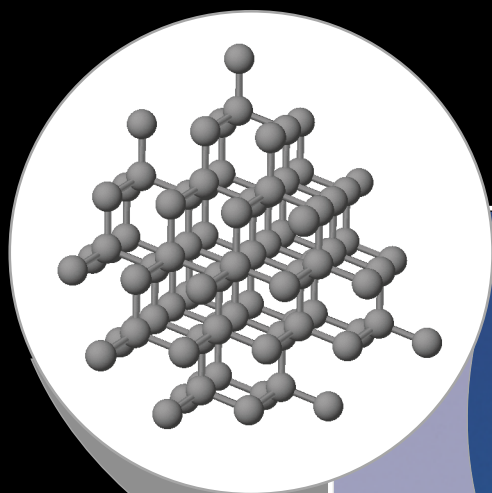


Chemical Bonding

7





Carbon atoms are covalently bonded together in a three-dimensional array to make diamond, the hardest substance known.

OUTLINE

- | | | | |
|-------------------------|--|------|--|
| 7-1 | Lewis Dot Formulas of Atoms | 7-6 | Resonance |
| Ionic Bonding | | 7-7 | Limitations of the Octet Rule for Lewis Formulas |
| 7-2 | Formation of Ionic Compounds | 7-8 | Polar and Nonpolar Covalent Bonds |
| Covalent Bonding | | 7-9 | Dipole Moments |
| 7-3 | Formation of Covalent Bonds | 7-10 | The Continuous Range of Bonding Types |
| 7-4 | Lewis Formulas for Molecules and Polyatomic Ions | | |
| 7-5 | The Octet Rule | | |

OBJECTIVES

After you have studied this chapter, you should be able to

- *Write Lewis dot representations of atoms*
- *Predict whether bonding between specified elements will be primarily ionic, covalent, or polar covalent*
- *Compare and contrast characteristics of ionic and covalent compounds*
- *Describe how the properties of compounds depend on their bonding*
- *Describe how the elements bond by electron transfer (ionic bonding)*
- *Describe energy relationships in ionic compounds*
- *Predict the formulas of ionic compounds*
- *Describe how elements bond by sharing electrons (covalent bonding)*
- *Write Lewis dot and dash formulas for molecules and polyatomic ions*
- *Recognize exceptions to the octet rule*
- *Write formal charges for atoms in covalent structures*
- *Describe resonance, and know when to write resonance structures and how to do so*
- *Relate the nature of bonding to electronegativity differences*

Chemical bonding refers to the attractive forces that hold atoms together in compounds. There are two major classes of bonding. (1) **Ionic bonding** results from electrostatic interactions among ions, which often results from the net *transfer* of one or more electrons from one atom or group of atoms to another. (2) **Covalent bonding** results from *sharing* one or more electron pairs between two atoms. These two classes represent two extremes; all bonds between atoms of different elements have at least some degree of both ionic and covalent character. Compounds containing predominantly ionic bonding are called **ionic compounds**. Those that are held together mainly by covalent bonds are called **covalent compounds**. Some nonmetallic elements, such as H_2 , Cl_2 , N_2 , and P_4 , also involve covalent bonding. Some properties usually associated with many simple ionic and covalent compounds are summarized in the following list. The differences in these properties can be accounted for by the differences in bonding between the atoms or ions.

As you study Chapters 7 and 8, keep in mind the periodic similarities that you learned in Chapters 4 and 6. What you learn about the bonding of an element usually applies to the other elements in the same column of the periodic table, with minor variations.

Ionic Compounds

1. They are solids with high melting points (typically $>400^\circ C$).
2. Many are soluble in polar solvents such as water.
3. Most are insoluble in nonpolar solvents, such as hexane, C_6H_{14} , and carbon tetrachloride, CCl_4 .
4. Molten compounds conduct electricity well because they contain mobile charged particles (ions).
5. Aqueous solutions conduct electricity well because they contain mobile charged particles (ions).
6. They are often formed between two elements with quite different electronegativities, usually a metal and a nonmetal.

Covalent Compounds

1. They are gases, liquids, or solids with low melting points (typically $<300^\circ C$).
2. Many are insoluble in polar solvents.
3. Most are soluble in nonpolar solvents, such as hexane, C_6H_{14} , and carbon tetrachloride, CCl_4 .
4. Liquid and molten compounds do not conduct electricity.
5. Aqueous solutions are *usually* poor conductors of electricity because most do not contain charged particles.
6. They are often formed between two elements with similar electronegativities, usually nonmetals.

The distinction between polar and nonpolar molecules is made in Section 7-8.

As we saw in Section 4-2, aqueous solutions of some covalent compounds do conduct electricity, because they react with water to some extent to form ions.

7-1 LEWIS DOT FORMULAS OF ATOMS

The number and arrangements of electrons in the outermost shells of atoms determine the chemical and physical properties of the elements as well as the kinds of chemical bonds they form. We write **Lewis dot formulas** (or **Lewis dot representations**, or just **Lewis formulas**) as a convenient bookkeeping method for keeping track of these “chemically important electrons.” We now introduce this method for atoms of elements; in our discussion of chemical bonding in subsequent sections, we will frequently use such formulas for atoms, molecules, and ions.

For the Group A elements, the number of valence electrons (dots in the Lewis formula) for the *neutral* atom is equal to the group number. Exceptions: H (one valence electron) and He (two valence electrons).

For example, Al has the electron configuration $[\text{Ar}] 3s^23p^1$. The three dots in the Lewis dot formula for Al represent the two *s* electrons (the pair of dots) and the *p* electron (the single dot) beyond the noble gas configuration. Because of the large numbers of dots, such formulas are not as useful for the transition and inner transition elements.

The chemical and physical properties of an ion are quite different from those of the atom from which the ion is derived. For example, an atom of Na and an Na^+ ion are quite different.

TABLE 7-1 Lewis Dot Formulas for Representative Elements

Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
<i>Number of electrons in valence shell</i>	1	2	3	4	5	6	7	8 (except He)
Period 1	H ·							He :
Period 2	Li ·	Be :	·B·	·C·	·N·	·O·	·F·	·Ne·
Period 3	Na ·	Mg :	·Al·	·Si·	·P·	·S·	·Cl·	·Ar·
Period 4	K ·	Ca :	·Ga·	·Ge·	·As·	·Se·	·Br·	·Kr·
Period 5	Rb ·	Sr :	·In·	·Sn·	·Sb·	·Te·	·I·	·Xe·
Period 6	Cs ·	Ba :	·Tl·	·Pb·	·Bi·	·Po·	·At·	·Rn·
Period 7	Fr ·	Ra :						

Chemical bonding usually involves only the outermost electrons of atoms, also called **valence electrons**. In Lewis dot representations, only the electrons in the outermost occupied *s* and *p* orbitals are shown as dots. Paired and unpaired electrons are also indicated. Table 7-1 shows Lewis dot formulas for the representative elements. All elements in a given group have the same outer-shell electron configuration. It is somewhat arbitrary on which side of the atom symbol we write the electron dots. We do, however, represent an electron pair as a pair of dots and an unpaired electron as a single dot.

IONIC BONDING

7-2 FORMATION OF IONIC COMPOUNDS

The first kind of chemical bonding we shall describe is **ionic bonding**. We recall (Section 2-3) that an **ion** is an atom or a group of atoms that carries an electrical charge. An ion in which the atom or group of atoms has fewer electrons than protons is positively charged, and is called a **cation**; one that has more electrons than protons is negatively charged, and is called an **anion**. An ion that consists of only one atom is described as a **monatomic ion**. Examples include the chloride ion, Cl^- , and the magnesium ion, Mg^{2+} . An ion that contains more than one atom is called a **polyatomic ion**. Examples include the ammonium ion, NH_4^+ ; the hydroxide ion, OH^- ; and the sulfate ion, SO_4^{2-} . The atoms of a polyatomic ion are held together by covalent bonds. In this section we shall discuss how ions can be formed from individual atoms; polyatomic ions will be discussed along with other covalently bonded species.

Ionic bonding is the attraction of oppositely charged ions (cations and anions) in large numbers to form a solid. Such a solid compound is called an *ionic solid*.

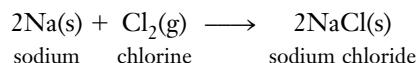
As our previous discussions of ionization energy, electronegativity, and electron affinity would suggest, ionic bonding can occur easily when elements that have low ionization energies (metals) react with elements having high electronegativities and very negative electron affinities (nonmetals). Many metals are easily *oxidized*—that is, they lose electrons to form cations; and many nonmetals are readily *reduced*—that is, they gain electrons to form anions.

When the electronegativity difference, $\Delta(\text{EN})$, between two elements is large, as between a metal and a nonmetal, the elements are likely to form a compound by ionic bonding (transfer of electrons).

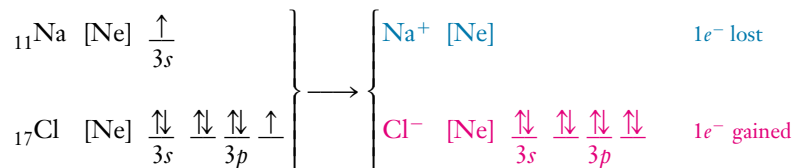
Let us describe some combinations of metals with nonmetals to form ionic compounds.

Group IA Metals and Group VIIA Nonmetals

Consider the reaction of sodium (a Group IA metal) with chlorine (a Group VIIA nonmetal). Sodium is a soft silvery metal (mp 98°C), and chlorine is a yellowish-green corrosive gas at room temperature. Both sodium and chlorine react with water, sodium vigorously. By contrast, sodium chloride is a white solid (mp 801°C) that dissolves in water with no reaction and with the absorption of just a little heat. We can represent the reaction for its formation as



We can understand this reaction better by showing electron configurations for all species. We represent chlorine as individual atoms rather than molecules, for simplicity.



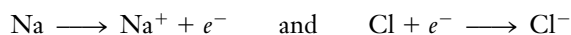
Freshly cut sodium has a metallic luster. A little while after being cut, the sodium metal surface turns white as it reacts with the air.

Some ionic compounds. Clockwise from front right: sodium chloride (NaCl, *white*); copper(II) sulfate pentahydrate (CuSO₄·5H₂O, *blue*); nickel(II) chloride hexahydrate (NiCl₂·6H₂O, *green*); potassium dichromate (K₂Cr₂O₇, *orange*); and cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, *red*). One mole of each substance is shown.

The loss of electrons is *oxidation* (Section 4-5). Na atoms are *oxidized* to form Na^+ ions.

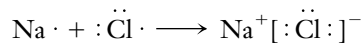
The gain of electrons is *reduction* (Section 4-5). Cl atoms are *reduced* to form Cl^- ions.

In this reaction, Na atoms lose one electron each to form Na^+ ions, which contain only ten electrons, the same number as the *preceding* noble gas, neon. We say that sodium ions have the neon electronic structure: Na^+ is *isoelectronic* with Ne (Section 6-5). In contrast, Cl atoms gain one electron each to form Cl^- ions, which contain 18 electrons. This is the same number as the *following* noble gas, argon; Cl^- is *isoelectronic* with Ar. These processes can be represented compactly as



Similar observations apply to most ionic compounds formed by reactions between *representative metals and representative nonmetals*.

We can use Lewis dot formulas (Section 7-1) to represent the reaction.



The formula for sodium chloride is NaCl because the compound contains Na^+ and Cl^- in a 1:1 ratio. This is the formula we predict based on the fact that each Na atom contains only one electron in its outermost occupied shell and each Cl atom needs only one electron to fill completely its outermost *p* orbitals.

The chemical formula NaCl does not explicitly indicate the ionic nature of the compound, only the ratio of ions. Furthermore, values of electronegativities are not always available. So we must learn to recognize, from positions of elements in the periodic table and known trends in electronegativity, when the difference in electronegativity is large enough to favor ionic bonding.

The noble gases are excluded from this generalization.

The farther apart across the periodic table two Group A elements are, the more ionic their bonding will be.

Formulas for some of these are

LiF	NaF	KF
LiCl	NaCl	KCl
LiBr	NaBr	KBr
LiI	NaI	KI

Coulomb's Law is $F \propto \frac{q^+ q^-}{d^2}$. The symbol \propto means "is proportional to."

The greatest difference in electronegativity occurs from the lower left to upper right, so CsF ($\Delta[\text{EN}] = 3.2$) is more ionic than LiI ($\Delta[\text{EN}] = 1.5$).

All the Group IA metals (Li, Na, K, Rb, Cs) will react with the Group VIIA elements (F, Cl, Br, I) to form ionic compounds of the same general formula, MX. All the resulting ions, M^+ and X^- , have noble gas configurations. Once we understand the bonding of one member of a group (column) in the periodic table, we know a great deal about the others in the family. Combining each of the five common alkali metals with each of the four common halogens gives $5 \times 4 = 20$ possible compounds. The discussion of NaCl presented here applies also to the other 19 such compounds.

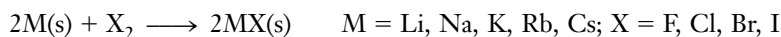
The collection of isolated positive and negative ions occurs at a higher energy than the elements from which they are formed. The ion formation alone is not sufficient to account for the formation of ionic compounds. Some other favorable factor must account for the observed stability of these compounds. Because of the opposite charges on Na^+ and Cl^- , an attractive force is developed. According to Coulomb's Law, the force of attraction, *F*, between two oppositely charged particles of charge magnitudes q^+ and q^- is directly proportional to the product of the charges and inversely proportional to the square of the distance separating their centers, *d*. Thus, the greater the charges on the ions and the smaller the ions are, the stronger the resulting ionic bonding. Of course, like-charged ions repel each other, so the distances separating the ions in ionic solids are those at which the attractions exceed the repulsions by the greatest amount.

The energy associated with the attraction of separated gaseous positive and negative ions to form an ionic solid is the *crystal lattice energy* of the solid. For NaCl, this energy

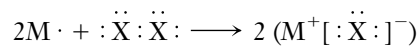
is -789 kJ/mol; that is, one mole of NaCl solid is 789 kJ lower in energy (*more stable*) than one mole of isolated Na^+ ions and one mole of isolated Cl^- ions. We could also say that it would require 789 kJ of energy to separate one mole of NaCl solid into isolated gaseous ions. The stability of ionic compounds is thus due to the interplay of the energy cost of ion formation and the energy repaid by the crystal lattice energy. The best trade-off usually comes when the monatomic ions of representative elements have noble gas configurations.

The structure of common table salt, sodium chloride (NaCl), is shown in Figure 7-1. Like other simple ionic compounds, NaCl(s) exists in a regular, extended array of positive and negative ions, Na^+ and Cl^- . Distinct molecules of solid ionic substances do not exist, so we must refer to *formula units* (Section 2-3) instead of molecules. The forces that hold all the particles together in an ionic solid are quite strong. This explains why such substances have quite high melting and boiling points (a topic that we will discuss more fully in Chapter 13). When an ionic compound is melted or dissolved in water, its charged particles are free to move in an electric field, so such a liquid shows high electrical conductivity (Section 4-2, part 1).

We can represent the general reaction of the IA metals with the VIIA elements as follows:

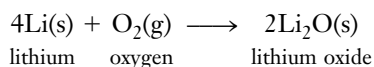


The Lewis dot representation for the generalized reaction is

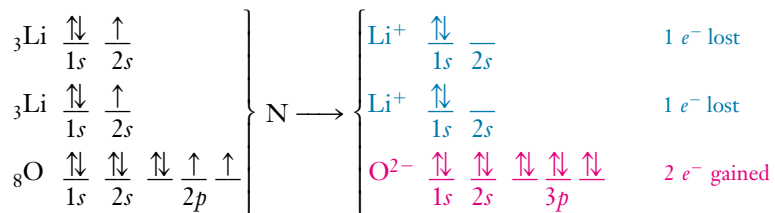


Group IA Metals and Group VIA Nonmetals

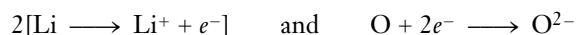
Next, consider the reaction of lithium (Group IA) with oxygen (Group VIA) to form lithium oxide, a solid ionic compound (mp $> 1700^\circ\text{C}$) (see next page). We may represent the reaction as



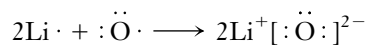
The formula for lithium oxide, Li_2O , indicates that two atoms of lithium combine with one atom of oxygen. If we examine the structures of the atoms before reaction, we can see the reason for this ratio.



In a compact representation,



The Lewis dot formulas for the atoms and ions are



Lithium ions, Li^+ , are isoelectronic with helium atoms ($2 e^-$). Oxide ions, O^{2-} , are isoelectronic with neon atoms ($10 e^-$).

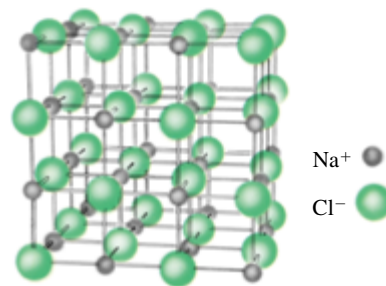


Figure 7-1 A representation of the crystal structure of NaCl. Each Cl^- ion (*green*) is surrounded by six sodium ions, and each Na^+ ion (*gray*) is surrounded by six chloride ions. Any NaCl crystal includes billions of ions in the pattern shown. Adjacent ions actually are in contact with one another; in this drawing, the structure has been expanded to show the spatial arrangement of ions. The lines *do not* represent covalent bonds. Compare with Figure 2-7, a space-filling drawing of the NaCl structure.

Although the oxides of the other Group IA metals are prepared by different methods, similar descriptions apply to compounds between the Group IA metals (Li, Na, K, Rb, Cs) and the Group VIA nonmetals (O, S, Se, Te, Po).

Each Li atom has $1 e^-$ in its valence shell, one more e^- than a noble gas configuration, [He]. Each O atom has $6 e^-$ in its valence shell and needs $2 e^-$ more to attain a noble gas configuration [Ne]. The Li^+ ions are formed by oxidation of Li atoms, and the O^{2-} ions are formed by reduction of O atoms.

Isoelectronic species have the same number of electrons (see Section 6-5). Some isoelectronic species:

O^{2-}	8 protons	10 electrons
F^-	9 protons	10 electrons
Ne	10 protons	10 electrons
Na^+	11 protons	10 electrons
Mg^{2+}	12 protons	10 electrons



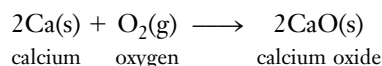
Lithium is a metal, as the shiny surface of freshly cut Li shows. Where it has been exposed to air, the surface is covered with lithium oxide.

This discussion also applies to other ionic compounds between any Group IIA metal (Be, Mg, Ca, Sr, Ba) and any Group VIA nonmetal (O, S, Se, Te).

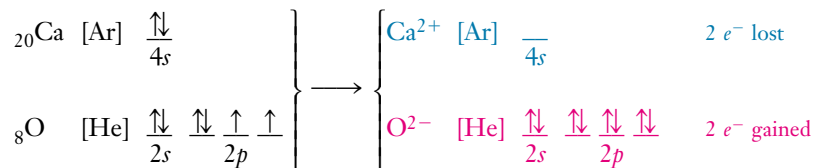
The very small size of the Li^+ ion gives it a much higher *charge density* (ratio of charge to size) than that of the larger Na^+ ion (Figure 6-1). Similarly, the O^{2-} ion is smaller than the Cl^- ion, so its smaller size and double negative charge give it a much higher charge density. These more concentrated charges and smaller sizes bring the Li^+ and O^{2-} ions closer together in Li_2O than the Na^+ and Cl^- ions are in NaCl . Consequently, the q^+q^- product in the numerator of Coulomb's Law is greater in Li_2O , and the d^2 term in the denominator is smaller. The net result is that the ionic bonding is much stronger (the lattice energy is much more negative) in Li_2O than in NaCl . This is consistent with the higher melting temperature of Li_2O ($>1700^\circ\text{C}$) compared to NaCl (801°C).

Group IIA Metals and Group VIA Nonmetals

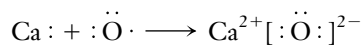
As our final illustration of ionic bonding, consider the reaction of calcium (Group IIA) with oxygen (Group VIA). This reaction forms calcium oxide, a white solid ionic compound with a very high melting point, 2580°C .



Again, we show the electronic structure of the atoms and ions, representing the inner electrons by the symbol of the preceding noble gas.



The Lewis dot notation for the reacting atoms and the resulting ions is



Calcium ions, Ca^{2+} , are isoelectronic with argon ($18 e^-$), the preceding noble gas. Oxide ions, O^{2-} , are isoelectronic with neon ($10 e^-$), the following noble gas.

Ca^{2+} is about the same size as Na^+ (see Figure 6-1) but carries twice the charge, so its charge density is higher. Because the attraction between the two small, highly charged ions Ca^{2+} and O^{2-} is quite high, the ionic bonding is very strong, accounting for the very high melting point of CaO , 2580°C .

Binary Ionic Compounds: A Summary

Table 7-2 summarizes the general formulas of binary ionic compounds formed by the representative elements. "M" represents metals, and "X" represents nonmetals from the indicated groups. In these examples of ionic bonding, each of the metal atoms has lost one, two, or three electrons, and each of the nonmetal atoms has gained one, two, or three electrons. *Simple (monatomic) ions rarely have charges greater than 3+ or 3-*. Ions with greater charges would interact so strongly with the electron clouds of other ions that the electron clouds would be very distorted, and considerable covalent character in the bonds would result. Distinct molecules of solid ionic substances do not exist. The sum of the attractive forces of all the interactions in an ionic solid is substantial. Therefore, binary ionic compounds have high melting and boiling points.

The *d*- and *f*-transition elements form many compounds that are essentially ionic in character. Many simple ions of transition metals do not have noble gas configurations.

Binary compounds contain *two* elements.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 8.8, Electron Configurations in Ions.

The distortion of the electron cloud of an anion by a small, highly charged cation is called *polarization*.

TABLE 7-2 Simple Binary Ionic Compounds

Metal		Nonmetal		General Formula	Ions Present	Example	mp (°C)
IA*	+	VIIA	→	MX	(M ⁺ , X ⁻)	LiBr	547
IIA	+	VIIA	→	MX ₂	(M ²⁺ , 2X ⁻)	MgCl ₂	708
IIIA	+	VIIA	→	MX ₃	(M ³⁺ , 3X ⁻)	GaF ₃	800 (subl)
IA [†]	+	VIA	→	M ₂ X	(2M ⁺ , X ²⁻)	Li ₂ O	>1700
IIA	+	VIA	→	MX	(M ²⁺ , X ²⁻)	CaO	2580
IIA	+	VIA	→	M ₂ X ₃	(2M ³⁺ , 3X ²⁻)	Al ₂ O ₃	2045
IA*	+	VA	→	M ₃ X	(3M ⁺ , X ³⁻)	Li ₃ N	840
IIA	+	VA	→	M ₃ X ₂	(3M ²⁺ , 2X ³⁻)	Ca ₃ P ₂	≈1600
IIIA	+	VA	→	MX	(M ³⁺ , X ³⁻)	AlP	

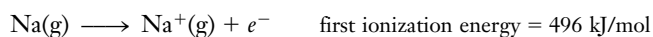
*Hydrogen is a nonmetal. All binary compounds of hydrogen are covalent, except for certain metal hydrides such as NaH and CaH₂, which contain hydride, H⁻, ions.

†As we saw in Section 6-8, the metals in Groups IA and IIA also commonly form peroxides (containing the O₂²⁻ ion) or superoxides (containing the O₂⁻ ion). See Table 6-4. The peroxide and superoxide ions contain atoms that are covalently bonded to one another.

Introduction to Energy Relationships in Ionic Bonding

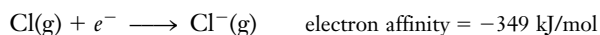
The following discussion may help you to understand why ionic bonding occurs between elements with low ionization energies and those with high electronegativities. There is a general tendency in nature to achieve stability. One way to do this is by lowering potential energy; lower energies generally represent *more stable* arrangements.

Let us use energy relationships to describe why the ionic solid NaCl is more stable than a mixture of individual Na and Cl atoms. Consider a gaseous mixture of one mole of sodium atoms and one mole of chlorine atoms, Na(g) + Cl(g). The energy change associated with the loss of one mole of electrons by one mole of Na atoms to form one mole of Na⁺ ions (step 1 in Figure 7-2) is given by the *first ionization energy* of Na (see Section 6-3).



This is a positive value, so the mixture Na⁺(g) + e⁻ + Cl(g) is 496 kJ/mol higher in energy than the original mixture of atoms (the mixture Na⁺ + e⁻ + Cl is *less stable* than the mixture of atoms).

The energy change for the gain of one mole of electrons by one mole of Cl atoms to form one mole of Cl⁻ ions (step 2) is given by the *electron affinity* of Cl (see Section 6-4).




This negative value, -349 kJ/mol, lowers the energy of the mixture, but the mixture of separated ions, Na⁺ + Cl⁻, is still *higher* in energy (*less stable*) by (496 - 349) kJ/mol = 147 kJ/mol than the original mixture of atoms (the red arrow in Figure 7-2). Thus, just the formation of ions does not explain why the process occurs. The strong attractive force between ions of opposite charge draws the ions together into the regular array shown in Figure 7-1. The energy associated with this attraction (step 3) is the *crystal lattice energy* of NaCl, -789 kJ/mol.



The crystal (solid) formation thus further *lowers* the energy to (147 - 789) kJ/mol = -642 kJ/mol. The overall result is that one mole of NaCl(s) is 642 kJ/mol lower in energy



 See the Saunders Interactive General Chemistry CD-ROM, Screen 8.17, Lattice Energy.

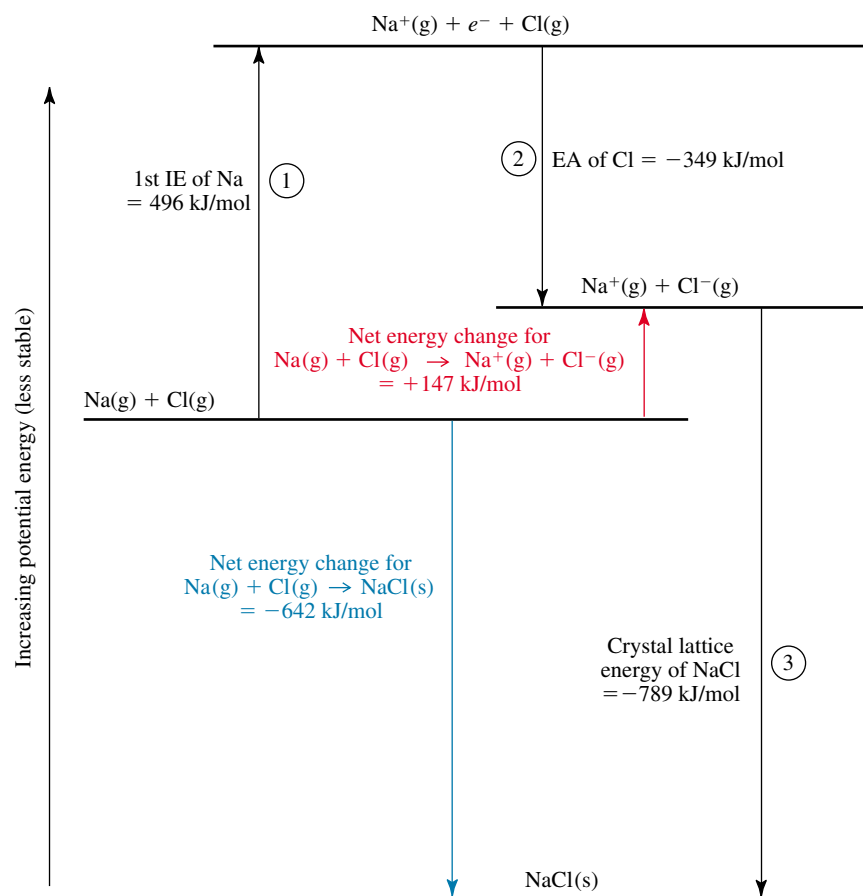
(Enrichment, continued)

Figure 7-2 A schematic representation of the energy changes that accompany the process $\text{Na}(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{NaCl}(\text{s})$. The red arrow represents the *positive* energy change (unfavorable) for the process of ion formation, $\text{Na}(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$. The blue arrow represents the *negative* energy change (favorable) for the overall process, including the formation of the ionic solid.

(more stable) than the original mixture of atoms (the blue arrow in Figure 7-2). Thus, we see that a major driving force for the formation of ionic compounds is the large electrostatic stabilization due to the attraction of the ionic charges (step 3).

In this discussion we have not taken into account the fact that sodium is a solid metal or that chlorine actually exists as diatomic molecules. The additional energy changes involved when these are changed to gaseous Na and Cl atoms, respectively, are small enough that the overall energy change starting from $\text{Na}(\text{s})$ and $\text{Cl}_2(\text{g})$ is still negative.

COVALENT BONDING

Ionic bonding cannot result from a reaction between two nonmetals, because their electronegativity difference is not great enough for electron transfer to take place. Instead, reactions between two nonmetals result in *covalent bonding*.

A **covalent bond** is formed when two atoms share one or more pairs of electrons. Covalent bonding occurs when the electronegativity difference, $\Delta(\text{EN})$, between elements (atoms) is zero or relatively small.

In predominantly covalent compounds the bonds between atoms *within* a molecule (*intramolecular* bonds) are relatively strong, but the forces of attraction *between* molecules (*intermolecular* forces) are relatively weak. As a result, covalent compounds have lower melting and boiling points than ionic compounds. The relation of bonding types to physical properties of liquids and solids will be developed more fully in Chapter 13.

7-3 FORMATION OF COVALENT BONDS

Let us look at the simplest case of covalent bonding, the reaction of two hydrogen atoms to form the diatomic molecule H_2 . As you recall, an isolated hydrogen atom has the ground state electron configuration $1s^1$, with the probability density for this one electron spherically distributed about the hydrogen nucleus (Figure 7-3a). As two hydrogen atoms approach each other, the electron of each hydrogen atom is attracted by the nucleus of the *other* hydrogen atom as well as by its own nucleus (Figure 7-3b). If these two electrons have opposite spins so that they can occupy the same region (orbital), both electrons can now preferentially occupy the region *between* the two nuclei (Figure 7-3c), because they are attracted by both nuclei. The electrons are *shared* between the two hydrogen atoms, and a single covalent bond is formed. We say that the $1s$ orbitals *overlap* so that both electrons are now in the orbitals of both hydrogen atoms. The closer together the atoms come, the more nearly this is true. In that sense, each hydrogen atom then has the helium configuration $1s^2$.

The bonded atoms are at lower energy (more stable) than the separated atoms. This is shown in the plot of energy versus distance in Figure 7-4. As the two atoms get closer together, however, the two nuclei, being positively charged, exert an increasing repulsion on each other. At some distance, a minimum energy, -435 kJ/mol, is reached; it corresponds to the most stable arrangement and occurs at 0.74 Å, the actual distance between two hydrogen nuclei in an H_2 molecule. At greater internuclear separation, the repulsive forces diminish, but the attractive forces decrease even faster. At smaller separations, repulsive forces increase more rapidly than attractive forces. The magnitude of this stabilization

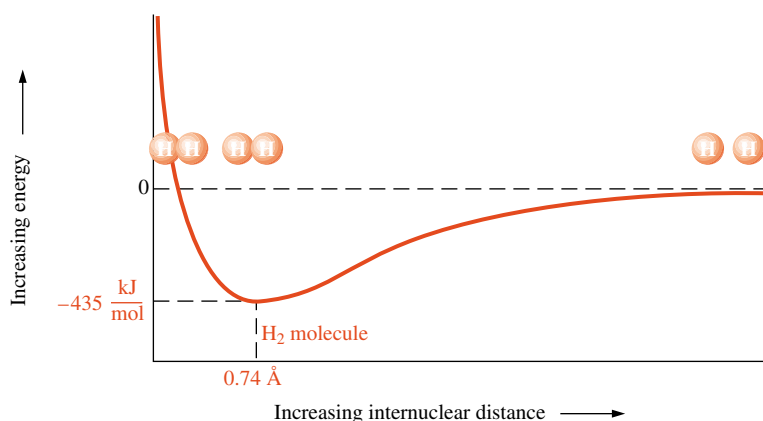


Figure 7-4 The potential energy of the H_2 molecule as a function of the distance between the two nuclei. The lowest point in the curve, -435 kJ/mol, corresponds to the internuclear distance actually observed in the H_2 molecule, 0.74 Å. (The minimum potential energy, -435 kJ/mol, corresponds to the value of -7.23×10^{-19} joule per H_2 molecule.) Energy is compared with that of two separated hydrogen atoms.

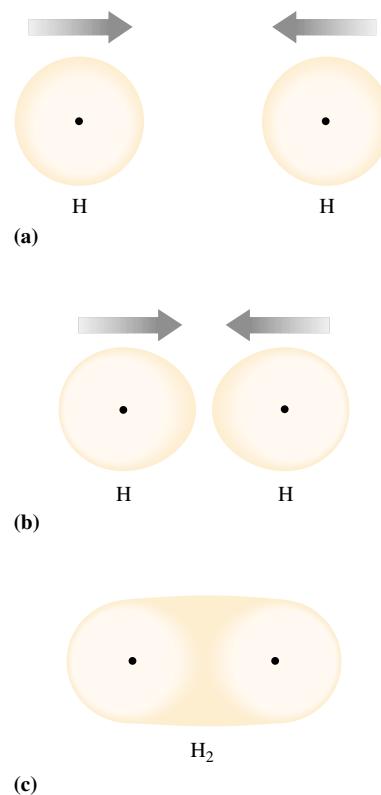



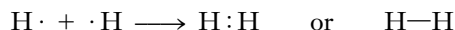
Figure 7-3 A representation of the formation of a covalent bond between two hydrogen atoms. The position of each positively charged nucleus is represented by a black dot. Electron density is indicated by the depth of shading. (a) Two hydrogen atoms separated by a large distance. (b) As the atoms approach each other, the electron of each atom is attracted by the positively charged nucleus of the other atom, so the electron density begins to shift. (c) The two electrons can both occupy the region where the two $1s$ orbitals overlap; the electron density is highest in the region between the nuclei of the two atoms.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 9.3, Chemical Bond Formation: Covalent Bonding, and Screen 10.3, Valence Bond Theory.

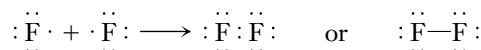
is called the H—H *bond energy*. Bond energies for covalent bonds will be discussed more extensively in Section 15-9.

Other pairs of nonmetal atoms share electron pairs to form covalent bonds. The result of this sharing is that each atom attains a more stable electron configuration—frequently the same as that of the nearest noble gas. This results in a more stable arrangement for the bonded atoms. (This is discussed in Section 7-5.) Most covalent bonds involve sharing of two, four, or six electrons—that is, one, two, or three *pairs* of electrons. Two atoms form a **single covalent bond** when they share one pair of electrons, a **double covalent bond** when they share two electron pairs, and a **triple covalent bond** when they share three electron pairs. These are usually called simply *single*, *double*, and *triple* bonds. Covalent bonds that involve sharing of one and three electrons are known, but are relatively rare.

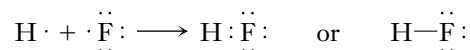
In a Lewis formula, we represent a covalent bond by writing *each shared electron pair* either as a pair of two dots between the two atom symbols or as a dash connecting them. Thus, the formation of H₂ from H atoms could be represented as



where the dash represents a single bond. Similarly, the combination of two fluorine atoms to form a molecule of fluorine, F₂, can be shown as



The formation of a hydrogen fluoride, HF, molecule from a hydrogen atom and a fluorine atom can be shown as




We will see many more examples of this representation.

In our discussion, we have postulated that bonds form by the **overlap** of two atomic orbitals. This is the essence of the **valence bond theory**, which we will describe in more detail in the next chapter. Another theory, **molecular orbital theory**, is discussed in Chapter 9. For now, let us concentrate on the *number* of electron pairs shared and defer the discussion of *which* orbitals are involved in the sharing until the next chapter.

The bonding in the other halogens, Cl₂, Br₂, and I₂, is analogous to that in F₂.

The bonding in gaseous HCl, HBr, and HI is analogous to that in HF.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 9.4, Lewis Electron Dot Structures.

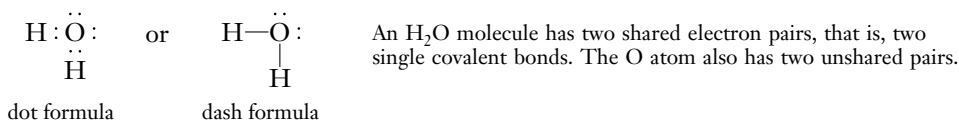
In H₂O, two of the six valence electrons of an oxygen atom are used in covalent bonding; the one valence electron of each hydrogen atom is used in covalent bonding.

In CO₂, the four valence electrons of a carbon atom are used in covalent bonding; two of the six valence electrons of each oxygen atom are used in covalent bonding.

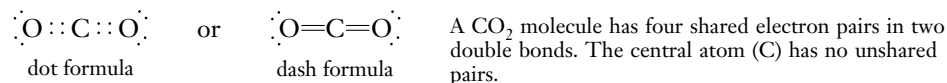
A polyatomic ion is an ion that contains more than one atom.

7-4 LEWIS FORMULAS FOR MOLECULES AND POLYATOMIC IONS

In Sections 7-1 and 7-2 we drew *Lewis formulas* for atoms and monatomic ions. In Section 7-3, we used Lewis formulas to show the *valence electrons* in three simple molecules. A water molecule can be represented by either of the following diagrams.

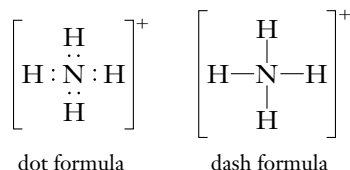


In *dash formulas*, a shared pair of electrons is indicated by a dash. There are two *double* bonds in carbon dioxide, and its Lewis formula is

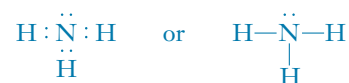


The covalent bonds in a polyatomic ion can be represented in the same way. The Lewis formula for the ammonium ion, NH₄⁺, shows only eight electrons, even though the N atom has five electrons in its valence shell and each H atom has one, for a total of

$5 + 4(1) = 9$ electrons. The NH_4^+ ion, with a charge of $1+$, has one less electron than the original atoms.



The NH_3 molecule, like the NH_4^+ ion, has eight valence electrons about the N atom.



The writing of Lewis formulas is an electron bookkeeping method that is useful as a first approximation to suggest bonding schemes. It is important to remember that Lewis dot formulas only show the number of valence electrons, the number and kinds of bonds, and the order in which the atoms are connected. *They are not intended to show the three-dimensional shapes of molecules and polyatomic ions.* We will see in Chapter 8, however, that the three-dimensional geometry of a molecule can be predicted from its Lewis formula.

7-5 THE OCTET RULE

Representative elements usually attain stable noble gas electron configurations when they share electrons. In the water molecule eight electrons are in the outer shell of the O atom, and it has the neon electron configuration; two electrons are in the valence shell of each H atom, and each has the helium electron configuration. Likewise, the C and O of CO_2 and the N of NH_3 and the NH_4^+ ion each have a share in eight electrons in their outer shells. The H atoms in NH_3 and NH_4^+ each share two electrons. Many Lewis formulas are based on the idea that

in *most* of their compounds, the representative elements achieve noble gas configurations.

In some compounds, the central atom does not achieve a noble gas configuration. Such exceptions to the octet rule are discussed in Section 7-7.

This statement is usually called the **octet rule**, because the noble gas configurations have $8 e^-$ in their outermost shells (except for He, which has $2 e^-$).

For now, we restrict our discussion to compounds of the *representative elements*. The octet rule alone does not let us write Lewis formulas. We still must decide how to place the electrons around the bonded atoms—that is, how many of the available valence electrons are **bonding electrons** (shared) and how many are **unshared electrons** (associated with only one atom). A pair of unshared electrons in the same orbital is called a **lone pair**. A simple mathematical relationship is helpful here:

The representative elements are those in the A groups of the periodic table.

$$S = N - A$$

S is the total number of electrons *shared* in the molecule or polyatomic ion.

N is the total number of valence shell electrons *needed* by all the atoms in the molecule or ion to achieve noble gas configurations ($N = 8 \times$ number of atoms that are not H, plus $2 \times$ number of H atoms).

A is the number of electrons *available* in the valence shells of all of the (representative) atoms. This is equal to the sum of their periodic group numbers. We must adjust A , if necessary, for ionic charges. We add electrons to account for negative charges and subtract electrons to account for positive charges.

Let us see how this relationship applies to some species whose Lewis formulas we have already shown.

For F_2 ,

$$N = 2 \times 8 \text{ (for two F atoms)} = 16 e^- \text{ needed}$$

$$A = 2 \times 7 \text{ (for two F atoms)} = 14 e^- \text{ available}$$

$$S = N - A = 16 - 14 = 2 e^- \text{ shared}$$



The Lewis formula for F_2 shows 14 valence electrons total, with $2 e^-$ shared in a single bond.

For HF,

$$N = 1 \times 2 \text{ (for one H atom)} + 1 \times 8 \text{ (for one F atom)} = 10 e^- \text{ needed}$$

$$A = 1 \times 1 \text{ (for one H atom)} + 1 \times 7 \text{ (for one F atom)} = 8 e^- \text{ available}$$

$$S = N - A = 10 - 8 = 2 e^- \text{ shared}$$



The Lewis formula for HF shows 8 valence electrons total, with $2 e^-$ shared in a single bond.

For H_2O ,

$$N = 2 \times 2 \text{ (for two H atoms)} + 1 \times 8 \text{ (for one O atom)} = 12 e^- \text{ needed}$$

$$A = 2 \times 1 \text{ (for two H atoms)} + 1 \times 6 \text{ (for one O atom)} = 8 e^- \text{ available}$$

$$S = N - A = 12 - 8 = 4 e^- \text{ shared}$$



The Lewis formula for H_2O shows 8 valence electrons total, with a total of $4 e^-$ shared, $2 e^-$ in each single bond.

For CO_2 ,

$$N = 1 \times 8 \text{ (for one C atom)} + 2 \times 8 \text{ (for two O atoms)} = 24 e^- \text{ needed}$$

$$A = 1 \times 4 \text{ (for one C atom)} + 2 \times 6 \text{ (for two O atoms)} = 16 e^- \text{ available}$$

$$S = N - A = 24 - 16 = 8 e^- \text{ shared}$$



The Lewis formula for CO_2 shows 16 valence electrons total, with a total of $8 e^-$ shared, $4 e^-$ in each double bond.

For NH_4^+ ,

$$N = 1 \times 8 \text{ (for one N atom)} + 4 \times 2 \text{ (for four H atoms)} = 16 e^- \text{ needed}$$

$$A = 1 \times 5 \text{ (for one N atom)} + 4 \times 1 \text{ (for four H atoms)} - 1 \text{ (for } 1+ \text{ charge)} = 8 e^- \text{ available}$$

$$S = N - A = 16 - 8 = 8 e^- \text{ shared}$$

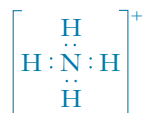
The Lewis formula for NH_4^+ shows 8 valence electrons total, with all $8 e^-$ shared, $2 e^-$ in each single bond.

The following general steps describe the use of the $S = N - A$ relationship in constructing dot formulas for molecules and polyatomic ions.

Writing Lewis Formulas

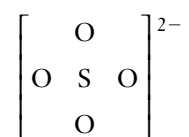
1. Select a reasonable (symmetrical) “skeleton” for the molecule or polyatomic ion.
 - a. The *least electronegative element* is usually the central element, except that H is never the central element, because it forms only one bond. The least elec-

The $1+$ ionic charge is due to a deficiency of one e^- relative to the neutral atoms.

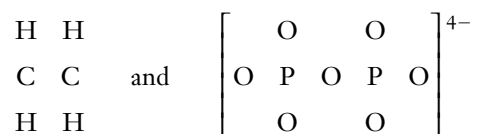


tronegative element is usually the one that needs the most electrons to fill its octet. Example: CS_2 has the skeleton $\text{S}-\text{C}-\text{S}$.

- b. Oxygen atoms do not bond to each other except in (1) O_2 and O_3 molecules; (2) hydrogen peroxide, H_2O_2 , and its derivatives, the peroxides, which contain the O_2^{2-} group; and (3) the rare superoxides, which contain the O_2^- group. Example: The sulfate ion, SO_4^{2-} , has the skeleton



- c. In *ternary oxoacids*, hydrogen usually bonds to an O atom, *not* to the central atom. Example: nitrous acid, HNO_2 , has the skeleton $\text{H}-\text{O}-\text{N}-\text{O}$. There are a few exceptions to this guideline, such as H_3PO_3 and H_3PO_2 .
- d. For ions or molecules that have more than one central atom, the most symmetrical skeletons possible are used. Examples: C_2H_4 and $\text{P}_2\text{O}_7^{4-}$ have the following skeletons:



A ternary oxoacid contains *three* elements—H, O, and another element, often a nonmetal.

2. Calculate N , the number of valence (outer) shell electrons needed by all atoms in the molecule or ion to achieve noble gas configurations. Examples:

For H_2SO_4 ,

$$N = 2 \times 2 \text{ (H atoms)} + 1 \times 8 \text{ (S atom)} + 4 \times 8 \text{ (O atoms)} = 4 + 8 + 32 = 44 e^- \text{ needed}$$

For ClO_4^- ,

$$N = 8 \text{ (Cl atoms)} + 32 \text{ (O atoms)} = 40 e^- \text{ needed}$$

For NO_3^- ,

$$N = 1 \times 8 \text{ (N atom)} + 3 \times 8 \text{ (O atoms)} = 32 e^- \text{ needed}$$

Calculate A , the number of electrons available in the valence (outer) shells of all the atoms. For negatively charged ions, add to this total the number of electrons equal to the charge on the anion; for positively charged ions, subtract the number of electrons equal to the charge on the cation. Examples:

For H_2SO_4 ,

$$A = 2 \times 1 \text{ (H atoms)} + 1 \times 6 \text{ (S atom)} + 4 \times 6 \text{ (O atoms)} = 2 + 6 + 24 = 32 e^- \text{ available}$$

For ClO_4^- ,

$$A = 1 \times 7 \text{ (Cl atom)} + 4 \times 6 \text{ (O atoms)} + 1 \text{ (for } 1^- \text{ charge)} = 7 + 24 + 1 = 32 e^- \text{ available}$$

For NO_3^- ,

$$A = 1 \times 5 \text{ (N atom)} + 3 \times 6 \text{ (O atoms)} + 1 \text{ (for } 1^- \text{ charge)} = 5 + 18 + 1 = 24 e^- \text{ available}$$

Calculate S , total number of electrons shared in the molecule or ion, using the relationship $S = N - A$. Examples:

For compounds containing only representative elements, N is equal to $8 \times$ number of atoms that are *not* H, plus $2 \times$ number of H atoms.

For the representative elements, the number of valence shell electrons in an atom is equal to its periodic group number. Exceptions: 1 for an H atom and 2 for He.

For H_2SO_4 ,

$$\begin{aligned} S &= N - A = 44 - 32 \\ &= 12 \text{ electrons shared (6 pairs of } e^- \text{ shared)} \end{aligned}$$

For ClO_4^- ,

$$\begin{aligned} S &= N - A = 40 - 32 \\ &= 8 \text{ electrons shared (4 pairs of } e^- \text{ shared)} \end{aligned}$$

For NO_3^- ,

$$S = N - A = 32 - 24 = 8 e^- \text{ shared (4 pairs of } e^- \text{ shared)}$$

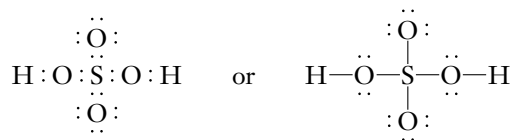
C, N, and O often form double and triple bonds. S can form double bonds with C, N, and O.

3. Place the S electrons into the skeleton as *shared pairs*. Use double and triple bonds only when necessary. Lewis formulas may be shown as either dot formulas or dash formulas.

Formula	Skeleton	Dot Formula ("bonds" in place, but incomplete)	Dash Formula ("bonds" in place, but incomplete)
H_2SO_4	$\begin{array}{c} \text{O} \\ \text{H O S O H} \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \text{H : O : } \ddot{\text{S}} \text{ : O : H} \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \text{H - O - S - O - H} \\ \text{O} \end{array}$
ClO_4^-	$\left[\begin{array}{c} \text{O} \\ \text{O Cl O} \\ \text{O} \end{array} \right]^-$	$\left[\begin{array}{c} \text{O} \\ \text{O : Cl : O} \\ \text{O} \end{array} \right]^-$	$\left[\begin{array}{c} \text{O} \\ \text{O - Cl - O} \\ \text{O} \end{array} \right]^-$
NO_3^-	$\left[\begin{array}{c} \text{O} \\ \text{O N O} \\ \text{O} \end{array} \right]^-$	$\left[\begin{array}{c} \text{O} \\ \text{O : N : O} \\ \text{O} \end{array} \right]^-$	$\left[\begin{array}{c} \text{O} \\ \text{O - N = O} \\ \text{O} \end{array} \right]^-$

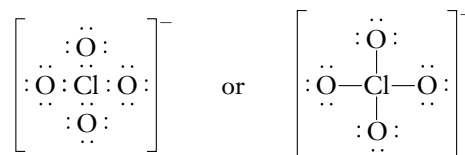
4. Place the additional electrons into the skeleton as *unshared (lone) pairs* to fill the octet of every A group element (except H, which can share only $2 e^-$). Check that the total number of electrons is equal to A , from step 2. Examples:

For H_2SO_4 ,



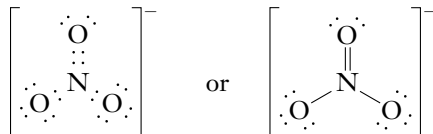
Check: 16 pairs of e^- have been used and all octets are satisfied. $2 \times 16 = 32 e^-$ available.

For ClO_4^- ,




Check: 16 pairs of e^- have been used and all octets are satisfied. $2 \times 16 = 32 e^-$ available.

For NO_3^- ,



Check: 12 pairs of e^- have been used and all octets are satisfied. $2 \times 12 = 24 e^-$ available.

 For a slightly different approach than the one used in this text, see the *Saunders Interactive General Chemistry CD-ROM*, Screen 9.5, Drawing Lewis Structures.

 **Problem-Solving Tip:** Be Careful of the Total Number of Electrons

A very common error in writing Lewis formulas is showing the wrong number of electrons. Always make a final check to be sure that the Lewis formula you write shows the same number of electrons you calculated as A .

EXAMPLE 7-1 Writing Lewis Formulas

Write the Lewis formula for the nitrogen molecule, N_2 .

Plan

We follow the stepwise procedure that was just presented for writing Lewis formulas.

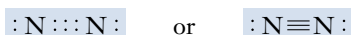
Solution

Step 1: The skeleton is N N.

Step 2: $N = 2 \times 8 = 16 e^-$ needed (total) by both atoms
 $A = 2 \times 5 = 10 e^-$ available (total) for both atoms
 $S = N - A = 16 e^- - 10 e^- = 6 e^-$ shared

Step 3: $\text{N}::\text{N}$ $6 e^-$ (3 pairs) are shared; a *triple* bond.

Step 4: The additional $4 e^-$ are accounted for by a lone pair on each N. The complete Lewis formula is



Check: 10 e^- (5 pairs) have been used.

EXAMPLE 7-2 Writing Lewis Formulas

Write the Lewis formula for carbon disulfide, CS_2 , a foul-smelling liquid.

Plan

Again, we follow the stepwise procedure to apply the relationship $S = N - A$.

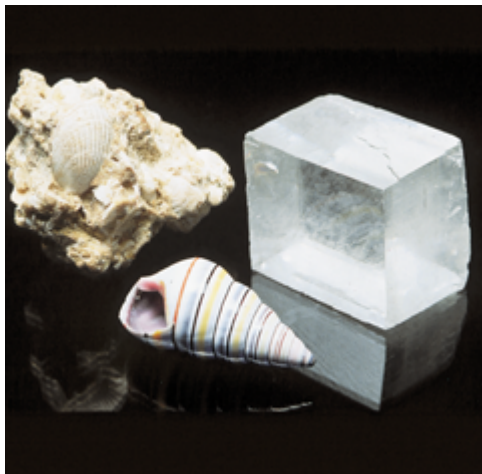
Solution

Step 1: The skeleton is S C S.

Step 2: $N = 1 \times 8$ (for C) + 2×8 (for S) = $24 e^-$ needed by all atoms
 $A = 1 \times 4$ (for C) + 2×6 (for S) = $16 e^-$ available
 $S = N - A = 24 e^- - 16 e^- = 8 e^-$ shared

Step 3: $\text{S} : \text{C} : \text{S}$ $8 e^-$ (4 pairs) are shared; two *double* bonds.

C is the central atom, or the element in the middle of the molecule. It needs four more electrons to acquire an octet, and each S atom needs only two more electrons.



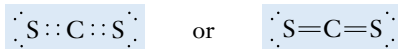
Calcium carbonate, CaCO_3 , occurs in several forms in nature. The mineral calcite forms very large clear crystals (*right*); in microcrystalline form it is the main constituent of limestone (*top left*). Seashells (*bottom*) are largely calcium carbonate.



Acetylene burns in oxygen with a flame so hot that it is used to weld metals.

For practice, apply the methods of this section to write these Lewis formulas.

Step 4: C already has an octet, so the remaining $8 e^-$ are distributed as lone pairs on the S atoms to give each S an octet. The complete Lewis formula is



Check: $16 e^-$ (8 pairs) have been used. The bonding picture is similar to that of CO_2 ; this is not surprising, because S is below O in Group VIA.

You should now work Exercise 29.

EXAMPLE 7-3 Writing Lewis Formulas

Write the Lewis formula for the carbonate ion, CO_3^{2-} .

Plan

The same stepwise procedure can be applied to ions. We must remember to adjust A , the total number of electrons, to account for the charge shown on the ion.

Solution



Step 1: The skeleton is $\text{O} \quad \text{C} \quad \text{O}$

Step 2: $N = 1 \times 8$ (for C) + 3×8 (for O) = $8 + 24 = 32 e^-$ needed by all atoms

$$A = 1 \times 4$$
 (for C) + 3×6 (for O) + 2 (for the $2-$ charge)

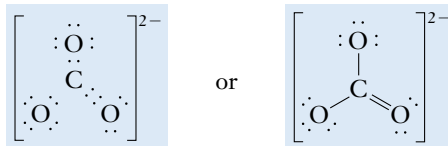
$$= 4 + 18 + 2 = 24 e^- \text{ available}$$

$$S = N - A = 32 e^- - 24 e^- = 8 e^- \text{ (4 pairs) shared}$$



Step 3: $\text{O} : \text{C} :: \text{O}$ (Four pairs are shared. At this point it doesn't matter which O is doubly bonded.)

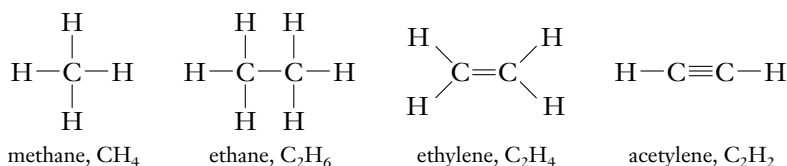
Step 4: The Lewis formula is



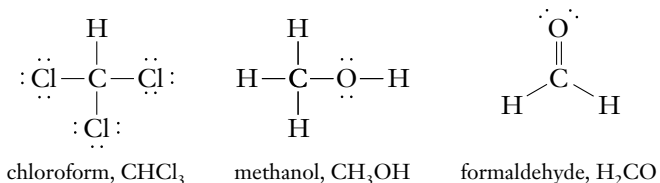
Check: $24 e^-$ (12 pairs) have been used.

You should now work Exercises 30 and 38.

You should practice writing many Lewis formulas. A few common types of organic compounds and their Lewis formulas are shown here. Each follows the octet rule. Methane, CH_4 , is the simplest of a huge family of organic compounds called *hydrocarbons* (composed solely of hydrogen and carbon). Ethane, C_2H_6 , is another hydrocarbon that contains only single bonds. Ethylene, C_2H_4 , has a carbon-carbon double bond, and acetylene, C_2H_2 , contains a carbon-carbon triple bond.



Halogen atoms can appear in place of hydrogen atoms in many organic compounds, because hydrogen and halogen atoms each need one more electron to attain noble gas configurations. An example is chloroform, CHCl_3 . Alcohols contain the group $\text{C}-\text{O}-\text{H}$; the simplest alcohol is methanol, CH_3OH . An organic compound that contains a carbon-oxygen double bond is formaldehyde, H_2CO .



✓ Problem-Solving Tip: Some Guidelines for Drawing Lewis Formulas

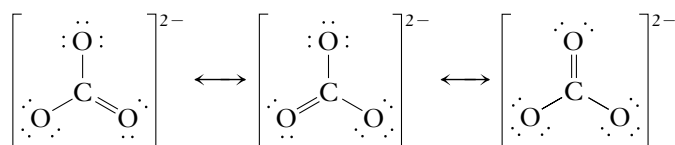
The following guidelines might help you draw Lewis formulas.

- In most of their covalent compounds, the representative elements follow the octet rule, except that hydrogen always shares only two electrons.
- Carbon always forms four bonds. This can be accomplished as:
 - four single bonds
 - two double bonds
 - two single bonds and one double bond or
 - one single bond and one triple bond
- Hydrogen forms only one bond to another element; thus hydrogen can never be a central atom.
- In neutral (uncharged) species, nitrogen forms three bonds, and oxygen forms two bonds.
- Nonmetals can form single, double, or triple bonds, but never quadruple bonds.
- Carbon forms double or triple bonds to C, N, O, or S atoms; oxygen can form double bonds with many other elements.


C, N, and O often form double and triple bonds. S can form double bonds with C, N, and O.

7-6 RESONANCE

In addition to the Lewis formula shown in Example 7-3, two other Lewis formulas with the same skeleton for the CO_3^{2-} ion are equally acceptable. In these formulas, the double bond could be between the carbon atom and either of the other two oxygen atoms.

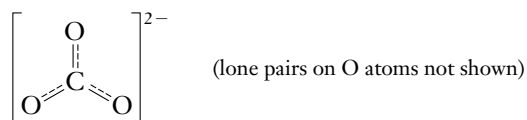


A molecule or polyatomic ion for which two or more Lewis formulas with the same arrangements of atoms can be drawn to describe the bonding is said to exhibit **resonance**. The three structures above are **resonance structures** of the carbonate ion. The relationship among them is indicated by the double-headed arrows, \leftrightarrow . This symbol *does not mean* that the ion flips back and forth among these three structures. The true structure can be described as an average, or hybrid, of the three.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 9.6, Resonance Structures.

When electrons are shared among more than two atoms, the electrons are said to be *delocalized*. The concept of delocalization is important in molecular orbital theory (Chapter 9).

Experiments show that the C—O bonds in CO_3^{2-} are *neither* double nor single bonds, but are intermediate in bond length and strength. Based on measurements in many compounds, the typical C—O single bond length is 1.43 Å, and the typical C=O double bond length is 1.22 Å. The C—O bond length for each bond in the CO_3^{2-} ion is intermediate at 1.29 Å. Another way to represent this situation is by **delocalization** of bonding electrons:



The dashed lines include that some of the electrons shared between C and O atoms are *delocalized* among all four atoms; that is, the four pairs of shared electrons are equally distributed among three C—O bonds.



The rose on the left is in an atmosphere of sulfur dioxide, SO_2 . Gaseous SO_2 and its aqueous solutions are used as bleaching agents. A similar process is used to bleach wood pulp before it is converted to paper.

EXAMPLE 7-4 Lewis Formulas, Resonance

Draw two resonance structures for the sulfur dioxide molecule, SO_2 .

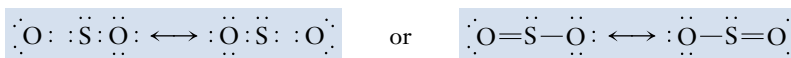
Plan

The stepwise procedure (Section 7-5) can be used to write each resonance structure.

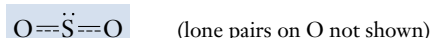
Solution

$$\begin{array}{l} \text{S} \quad \text{O} \\ \searrow \quad \searrow \\ N = 1(8) + 2(8) = 24 e^- \\ A = 1(6) + 2(6) = 18 e^- \\ \hline S = N - A = 6 e^- \text{ shared} \end{array}$$

The resonance structures are



We could show delocalization of electrons as follows:



Remember that Lewis formulas *do not necessarily show shapes*. SO_2 molecules are angular, not linear.

You should now work Exercises 50 and 52.



Problem-Solving Tip: Some Guidelines for Resonance Structures

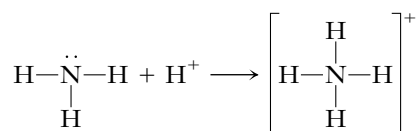
Resonance involves several different acceptable Lewis formulas with the same arrangement of atoms. They differ only in the arrangements of electron pairs, never in atom positions. The actual structure of such a molecule or ion is the average, or composite, of its resonance structures, but this does not mean that the electrons are moving from one place to another. This average structure is more stable than any of the individual resonance structures.



Formal Charges

An experimental determination of the structure of a molecule or polyatomic ion is necessary to establish unequivocally its correct structure. We often do not have these results available, however. **Formal charge** is the hypothetical charge on an atom *in a molecule or polyatomic ion*; to find the formal charge, we count bonding electrons as though they were equally shared between the two bonded atoms. The concept of formal charges helps us to write correct Lewis formulas in most cases. The most energetically favorable formula for a molecule is usually one in which the formal charge on each atom is zero or as near zero as possible.

Consider the reaction of NH_3 with hydrogen ion, H^+ , to form the ammonium ion, NH_4^+ .



The previously unshared pair of electrons on the N atom in the NH_3 molecule is shared with the H^+ ion to form the NH_4^+ ion, in which the N atom has four covalent bonds. Because N is a Group VA element, we expect it to form three covalent bonds to complete its octet. How can we describe the fact that N has four covalent bonds in species like NH_4^+ ? The answer is obtained by calculating the *formal charge* on each atom in NH_4^+ by the following rules:

Rules for Assigning Formal Charges to Atoms of A Group Elements

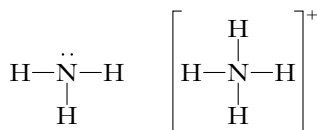
1. The formal charge, abbreviated FC, on an atom in a Lewis formula is given by the relationship

$$\text{FC} = (\text{group number}) - [(\text{number of bonds}) + (\text{number of unshared } e^-)]$$

Formal charges are represented by \oplus and \ominus to distinguish them from real charges on ions.

2. In a Lewis formula, an atom that has the same number of bonds as its periodic group number has a formal charge of zero.
3. a. In a molecule, the sum of the formal charges is zero.
b. In a polyatomic ion, the sum of the formal charges is equal to the charge.

Let us apply these rules to the ammonia molecule, NH_3 , and to the ammonium ion, NH_4^+ . Because N is a Group VA element, its group number is 5.



In NH_3 the N atom has 3 bonds and 2 unshared e^- , and so for N,

$$\begin{aligned} \text{FC} &= (\text{group number}) - [(\text{number of bonds}) + (\text{number of unshared } e^-)] \\ &= 5 - (3 + 2) = 0 \text{ (for N)} \end{aligned}$$

The H^+ ion has a vacant orbital, which accepts a share in the lone pair on nitrogen. The formation of a covalent bond by the sharing of an electron pair that is provided by one atom is called *coordinate covalent bond formation*. This type of bond formation is discussed again in Chapters 10 and 25.

For H,

$$\begin{aligned}\text{FC} &= (\text{group number}) - [(\text{number of bonds}) + (\text{number of unshared } e^-)] \\ &= 1 - (1 + 0) = 0 \text{ (for H)}\end{aligned}$$

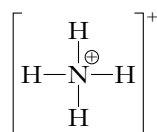
The formal charges of N and H are both zero in NH_3 , so the sum of the formal charges is $0 + 3(0) = 0$, consistent with rule 3a.

In NH_4^+ the atom has 4 bonds and no unshared e^- , and so for N,

$$\begin{aligned}\text{FC} &= (\text{group number}) - [(\text{number of bonds}) + (\text{number of unshared } e^-)] \\ &= 5 - (4 + 0) = +1 \text{ (for N)}\end{aligned}$$

Calculation of the FC for H atoms gives zero, as shown previously. The sum of the formal charges in NH_4^+ is $(1+) + 4(0) = 1+$. This is consistent with rule 3b.

FCs are indicated by \oplus and \ominus . The sum of the formal charges in a polyatomic ion is equal to the charge on the ion: +1 in NH_4^+ .

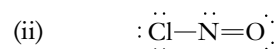


Thus, we see the octet rule is obeyed in both NH_3 and NH_4^+ . The sum of the formal charges in each case is that predicted by rule 3, even though nitrogen has four covalent bonds in the NH_4^+ ion.

This bookkeeping system helps us to choose among various Lewis formulas for a molecule or ion, according to the following guidelines.

- The most likely formula for a molecule or ion is usually one in which the formal charge on each atom is zero or as near zero as possible.
- Negative formal charges are more likely to occur on the more electronegative elements.
- Lewis formulas in which adjacent atoms have formal charges of the same sign are usually *not* accurate representations (the *adjacent charge rule*).

Let us now write some Lewis formulas for, and assign formal charges to, the atoms in nitrosyl chloride, NOCl , a compound often used in organic synthesis. The Cl atom and the O atom are both bonded to the N atom. Two Lewis formulas that satisfy the octet rule are



For Cl, $\text{FC} = 7 - (2 + 4) = +1$

For Cl, $\text{FC} = 7 - (1 + 6) = 0$

For N, $\text{FC} = 5 - (3 + 2) = 0$

For N, $\text{FC} = 5 - (3 + 2) = 0$

For O, $\text{FC} = 6 - (1 + 6) = -1$

For O, $\text{FC} = 6 - (2 + 4) = 0$

We believe that (ii) is a preferable Lewis formula, because it has smaller formal charges than (i). We see that a double-bonded terminal Cl atom would have its electrons arranged as $\text{:Cl}=\text{X}$, with the formal charge of Cl equal to $7 - (2 + 4) = +1$. A positive formal charge on such an electronegative element is quite unlikely, and double bonding to chlorine does not occur. The same reasoning would apply to the other halogens.

7-7 LIMITATIONS OF THE OCTET RULE FOR LEWIS FORMULAS

Recall that representative elements achieve noble gas electron configurations in *most* of their compounds. But when the octet rule is not applicable, the relationship $S = N - A$ is not valid without modification. The following are general cases for which the procedure in Section 7-5 *must be modified*—that is, there are four types of limitations of the octet rule.

- A. Most covalent compounds of beryllium, Be. Because Be contains only two valence shell electrons, it usually forms only two covalent bonds when it bonds to two other atoms. We therefore use *four electrons* as the number *needed* by Be in step 2, Section 7-5. In steps 3 and 4 we use only two pairs of electrons for Be.
- B. Most covalent compounds of the Group IIIA elements, especially boron, B. The IIIA elements contain only three valence shell electrons, so they often form three covalent bonds when they bond to three other atoms. We therefore use *six electrons* as the number *needed* by the IIIA elements in step 2; and in steps 3 and 4 we use only three pairs of electrons for the IIIA elements.
- C. Compounds or ions containing an odd number of electrons. Examples are NO, with 11 valence shell electrons, and NO₂, with 17 valence shell electrons.
- D. Compounds or ions in which the central element needs a share in more than eight valence shell electrons to hold all the available electrons, *A*. Extra rules are added to steps 2 and 4 of the procedure in Section 7-5 when this is encountered.
 - Step 2a: If *S*, the number of electrons shared, is less than the number needed to bond all atoms to the central atom, then *S* is increased to the number of electrons needed.
 - Step 4a: If *S* must be increased in step 2a, then the octets of all the atoms might be satisfied before all of the electrons (*A*) have been added. Place the extra electrons on the central element.

Many species that violate the octet rule are quite reactive. For instance, compounds containing atoms with only four valence shell electrons (limitation type A above) or six valence shell electrons (limitation type B above) frequently react with other species that supply electron pairs. Compounds such as these that accept a share in a pair of electrons are called *Lewis acids*; a *Lewis base* is a species that makes available a share in a pair of electrons. (This kind of behavior will be discussed in detail in Section 10-10.) Molecules with an odd number of electrons often *dimerize* (combine in pairs) to give products that do satisfy the octet rule. Examples are the dimerization of NO to form N₂O₂ (Section 24-15) and NO₂ to form N₂O₄ (Section 24-15). Examples 7-5 through 7-9 illustrate some limitations and show how such Lewis formulas are constructed.

EXAMPLE 7-5 Limitations of the Octet Rule

Write the Lewis formula for gaseous beryllium chloride, BeCl₂, a covalent compound.

Plan

This is an example of limitation type A. So, as we follow the steps in writing the Lewis formula, we must remember to use *four electrons* as the number *needed* by Be in step 2. Steps 3 and 4 should show only two pairs of electrons for Be.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 9.8, Free Radicals—Exceptions to the Octet Rule.

Lewis formulas are not normally written for compounds containing *d*- and *f*-transition metals. The *d*- and *f*-transition metals utilize *d* or *f* orbitals (or both) in bonding as well as *s* and *p* orbitals. Thus, they can accommodate more than eight valence electrons.

Solution

Step 1: The skeleton is Cl Be Cl

see limitation type A

↓

Step 2: $N = 2 \times 8$ (for Cl) + 1×4 (for Be) = $20 e^-$ needed

$A = 2 \times 7$ (for Cl) + 1×2 (for Be) = $16 e^-$ available


$S = N - A = 20 e^- - 16 e^- = 4 e^-$ shared

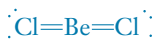
Step 3: Cl : Be : Cl

Step 4: $\begin{array}{c} \cdot\cdot \\ \cdot\cdot \\ \text{Cl} \\ \cdot\cdot \\ \cdot\cdot \end{array} : \text{Be} : \begin{array}{c} \cdot\cdot \\ \cdot\cdot \\ \text{Cl} \\ \cdot\cdot \\ \cdot\cdot \end{array}$ or $\begin{array}{c} \cdot\cdot \\ \cdot\cdot \\ \text{Cl} \\ \cdot\cdot \\ \cdot\cdot \end{array} - \text{Be} - \begin{array}{c} \cdot\cdot \\ \cdot\cdot \\ \text{Cl} \\ \cdot\cdot \\ \cdot\cdot \end{array}$

Calculation of formal charges shows that

$$\text{for Be, FC} = 2 - (2 + 0) = 0 \quad \text{and} \quad \text{for Cl, FC} = 7 - (1 + 6) = 0$$

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 9.7, Electron-Deficient Compounds.



BF_3 and BCl_3 are gases at room temperature. Liquid BBr_3 and solid BI_3 are shown here.

In BeCl_2 , the chlorine atoms achieve the argon configuration, [Ar], and the beryllium atom has a share of only four electrons. Compounds such as BeCl_2 , in which the central atom shares fewer than $8 e^-$, are sometimes referred to as **electron deficient** compounds. This “deficiency” refers only to satisfying the octet rule for the central atom. The term does not imply that there are fewer electrons than there are protons in the nuclei, as in the case of a cation, because the molecule is neutral.

A Lewis formula can be written for BeCl_2 that *does* satisfy the octet rule (see structure shown in the margin). Let us evaluate the formal charges for that formula:

$$\text{for Be, FC} = 2 - (4 + 0) = -2 \quad \text{and} \quad \text{for Cl, FC} = 7 - (2 + 4) = +1$$

We have said that the most favorable structure for a molecule is one in which the formal charge on each atom is zero, if possible. In case some atoms did have nonzero formal charges, we would expect that the more electronegative atoms (Cl) would be the ones with lowest formal charge. Thus, we prefer the Lewis structure shown in Example 7-5 over the one in the margin.

One might expect a similar situation for compounds of the other IIA metals, Mg, Ca, Sr, Ba, and Ra. These elements, however, have *lower ionization energies* and *larger radii* than Be, so they usually form ions by losing two electrons.

EXAMPLE 7-6 Limitations of the Octet Rule

Write the Lewis formula for boron trichloride, BCl_3 , a covalent compound.

Plan

This covalent compound of boron is an example of limitation type B. As we follow the steps in writing the Lewis formula, we use *six electrons* as the number *needed* by boron in step 2. Steps 3 and 4 should show only three pairs of electrons for boron.

Solution

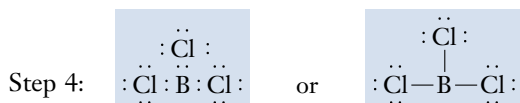
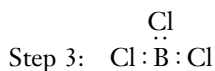
Cl

Step 1: The skeleton is Cl B Cl

see limitation type B



Step 2: $N = 3 \times 8$ (for Cl) + 1×6 (for B) = $30 e^-$ needed
 $A = 3 \times 7$ (for Cl) + 1×3 (for B) = $24 e^-$ available
 $S = N - A = 30 e^- - 24 e^- = 6 e^-$ shared



Each chlorine atom achieves the Ne configuration. The boron (central) atom acquires a share of only six valence shell electrons. Calculation of formal charges shows that

$$\text{for B, FC} = 3 - (3 + 0) = 0 \quad \text{and} \quad \text{for Cl, FC} = 7 - (1 + 6) = 0$$

You should now work Exercise 54.

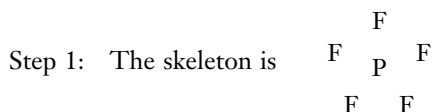
EXAMPLE 7-7 Limitations of the Octet Rule

Write the Lewis formula for phosphorus pentafluoride, PF_5 , a covalent compound.

Plan

We apply the usual stepwise procedure to write the Lewis formula. In PF_5 , all five F atoms are bonded to P. This requires the sharing of a minimum of $10 e^-$, so this is an example of limitation type D. We therefore add the extra step 2a, and increase S from the calculated value of $8 e^-$ to $10 e^-$.

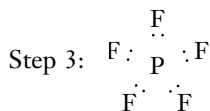
Solution

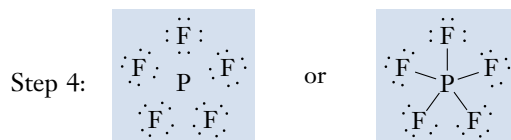


Step 2: $N = 5 \times 8$ (for F) + 1×8 (for P) = $48 e^-$ needed
 $A = 5 \times 7$ (for F) + 1×5 (for P) = $40 e^-$ available
 $S = N - A = 8 e^-$ shared

Five F atoms are bonded to P. This requires the sharing of a minimum of $10 e^-$. But only $8 e^-$ have been calculated. This is therefore an example of limitation type D.

Step 2a: Increase S from $8 e^-$ to $10 e^-$, the number required to bond five F atoms to one P atom. The number of electrons available, 40, does not change.





When the octets of the five F atoms have been satisfied, all 40 of the available electrons have been added. The phosphorus (central) atom has a share of ten electrons.

Calculation of formal charges shows that

$$\text{for P, FC} = 5 - (5 + 0) = 0 \quad \text{and} \quad \text{for F, FC} = 7 - (1 + 6) = 0$$

This is sometimes referred to as *hypervalence*.

When an atom has a share of more than eight electrons, as does P in PF_5 , we say that it exhibits an *expanded valence shell*. The electronic basis of the octet rule is that one s and three p orbitals in the valence shell of an atom can accommodate a maximum of eight electrons. The valence shell of phosphorus has $n = 3$, so it also has $3d$ orbitals available that can be involved in bonding. It is for this reason that phosphorus (and many other representative elements of Period 3 and beyond) can exhibit an expanded valence shell. By contrast, elements in the *second row* of the periodic table can *never* exceed eight electrons in their valence shells, because each atom has only one s and three p orbitals in that shell. Thus, we understand why PF_5 can exist but NF_5 cannot.

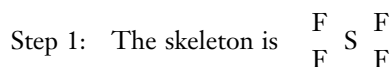
EXAMPLE 7-8 Limitations of the Octet Rule

Write the Lewis formula for sulfur tetrafluoride, SF_4 .

Plan

We apply the usual stepwise procedure. The calculation of $S = N - A$ in step 2 shows only $6 e^-$ shared, but a minimum of $8 e^-$ are required to bond four F atoms to the central S atom. Limitation type D applies, and we proceed accordingly.

Solution

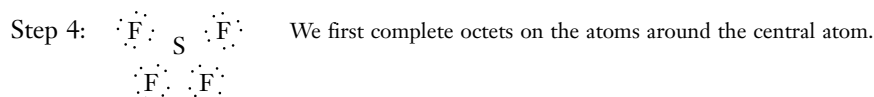
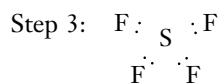


Step 2: $N = 1 \times 8$ (S atom) + 4×8 (F atoms) = $40 e^-$ needed

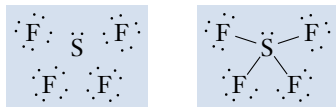
$$A = 1 \times 6$$
 (S atom) + 4×7 (F atoms) = $34 e^-$ available

$S = N - A = 40 - 34 = 6 e^-$ shared. Four F atoms are bonded to the central S. This requires a minimum of $8 e^-$, but only $6 e^-$ have been calculated in step 2. This is therefore an example of limitation type D.

Step 2a: We increase S from $6 e^-$ to $8 e^-$.



Step 4a: Now we have satisfied the octet rule, but we have used only 32 of the 34 e^- available. We place the other two electrons on the central S atom.



In SF_4 , sulfur has an expanded valence shell.

Calculation of the formal charge shows that

$$\text{for S, FC} = 6 - (4 + 2) = 0$$

$$\text{for F, FC} = 7 - (1 + 6) = 0$$

EXAMPLE 7-9 Limitations of the Octet Rule

Write the Lewis formula for the triiodide ion, I_3^- .

Plan

We apply the usual stepwise procedure. The calculation of $S = N - A$ in step 2 shows only 2 e^- shared, but a minimum of 4 e^- are required to bond two I atoms to the central I. Limitation type D applies, and we proceed accordingly.

Solution

Step 1: The skeleton is $[\text{I} \quad \text{I} \quad \text{I}]^-$

Step 2: $N = 3 \times 8$ (for I) = 24 e^- needed

$$A = 3 \times 7$$
 (for I) + 1 (for the 1- charge) = 22 e^- available

$S = N - A = 2 e^-$ shared. Two I atoms are bonded to the central I. This requires a minimum of 4 e^- , but only 2 e^- have been calculated in step 4. This is therefore an example of limitation type D.

Step 2a: Increase S from 2 e^- to 4 e^- .

Step 3: $[\text{I} : \text{I} : \text{I}]^-$

Step 4: $[\text{:}\ddot{\text{I}}:\ddot{\text{I}}:\ddot{\text{I}}:]^-$

Step 4a: Now we have satisfied the octets of all atoms using only 20 of the 22 e^- available. We place the other two electrons on the central I atom.



The central iodine atom in I_3^- has an expanded valence shell.


Calculation of the formal charge shows that

$$\text{for I on ends, FC} = 7 - (1 + 6) = 0$$

$$\text{for I in middle, FC} = 7 - (2 + 6) = -1$$

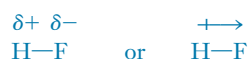
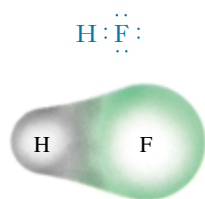
You should now work Exercise 58.

We have seen that *atoms attached to the central atom nearly always attain noble gas configurations*, even when the central atom does not.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 9.11, Bond Polarity and Electronegativity.

A **homonuclear** molecule contains only one kind of atom. A molecule that contains two or more kinds of atoms is described as **heteronuclear**.

Remember that ionic compounds are solids at room temperature.



The word “dipole” means “two poles.” Here it refers to the positive and negative poles that result from the separation of charge within a molecule.

The values of electronegativity are obtained from Table 6-3.

7-8 POLAR AND NONPOLAR COVALENT BONDS

Covalent bonds may be either *polar* or *nonpolar*. In a **nonpolar bond** such as that in the hydrogen molecule, H_2 , ($\text{H}:\text{H}$ or $\text{H}-\text{H}$) the electron pair is *shared equally* between the two hydrogen nuclei. We defined electronegativity as the tendency of an atom to attract electrons to itself in a chemical bond (see Section 6-6). Both H atoms have the same electronegativity. This means that the shared electrons are equally attracted to both hydrogen nuclei and therefore spend equal amounts of time near each nucleus. In this nonpolar covalent bond, the **electron density** is symmetrical about a plane that is perpendicular to a line between the two nuclei. This is true for all homonuclear *diatomic molecules*, such as H_2 , O_2 , N_2 , F_2 , and Cl_2 , because the two identical atoms have identical electronegativities. We can generalize:

The covalent bonds in all homonuclear diatomic molecules must be nonpolar.

Let us now consider *heteronuclear diatomic molecules*. Start with the fact that hydrogen fluoride, HF, is a gas at room temperature. This tells us that it is a covalent compound. We also know that the $\text{H}-\text{F}$ bond has some degree of polarity because H and F are not identical atoms and therefore do not attract the electrons equally. But how polar will this bond be?

The electronegativity of hydrogen is 2.1, and that of fluorine is 4.0 (see Table 6-3). Clearly, the F atom, with its higher electronegativity, attracts the shared electron pair much more strongly than does the H atom. We can represent the structure of HF as shown in the margin. The electron density is distorted in the direction of the more electronegative F atom. This small shift of electron density leaves H somewhat positive.

Covalent bonds, such as the one in HF, in which the *electron pairs are shared unequally* are called **polar covalent bonds**. Two kinds of notation used to indicate polar bonds are shown in the margin.

The δ^- over the F atom indicates a “partial negative charge.” This means that the F end of the molecule is somewhat more negative than the H end. The δ^+ over the H atom indicates a “partial positive charge,” or that the H end of the molecule is positive *with respect to* the F end. We are *not* saying that H has a charge of +1 or that F has a charge of -1! A second way to indicate the polarity is to draw an arrow so that the head points toward the negative end (F) of the bond and the crossed tail indicates the positive end (H).

The separation of charge in a polar covalent bond creates an electric **dipole**. We expect the dipoles in the covalent molecules HF, HCl, HBr, and HI to be different because F, Cl, Br, and I have different electronegativities. This tells us that atoms of these elements have different tendencies to attract an electron pair that they share with hydrogen. We indicate this difference as shown here, where $\Delta(\text{EN})$ is the difference in electronegativity between two atoms that are bonded together.

	Most polar		Least polar	
	\longleftrightarrow	\longleftrightarrow	\longleftrightarrow	\longleftrightarrow
	$\text{H}-\text{F}$	$\text{H}-\text{Cl}$	$\text{H}-\text{Br}$	$\text{H}-\text{I}$
EN:	$\frac{2.1}{\quad} \frac{4.0}{\quad}$	$\frac{2.1}{\quad} \frac{3.0}{\quad}$	$\frac{2.1}{\quad} \frac{2.8}{\quad}$	$\frac{2.1}{\quad} \frac{2.5}{\quad}$
$\Delta(\text{EN})$	1.9	0.9	0.7	0.4

The longest arrow indicates the largest dipole, or greatest separation of electron density in the molecule (see Table 7-3). For comparison, the $\Delta(\text{EN})$ values for some typical 1:1 ionic compounds are RbCl, 2.1; NaF, 3.0; and KCl, 2.1

EXAMPLE 7-10 Polar Bonds

Each halogen can form single covalent bonds with other halogens, to form compounds called *interhalogens*; some examples are ClF and BrF. Use the electronegativity values in Table 6-3 to rank the following single bonds from most polar to least polar: F—F, F—Cl, F—Br, Cl—Br, Cl—I, and Cl—Cl.

Plan

The bond polarity decreases as the electronegativity difference between the two atoms decreases. We can calculate $\Delta(\text{EN})$ for each bond, and then arrange them according to decreasing $\Delta(\text{EN})$ value.

Solution

We know that two F atoms have the same electronegativity, so $\Delta(\text{EN})$ for F—F must be zero, and the F—F bond is nonpolar; the same reasoning applies to Cl—Cl. We use the values from Table 6-3 to calculate $\Delta(\text{EN})$ for each of the other pairs, always subtracting the smaller from the larger value:

Elements	$\Delta(\text{EN})$
F, Cl	$4.0 - 3.0 = 1.0$
F, Br	$4.0 - 2.8 = 1.2$
Cl, Br	$3.0 - 2.8 = 0.2$
Cl, I	$3.0 - 2.5 = 0.5$

The bonds, arranged from most polar to least polar, are:

	F—Br	F—Cl	Cl—I	Cl—Br	Cl—Cl	F—F
EN:	$\frac{4.0}{\quad} \frac{2.8}{\quad}$	$\frac{4.0}{\quad} \frac{3.0}{\quad}$	$\frac{3.0}{\quad} \frac{2.5}{\quad}$	$\frac{3.0}{\quad} \frac{2.8}{\quad}$	$\frac{3.0}{\quad} \frac{3.0}{\quad}$	$\frac{4.0}{\quad} \frac{4.0}{\quad}$
$\Delta(\text{EN})$:	1.2	1.0	0.5	0.2	0	0

You should now work Exercise 74.

TABLE 7-3 $\Delta(\text{EN})$ Values and Dipole Moments for Some Pure (Gaseous) Substances

Substance	$\Delta(\text{EN})$	Dipole Moment (μ)*
HF	1.9	1.91 D
HCl	0.9	1.03 D
HBr	0.7	0.79 D
HI	0.4	0.38 D
H—H	0	0 D

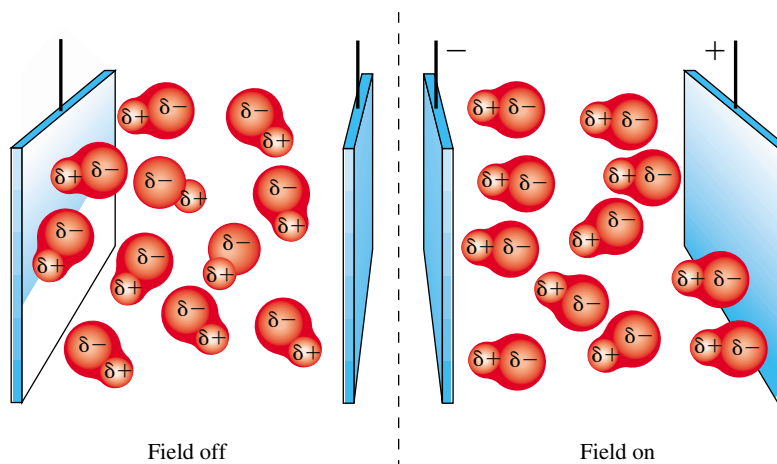
*The magnitude of a dipole moment is given by the product of charge \times distance of separation. Molecular dipole moments are usually expressed in debyes (D).

7-9 DIPOLE MOMENTS

It is convenient to express bond polarities on a numerical scale. We indicate the polarity of a molecule by its dipole moment, which measures the separation of charge within the molecule. The **dipole moment**, μ , is defined as the product of the distance, d , separating charges of equal magnitude and opposite sign, and the magnitude of the charge, q . A dipole moment is measured by placing a sample of the substance between two plates and applying a voltage. This causes a small shift in electron density of any molecule, so the applied voltage is diminished very slightly. Diatomic molecules that contain polar bonds, however, such as HF, HCl, and CO, tend to orient themselves in the electric field (Figure 7-5). This causes the measured voltage between the plates to decrease more markedly for these substances, and we say that these molecules are *polar*. Molecules such as F₂ or N₂

$$\mu = d \times q$$

Figure 7-5 If polar molecules, such as HF, are subjected to an electric field, they tend to line up very slightly in a direction opposite to that of the field. This minimizes the electrostatic energy of the molecules. Nonpolar molecules are not oriented by an electric field. The effect is greatly exaggerated in this drawing.



do not reorient, so the change in voltage between the plates remains slight; we say that these molecules are *nonpolar*.

Generally, as electronegativity differences increase in diatomic molecules, the measured dipole moments increase. This can be seen clearly from the data for the hydrogen halides (see Table 7-3).

Unfortunately, the dipole moments associated with *individual bonds* can be measured only in simple diatomic molecules. *Entire molecules* rather than selected pairs of atoms must be subjected to measurement. Measured values of dipole moments reflect the *overall* polarities of molecules. For polyatomic molecules they are the result of all the bond dipoles in the molecules. In Chapter 8, we will see that structural features, such as molecular geometry and the presence of lone (unshared) pairs of electrons, also affect the polarity of a molecule.

7-10 THE CONTINUOUS RANGE OF BONDING TYPES

Let us now clarify our classification of bonding types. The degree of electron sharing or transfer depends on the electronegativity difference between the bonding atoms. Nonpolar covalent bonding (involving *equal sharing* of electron pairs) is one extreme, occurring when the atoms are identical ($\Delta(\text{EN})$ is zero). Ionic bonding (involving *complete transfer* of electrons) represents the other extreme, and occurs when two elements with very different electronegativities interact ($\Delta(\text{EN})$ is large).

Polar covalent bonds may be thought of as intermediate between pure (nonpolar) covalent bonds and pure ionic bonds. In fact, bond polarity is sometimes described in terms of **partial ionic character**. This usually increases with increasing difference in electronegativity between bonded atoms. Calculations based on the measured dipole moment of gaseous HCl indicate about 17% “ionic character.”

When cations and anions interact strongly, some amount of electron sharing takes place; in such cases we can consider the ionic compound as having some **partial covalent character**. For instance, the high charge density of the very small Li^+ ion causes it to distort large anions that it approaches. The distortion attracts electron density from the anion to the region between it and the Li^+ ion, giving lithium compounds a higher degree of covalent character than in other alkali metal compounds.

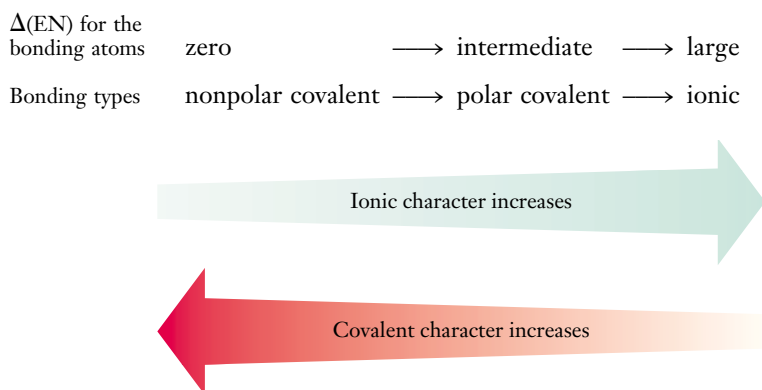
Almost all bonds have both ionic and covalent character. By experimental means, a given type of bond can usually be identified as being “closer” to one or the other extreme type. We find it useful and convenient to use the labels for the major classes of bonds to describe simple substances, keeping in mind that they represent ranges of behavior.

Above all, we must recognize that any classification of a compound that we might suggest based on electronic properties *must* be consistent with the physical properties of ionic and covalent substances described at the beginning of the chapter. For instance, HCl has a rather large electronegativity difference (0.9), and its aqueous solutions conduct electricity. But we know that we cannot view it as an ionic compound because it is a gas, and not a solid, at room temperature. Liquid HCl is a nonconductor.

HCl *ionizes* in aqueous solution. We will study more about this behavior in Chapter 10.

Let us point out another aspect of the classification of compounds as ionic or covalent. Not all ions consist of single charged atoms. Many are small groups of atoms that are covalently bonded together, yet they still have excess positive or negative charge. Examples of such *polyatomic ions* are ammonium ion, NH_4^+ , sulfate ion, SO_4^{2-} , and nitrate ion, NO_3^- . A compound such as potassium sulfate, K_2SO_4 , contains potassium ions, K^+ , and sulfate ions, SO_4^{2-} , in a 2:1 ratio. We should recognize that this compound contains both covalent bonding (electron sharing *within* each sulfate ion) and ionic bonding (electrostatic attractions *between* potassium and sulfate ions). We classify this compound as *ionic*, however, because it is a high-melting solid (mp 1069°C), it conducts electricity both in molten form and in aqueous solution, and it displays other properties that we generally associate with ionic compounds. Put another way, covalent bonding holds each sulfate ion together, but the forces that hold the *entire* substance together are ionic.

In summary, we can describe chemical bonding as a continuum that may be represented as



Key Terms

Anion A negatively charged ion; that is, an ion in which the atom or group of atoms has more electrons than protons.

Binary compound A compound consisting of two elements; may be ionic or covalent.

Bonding pair A pair of electrons involved in a covalent bond. Also called *shared pair*.

Cation A positively charged ion; that is, an ion in which the atom or group of atoms has fewer electrons than protons.

Chemical bonds Attractive forces that hold atoms together in elements and compounds.

Covalent bond A chemical bond formed by the sharing of one or more electron pairs between two atoms.

Covalent compound A compound containing predominantly covalent bonds.

Debye The unit used to express dipole moments.

Delocalization of electrons Refers to bonding electrons distributed among more than two atoms that are bonded together; occurs in species that exhibit resonance.

Dipole Refers to the separation of charge between two covalently bonded atoms.

Dipole moment (μ) The product of the distance separating opposite charges of equal magnitude and the magnitude of the charge; a measure of the polarity of a bond or molecule. A measured dipole moment refers to the dipole moment of an entire molecule.

Double bond A covalent bond resulting from the sharing of four electrons (two pairs) between two atoms.

Electron-deficient compound A compound containing at least one atom (other than H) that shares fewer than eight electrons.

Formal charge The hypothetical charge on an atom in a covalently bonded molecule or ion; bonding electrons are counted as though they were shared equally between the two bonded atoms.

Heteronuclear Consisting of different elements.

Homonuclear Consisting of only one element.

Ion An atom or a group of atoms that carries an electrical charge.

Ionic bonding The attraction of oppositely charged ions (cations and anions) in large numbers to form a solid. Ions result from the transfer of one or more electrons from one atom or group of atoms to another.

Ionic compound A compound containing predominantly ionic bonding.

Isoelectronic Having the same number of electrons.

Lewis acid A substance that accepts a share in a pair of electrons from another species.

Lewis base A substance that makes available a share in an electron pair.

Lewis formula The representation of a molecule, ion, or formula unit by showing atomic symbols and only outer-shell electrons; does not represent the shape of the molecule or ion.

Lone pair A pair of electrons residing on one atom and not shared by other atoms; unshared pair.

Monatomic ion An ion that consists of only one atom.

Nonpolar bond A covalent bond between two atoms with the same electronegativity, so that the electron density is symmetrically distributed.

Octet rule Many representative elements attain at least a share of eight electrons in their valence shells when they form molecular or ionic compounds; there are some limitations.

Polar bond A covalent bond between two atoms with different electronegativities, so that the electron density is unsymmetrically distributed.

Polyatomic ion An ion that consists of more than one atom.

Resonance A concept in which two or more Lewis formulas for the same arrangement of atoms (resonance structures) are used to describe the bonding in a molecule or ion.

Single bond A covalent bond resulting from the sharing of two electrons (one pair) between two atoms.

Triple bond A covalent bond resulting from the sharing of six electrons (three pairs) between two atoms.

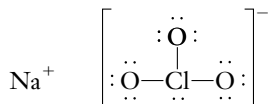
Unshared pair See *Lone pair*.

Valence electrons The *s* and *p* electrons in the outermost shell of an atom.

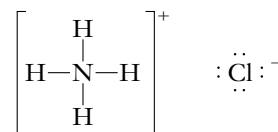
Exercises

Chemical Bonding: Basic Ideas

- What type of force is responsible for chemical bonding? Explain the differences between ionic bonding and covalent bonding.
- What kind of bonding (ionic or covalent) would you predict for the products resulting from the following combinations of elements?
 - $\text{Na} + \text{Cl}_2$;
 - $\text{C} + \text{O}_2$;
 - $\text{N}_2 + \text{O}_2$;
 - $\text{S} + \text{O}_2$.
- Why are covalent bonds called directional bonds, whereas ionic bonding is termed nondirectional?
- What do Lewis dot formulas for atoms show? (b) Write Lewis dot formulas for the following atoms: He; Si; P; Ne; Mg; Br.
- Write Lewis dot formulas for the following atoms: Li; B; As; K; Xe; Al.
- Describe the types of bonding in sodium chlorate, NaClO_3 .



- Describe the types of bonding in ammonium chloride, NH_4Cl .



- Based on the positions in the periodic table of the following pairs of elements, predict whether bonding between the two would be primarily ionic or covalent. Justify your answers. (a) Ca and Cl; (b) P and O; (c) Br and I; (d) Li and I; (e) Si and Br; (f) Ba and F.
- Predict whether the bonding between the following pairs of elements would be primarily ionic or covalent. Justify your answers. (a) Rb and Cl; (b) N and O; (c) Ca and F; (d) P and S; (e) C and F; (f) K and O.
- Classify the following compounds as ionic or covalent: (a) $\text{Ca}(\text{NO}_3)_2$; (b) H_2S ; (c) KNO_3 ; (d) CaCl_2 ; (e) H_2CO_3 ; (f) PCl_3 ; (g) Li_2O ; (h) N_2H_4 ; (i) SOCl_2 .

Ionic Bonding

- Describe what happens to the valence electron(s) as a metal atom and a nonmetal atom combine to form an ionic compound.
- Describe an ionic crystal. What factors might determine the geometrical arrangement of the ions?
- Why are solid ionic compounds rather poor conductors of electricity? Why does conductivity increase when an ionic compound is melted or dissolved in water?
- Write the formula for the ionic compound that forms between each of the following pairs of elements: (a) Ca and Br₂; (b) Ba and Cl₂; (c) Na and Cl₂.
- Write the formula for the ionic compound that forms between each of the following pairs of elements: (a) Cs and F₂; (b) Sr and S; (c) Na and Se.
- When a *d*-transition metal ionizes, it loses its outer *s* electrons before it loses any *d* electrons. Using [noble gas] (*n* - 1) *d^x* representations, write the outer-electron configurations for the following ions: (a) Cr³⁺; (b) Mn²⁺; (c) Ag⁺; (d) Fe³⁺; (e) Cu²⁺; (f) Sc³⁺; (g) Fe²⁺.
- Which of the following do not accurately represent stable binary ionic compounds? Why? BaCl₂; NaS; AlF₄; SrS₂; Ca₂O₃; NaBr₂; LiSe₂.
- Which of the following do not accurately represent stable binary ionic compounds? Why? MgI; Al(OH)₂; InF₂; CO₂; RbCl₂; CsSe; Be₂O.
- (a) Write Lewis formulas for the positive and negative ions in these compounds: SrBr₂; K₂O; Ca₃P₂; PbCl₂; Bi₂O₃. (b) Which ions do not have a noble gas configuration?
- Write formulas for two cations and two anions that are isoelectronic with argon.
- Write formulas for two cations and two anions that are isoelectronic with krypton.
- Write formulas for two cations that have each of the following electron configurations in their *highest* occupied energy level: (a) 3s²3p⁶; (b) 4s²4p⁶.
- Write formulas for two anions that have each of the electron configurations listed in Exercise 22.

Covalent Bonding: General Concepts

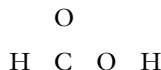
- What does Figure 7-4 tell us about the attractive and repulsive forces in a hydrogen molecule?
- Distinguish between heteronuclear and homonuclear diatomic molecules.
- How many electrons are shared between two atoms in (a) a single covalent bond, (b) a double covalent bond, and (c) a triple covalent bond?
- What is the maximum number of covalent bonds that a second-period element could form? How can the representative elements beyond the second period form more than this number of covalent bonds?

Lewis Formulas for Molecules and Polyatomic Ions

- What information about chemical bonding can a Lewis formula give for a compound or ion? What information about bonding is not directly represented by a Lewis formula?
- Write Lewis formulas for the following: H₂; N₂; Cl₂; HCl; HBr.
- Write Lewis formulas for the following: H₂O; NH₃; OH⁻; F⁻.
- Use Lewis formulas to represent the covalent molecules formed by these pairs of elements. Write only structures that satisfy the octet rule. (a) P and H; (b) Se and Br; (c) N and Cl; (d) Si and Cl.
- Use Lewis formulas to represent the covalent molecules formed by these pairs of elements. Write only structures that satisfy the octet rule. (a) S and Cl; (b) As and F; (c) I and Cl; (d) P and Cl.
- Find the total number of valence electrons in each of the following molecules or ions.
(a) NH₂⁻ (b) ClO₃⁻
(c) HCN (d) SnCl₄
- How many valence electrons does each of these molecules or ions have?
(a) H₂S (b) PCl₃
(c) NOCl (d) OH⁻
- Write Lewis structures for the molecules or ions in Exercise 33.
- Write Lewis structures for the molecules or ions in Exercise 34.
- Write Lewis structures for the following molecules or ions: (a) ClO₄⁻; (b) C₂H₆O (two possibilities); (c) HOCl; (d) SO₃²⁻.
- Write Lewis structures for the following molecules or ions: (a) H₂CO; (b) ClF; (c) BF₄⁻; (d) PO₄³⁻.
- (a) Write the Lewis formula for AlCl₃, a molecular compound. Note that in AlCl₃, the aluminum atom is an exception to the octet rule. (b) In the gaseous phase, two molecules of AlCl₃ join together (dimerize) to form Al₂Cl₆. (The two molecules are joined by two "bridging" Al—Cl—Al bonds.) Write the Lewis formula for this molecule.
- Write the Lewis formula for molecular ClO₂. There is a single unshared electron on the chlorine atom in this molecule.
- Write Lewis formulas for CH₄ and SiH₄; explain the similarity.
- Write Lewis formulas for CCl₄, SiF₄, and PbI₄; explain the similarity.
- Write Lewis formulas for the fluorine molecule and for sodium fluoride. Describe the nature of the chemical bonding involved in each substance.
- Write Lewis formulas for butane, CH₃CH₂CH₂CH₃, and propane, CH₃CH₂CH₃. Describe the nature of the bond indicated: CH₃CH₂—CH₂CH₃ and CH₃—CH₂CH₃.

45. Write Lewis structures for the following molecules:

(a) Formic acid, HCOOH, in which the atomic arrangement is



(b) Acetonitrile, CH₃CN;

(c) Vinyl chloride, CH₂CHCl, the molecule from which PVC plastics are made.

46. Write Lewis structures for the following molecules:

(a) Tetrafluoroethylene, C₂F₄, the molecule from which Teflon is made;

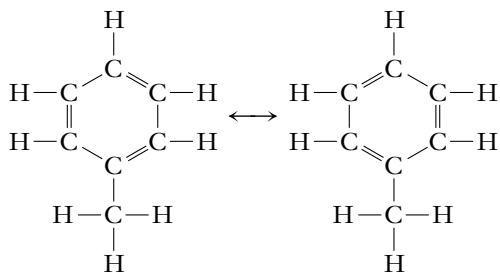
(b) Acrylonitrile, CH₂CHCN, the molecule from which Orlon is made.

47. What do we mean by the term “resonance”? Do the resonance structures that we draw actually represent the bonding in the substance? Explain your answer.

48. Careful examination of the ozone molecule indicates that the two outer oxygens are the same distance from the central oxygen. Write Lewis formulas or resonance structures that are consistent with this finding.

49. Draw resonance structures for the nitric acid molecule.

*50. We can write two resonance structures for toluene, C₆H₅CH₃:



How would you expect the carbon-carbon bond lengths in the six-membered ring to compare with the carbon-carbon bond length between the CH₃ group and the carbon atom on the ring?

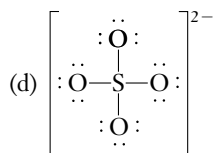
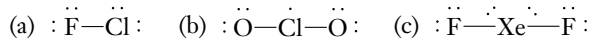
51. Write resonance structures for the formate ion, HCOO⁻.

52. Write resonance structures for the nitrate ion, NO₃⁻.

53. Write Lewis formulas for (a) H₂NOH (i.e., one H bonded to O); (b) S₈ (a ring of eight atoms); (c) PCl₃; (d) F₂O₂ (O atoms in center, F atoms on outside); (e) CO; (f) SeCl₆.

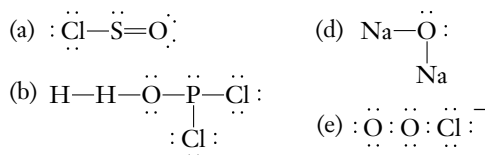
54. Write the Lewis formula for each of the following covalent compounds. Which ones contain at least one atom with a share in less than an octet of valence electrons? (a) BeBr₂; (b) BBr₃; (c) NCl₃; (d) AlCl₃.

55. Which of the following species contain at least one atom that violates the octet rule?



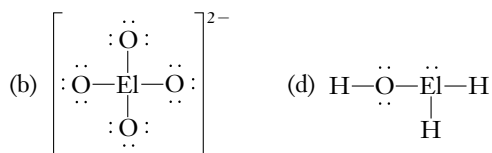
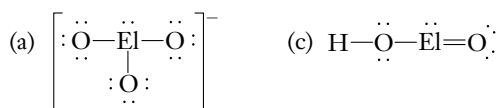
56. Write the Lewis formula for each of the following molecules or ions. Which ones contain at least one atom with a share in less than an octet of valence electrons? (a) CH₂Cl₂; (b) BF₃; (c) BCl₄⁻; (d) AlF₄⁻.

*57. None of the following is known to exist. What is wrong with each one?

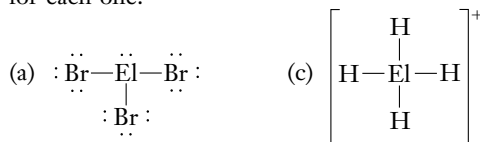


58. Write the Lewis formula for each of the following molecules or ions. Which ones contain at least one atom with a share in more than an octet of valence electrons? (a) PF₆⁻; (b) AsCl₅; (c) ICl₃; (d) C₂H₆.

*59. Suppose that “El” is the general symbol for a representative element. In each case, in which periodic group is El located? Justify your answers and cite a specific example for each one.



*60. Suppose that “El” is the general symbol for a representative element. In each case, in which periodic group is El located? Justify your answers and cite a specific example for each one.

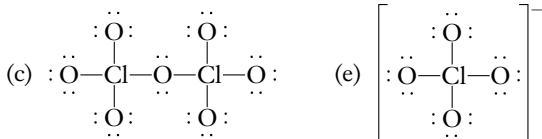
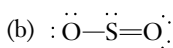


61. Many common stains, such as those of chocolate and other fatty foods, can be removed by dry-cleaning solvents such as tetrachloroethylene, C₂Cl₄. Is C₂Cl₄ ionic or covalent? Write its Lewis formula.

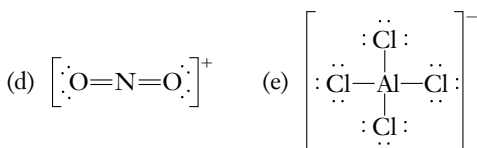
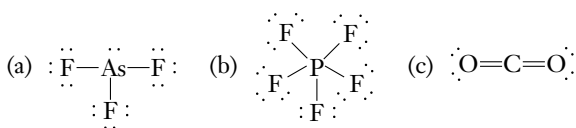
- *62. Write acceptable Lewis formulas for the following common air pollutants: (a) SO_2 ; (b) NO_2 ; (c) CO ; (d) O_3 (ozone); (e) SO_3 ; (f) $(\text{NH}_4)_2\text{SO}_4$. Which one is a solid? Which ones exhibit resonance? Which ones violate the octet rule?

Formal Charges

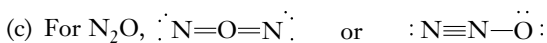
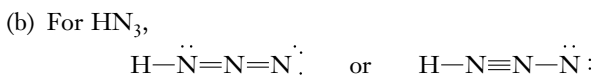
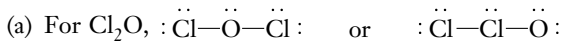
63. Assign a formal charge to each atom in the following:



64. Assign a formal charge to each atom in the following:



- *65. With the aid of formal charges, explain which Lewis formula is more likely to be correct for each given molecule.



66. Write Lewis formulas for three different atomic arrangements with the molecular formula HCNO . Indicate all formal charges. Predict which arrangement is likely to be the least stable and justify your selection.

Ionic Versus Covalent Character and Bond Polarities

67. Distinguish between polar and nonpolar covalent bonds.
68. Why is an HCl molecule polar but a Cl_2 molecule is nonpolar?
69. How does one predict that the chemical bonding between two elements is likely to be ionic?

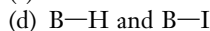
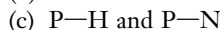
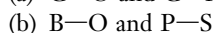
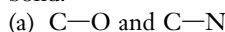
70. How does one predict that a covalent bond between two atoms is polar?

71. Ionic compounds generally have a higher melting point than covalent compounds. What is the major difference in the structures of ionic and covalent compounds that explains the difference in melting points?

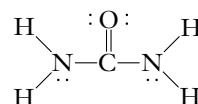
72. Explain why the electrons in the carbon–fluorine covalent bond tend to move more toward the halogen atom than do the electrons in the carbon–bromine covalent bond.

73. Why do we show only partial charges, and not full charges, on the atoms of a polar molecule?

74. In each pair of bonds, indicate the more polar bond, and use $\delta+$ and $\delta-$ to show the direction of polarity in each bond.



75. The molecule below is urea, a compound used in plastics and fertilizers.



- (a) Which bonds in this molecule are polar and which are nonpolar?

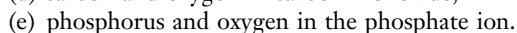
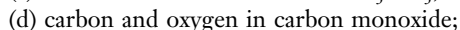
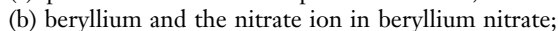
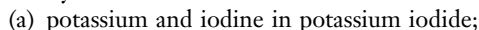
- (b) Which is the most polar bond in the molecule? Which atom is the partial negative end of this bond?

76. (a) Which two of the following pairs of elements are most likely to form ionic bonds? Te and H ; C and F ; Ba and F ; N and F ; K and O . (b) Of the remaining three pairs, which one forms the least polar, and which the most polar, covalent bond?

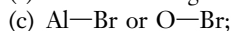
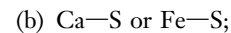
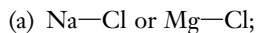
77. (a) List three reasonably nonpolar covalent bonds between dissimilar atoms. (b) List three pairs of elements whose compounds should exhibit extreme ionic character.

78. Classify the bonding between the following pairs of atoms as ionic, polar covalent, or nonpolar covalent. (a) Li and O ; (b) Br and I ; (c) Na and H ; (d) O and O ; (e) H and O .

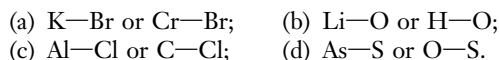
79. For each of the following, tell whether the bonding is primarily ionic or covalent.



80. Identify the bond in each of the following bonded pairs that is likely to have the greater proportion of “ionic character.”

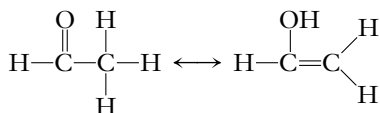


81. Identify the bond in each of the following bonded pairs that is likely to have the greater proportion of “covalent character.”

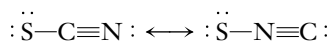


CONCEPTUAL EXERCISES

82. When asked to give an example of resonance structures, a student drew the following. Why is this example incorrect?



83. Why is the following not an example of resonance structures?



84. Describe the circumstances under which one would expect a bond to exhibit 100% “covalent character” and 0% “ionic character.” Give an example of two bonded atoms that would be predicted to exhibit 0% “ionic character.”
85. The following properties can be found in a handbook of chemistry:



Camphor sublimes readily.

camphor, $\text{C}_{10}\text{H}_{16}\text{O}$ —colorless crystals; specific gravity, 0.990 at 25°C; sublimes, 204°C; insoluble in water; very soluble in alcohol and ether.

praseodymium chloride, PrCl_3 —blue-green needle crystals; specific gravity, 4.02; melting point, 786°C; boiling point, 1700°C; solubility in cold water, 103.9 g/100 mL H_2O ; very soluble in hot water.

Would you describe each of these as ionic or covalent? Why?

BUILDING YOUR KNOWLEDGE

86. Look up the properties of NaCl and PCl_3 in a handbook of chemistry. Why do we describe NaCl as an ionic compound and PCl_3 as a covalent compound?
87. (a) How many moles of electrons are transferred when 10.0 g of magnesium react as completely as possible with 10.0 g of fluorine to form MgF_2 ? (b) How many electrons is this? (c) Look up the charge on the electron in coulombs. What is the total charge, in coulombs, that is transferred?
88. Write the formula for the compound that forms between (a) calcium and nitrogen, (b) aluminum and oxygen, (c) potassium and selenium, and (d) strontium and chlorine. Classify each compound as covalent or ionic.
- *89. Write the Lewis formulas for the nitric acid molecule (HNO_3) that are consistent with the following bond length data: 1.405 Å for the bond between the nitrogen atom and the oxygen atom that is attached to the hydrogen atom; 1.206 Å for the bonds between the nitrogen atom and each of the other oxygen atoms.
90. Write the total ionic and net ionic equations for the reaction between each of the following pairs of compounds in aqueous solution. Then give the Lewis formula for each species in these equations. (a) HCN and NaOH ; (b) HCl and NaOH ; (c) CaCl_2 and Na_2CO_3 .
91. Sketch a portion of an aqueous solution of NaCl . Show the Lewis formulas of the solute and solvent species. Suggest the relative location of each species with respect to the others.
92. Sketch a portion of an aqueous solution of CH_3COOH . Show the Lewis formulas of the solute and solvent species. Suggest the relative location of each species with respect to the others.
93. Determine the oxidation number of each element in the following compounds: (a) CO_2 ; (b) CH_4 ; (c) PF_3 ; (d) PF_5 ; (e) Na_2O ; (f) Na_2O_2 .