization energy for M
  - an increasing bond energy for the halogen
  - a decreasing electron affinity for the halogen
  - an increasing size of the anion formed by the halogen

16. The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4008 kJ/mol? Explain your choice.

**Check Answer:** <sup>41</sup>

17. Which compound in each of the following pairs has the larger lattice energy? Note: Mg<sup>2+</sup> and Li<sup>+</sup> have similar radii; O<sup>2-</sup> and F<sup>-</sup> have similar radii. Explain your choices.
- MgO or MgSe
  - LiF or MgO
  - Li<sub>2</sub>O or LiCl
  - Li<sub>2</sub>Se or MgO

18. Which compound in each of the following pairs has the larger lattice energy? Note: Ba<sup>2+</sup> and K<sup>+</sup> have similar radii; S<sup>2-</sup> and Cl<sup>-</sup> have similar radii. Explain your choices.
- K<sub>2</sub>O or Na<sub>2</sub>O
  - K<sub>2</sub>S or BaS
  - KCl or BaS
  - BaS or BaCl<sub>2</sub>

**Check Answer:** <sup>42</sup>

19. Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

- a. MgO
  - b. SrO
  - c. KF
  - d. CsF
  - e. MgF<sub>2</sub>
20. Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?
- a. K<sub>2</sub>S
  - b. K<sub>2</sub>O
  - c. CaS
  - d. Cs<sub>2</sub>S
  - e. CaO

**Check Answer:** <sup>43</sup>

21. The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF: 682 kJ/mol, 794 kJ/mol, 924 kJ/mol, 1588 kJ/mol, or 3175 kJ/mol? Explain your answer.

## 11.6 Molecular Structure and Polarity

1. Explain why the HOH molecule is bent, whereas the HBeH molecule is linear. **Check Answer:** <sup>44</sup>
2. What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?
3. Explain the difference between electron-pair geometry and molecular structure. **Check Answer:** <sup>45</sup>
4. Why is the H–N–H angle in NH<sub>3</sub> smaller than the H–C–H bond angle in CH<sub>4</sub>? Why is the H–N–H angle in NH<sub>4</sub><sup>+</sup> identical to the H–C–H bond angle in CH<sub>4</sub>?
5. Explain how a molecule that contains polar bonds can be nonpolar. **Check Answer:** <sup>46</sup>
6. As a general rule, MX<sub>n</sub> molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH<sub>3</sub> (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?
7. Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:
  - a. SF<sub>6</sub>
  - b. PCl<sub>5</sub>
  - c. BeH<sub>2</sub>
  - d. CH<sub>3</sub><sup>+</sup>



**Check Answer:**<sup>47</sup>

8. Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

- a.  $\text{IF}_6^+$
- b.  $\text{CF}_4$
- c.  $\text{BF}_3$
- d.  $\text{SiF}_5^-$
- e.  $\text{BeCl}_2$

9. What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

- a.  $\text{ClF}_5$
- b.  $\text{ClO}_2^-$
- c.  $\text{TeCl}_4^{2-}$
- d.  $\text{PCl}_3$
- e.  $\text{SeF}_4$
- f.  $\text{PH}_2^-$

**Check Answer:**<sup>48</sup>

10. Predict the electron pair geometry and the molecular structure of each of the following ions:

- a.  $\text{H}_3\text{O}^+$
- b.  $\text{PCl}_4^-$
- c.  $\text{SnCl}_3^-$
- d.  $\text{BrCl}_4^-$
- e.  $\text{ICl}_3$
- f.  $\text{XeF}_4$
- g.  $\text{SF}_2$

11. Identify the electron pair geometry and the molecular structure of each of the following molecules:

- a.  $\text{ClNO}$  (N is the central atom)
- b.  $\text{CS}_2$
- c.  $\text{Cl}_2\text{CO}$  (C is the central atom)
- d.  $\text{Cl}_2\text{SO}$  (S is the central atom)
- e.  $\text{SO}_2\text{F}_2$  (S is the central atom)
- f.  $\text{XeO}_2\text{F}_2$  (Xe is the central atom)
- g.  $\text{ClOF}_2^+$  (Cl is the central atom)

**Check Answer:**<sup>49</sup>

12. Predict the electron pair geometry and the molecular structure of each of the following:

- a.  $\text{IOF}_5$  (I is the central atom)
- b.  $\text{POCl}_3$  (P is the central atom)

- c.  $\text{Cl}_2\text{SeO}$  (Se is the central atom)
- d.  $\text{ClSO}^+$  (S is the central atom)
- e.  $\text{F}_2\text{SO}$  (S is the central atom)
- f.  $\text{NO}_2^-$
- g.  $\text{SiO}_4^{4-}$

13. Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

- a.  $\text{ClF}_5$
- b.  $\text{ClO}_2^-$
- c.  $\text{TeCl}_4^{2-}$
- d.  $\text{PCl}_3$
- e.  $\text{SeF}_4$
- f.  $\text{PH}_2^-$
- g.  $\text{XeF}_2$

**Check Answer:** <sup>50</sup>

14. Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

- a.  $\text{H}_3\text{O}^+$
- b.  $\text{PCl}_4^-$
- c.  $\text{SnCl}_3^-$
- d.  $\text{BrCl}_4^-$
- e.  $\text{ICl}_3$
- f.  $\text{XeF}_4$
- g.  $\text{SF}_2$

15. Which of the following molecules have dipole moments?

- a.  $\text{CS}_2$
- b.  $\text{SeS}_2$
- c.  $\text{CCl}_2\text{F}_2$
- d.  $\text{PCl}_3$  (P is the central atom)
- e.  $\text{ClNO}$  (N is the central atom)

**Check Answer:** <sup>51</sup>

16. Identify the molecules with a dipole moment:

- a.  $\text{SF}_4$
- b.  $\text{CF}_4$
- c.  $\text{Cl}_2\text{CCBr}_2$
- d.  $\text{CH}_3\text{Cl}$
- e.  $\text{H}_2\text{CO}$

17. The molecule  $\text{XF}_3$  has a dipole moment. Is X boron or phosphorus? **Check Answer:** <sup>52</sup>
18. The molecule  $\text{XCl}_2$  has a dipole moment. Is X beryllium or sulfur?
19. Is the  $\text{Cl}_2\text{BBCl}_2$  molecule polar or nonpolar? **Check Answer:** <sup>53</sup>
20. There are three possible structures for  $\text{PCl}_2\text{F}_3$  with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.
21. Describe the molecular structure around the indicated atom or atoms:
- the sulfur atom in sulfuric acid,  $\text{H}_2\text{SO}_4$  [ $(\text{HO})_2\text{SO}_2$ ]
  - the chlorine atom in chloric acid,  $\text{HClO}_3$  [ $\text{HOClO}_2$ ]
  - the oxygen atom in hydrogen peroxide,  $\text{HOOH}$
  - the nitrogen atom in nitric acid,  $\text{HNO}_3$  [ $\text{HONO}_2$ ]
  - the oxygen atom in the OH group in nitric acid,  $\text{HNO}_3$  [ $\text{HONO}_2$ ]
  - the central oxygen atom in the ozone molecule,  $\text{O}_3$
  - each of the carbon atoms in propyne,  $\text{CH}_3\text{CCH}$
  - the carbon atom in Freon,  $\text{CCl}_2\text{F}_2$
  - each of the carbon atoms in allene,  $\text{H}_2\text{CCCH}_2$
- Check Answer:** <sup>54</sup>
22. Draw the Lewis structures and predict the shape of each compound or ion:
- $\text{CO}_2$
  - $\text{NO}_2^-$
  - $\text{SO}_3$
  - $\text{SO}_3^{2-}$
23. A molecule with the formula  $\text{AB}_2$ , in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape. **Check Answer:** <sup>55</sup>
24. A molecule with the formula  $\text{AB}_3$ , in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.
25. Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:
- $\text{CS}_3^{2-}$
  - $\text{CS}_2$
  - $\text{CS}$
  - predict the molecular shapes for  $\text{CS}_3^{2-}$  and  $\text{CS}_2$  and explain how you arrived at your predictions
- Check Answer:** <sup>56</sup>
26. What is the molecular structure of the stable form of  $\text{FNO}_2$ ? (N is the central atom.)
27. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure? **Check Answer:** <sup>57</sup>

28. Use the Molecule Polarity simulation ([https://phet.colorado.edu/sims/html/molecule-polarity/latest/molecule-polarity\\_en.html](https://phet.colorado.edu/sims/html/molecule-polarity/latest/molecule-polarity_en.html)) to perform the following exercises for a two-atom molecule:
- Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
  - With a partial positive charge on A, turn on the electric field and describe what happens.
  - With a small partial negative charge on A, turn on the electric field and describe what happens.
  - Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.
29. Use the Molecule Polarity simulation ([https://phet.colorado.edu/sims/html/molecule-polarity/latest/molecule-polarity\\_en.html](https://phet.colorado.edu/sims/html/molecule-polarity/latest/molecule-polarity_en.html)) to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.
- Sketch the bond dipoles and molecular dipole (if any) for  $O_3$ . Explain your observations.
  - Look at the bond dipoles for  $NH_3$ . Use these dipoles to predict whether N or H is more electronegative.
  - Predict whether there should be a molecular dipole for  $NH_3$  and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.
- Check Answer:**<sup>58</sup>
30. Use the Molecule Shape simulator ([https://phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes\\_en.html](https://phet.colorado.edu/sims/html/molecule-shapes/latest/molecule-shapes_en.html)) to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

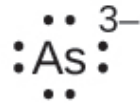
## Attribution & References

Except where otherwise noted, this page is adapted by JR van Haarlem from “4.1 Ionic Bonding (<https://boisestate.pressbooks.pub/chemistry/chapter/4-1-ionic-bonding/>)”, “4.2 Covalent Bonding (<https://boisestate.pressbooks.pub/chemistry/chapter/4-2-covalent-bonding/>)”, “4.3 Lewis Symbols and Structures (<https://boisestate.pressbooks.pub/chemistry/chapter/4-3-chemical-nomenclature/>)”, “4.4 Lewis Symbols and Structures (<https://boisestate.pressbooks.pub/chemistry/chapter/4-4-lewis-symbols-and-structures/>)”, “4.5 Formal Charges and Resonance (<https://boisestate.pressbooks.pub/chemistry/chapter/4-5-formal-charges-and-resonance/>)”, “4.6 Strengths of Ionic and Covalent Bonds (<https://boisestate.pressbooks.pub/chemistry/chapter/4-6-strengths-of-ionic-and-covalent-bonds/>)” and “4.7 Molecular Structure and Polarity” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>). / Extracted exercises from each section for this page.

## Notes

- The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.
- P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.
- (a)  $P^{3-}$ ; (b)  $Mg^{2+}$ ; (c)  $Al^{3+}$ ; (d)  $O^{2-}$ ; (e)  $Cl^{-}$ ; (f)  $Cs^{+}$
- (a)  $[Ar]4s^2 3d^{10} 4p^6$ ; (b)  $[Kr]4d^{10} 5s^2 5p^6$ ; (c)  $1s^2$ ; (d)  $[Kr]4d^{10}$ ; (e)  $[He]2s^2 2p^6$ ; (f)  $[Ar]3d^{10}$ ; (g)  $1s^2$ ; (h)  $[He]2s^2 2p^6$ ; (i)  $[Kr]4d^{10} 5s^2$ ; (j)  $[Ar]3d^7$ ; (k)  $[Ar]3d^6$ ; (l)  $[Ar]3d^{10} 4s^2$
- (a)  $1s^2 2s^2 2p^6 3s^2 3p^1$ ;  $Al^{3+}$ :  $1s^2 2s^2 2p^6$ ; (b)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$ ;  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ ; (c)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$ ;  $Sr^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ ; (d)  $1s^2 2s^1$ ;  $Li^{+}$ :  $1s^2$ ; (e)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ ;  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ ; (f)  $1s^2 2s^2 2p^6 3s^2 3p^4$ ;  $1s^2 2s^2 2p^6 3s^2 3p^6$
- NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.
- ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)
- (a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N
- (a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O
- N, O, F, and Cl
- (a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

12. 1. (a) eight electrons:



;

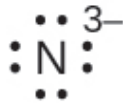
(b) eight electrons:

; (c) no electrons  $Be^{2+}$ ; (d) eight

electrons:

; (e) no electrons  $Ga^{3+}$ ; (f) no electrons  $Li^{+}$ ; (g)

eight electrons:



13. 3. (a)

 $Mg^{2+}$ 

;

(b)

 $Al^{3+}$ 

; (c)

 $Ga^{3+}$ 

; (d)

 $K^{+}$ 

&gt;; (e)

 $Li^{+}$ 

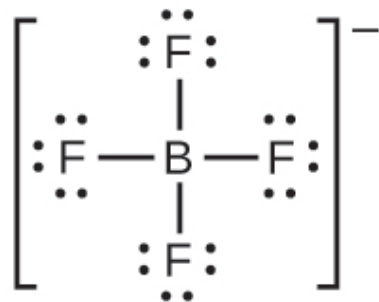
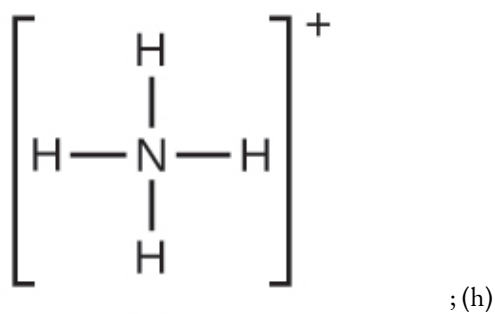
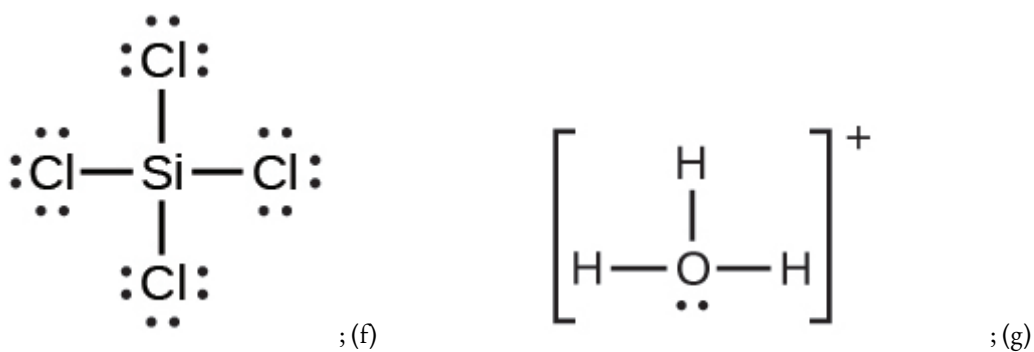
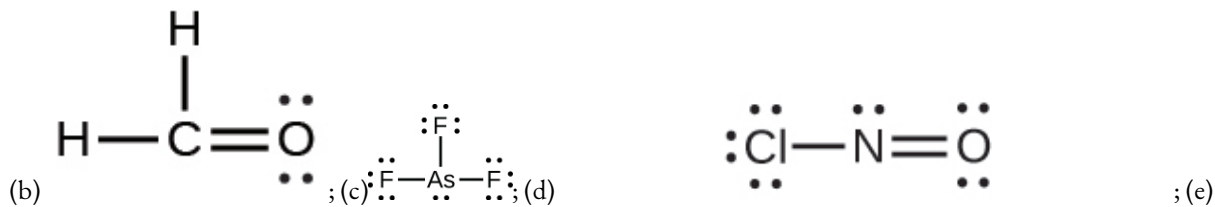
; (f)

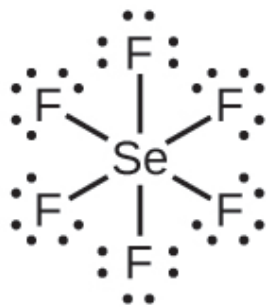
 $K^{+}$ 

- 14.

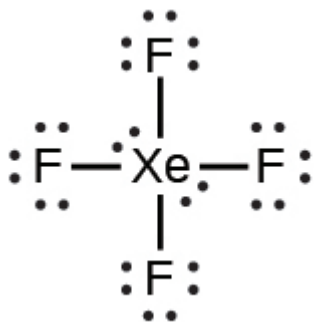
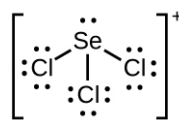
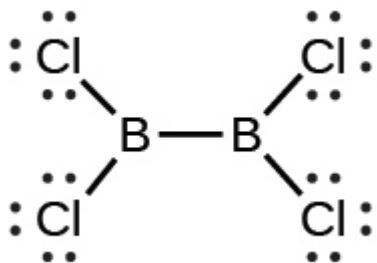


15. (a)  $\text{:}\ddot{\text{O}}=\ddot{\text{O}}\text{:}$  In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

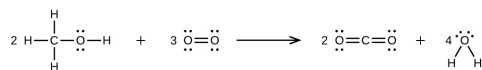


16. (a)  $\text{SeF}_6$ :

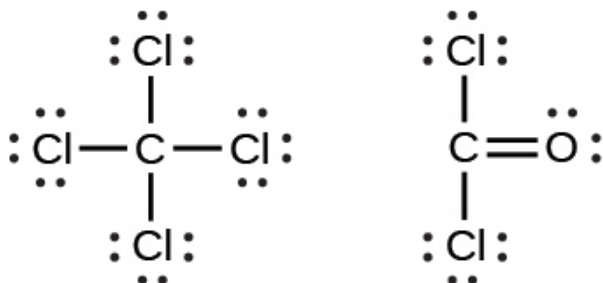
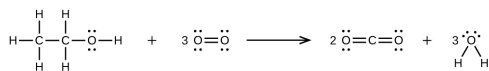
;

(b)  $\text{XeF}_4$ :; (c)  $\text{SeCl}_3^+$ :; (d)  $\text{Cl}_2\text{BBCl}_2$ :

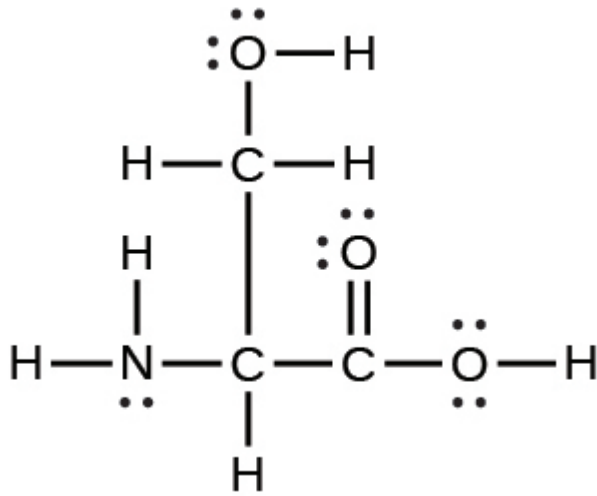
17. Two valence electrons per Pb atom are transferred to Cl atoms; the resulting  $\text{Pb}^{2+}$  ion has a  $6s^2$  valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.



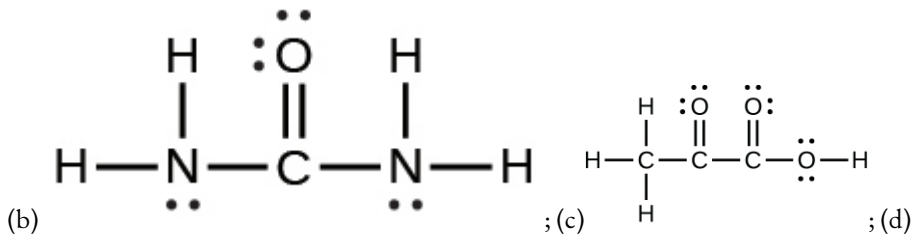
18.



19.



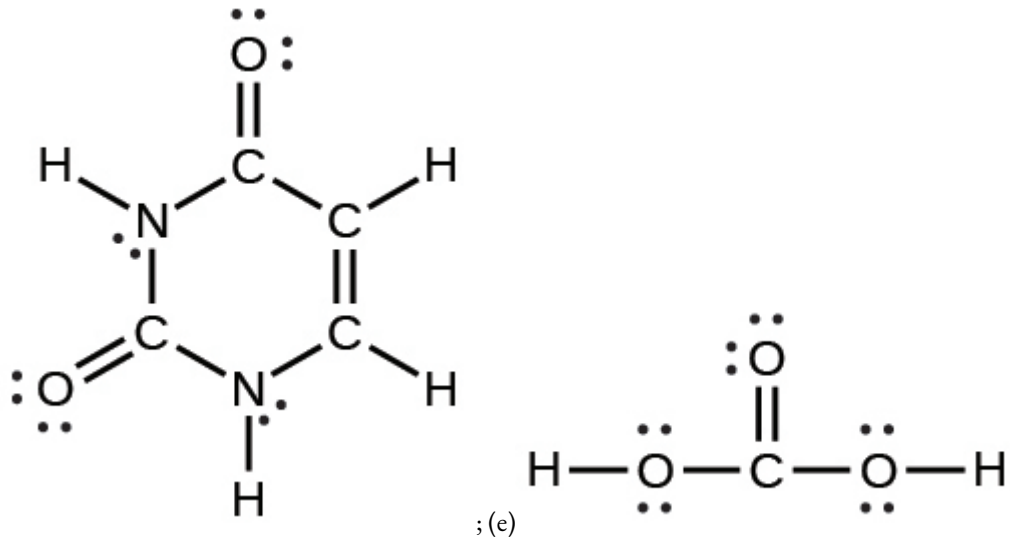
20. (a) ;



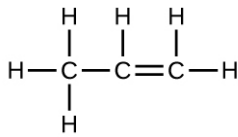
(b)

;(c)

;(d)

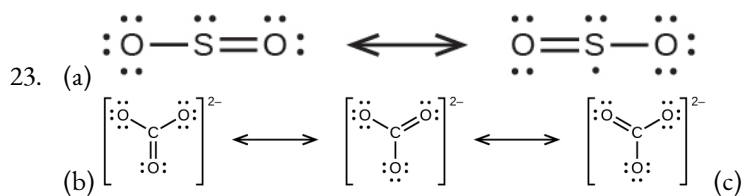


;(e)

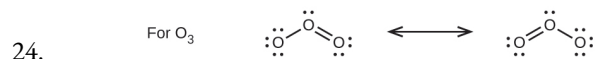
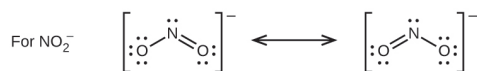
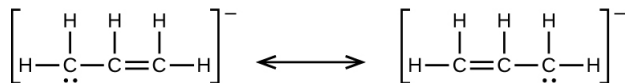
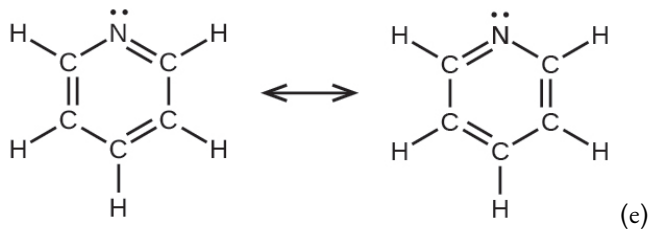
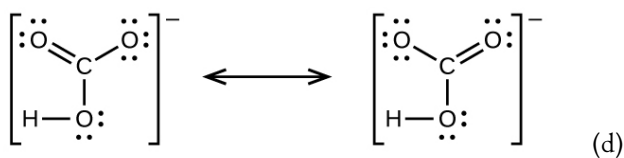


21.

22. Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.



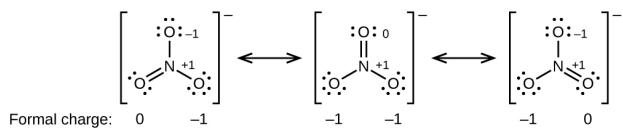
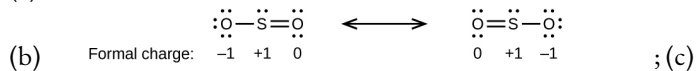
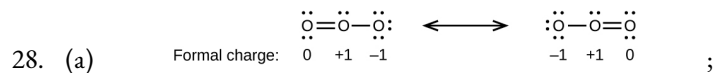




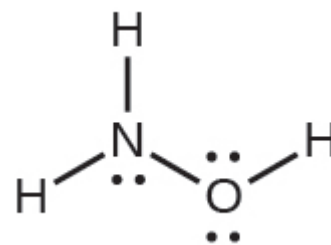
(b)  $\text{C}\equiv\text{O}$  CO has the strongest carbon-oxygen bond because there is a triple bond joining C and O.  $\text{CO}_2$  has double bonds.

26. (a) H: 0, Cl: 0; (b) C: 0, F: 0; (c) P: 0, Cl: 0; (d) P: 0, F: 0

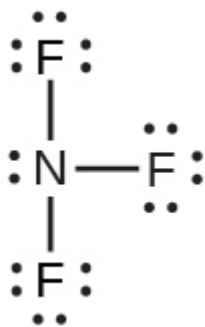
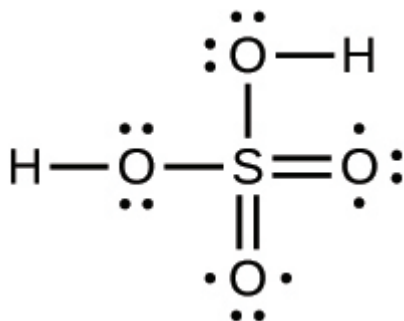
27. Cl in  $\text{Cl}_2$ : 0; Cl in  $\text{BeCl}_2$ : 0; Cl in  $\text{ClF}_5$ : 0



29. HOCl



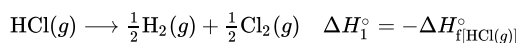
30. The structure that gives zero formal charges is consistent with the actual structure:

31.  $\text{NF}_3$ ;

32.

33. (a)  $-114 \text{ kJ}$ ; (b)  $30 \text{ kJ}$ ; (c)  $-1055 \text{ kJ}$ 

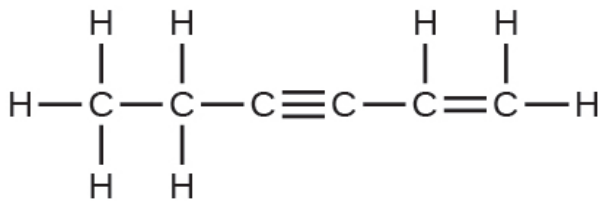
34. The greater bond energy is in the figure on the left. It is the more stable form.



35.



$$\begin{aligned} D_{\text{HCl}} &= \Delta H_{298}^\circ = -\Delta H_{\text{f}[\text{HCl}(g)]}^\circ + \Delta H_{\text{f}[\text{H}(g)]}^\circ + \Delta H_{\text{f}[\text{Cl}(g)]}^\circ \\ &= -(-92.307 \text{ kJ}) + 217.97 \text{ kJ} + 121.3 \text{ kJ} \\ &= 431.6 \text{ kJ} \end{aligned}$$

36. The S-F bond in  $\text{SF}_4$  is stronger.

37.

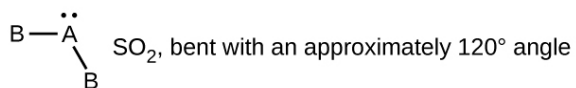
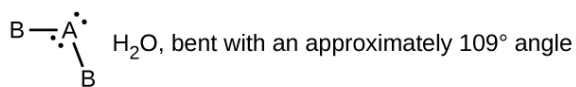
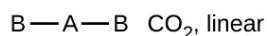
The C-C single bonds are longest.

38. This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

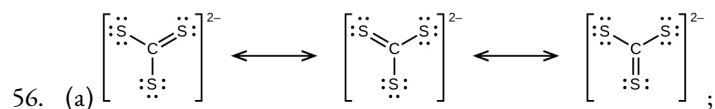
39. (a) When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower  $n = 3$  level, which is much smaller in radius. (b) The  $+2$  charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion. (c) Removal of the  $4s$  electron in Ca requires more energy than removal of the  $4s$  electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level. (d) In Al, the removed electron is relatively unprotected and unpaired in a  $p$  orbital. The higher energy for Mg mainly reflects the unpairing of the  $2s$  electron.

40. (d)

41. 4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy
42. (a) Na<sub>2</sub>O; Na<sup>+</sup> has a smaller radius than K<sup>+</sup>; (b) BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; (d) BaS; S has a larger charge
43. (e)
44. The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.
45. Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.
46. As long as the polar bonds are compensated (for example, two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.
47. (a) Both the electron geometry and the molecular structure are octahedral. (b) Both the electron geometry and the molecular structure are trigonal bipyramid. (c) Both the electron geometry and the molecular structure are linear. (d) Both the electron geometry and the molecular structure are trigonal planar.
48. (a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)
49. (a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal
50. All of these molecules and ions contain polar bonds. Only ClF<sub>5</sub>, ClO<sub>2</sub><sup>-</sup>, PCl<sub>3</sub>, SeF<sub>4</sub>, and PH<sub>2</sub><sup>-</sup> have dipole moments.
51. SeS<sub>2</sub>, CCl<sub>2</sub>F<sub>2</sub>, PCl<sub>3</sub>, and ClNO all have dipole moments.
52. P
53. nonpolar
54. (a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; (e) bent (109°); (f) bent (109°); (g) CH<sub>3</sub>CCH - first carbon on left is tetrahedral, middle carbon and carbon on right are linear; (h) tetrahedral; (i) H<sub>2</sub>CCCH<sub>2</sub> - middle carbon is linear; carbons on left and right are trigonal planar

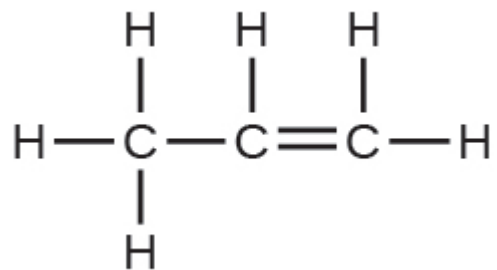


55.



- (b)  $\ddot{\text{S}}=\text{C}=\ddot{\text{S}}$  ; (c)  $:\text{C}\equiv\text{S}:$  ; (d) CS<sub>3</sub><sup>2-</sup> includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS<sub>2</sub> has only two regions of electron density (all bonds with no lone pairs); the shape is linear

57. The Lewis structure is made from three units, but the atoms must be rearranged:



58. The molecular dipole points away from the hydrogen atoms.