

Part III

Blessed Be the Bonds That Tie

The 5th Wave

By Rich Tennant



In this part . . .

Chemists operate in the microscopic world of atoms and molecules. I show you in this part the modern atomic theory — the quantum theory and how a radio wave and a locomotive are similar. I then give you the opportunity to explore chemical bonding — the ionic bonds that hold together the ions in a salt crystal and the covalent bonds that hold together a sugar molecule.

This part also shows you how to predict the shape of molecules. In chemistry, especially biochemistry, shape really does matter, and you discover how to determine the shape of molecules. You also uncover hybridization and molecular orbitals, theories about bonding. I revisit the periodic table and discuss periodic trends and finally end up talking about intermolecular forces, those forces that allow water to help support life on earth and make your hair curly or straight.

Chapter 12

Where Did I Put That Electron? Quantum Theory

In This Chapter

- ▶ Taking a closer look at matter and light
 - ▶ Getting acquainted with Bohr
 - ▶ Finding out about the quantum mechanical model
-

The development of Rutherford's nuclear model that I discuss in Chapter 4 was an important step toward understanding the atom. In this model, protons and neutrons are located in a dense central core of the atom called the *nucleus*, while the electrons are located outside the nucleus. These electrons interact (or react) with electrons from other atoms. The nuclei are really only indirectly involved in chemical reactions.

Because the behavior of electrons is so very important, understanding this behavior is crucial. Scientists discovered that the behavior of electrons is very closely related to the behavior of light. The investigation of light and electrons led to a fundamental revision of physics known as quantum mechanics. This chapter gives you just the basics you may need to know about quantum mechanics during your Chem I class. As you venture deeper into your chemistry studies, you'll encounter more in-depth and complicated matters about quantum mechanics.

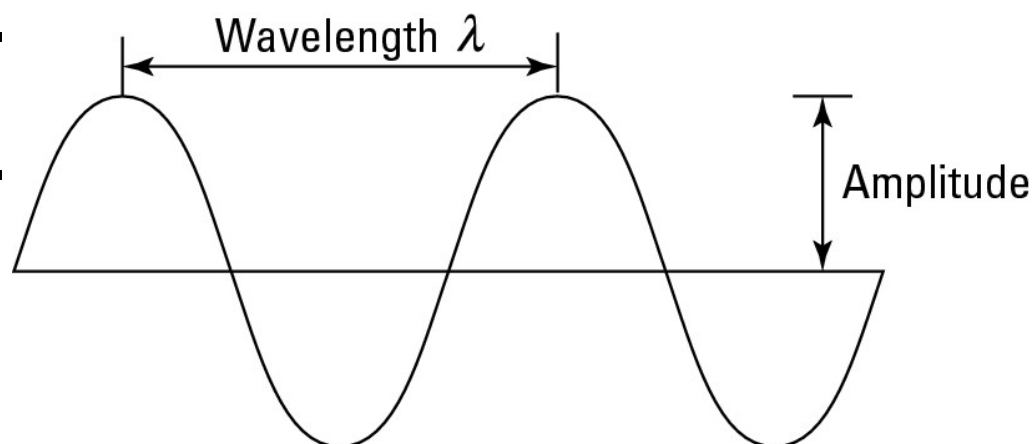
Facing the Concepts of Matter and Light

Before you can understand the behavior of the electron, you need to look first at the properties of light. Here I define a few terms and relationships concerning light, and then I focus on spectroscopy as the interaction of light and electrons.

Understanding the components

To begin to grasp the nature of electrons, examining the nature of light is necessary. Visible light, X-rays, microwaves, radio waves, and so on are all various forms of electromagnetic radiation. *Electromagnetic radiation*, sometimes referred to as *radiant energy*, carries energy through space. If that space is a vacuum, all types of electromagnetic radiation travel at the speed of light, denoted by c , 3.00×10^8 m/s. These waves of electromagnetic radiation also have the following three properties (see Figure 12-1):

Figure 12-1:
Properties of
waves.



- ✓ **Amplitude:** The *amplitude* of a wave is the height of the wave from the midpoint or baseline of the wave to its peak (highpoint). Think of it as a measure of the strength

of the electromagnetic radiation. For the visible part of the spectrum, you interpret the amplitude as the intensity or brightness of the light.

- ✓ **Wavelength:** *Wavelength*, λ (lambda), is the distance between two identical adjacent points of a wave, such as peaks (high points) or troughs (low points). You may express the wavelength in any unit of length, although many times chemists choose a specific unit for a specific type of electromagnetic radiation (meters for radio and TV waves or angstroms [10^{-10} m] for X-rays).
- ✓ **Frequency:** The *frequency*, ν (nu), is the number of waves that pass a given point during a specified time interval. Frequency has units of cycles per time, but chemists generally accept the cycles part as understood and omit it, leaving frequency expressed as reciprocal time (1/time). The SI base unit for time is the second, so frequency is measured in cycles per second and has the units of 1/s or s^{-1} .

Because these electromagnetic waves are all traveling at the speed of light, the wavelength and the frequency of the light have a direct relationship. If the wavelength is short, many waves pass a reference point per given amount of time and the frequency is high. If the wavelength is long, fewer waves pass the reference point during the same amount of time and the frequency is lower. You can see the relationship between the wavelength and frequency with this equation:

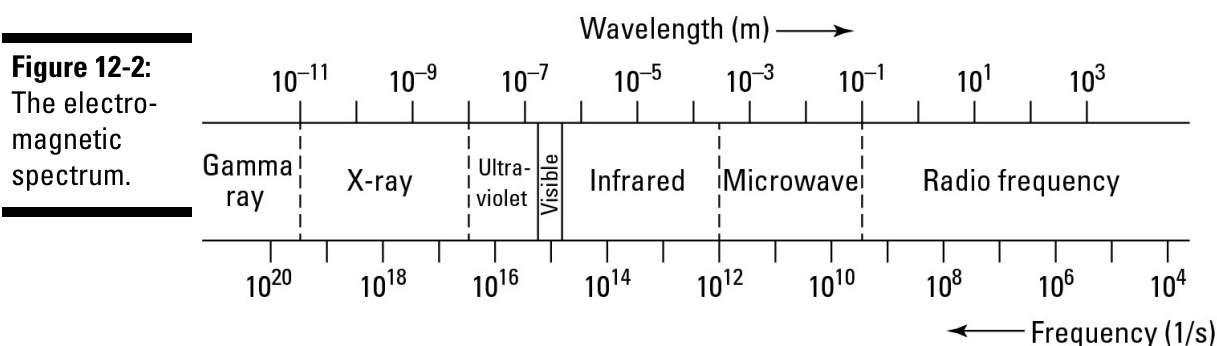
$$\lambda\nu = c$$

where λ is the wavelength (in meters), ν is the frequency (in s^{-1}), and c is the speed of light (in m/s).



In working problems with this direct relationship between wavelength and frequency, expressing the wavelength, frequency, and speed of light in the units of meters, cycles per second, and meters per second is easiest.

Figure 12-2 shows the electromagnetic spectrum in order of increasing wavelength. Notice that gamma rays have the shortest wavelength (highest frequency) and radio waves have the longest wavelength (lowest frequency). Also notice the visible spectrum (the part of the electromagnetic spectrum that you can detect with your eyes) is a relatively small part of the entire electromagnetic spectrum. Scientists generally express the wavelength of the visible part of the spectrum in nanometers (10^{-9} meters), and the wavelength ranges from violet at about 400 nm to red at 750 nm.



As mentioned previously, frequency is usually in cycles per second (or simply s^{-1}). This unit of cycles per second is a hertz (Hz), and thus frequency can be in hertz or as any combination with SI prefixes (such as kilohertz). Chemists commonly express the frequency of radio stations in this fashion. Thus, 900 on the AM dial would be 900 kHz (kilohertz) or $900,000 s^{-1}$.

Spectroscopy

In the early 1900s, Max Planck, a German scientist, found that energy came in discrete units. Planck labeled each of these units a *quantum*. He was able to relate the energy of these quanta to the frequency of the light with a simple constant. His theory of quantized energy of the electrons helped explain the fact that elements sometimes gave off light of certain distinct wavelengths. This relationship is

$$E = h\nu$$

E is the energy of the radiation in joules, h is Planck's constant ($6.626 \times 10^{-34} \text{ J} \times \text{s}$), and ν is the frequency of the radiation in s^{-1} .

The energy of a photon may also relate to its wavelength if you combine the following equations:

$$\lambda\nu = c \text{ and } E = h\nu$$

to get

$$E = \frac{hc}{\lambda}$$

Einstein extended Planck's work to say that particles of light known as *photons* carry Planck's quanta of energy. Thus, light has both wave properties (λ and ν) and particle (photon) properties. This dual nature of light is very important in helping you understand the behavior of light, and a better understanding of the behavior of light leads to a better understanding of how light interacts with electrons.

According to Planck's theory, matter could only release or absorb energy in multiples of this quantum (packet) of energy. It's like a one-legged person going up the stairs. The individual can rest on one stair or another but not between the stair steps. Planck's theory means that the energy is *quantized*; that is, only certain values (multiples of the quantum) are allowed. A logical

extension of Planck's theory is that the electrons in an atom can have only certain quantized energies associated with them.

Support for Planck's theory is found in the emission and absorption of elements.

Emission spectra

Light from most sources contains many different frequencies. You can separate these different frequencies into a *spectrum* (a range or band of wavelengths) using a prism or diffraction grating. The type of spectrum that you get depends upon the source of the light. For example, light from the sun or some other very hot object produces a *continuous spectrum*, a spectrum consisting of all frequencies of light.

When you excite elements in the gas phase by heating them or using electricity, the elements also emit light at various frequencies. The separation of this light yields a spectrum with only certain distinct frequencies, not a continuous spectrum. These separate frequencies appear as separate lines in the spectrum, so this type of spectrum is named a *line spectrum*. Because the spectrum results from individual atoms emitting light, it's also called an *emission spectrum*. The lines observed are characteristic of the element; each element gives a different combination of lines.

Absorption spectra

Another type of spectrum is an *absorption spectrum*. To yield this type of spectrum, the atoms must be in the gaseous state (as for an emission spectrum). However, instead of the thermal or electrical energy needed to produce an emission spectrum, light from a continuous spectrum source is used. The passage of this light through the gaseous atoms results in the absorption

of some of the frequencies. The absorption spectrum results from this transmitted light.

If you use atoms of the same element for an emission spectrum and an absorption spectrum, you find that the lines in the emission spectrum correspond to the absorbed frequencies in the absorption spectrum. This correspondence of frequencies indicates that a relationship must exist between the emission of light and the absorption of light. Because specific frequencies are involved, according to Planck's theory, the element can emit or absorb only specific quanta of energy.

The first step toward understanding the spectra of the elements came from an examination of the spectrum of the simplest element — hydrogen. The spectrum of hydrogen consists of groups of lines in different regions of the spectrum. Analysis of this repeated pattern led Niels Bohr to develop a theory to explain not only the spectrum of the hydrogen atom but also a structure of the atom itself (see the next section for more information).

Grasping Bohr's Atomic Model

Niels Bohr, attempting to explain the line spectrum of hydrogen, developed a model combining the concepts developed by Planck and Einstein (addressed previously under "Spectroscopy"). Bohr assumed that the atom contained a nucleus and that the electrons circled the nucleus in circular orbits. He had to introduce three postulates in order to make his model consistent with observations:

- ✓ The electron in a hydrogen atom may only occupy orbits of certain radii that corresponded to certain discrete energies.

- ✓ While an electron is in an allowed energy state (orbit), it does not radiate energy and it remains in that orbit without spiraling into the nucleus.
- ✓ An electron may move from one energy state to another by absorbing or releasing energy. The energy needed is the difference between one energy level and another and is equal to a photon, $E = h\nu$.



In Bohr's atomic model, the number n designates the energy state (level) occupied by an electron. The smaller the n value, the smaller the radius (closer to the nucleus) and the lower the energy associated with the electron. An electron that occupies its lowest possible energy level is in its *ground state*. It may absorb energy to give an absorption spectra, and when it does, the energy absorbed must equal the difference between the ground state energy and a higher energy level. The electron will then move from the lower state to the higher one, which is an *excited state*. The electron can return to its ground state by emitting a photon of energy equal to the energy difference in these two states. These transitions explain the emission line spectra that occur when atoms emit distinct lines of frequencies (which I discuss in "Emission spectra").

The Bohr model works well in predicting the spectral lines of hydrogen but not nearly as well for any other atom. In other atoms, the additional electron-nucleus attractions and the electron-electron repulsions introduce complications that Bohr's model can't handle. In addition, the critical assumption of the Bohr model, that electrons travel in discrete orbits, was found to be incorrect. The motion of the electrons is far more complex. It was up to other scientists to build upon this notion. The following sections identify a couple other scientists' work with the atomic model.

De Broglie's contribution

The work of Planck and Einstein firmly established the dual nature of radiant energy. Light had properties of both particles (photons) and waves. Louis de Broglie in the early 1920s proposed the idea that if light waves had properties of particles, then particles could have the properties of waves (wavelength and so on). De Broglie put forth the idea that a simple equation relates the wavelength, λ , associated with an object, the object's mass, m , and its velocity, v :

$$\lambda = \frac{h}{mv}$$

where h is Planck's constant. This equation is the de Broglie relationship.



Don't confuse ν (frequency) with v (velocity).

De Broglie introduced the concept that all matter, even you, has both wave-like and particle-like properties. Looking at the mathematical relationship, note that the wavelength is inversely proportional to the mass. The larger the mass, the smaller the wave nature becomes and the more important the particle nature of the object. Therefore, you can describe a train, a car, or even a gold ball in terms of its wave nature, but the description wouldn't be very useful, because the wave nature of these objects is very small. They can best be described in terms of their particle nature. However, an electron, with its extremely tiny mass, has a much larger wave nature associated with it and may be better described with its wave properties.

De Broglie's hypothesis of the dual properties of electrons gained acceptance in 1927 when scientists found that a stream of electrons passing through a crystal exhibited the same behavior as a stream of X-rays. The scientific community began

to embrace the concept of the dual properties of both energy and matter.

Heisenberg's contribution

Planck's theory, even the wave portion, was still based on classical physics, but along came Heisenberg and his introduction of uncertainty.

The concept of the wave-like nature of the electron had a major impact on modern physics and the view of the world. In classical mechanics, scientists treated the electron as a particle with a certain measurable position and momentum. If they knew the position and momentum, physicists could then calculate the position and momentum at points in the past and in the future with a great deal of accuracy. However, the German physicist Werner Heisenberg realized that with something as small as an electron, the location of the particle can't be measured with accuracy.

Heisenberg formalized his ideas in his 1927 paper on the uncertainty principle, which states that accurately determining both the position and momentum of a particle simultaneously is impossible. You may determine one, but in doing so your measurement techniques influence and change the other. Heisenberg's uncertainty principle means that you can't determine the precise position of the electron; the best you can do is assign probabilities to volumes of space in which you may find electrons.

Understanding the Quantum Mechanical Model

In 1926, Erwin Schrödinger introduced a mathematical relationship called a *wave equation* that takes into account both the wave and particle nature of the electron. That equation was instrumental in the development of a completely new way of representing the behavior of subatomic particles. This new field is *wave mechanics* or *quantum mechanics*.

Solving Schrödinger's wave equation for the electron in hydrogen results in the generation of a mathematical expression called a *wave function*, represented by Greek ψ (psi). The square of this wave function, ψ^2 , provides you with information concerning the probability of finding an electron at a certain location in hydrogen. Because of the Heisenberg uncertainty principle, Schrödinger represented this information in terms of a volume of space in which it is more probable to find the electron (not in terms of distinct orbits as described by Bohr).



In order to solve Schrödinger's wave equation for a specific electron in an atom, you must specify three numbers, called *quantum numbers*. In addition, you must use a fourth quantum number to differentiate between the two electrons sharing a specific volume of space. The four quantum numbers and their mathematically allowed values are as follows:

- ✓ **Principal quantum number:** This number, n , denotes the energy level or shell that the electron occupies. The values of n are positive integers 1, 2, 3, 4, and so on. The larger the value of n , the greater the average distance the electron is from the nucleus and the higher the energy associated with the electrons.
- ✓ **Angular momentum quantum number:** This number, l , designates the shape of the volume of space within an energy level that most likely contains the electrons. This volume of space is a *subshell*. The allowed values of l

range from 0 to $n - 1$ in integer steps. For example, if $n = 1$, then the only allowed value of l is 0. If $n = 3$, then l may have the values of 0, 1, and 2 ($= 3 - 1$). The various values of l correspond to different shapes. In addition, each subshell contains one or more orbitals, volumes of space in which electrons may be found. The orbitals contained in a specific subshell have the same energy. An individual orbital may contain a maximum of two electrons.

✓ **Magnetic quantum number:** This number, m_l , describes the orientation of the orbital in space. It may have values of $-l$ to 0 to $+l$ in integer steps. For example if $l = 0$, then the only allowed value for m_l is 0. If $l = 3$, then m_l may have values of $-3, -2, -1, 0, +1, +2$, and $+3$. This means that when considering a subshell of $l = 3$, seven different orbitals (seven different allowed values of m_l) are within that subshell.

✓ **Electron spin quantum number:** This number, m_s , designates the direction of the magnetic field that the electron is generating. It may align either with or against the field of the atom. Therefore, two values are allowed, $+\frac{1}{2}$ and $-\frac{1}{2}$.

Probabilities: In science and the real world

The idea of probabilities associated with the location of an electron may seem strange, but you deal with probabilities of location in your macroscopic life every day. Do you ever ride trains? Can you predict the *exact* time the train will arrive at the station? Probably not. However, you can easily establish an interval of time (perhaps ten minutes or so) that is most probable for the train to arrive. Your friends may know that the movie you plan to attend is showing from 7:00 to 9:15 p.m. Does this mean that they know without a doubt that you'll be sitting in that movie theater at 7:05 that evening? Probably not. You may be in the restroom or standing in line at the concession stand. It is most probable that you are in that movie

theater, but not certain. Scientists use probabilities in a similar way in the microscopic world.

Under the quantum mechanical model, chemists and physicists speak of probability densities or electron densities instead of an exact location. Scientists commonly calculate probability densities at a 90 percent probability level, meaning that the size of the three-dimensional figure is such that you can probably find the electron within that volume of space 90 percent of the time. Scientists sometimes call these electron density plots *electron clouds* and quite commonly use them in representing the probabilities of finding various electrons within an atom.

Chapter 13

Opposites Do Attract: Ionic Bonding

In This Chapter

- ▶ Finding out why and how ions are formed
 - ▶ Discovering how cations and anions are formed
 - ▶ Understanding ions made of groups of atoms
 - ▶ Deciphering the formulas of ionic compounds
 - ▶ Seeing how to name ionic compounds
 - ▶ Clarifying the difference between electrolytes and nonelectrolytes
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If I had to point to the one thing that made me want to major in chemistry, it would be the reactions of salts. I remember the day clearly: It was the second half of general chemistry, and I was doing qualitative analysis (finding out what's in a sample) of salts. I really enjoyed the colors of the compounds formed in the reactions I was doing, and the labs were fun and challenging. I was hooked.

In this chapter, I introduce you to *ionic bonding*, the type of bonding that holds salts together. I discuss simple ions and polyatomic ions: how they form and how they combine. I also show you how to predict the formulas of ionic compounds and how chemists detect ionic bonds. You may not decide to devote your life to chemistry after reading this chapter, but it will definitely help you get through your class.

Magically Bonding Ions: Sodium + Chlorine = Table Salt

Sodium is a fairly typical metal. It's silvery, soft, and a good conductor. It's also highly reactive. Sodium is normally stored under oil to keep it from reacting with the water in the atmosphere. If you melt a freshly cut piece of sodium and put it into a beaker filled with greenish-yellow chlorine gas, something very impressive happens. The molten sodium begins to glow with a white light that gets brighter and brighter. The chlorine gas swirls, and soon the color of the gas begins to disappear. In a couple of minutes, the reaction is over, and the beaker can be safely uncovered. You find a white crystalline substance, table salt (NaCl), deposited on the inside of the beaker.

In the following sections, I show you what happens during the chemical reaction to create table salt and, more importantly, why it occurs. Understanding these concepts will go a long way in your investigation into ionic bonding.

Meeting the components

If you really stop and think about it, the process of creating table salt is pretty remarkable. You take the following two substances that are both very hazardous (the Germans used chlorine gas against the opposing troops during World War I), and from them you make a substance that's necessary for life.

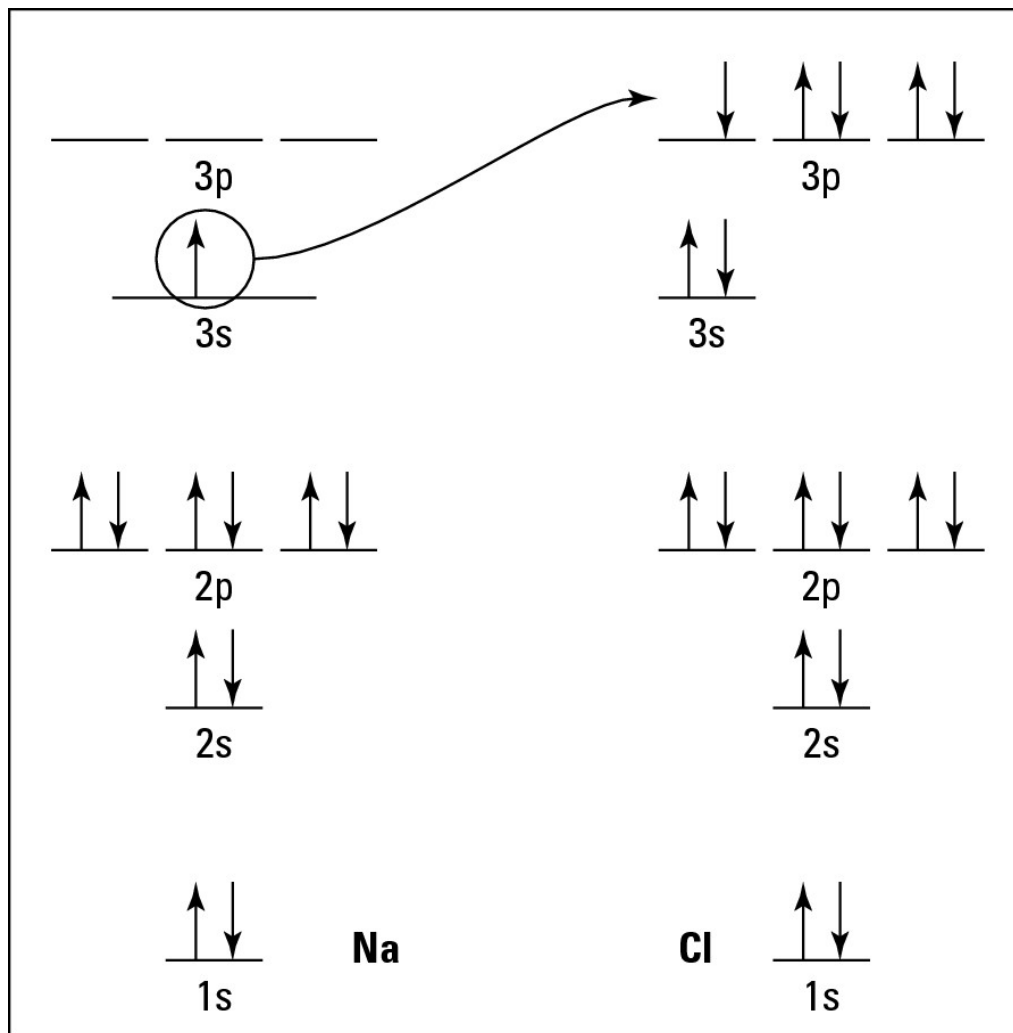
✓ **Sodium** is an alkali metal, a member of the IA family on the periodic table. The Roman numerals at the top of the A families show the number of valence electrons (s and p electrons in the outermost energy level) in the particular element (see Chapter 5 for details). So sodium has 1

valence electron and 11 total electrons because its atomic number is 11.

You can use an energy-level diagram to represent the distribution of electrons in an atom. Sodium's energy-level diagram is shown in Figure 13-1. (If energy-level diagrams are new to you, check out Chapter 4. A number of minor variations are commonly used in writing energy-level diagrams, so don't worry if the diagrams in Chapter 4 are slightly different than the ones I show you here.)

Chlorine is a member of the halogen family — the VIIA family on the periodic table. It has 7 valence electrons and a total of 17 electrons. The energy-level diagram for chlorine is also shown in Figure 13-1.

Figure 13-1:
Energy-level
diagrams for
sodium and
chlorine.



If you want, instead of using the bulky energy-level diagram to represent the distribution of electrons in an atom, you can use the electron configuration. (For a complete discussion of electron configurations, see Chapter 4.) Write, *in order*, the energy levels being used, the orbital types (s, p, d, and so on), and — in superscript — the number of electrons in each orbital. Here are the electronic configurations for sodium and chlorine:

Sodium (Na) $1s^2 2s^2 2p^6 3s^1$

Chlorine (Cl) $1s^2 2s^2 2p^6 3s^2 3p^5$

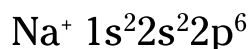
Understanding the reaction

The noble gases are the VIIIA elements on the periodic table. They're extremely unreactive because each atom's *valence* energy level (outermost energy level) is filled. Achieving a filled (complete) valence energy level is a driving force in nature in terms of chemical reactions, because that's when elements become stable, or *unreactive*. They don't lose, gain, or share electrons.

The other elements in the A families on the periodic table do gain, lose, or share valence electrons in order to fill their valence energy level and become stable. Because this process, in most cases, involves filling the outermost s and p orbitals, it's sometimes called the *octet rule* — elements gain, lose, or share electrons to reach a full octet (eight valence electrons: two in the s orbital and six in the p orbital).

Sodium's role

Sodium has one valence electron; by the octet rule, it becomes stable when it has eight valence electrons. Two possibilities exist for sodium to become stable: It can gain seven more electrons to fill energy level 3, or it can lose the one 3s electron so that energy level 2 (which is already filled with eight electrons) becomes the valence energy level. In general, the loss or gain of one, two, or sometimes even three electrons can occur, but an element doesn't ordinarily lose or gain more than three electrons. So to gain stability, sodium loses its 3s electron. At this point, it has 11 protons (11 positive charges) and 10 electrons (10 negative charges). The once-neutral sodium atom now has a single positive charge [11(+) plus 10(−) equals 1+]. It's now an *ion*, an atom that has a charge due to the loss or gain of electrons. And ions that have a positive charge (such as sodium) due to the loss of electrons are called *cations*. You can write an electron configuration for the sodium cation:

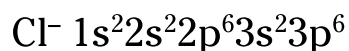


The sodium ion (cation) has the same electron configuration as neon, so it's *isoelectronic* with neon. So has sodium become neon by losing an electron? No. Sodium still has 11 protons, and the number of protons determines the identity of the element.

The neutral sodium atom and the sodium cation have the difference of one electron. In addition, their chemical reactivities are different *and* their sizes are different. The cation is smaller. The outermost energy level determines the size of an atom or ion (or, in this case, cation). Because sodium loses an entire energy level to change from an atom to a cation, the cation is smaller.

Chlorine's role

Chlorine has seven valence electrons. To obtain its full octet, it must lose the seven electrons in energy level 3 or gain one at that level. Because elements don't generally gain or lose more than three electrons, chlorine must gain a single electron to fill energy level 3. At this point, chlorine has 17 protons (17 positive charges) and 18 electrons (18 negative charges). So chlorine becomes an ion with a single negative charge (Cl^-). The neutral chlorine atom becomes the chloride ion. Ions with a negative charge due to the gain of electrons are called *anions*. The electronic configuration for the chloride anion is



The chloride anion is isoelectronic with argon. The chloride anion is also slightly larger than the neutral chlorine atom. To complete the octet, the one electron gained went into energy level 3, but now 17 protons are attracting 18 electrons. The attractive force on each electron has been reduced slightly, and the electrons are free to move outward a little, making the anion a little larger.



In general, a cation is smaller than its corresponding atom, and an anion is slightly larger.

Ending up with a bond

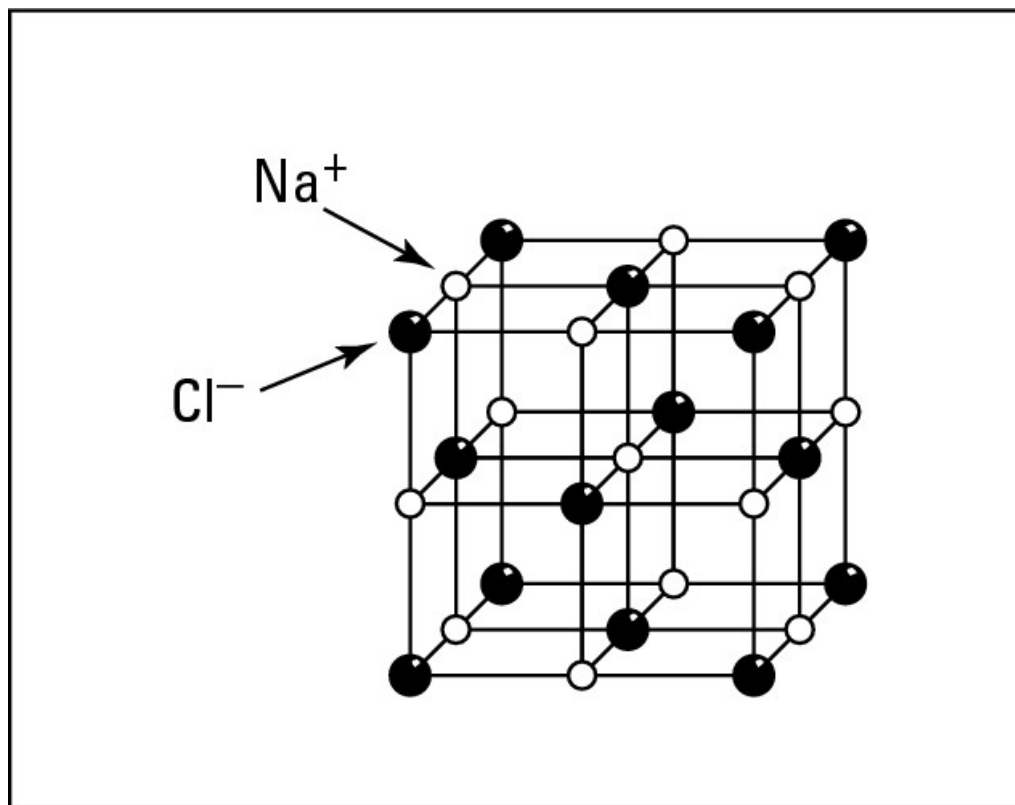
Sodium can achieve its full octet and stability by losing an electron. Chlorine can fill its octet by gaining an electron. If the two are in the same container, then the electron sodium loses can be the same electron chlorine gains. I show this process in Figure 13-1, indicating that the 3s electron in sodium is transferred to the 3p orbital of chlorine.

The transfer of an electron creates ions — cations (positive charge) and anions (negative charge) — and opposite charges attract each other. The Na^+ cation attracts the Cl^- anion and forms the compound NaCl , or table salt. This is an example of an *ionic bond*, which is a *chemical bond* (a strong attractive force that keeps two chemical elements together) that comes from the *electrostatic attraction* (attraction of opposite charges) between cations and anions.

The compounds that have ionic bonds are commonly called *salts*. In sodium chloride, a crystal is formed in which each sodium cation is surrounded by six different chloride anions, and each chloride anion is surrounded by six different sodium cations. The crystal structure is shown in Figure 13-2.

Figure 13-2:

Crystal
structure of
sodium
chloride.



Notice the regular, repeating structure. Different types of salts have different crystal structures. Cations and anions can have more than one unit of positive or negative charge if they lose or gain more than one electron. In this fashion, many different kinds of salts are possible.

Ionic bonding, the bonding that holds the cations and anions together in a salt, is one of the two major types of bonding in chemistry. The other type, *covalent bonding*, is described in Chapter 14. Grasping the concepts involved in ionic bonding makes understanding covalent bonding much easier.

Identifying Positive and Negative Ions: Cations and Anions

The basic process that occurs when sodium chloride is formed also occurs when other salts are formed. A metal loses electrons, and a nonmetal gains those electrons. Cations and anions are formed, and the electrostatic attraction between the positives and negatives brings the particles together and creates the ionic compound.



A metal reacts with a nonmetal to form an ionic bond.

You can often determine the charge an ion normally has by the element's position on the periodic table. For example, all the alkali metals (the IA elements) lose a single electron to form a cation with a $1+$ charge. In the same way, the alkaline earth metals (IIA elements) lose two electrons to form a $2+$ cation. Aluminum, a member of the IIIA family, loses three electrons to form a $3+$ cation.

By the same reasoning, the halogens (VIIA elements) all have seven valence electrons. All the halogens gain a single electron to fill their valence energy level. And all of them form an anion with a single negative charge. The VIA elements gain two electrons to form anions with a $2-$ charge, and the VA elements gain three electrons to form anions with a $3-$ charge.

Table 13-1 shows the family, element, ion name, and ion symbol for some common monoatomic (one atom) cations, and Table 13-2 gives the same information for some common monoatomic anions.

Table 13-1		Some Common Monoatomic Cations	
<i>Family</i>	<i>Element</i>	<i>Ion Name</i>	<i>Ion Symbol</i>
IA	Lithium	Lithium cation	Li ⁺
	Sodium	Sodium cation	Na ⁺
	Potassium	Potassium cation	K ⁺
IIA	Beryllium	Beryllium cation	Be ²⁺
	Magnesium	Magnesium cation	Mg ²⁺
	Calcium	Calcium cation	Ca ²⁺
	Strontium	Strontium cation	Sr ²⁺
	Barium	Barium cation	Ba ²⁺
IB	Silver	Silver cation	Ag ⁺
IIB	Zinc	Zinc cation	Zn ²⁺
IIIA	Aluminum	Aluminum cation	Al ³⁺

Table 13-2		Some Common Monoatomic Anions	
<i>Family</i>	<i>Element</i>	<i>Ion Name</i>	<i>Ion Symbol</i>
VA	Nitrogen	Nitride anion	N ³⁻
	Phosphorus	Phosphide anion	P ³⁻
VIA	Oxygen	Oxide anion	O ²⁻
	Sulfur	Sulfide anion	S ²⁻
VIIA	Fluorine	Fluoride anion	F ⁻
	Chlorine	Chloride anion	Cl ⁻
	Bromine	Bromide anion	Br ⁻
	Iodine	Iodide anion	I ⁻



Determining the number of electrons that members of the transition metals (the B families) lose is more difficult. In fact, many of these elements lose a varying number of electrons so that they form two or more cations with different charges.

The electrical charge that an atom achieves is sometimes called its *oxidation state*. Many of the transition metal ions have varying oxidation states. Table 13-3 shows some common transition metals that have more than one oxidation state.

Table 13-3 Some Common Metals with More Than One Oxidation State			
<i>Family</i>	<i>Element</i>	<i>Ion Name</i>	<i>Ion Symbol</i>
VIB	Chromium	Chromium(II) or chromous	Cr ²⁺
		Chromium(III) or chromic	Cr ³⁺
VIIB	Manganese	Manganese(II) or manganous	Mn ²⁺
		Manganese(III) or manganic	Mn ³⁺
VIIIB	Iron	Iron(II) or ferrous	Fe ²⁺
		Iron(III) or ferric	Fe ³⁺
	Cobalt	Cobalt(II) or cobaltous	Co ²⁺
		Cobalt(III) or cobaltic	Co ³⁺
IB	Copper	Copper(I) or cuprous	Cu ⁺
		Copper(II) or cupric	Cu ²⁺
IIB	Mercury	Mercury(I) or mercurous	Hg ₂ ²⁺
		Mercury(II) or mercuric	Hg ²⁺
IVA	Tin	Tin(II) or stannous	Sn ²⁺
		Tin(IV) or stannic	Sn ⁴⁺
	Lead	Lead(II) or plumbous	Pb ²⁺
		Lead(IV) or plumbic	Pb ⁴⁺

Notice that these cations can have more than one name. The current way of naming ions is to use the metal name, such as chromium, followed in parentheses by the ionic charge written as a Roman numeral, such as (II). An older way of naming ions uses *-ous* and *-ic* endings. When an element has more than one ion — chromium, for example — the ion with the lower oxidation state (lower numerical charge, ignoring the + or –) is given an *-ous* ending, and the ion with the higher oxidation state (higher numerical charge) is given an *-ic* ending. So for

chromium, the Cr^{2+} ion is named *chromous* and the Cr^{3+} ion is named *chromic*. (See the section “Naming Ionic Compounds,” later in this chapter, for more on naming ions.)

Grasping Polyatomic Ions

Ions aren’t always *monoatomic*, composed of just one atom. Ions can also be *polyatomic*, composed of a group of atoms. For example, refer to Table 13-3. Notice anything about the mercury(I) ion? Its ion symbol, Hg_2^{2+} , shows that two mercury atoms are bonded together. This group has a 2+ charge, with each mercury cation having a 1+ charge. The mercurous ion is classified as a polyatomic ion.

Polyatomic ions are treated the same as monoatomic ions (see “Naming Ionic Compounds,” later in this chapter). Table 13-4 lists some important polyatomic ions. Many of the compounds you’ll encounter in chemistry contain polyatomic ions.

Table 13-4 Some Important Polyatomic Ions

Ion Name	Ion Symbol
Sulfate	SO_4^{2-}
Sulfite	SO_3^{2-}
Nitrate	NO_3^-
Nitrite	NO_2^-
Hypochlorite	ClO^-
Chlorite	ClO_2^-
Chlorate	ClO_3^-
Perchlorate	ClO_4^-

Acetate	$\text{C}_2\text{H}_3\text{O}_2^-$
Chromate	CrO_4^{2-}
Dichromate	$\text{Cr}_2\text{O}_7^{2-}$
Arsenate	AsO_4^{3-}
Hydrogen phosphate	HPO_4^{2-}
Dihydrogen phosphate	H_2PO_4^-
Bicarbonate or hydrogen carbonate	HCO_3^-
Bisulfate or hydrogen sulfate	HSO_4^-
Mercury(I)	Hg_2^{2+}
Ammonium	NH_4^+
Phosphate	PO_4^{3-}
Carbonate	CO_3^{2-}
Permanganate	MnO_4^-
Cyanide	CN^-
Cyanate	OCN^-
Thiocyanate	SCN^-
Oxalate	$\text{C}_2\text{O}_4^{2-}$
Thiosulfate	$\text{S}_2\text{O}_3^{2-}$
Hydroxide	OH^-
Arsenite	AsO_3^{3-}
Peroxide	O_2^{2-}

The symbol for the sulfate ion, SO_4^{2-} , indicates that one sulfur atom and four oxygen atoms are bonded together and that the whole polyatomic ion has two extra electrons.

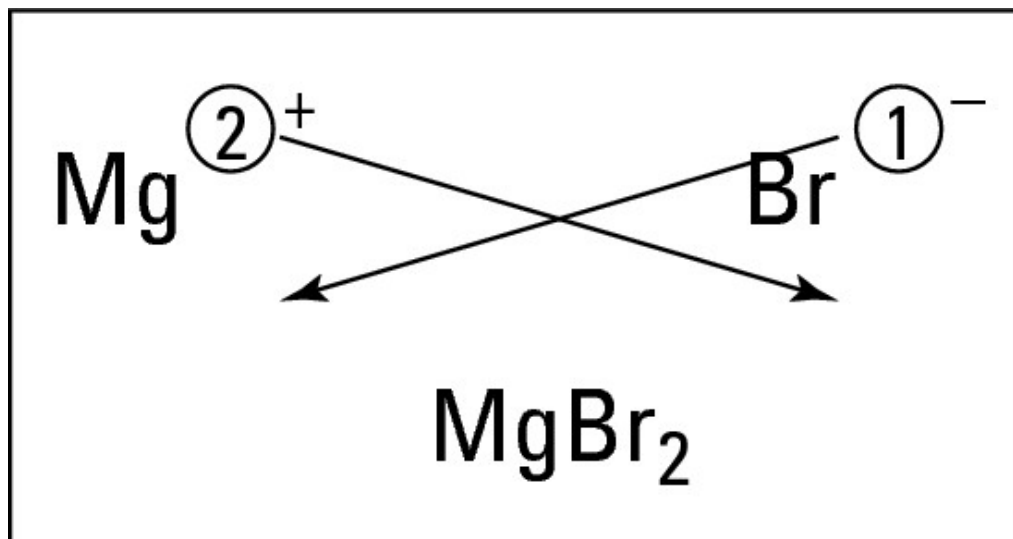
Putting Ions Together: Ionic Compounds

When an ionic compound is formed, the cation and anion attract each other, resulting in the formation of a salt (see “Magically Bonding Ions: Sodium + Chlorine = Table Salt,” earlier in this chapter). An important thing to remember is that the compound must be *neutral* — it must have equal numbers of positive and negative charges. In the following sections I show you how to predict the formula of an ionic compound simply by considering the electronic configurations and/or the charges on the cations and anions.

Putting magnesium and bromine together

Suppose you want to know the *formula*, or composition, of the compound that results from reacting magnesium with bromine. You start by putting the two atoms side by side, with the metal on the left, and then adding their charges. Figure 13-3 shows this process. (Forget about the crisscrossing lines for now. Well, if you’re really curious, check out the next section.)

Figure 13-3:
Figuring the
formula of
magnesium
bromide.



The electron configurations for magnesium and bromine are

Magnesium (Mg) $1s^2 2s^2 2p^6 3s^2$

Bromine (Br) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

Magnesium, an alkaline earth metal, has two valence electrons that it loses to form a cation with a 2+ charge. The electron configuration for the magnesium cation is

$\text{Mg}^{2+} 1s^2 2s^2 2p^6$

Bromine, a halogen, has seven valence electrons, so it gains one to complete its octet (eight valence electrons) and forms the bromide anion with a 1- charge. The electron configuration for the bromide anion is

$\text{Br}^{-} 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

Note that if the anion simply has 1 unit of charge, positive or negative, you normally don't write the 1; you just use the plus or minus symbol, with the 1 being understood. But for the example of the bromide ion, I use the 1.

The compound must be neutral; it must have the same number of positive and negative charges so that, overall, it has a zero charge. The magnesium ion has a 2+ charge, so it requires 2 bromide anions, each with a single negative charge, to balance the 2 positive charges of magnesium. So the formula of the compound that results from reacting magnesium with bromine is MgBr_2 .

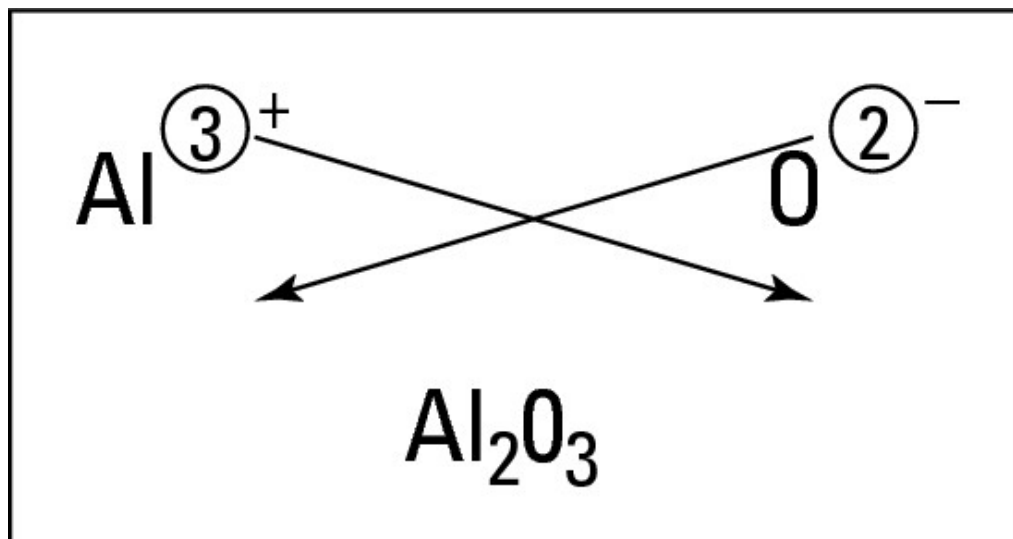
Applying the crisscross rule

A quick way to determine the formula of an ionic compound is to use the *crisscross rule*. The crisscross rule uses the ionic charges of the ions to predict the formula of the ionic compound. It doesn't work all the time, but it's a good way of checking your result using the previous method.

Refer to Figure 13-3 for an example of using this rule. Take the numerical value of the metal ion's superscript (forget about the charge symbol) and move it to the bottom right-hand side of the nonmetal's symbol — as a subscript. Then take the numerical value of the nonmetal's superscript and make it the subscript of the metal. (Note that if the numerical value is 1, it's just understood and not shown.) So in this example, you make magnesium's 2 a subscript of bromine and make bromine's 1 a subscript of magnesium (but because it's 1, you don't show it), and you get the formula MgBr_2 .

So what happens if you react aluminum and oxygen? Figure 13-4 shows the crisscross rule used for this reaction.

Figure 13-4:
Figuring the
formula of
aluminum
oxide.



Compounds involving polyatomic ions work exactly the same way. For example, here's the compound made from the ammonium cation (NH_4^+) and the sulfide anion (S^{2-}):



Notice that because two ammonium ions (two positive charges) are needed to neutralize the two negative charges of the sulfide ion, the ammonium ion is enclosed in parentheses and a subscript 2 is added.



The crisscross rule works very well, but you have to be careful if both ions have the same numeral in the superscript. Suppose that you want to write the compound formed when calcium reacts with oxygen. Magnesium, an alkaline earth metal, forms a $2+$ cation, and oxygen forms a $2-$ anion. So you might predict that the formula is



But this formula is incorrect. After you use the crisscross rule, you need to reduce all the subscripts by a common factor, if

possible. In this case, you divide each subscript by 2 and get the correct formula:



Naming Ionic Compounds

When you name inorganic compounds, you write the name of the metal first and then the nonmetal. Suppose, for example, that you want to name Li_2S , the compound that results from the reaction of lithium and sulfur. You first write the name of the metal, lithium, and then write the name of the nonmetal, adding an *-ide* ending so that *sulfur* becomes *sulfide*.



Ionic compounds involving polyatomic ions follow the same basic rule: Write the name of the metal first, and then simply add the name of the nonmetal (with the polyatomic anions, adding the *-ide* ending is unnecessary).



When the metal involved is a transition metal with more than one oxidation state (see “Identifying Positive and Negative Ions: Cations and Anions,” earlier in the chapter, for more info about that), the compound can be correctly named in more than one way. For example, suppose that you want to name the compound formed between the Fe^{3+} cation and the cyanide ion, CN^- . The preferred method is to use the metal name followed in parentheses by the ionic charge written as a Roman numeral: iron(III). But an older

naming method that is still sometimes used (so knowing it is a good idea) uses *-ous* and *-ic* endings. The ion with the lower oxidation state (lower numerical charge, ignoring the + or -) gets an *-ous* ending, and the ion with the higher oxidation state (higher numerical charge) gets an *-ic* ending. So, because Fe^{3+} has a higher oxidation state than Fe^{2+} , it's called a *ferric ion*. So the compound can be named

$\text{Fe}(\text{CN})_3$ iron(III) cyanide or ferric cyanide

Sometimes figuring out the charge on an ion can be a little challenging (and fun), so now I want to show you how to name $\text{FeNH}_4(\text{SO}_4)_2$.

I show you back in Table 13-4 that the sulfate ion has a 2- charge, and from the formula you can see that there are two of them. Therefore, you have a total of four negative charges. Table 13-4 also indicates that the ammonium ion has a 1+ charge, so you can figure out the charge on the iron cation.

<i>Ion</i>	<i>Charge</i>
Fe	?
NH_4	1+
$(\text{SO}_4)_2$	$(2-) \times 2$

Because you have a 4- for the sulfates and a 1+ for the ammonium, the iron must be a 3+ to make the compound neutral. So the iron is in the iron(III), or ferric, oxidation state. You can name the compound

$\text{FeNH}_4(\text{SO}_4)_2$ iron(III) ammonium sulfate or ferric ammonium sulfate

And, finally, if you have the name, you can derive the formula and the charge on the ions. For example, suppose that you're given the name *cuprous oxide*. You know that the cuprous ion is

Cu^+ and the oxide ion is O^{2-} . Applying the crisscross rule, you get the following formula:

Cuprous oxide Cu_2O

Contrasting Electrolytes and Nonelectrolytes

When an ionic compound such as sodium chloride is put into water, the water molecules attract both the cations and anions in the crystal (the crystal is shown in Figure 13-2) and pull them into the solution. (In Chapter 14, I talk a lot about water molecules and show you why they attract the NaCl ions.) The cations and anions get distributed throughout the solution. Substances that conduct electricity in the molten state or when dissolved in water are called *electrolytes*. Substances that don't conduct electricity when in these states are called *nonelectrolytes*.

You can detect the presence of these ions by using an instrument called a conductivity tester. A *conductivity tester* tests whether water solutions of various substances conduct electricity. It's composed of a light bulb with two electrodes attached. The light bulb is plugged into a wall outlet, but it doesn't light until some type of conductor (substance capable of transmitting electricity) between the electrodes completes the circuit. (A finger also completes the circuit, so this experiment should be done carefully. If you're not careful, it can be a shocking experience!)

When you place the electrodes in pure water, nothing happens, because there's no conductor between the electrodes. Pure water is a nonconductor. But if you put the electrodes in the NaCl solution, the light bulb lights, because the ions conduct

the electricity (carry the electrons) from one electrode to the other.

In fact, you don't even really need the water. If you were to melt pure NaCl (it requires a *lot* of heat!) and then place the electrodes into it, you'd find that the molten table salt also conducts electricity. In the molten state, the NaCl ions are free to move and carry electrons, just as they are in the saltwater solution.

Scientists can get some good clues as to the type of bonding in a compound by discovering whether a substance is an electrolyte or a nonelectrolyte. Ionically bonded substances act as electrolytes. But covalently bonded compounds (see Chapter 14), in which no ions are present, are commonly nonelectrolytes. Table sugar, or sucrose, is a good example of a nonelectrolyte. You can dissolve sugar in water or melt it, but it won't have conductivity. No ions are present to transfer the electrons. However, as you discover in Chapter 14, a few covalent compounds ionize (produce ions) when put into water.

Chapter 14

Sharing Nicely: Covalent Bonding

In This Chapter

- ▶ Looking at covalent bonding
 - ▶ Discovering the naming of covalent compounds
 - ▶ Finding out about the different types of chemical formulas
 - ▶ Taking a look at polar covalent bonding and electronegativity
-

Sometimes when I'm cooking, I have one of my chemistry nerd moments and start reading the ingredients on food labels. I usually find lots of salts, such as sodium chloride, and lots of other compounds, such as potassium nitrate, that are all ionically bonded (see Chapter 13). But I also find many compounds, such as sugar, that aren't ionically bonded.

If no ions are holding a compound together, what does hold it together? What holds together sugar, vinegar, and even DNA? In this chapter, I discuss the other major type of bonding: covalent bonding. I explain the basics with an extremely simple covalent compound, hydrogen, and I tell you some cool stuff about one of the most unusual covalent compounds I know — water.

Eyeing Covalent Bond Basics

An *ionic bond* is a chemical bond that comes from the transfer of electrons from a metal to a nonmetal, resulting in the formation of oppositely charged ions — cations (positive

charge) and anions (negative charge) — and the attraction between those oppositely charged ions. The driving force in this whole process is achieving a filled valence energy level, completing the atom's octet. (For a more complete explanation of this concept, see Chapter 13.)

But many other compounds exist in which electron transfer hasn't occurred. The driving force is still the same: achieving a filled valence energy level. But instead of achieving it by gaining or losing electrons, the atoms in these compounds *share* electrons. That's the basis of a *covalent bond*. The following sections provide more insight into covalent bonds.

Considering a hydrogen example

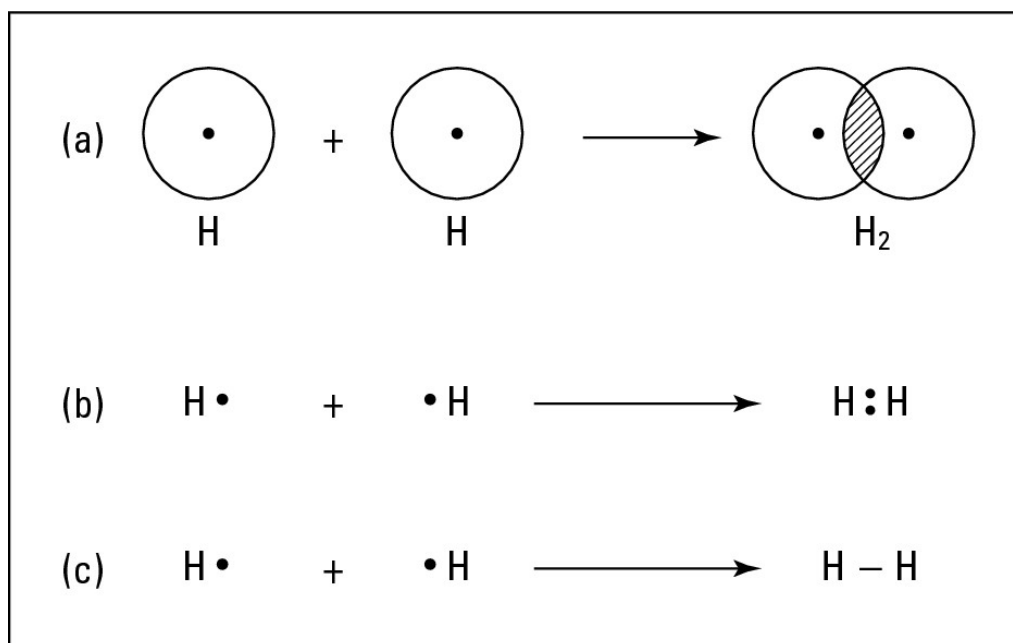
Hydrogen is #1 on the periodic table — upper left corner. The hydrogen found in nature is often not comprised of an individual atom. It's primarily found as H_2 , a *diatomic* (two atom) element. (Taken one step further, because a *molecule* is a combination of two or more atoms, H_2 is called a *diatomic molecule*.)

Hydrogen has one valence electron. It'd love to gain another electron to fill its 1s energy level, which would make it *isoelectronic* with helium (because the two would have the same electronic configuration), the nearest noble gas. Energy level 1 can only hold two electrons in the 1s orbital, so gaining another electron fills it. The driving force of hydrogen is filling the valence energy level and achieving the same electron arrangement as the nearest noble gas.

Imagine one hydrogen atom transferring its single electron to another hydrogen atom. The hydrogen atom receiving the electron fills its valence shell and reaches stability while becoming an anion (H^-). However, the other hydrogen atom now has no electrons (H^+) and moves further away from stability.

This process of electron loss and gain simply won't happen, because the driving force of *both* atoms is to fill their valence energy level. So the H_2 compound can't result from the loss or gain of electrons. What *can* happen is that the two atoms share their electrons. At the atomic level, this sharing is represented by the overlap of the electron orbitals (sometimes called *electron clouds*). The two electrons (one from each hydrogen atom) "belong" to both atoms. Each hydrogen atom feels the effect of the two electrons; each has, in a way, filled its valence energy level. A *covalent bond* is formed — a chemical bond that comes from the sharing of one or more electron pairs between two atoms. The overlapping of the electron orbitals and the sharing of an electron pair are represented in Figure 14-1a.

Figure 14-1:
The formation
of a covalent
bond in
hydrogen.



Another way to represent this process is through the use of an *electron-dot formula*. In this type of formula, valence electrons are represented as dots surrounding the atomic symbol, and the shared electrons are shown between the two atoms involved in the covalent bond. The electron-dot formula representations of H_2 are shown in Figure 14-1b.

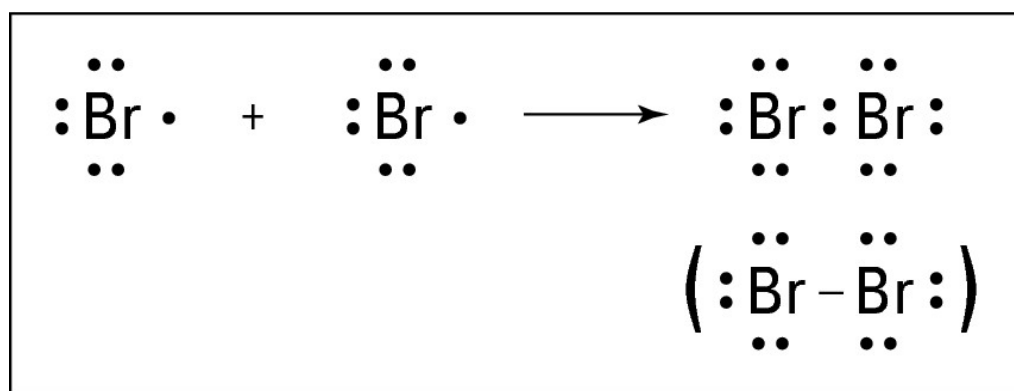
Most of the time, I use a slight modification of the electron-dot formula called the *Lewis structural formula*; it's basically the same as the electron-dot formula, but the shared pair of electrons (the covalent bond) is represented by a dash. The Lewis structural formula of diatomic hydrogen is shown in Figure 14-1c. (Check out the section, "Structural formula: Add the bonding pattern," for more about writing structural formulas of covalent compounds.)



In addition to hydrogen, six other elements are found in nature in the diatomic form: oxygen (O_2), nitrogen (N_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). So when I talk about oxygen gas or liquid bromine, I'm talking about the diatomic element (diatomic molecule).

For another example of using the electron-dot formula to represent the shared electron pair of a diatomic compound, look at bromine (Br_2), which is a member of the halogen family (see Figure 14-2). The two halogen atoms, each with seven valence electrons, share an electron pair and fill their octet.

Figure 14-2:
The covalent
bond
formation of
 Br_2 .



Comparing covalent bonds with other bonds

Ionic bonding occurs between a metal and a nonmetal. Covalent bonding, on the other hand, occurs between two nonmetals. The properties of these two types of compounds are different. Ionic compounds are usually solids at room temperature, whereas covalently bonded compounds can be solids, liquids, or gases. There's more. Ionic compounds (salts) usually have a much higher melting point than covalent compounds. In addition, ionic compounds tend to be electrolytes, and covalent compounds tend to be nonelectrolytes. (Chapter 13 explains all about ionic bonds, electrolytes, and nonelectrolytes.)

I know just what you're thinking: "If metals react with nonmetals to form ionic bonds, and nonmetals react with other nonmetals to form covalent bonds, do metals react with other metals?" The answer is yes and no.

Metals don't really react with other metals to form compounds. Instead, metals combine to form *alloys*, solutions of one metal in another. But in a situation called *metallic bonding*, which affects both alloys and pure metals, the valence electrons of each metal atom are donated to an electron pool, commonly called a *sea of electrons*, and are shared by all the atoms in the metal. These valence electrons are free to move throughout the sample instead of being tightly bound to an individual metal nucleus. The ability of the valence electrons to flow throughout the entire metal sample is why metals tend to be conductors of electricity and heat and is responsible for the luster of metals.

Understanding multiple bonds

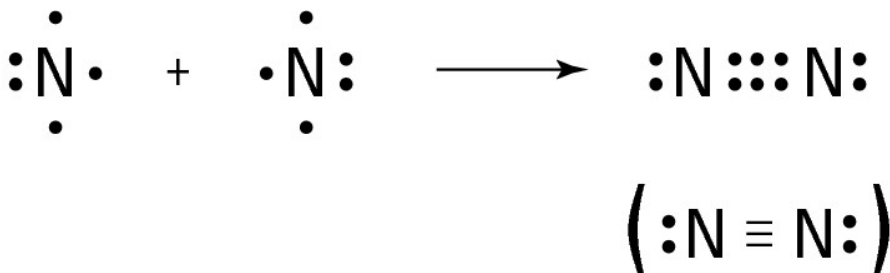
Covalent bonding is the sharing of one *or more* electron pairs. In hydrogen and most other diatomic molecules, only one electron pair is shared. But in many covalent bonding situations, more than one electron pair is shared. This section shows you an example of a molecule in which more than one electron pair is shared.

Energy is needed to break a covalent bond. The resistance of the bond to breaking is called its bond strength. In general, more energy is needed to break a double bond than a single bond if the same elements are involved. For example, a carbon-to-carbon double bond (two shared pairs of electrons) has a higher bond strength (requires more energy to break the bond) than a carbon-to-carbon single bond. The double bond isn't twice as strong as a single bond, but its strength is considerably greater. And a triple bond is stronger yet. Chemists also observe that multiple bonds are shorter in bond length (the distance between the nuclei of the bonded atoms) than single bonds — double bonds are shorter than single bonds, and triple bonds are shorter than double bonds.

Nitrogen (N_2) is a diatomic molecule in the *VA family* on the periodic table, meaning that it has five valence electrons (see Chapter 5 for a discussion of families on the periodic table). So nitrogen needs three more valence electrons to complete its octet. A nitrogen atom can fill its octet by sharing three electrons with another nitrogen atom, forming three covalent bonds, a triple bond. The triple-bond formation of nitrogen is shown in Figure 14-3.

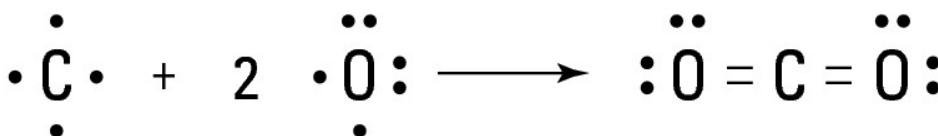
A triple bond isn't quite three times as strong as a single bond, but it's a very strong bond. In fact, the triple bond in nitrogen is one of the strongest bonds known. This strong bond is what makes nitrogen gas very stable and resistant to reaction with other chemicals. It's also why many explosive compounds (such as TNT and ammonium nitrate) contain nitrogen. When these compounds break apart in a chemical reaction, nitrogen gas (N_2) is formed and a large amount of energy is released.

Figure 14-3:
Triple bond
formation in
 N_2 .



Carbon dioxide (CO₂) is another example of a compound containing a multiple bond. Carbon can react with oxygen to form carbon dioxide. Carbon has four valence electrons, and oxygen has six. Carbon can share two of its valence electrons with each of the two oxygen atoms, forming two double bonds. These double bonds are shown in Figure 14-4.

Figure 14-4:
Formation of
carbon
dioxide.



There are no salt molecules!

A *molecule* is a compound that's covalently bonded. Referring to sodium chloride, which has ionic bonds, as a molecule is technically incorrect, but lots of chemists (and chemistry students) do it anyway. The mistake is kind of like using the wrong fork at a formal dinner. Some people may notice, but most don't notice or don't care. But just so you know, the correct term for ionic compounds is *formula unit*.

Naming Binary Covalent Compounds

Binary compounds are compounds made up of only two elements, such as carbon dioxide (CO₂). Prefixes are used in the names of binary compounds to indicate the number of atoms of each nonmetal present, so being able to recognize binary compounds and apply the correct naming rules is important. Table 14-1 lists the most common prefixes for binary covalent compounds.

Table 14-1 Common Prefixes for Binary Covalent Compounds

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

In general, the prefix *mono-* is rarely used. Carbon monoxide is one of the few compounds that uses it.

Take a look at the following examples to see how to use the prefixes when naming binary covalent compounds (I've bolded

the prefixes for you):

CO_2 carbon **d**ioxide

P_4O_{10} **tetr**aphosphorus **dec**oxide (Chemists try to avoid putting an *a* and an *o* together with the oxide name, as in **decaoxide**, so they normally drop the *a* off the prefix.)

SO_3 sulfur **tri**oxide

N_2O_4 **d**initrogen **tet**roxide

This naming system is used only with binary, nonmetal compounds, with one exception — MnO_2 is commonly called manganese dioxide.

Learning Many Formulas in a Little Time

In Chapter 13, I show you how to predict the formula of an ionic compound, based on the loss and gain of electrons, to reach a noble gas configuration. (For example, if you react Ca with Cl, you can predict the formula of the resulting salt — CaCl_2 .) You really can't make that type of prediction with covalent compounds, because they can combine in many ways, and many different possible covalent compounds may result.

Most of the time, you have to know the formula of the molecule you're studying. But you may have several different types of formulas, and each gives a slightly different amount of information. Oh joy. Not to worry though. I provide the 411 on what you need to know about formulas in the following sections to make the prediction easier.

Empirical formula: Just the elements

The *empirical formula* indicates the different types of elements in a molecule and the lowest whole-number ratio of each kind of atom in the molecule. For example, suppose you have a compound with the empirical formula $\text{C}_2\text{H}_6\text{O}$. Three different kinds of atoms are in the compound, C, H, and O, and they're in the lowest whole-number ratio of 2 C to 6 H to 1 O. So the actual formula (called the *molecular formula* or *true formula*) may be $\text{C}_2\text{H}_6\text{O}$, $\text{C}_4\text{H}_{12}\text{O}_2$, $\text{C}_6\text{H}_{18}\text{O}_3$, $\text{C}_8\text{H}_{24}\text{O}_4$, or another multiple of 2:6:1.

Molecular or true formula: Inside the numbers

The *molecular formula*, or *true formula*, tells you the kinds of atoms in the compound and the actual number of each atom. You may determine, for example, that the empirical formula $\text{C}_2\text{H}_6\text{O}$ is actually the molecular formula, too, meaning that the compound actually has two carbon atoms, six hydrogen atoms, and one oxygen atom.

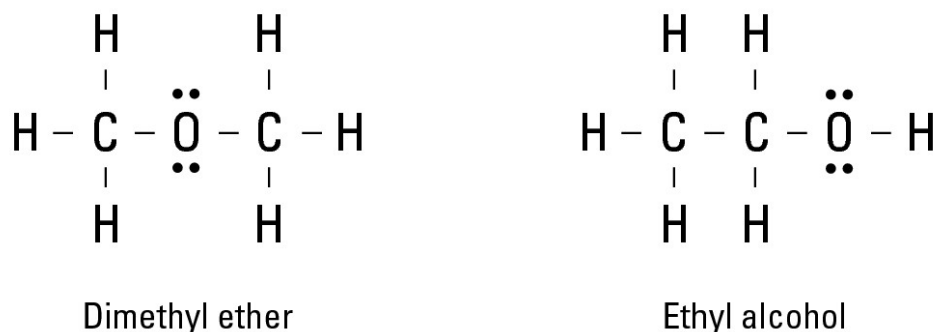
For ionic compounds, this formula is enough to fully identify the compound, but it's not enough to identify covalent compounds. Look at the Lewis formulas presented in Figure 14-5. Both compounds have the molecular formula of $\text{C}_2\text{H}_6\text{O}$.

It's always important to KISS

A lot of molecules obey the octet rule: Each atom in the compound ends up with a full octet of eight electrons filling its valence energy level. However, like most rules, the octet rule does have exceptions. Some stable molecules have atoms with just 6 electrons, and some have 10 or 12. Take a peek at Chapter 15 for some specific examples of compounds that do not obey the octet rule. For the most part in this book, I concentrate on situations in which the octet rule is obeyed.

I pretty much stick to the KISS principle — Keep It Simple, Silly. Electron-dot formulas are used quite a bit by organic chemists in explaining why certain compounds react the way they do and are the first step in determining the molecular geometry of a compound (which I describe in Chapter 15).

Figure 14-5:
Two possible
compounds of
 C_2H_6O .



Both compounds in Figure 14-5 have two carbon atoms, six hydrogen atoms, and one oxygen atom. The difference is in the way the atoms are bonded, or what's bonded to what, and it makes them two entirely different compounds with two entirely different sets of properties. The one on the left is called dimethyl ether. This compound is used in some refrigeration units and is highly flammable. The one on the right is ethyl alcohol, the drinking variety of alcohol. Simply knowing the molecular formula isn't enough to distinguish between the two compounds. Can you imagine going into a restaurant and ordering a shot of C_2H_6O and getting dimethyl ether instead of tequila?



Compounds that have the same molecular formula but different structures are called *isomers* of each other. To identify the *exact* covalent compound, you need its structural formula, which I discuss in the next section.

Structural formula: Add the bonding pattern

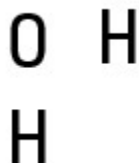
To write a formula that stands for the exact compound you have in mind, you often must write the structural formula instead of the molecular formula. The *structural formula* shows the elements in the compound, the exact number of each atom in the compound, and the bonding pattern for the compound. The electron-dot formula and Lewis formula are examples of structural formulas.

Writing the electron-dot formula for water

The following steps explain how to write the electron-dot formula for a simple molecule — water — and provide some general guidelines and rules to follow:

1. Write a skeletal structure showing a reasonable bonding pattern using just the element symbols.

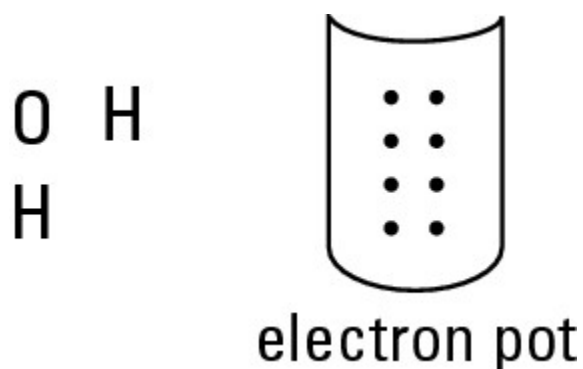
The skeletal structure involves only the atomic symbols and not the valence electrons. Often, most atoms are bonded to a single atom. This atom is called the *central atom*. Hydrogen and the halogens are very rarely, if ever, central atoms. Carbon, silicon, nitrogen, phosphorus, oxygen, and sulfur are always good candidates, because they form more than one covalent bond to fill their valence energy level. In the case of water, H_2O , oxygen is the central element and the hydrogen atoms are both bonded to it. The bonding pattern looks like this:



The hydrogen atoms can go anywhere around the oxygen. I put the hydrogen atoms at a 90-degree angle to each other, but it really doesn't matter when writing electron-dot (or Lewis) formulas.

2. Take all the valence electrons from all the atoms and throw them into an electron pot.

Each hydrogen atom has 1 electron, and the oxygen atom has 6 valence electrons (VIA family), so you have 8 electrons in your electron pot. You use those electrons to make your bonds and complete each atom's octet.



3. Use the $N - A = S$ equation to figure the number of bonds in this molecule. In this equation,

- N equals the sum of the number of valence electrons needed by each atom. N has only two possible values — 2 or 8. If the atom is hydrogen, it's 2; if it's anything else, it's 8.
- A is the number of valence electrons in your electron pot — the sum of the number of valence electrons *available* for each atom. If you're doing the structure of an ion, you add one electron for every unit of negative charge if it's an anion or subtract one electron for every unit of positive charge if it's a cation.
- S equals the number of electrons shared in the molecule. And if you divide S by 2, you have the number of covalent bonds in the molecule.

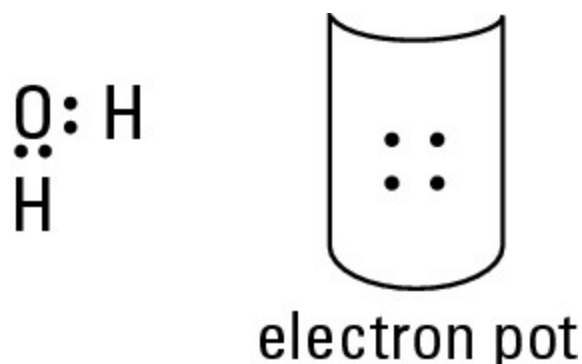
So in the case of water,

- $N = 8 + 2(2) = 12$ (8 valence electrons for the oxygen atom, plus 2 each for the two hydrogen atoms)
- $A = 6 + 2(1) = 8$ (6 valence electrons for the oxygen atom, plus 1 for each of the two hydrogen atoms)
- $S = 12 - 8 = 4$ (four electrons shared in water), and $S/2 = 4/2 = 2$ bonds

You now know that water molecules have two bonds (two shared pairs of electrons).

4. Distribute the electrons from your electron pot to account for the bonds.

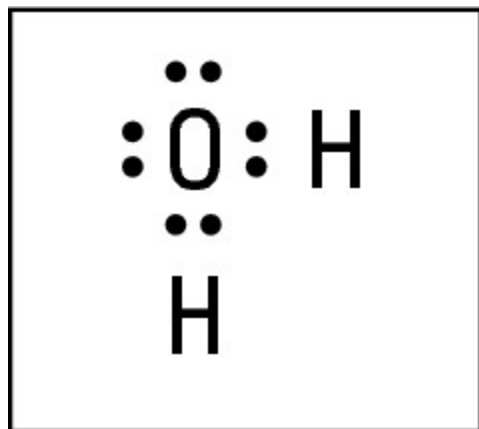
You use 4 electrons from the 8 in the pot, which leaves you with 4 to distribute later. At least one bond must connect your central atom to the atoms surrounding it.



5. Distribute the rest of the electrons (normally in pairs) so that each atom achieves its full octet of electrons.

Remember that hydrogen needs only 2 electrons to fill its valence energy level. In this case, each hydrogen atom has 2 electrons, but the oxygen atom has only 4 electrons, so the remaining 4 electrons are placed around the oxygen, emptying your electron pot. The completed electron-dot formula for water is shown in Figure 14-6.

Figure 14-6:
Electron-dot
formula of
 H_2O .

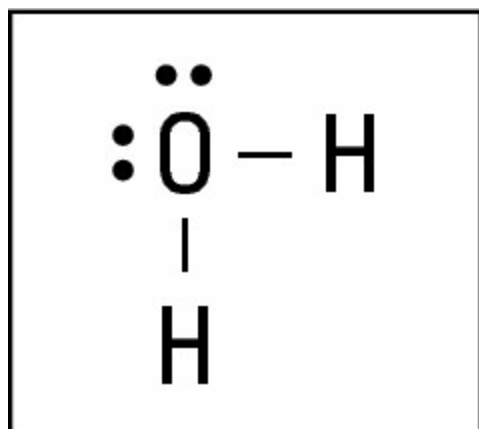


Notice that this structural formula actually shows two types of electrons: *bonding electrons*, the electrons that are shared between two atoms, and *nonbonding electrons*, the electrons that are not being shared. The last 4 electrons (2 electron pairs) that you put around oxygen are not being shared, so they're nonbonding electrons.

Writing the Lewis formula for water

If you want the Lewis formula for water, all you have to do is substitute a dash for every bonding pair of electrons. This structural formula is shown in Figure 14-7.

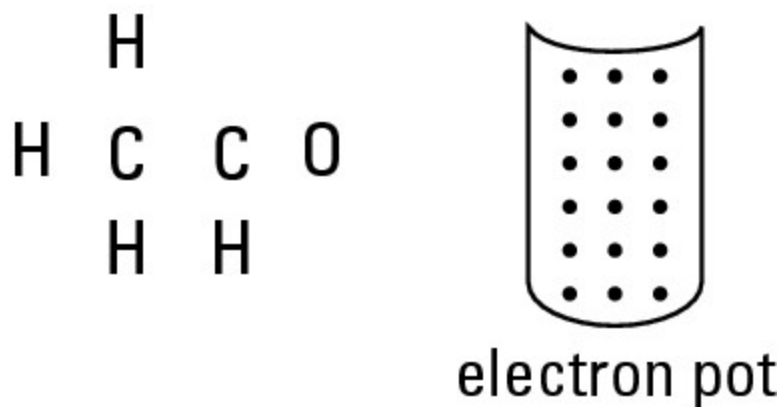
Figure 14-7:
The Lewis
formula for
 H_2O .



Writing the Lewis formula for C_2H_4O

Here's an example of a Lewis formula that's a little more complicated — C_2H_4O .

The compound has the following framework:



Notice that the compound has not 1 but 2 central atoms — the 2 carbon atoms. You can put 18 valence electrons into the electron pot: 4 for each carbon atom, 1 for each hydrogen atom, and 6 for the oxygen atom.

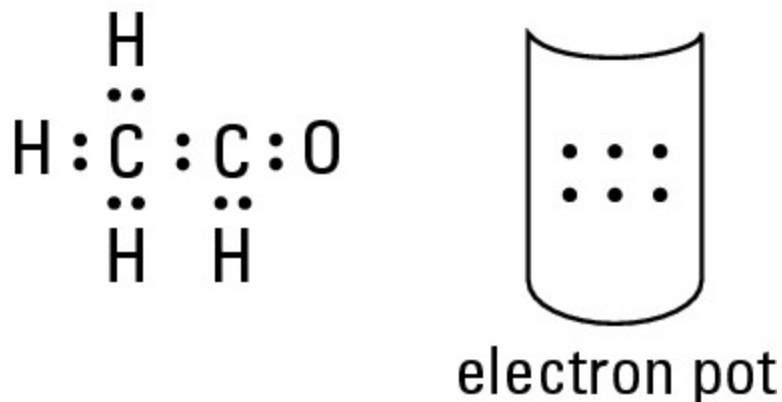
Now apply the $N - A = S$ equation:

$$N = 2(8) + 4(2) + 8 = 32 \text{ (2 carbon atoms with 8 valence electrons each, plus 4 hydrogen atoms with 2 valence electrons each, plus an oxygen atom with 8 electrons)}$$

$$A = 2(4) + 4(1) + 6 = 18 \text{ (4 electrons for each of the two carbon atoms, plus 1 electron for each of the 4 hydrogen atoms, plus 6 valence electrons for the oxygen atom)}$$

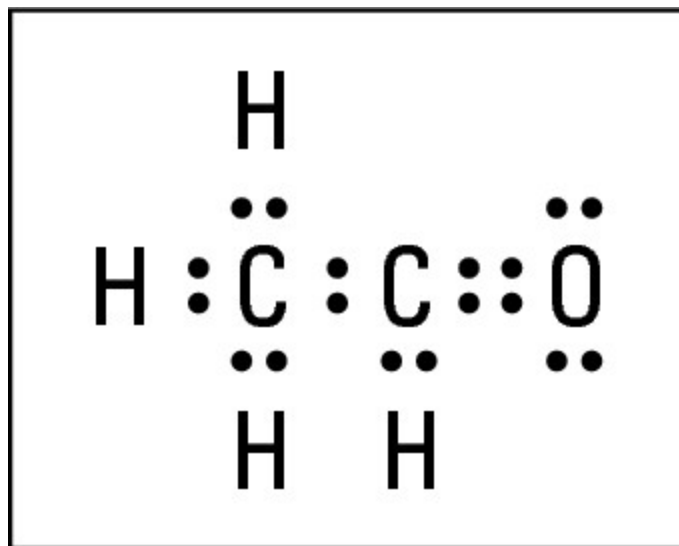
$$S = 32 - 18 = 14, \text{ and } S/2 = 14/2 = 7 \text{ bonds}$$

Add single bonds between the carbon atoms and the hydrogen atom, between the 2 carbon atoms, and between the carbon atom and oxygen atom. That's 6 of your 7 bonds.



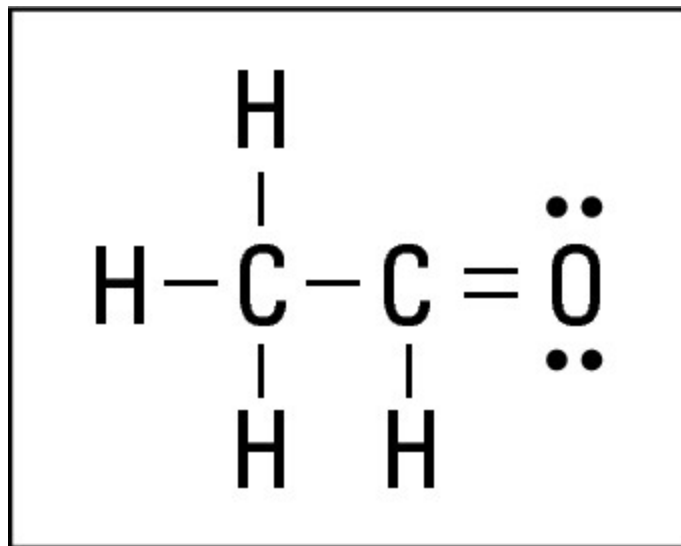
The seventh bond can go only one place, and that's between the carbon atom and the oxygen atom. It can't be between a carbon atom and a hydrogen atom, because that would overfill hydrogen's valence energy level. And it can't be between the two carbon atoms, because that would give the carbon on the left 10 electrons instead of 8. So there must be a double bond between the carbon atom and the oxygen atom. The 4 remaining electrons in the pot must be distributed around the oxygen atom, because all the other atoms have reached their octet. The electron-dot formula is shown in Figure 14-8.

Figure 14-8:
Electron-dot
formula of
 $\text{C}_2\text{H}_4\text{O}$.



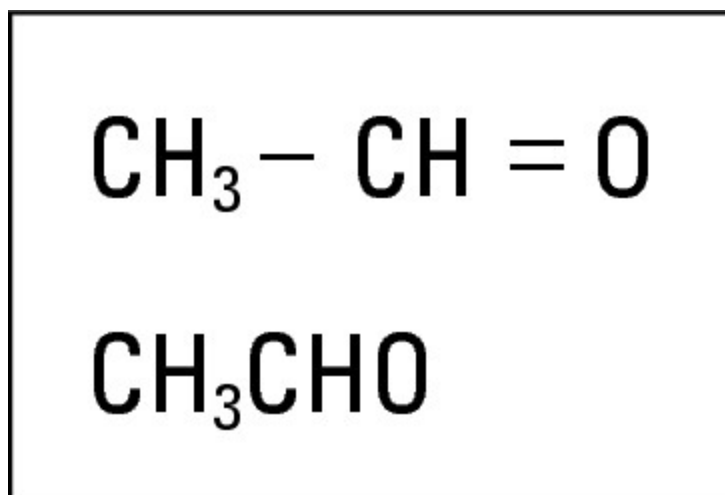
If you convert the bonding pairs to dashes, you have the Lewis formula of $\text{C}_2\text{H}_4\text{O}$, as shown in Figure 14-9.

Figure 14-9:
The Lewis
formula for
 C_2H_4O .



I like the Lewis formula because it enables you to show a lot of information without having to write all those little dots. But it, too, is rather bulky. Sometimes chemists (who are, in general, a lazy lot) use *condensed structural formulas* to show bonding patterns. They may condense the Lewis formula by omitting the nonbonding electrons and grouping atoms together and/or by omitting certain dashes (covalent bonds). A couple of condensed formulas for C_2H_4O are shown in Figure 14-10.

Figure 14-10:
Condensed
structural
formulas for
 C_2H_4O .



Sharing Electron Pairs — Sometimes Equally and Sometimes Not

One of my favorite lines from the book *Animal Farm* is “All animals are equal, but some animals are more equal than others.” The same is true of covalent bonds — electron pairs may be shared, but not always equally.

When a chlorine atom covalently bonds to another chlorine atom, the shared electron pair is shared equally. The electron density that comprises the covalent bond is located halfway between the two atoms. Each atom attracts the two bonding electrons equally because each nuclei has the same number of protons.

But what happens when the two atoms involved in a bond aren't the same? The two positively charged nuclei have different attractive forces; they “pull” on the electron pair to different degrees. The end result is that the electron pair is shifted toward one atom. But the question is, “Which atom does the electron pair shift toward?” Electronegativities provide the answer.

Attracting electrons: Electronegativities

Electronegativity is the strength an atom has to attract a bonding pair of electrons to itself. The larger the value of the electronegativity, the greater the atom's strength to attract a bonding pair of electrons. Figure 14-11 shows the electronegativity values of the various elements below each element symbol on the periodic table. Notice that, with a few

exceptions, the electronegativities increase from left to right, in a period, and decrease from top to bottom, in a family.

Figure 14-11:
Electro-
negativities of
the elements.

[illegible]



Electronegativities are useful because they give information about what will happen to the bonding pair of electrons when two atoms bond. Basically three types of bonds can be formed.

✓ **Nonpolar covalent bond:** This bond has an electron pair that's equally shared. You have a nonpolar covalent bond anytime the two atoms involved in the bond are the same or anytime the difference in the electronegativities of the atoms involved in the bond is very small. For example, look at the Cl_2 molecule. Chlorine has an electronegativity value of 3.0, as shown in Figure 14-11. Each chlorine atom attracts the bonding electrons with a force of 3.0. Because there's an equal attraction, the bonding electron pair is shared equally between the two chlorine atoms and is located halfway between the two atoms.

✓ **Polar covalent bond:** The electron pair in this bond is shifted toward one atom. The atom that more strongly attracts the bonding electron pair is slightly more negative, while the other atom is slightly more positive. The larger the difference in the electronegativities, the more negative and positive the atoms become.

Consider hydrogen chloride (HCl). Hydrogen has an electronegativity of 2.1, and chlorine has an electronegativity of 3.0. The electron pair that is bonding HCl together shifts toward the chlorine atom because it has a larger electronegativity value. Check out the next section for more information on these types of bonds.

✓ **Ionic bond:** In this case, the bonding electrons are totally removed from one of the atoms and ions are formed. Now look at a case in which the two atoms have

extremely different electronegativities — sodium chloride (NaCl). Sodium chloride is ionically bonded (see Chapter 13 for information on ionic bonds). An electron has transferred from sodium to chlorine. Sodium has an electronegativity of 1.0, and chlorine has an electronegativity of 3.0. That's an electronegativity difference of 2.0 ($3.0 - 1.0$), making the bond between the two atoms very, very polar. In fact, the electronegativity difference provides another way of predicting the kind of bond that will form between two elements.

The following table breaks down these three types of bonds that are formed and shows their electronegativity difference:

<i>Electronegativity Difference</i>	<i>Type of Bond Formed</i>
0.0 to 0.2	Nonpolar covalent
0.3 to 1.4	Polar covalent
> 1.5	Ionic

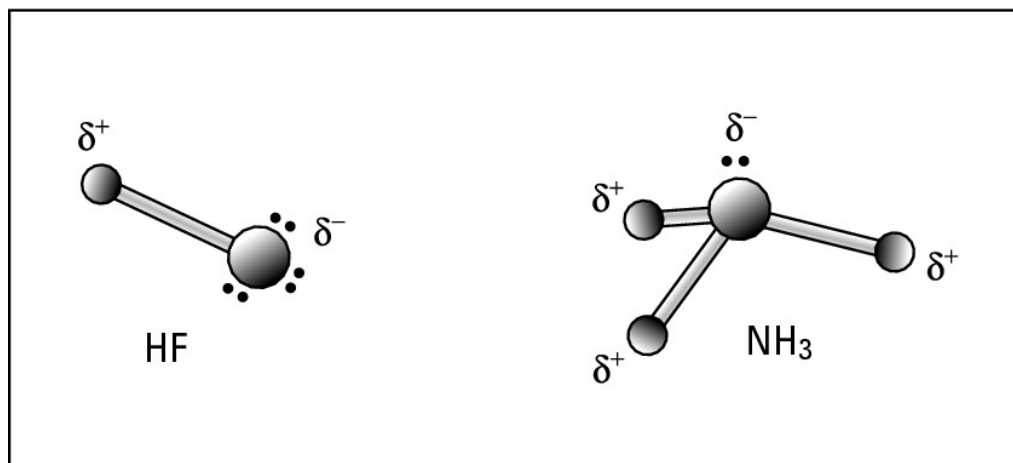
The presence of a polar covalent bond in a molecule can have some pretty dramatic effects on the properties of a molecule.

Polar covalent bonding

If the two atoms involved in the covalent bond are not the same, the bonding pair of electrons are pulled toward one atom, with that atom taking on a slight (partial) negative charge and the other atom taking on a partial positive charge. In many cases, the molecule then has a positive end and a negative end, and can be referred to as a *dipole* (think of a magnet). Figure 14-12 shows a couple of examples of molecules in which dipoles have formed. (The little Greek symbol by the charges refers to a *partial* charge.)

Figure 14-12:
Polar

covalent
bonding in HF
and NH₃.



In hydrogen fluoride (HF), the bonding electron pair is pulled much closer to the fluorine atom than to the hydrogen atom, so the fluorine end becomes partially negatively charged and the hydrogen end becomes partially positively charged. The same thing takes place in ammonia (NH₃); the nitrogen has a greater electronegativity than hydrogen, so the bonding pairs of electrons are more attracted to it than to the hydrogen atoms. The nitrogen atom takes on a partial negative charge, and the hydrogen atoms take on a partial positive charge.

The presence of a polar covalent bond explains why some substances act the way they do in a chemical reaction: Because this type of molecule has a positive end and a negative end, it can attract the part of another molecule with the opposite charge.

In addition, this type of molecule can act as a weak electrolyte because a polar covalent bond allows the substance to act as a conductor. So if a chemist wants a material to act as a good *insulator* (a device used to separate conductors), the chemist looks for a material with as weak a polar covalent bond as possible.

Wondering about water: A really strange molecule

Water (H_2O) has some very strange chemical and physical properties. It can exist in all three states of matter at the same time. Imagine that you're sitting in your hot tub (filled with *liquid* water) watching the steam (*gas*) rise from the surface as you enjoy a cold drink from a glass filled with ice (*solid*) cubes. Very few other chemical substances can exist in all these physical states in this close of a temperature range.

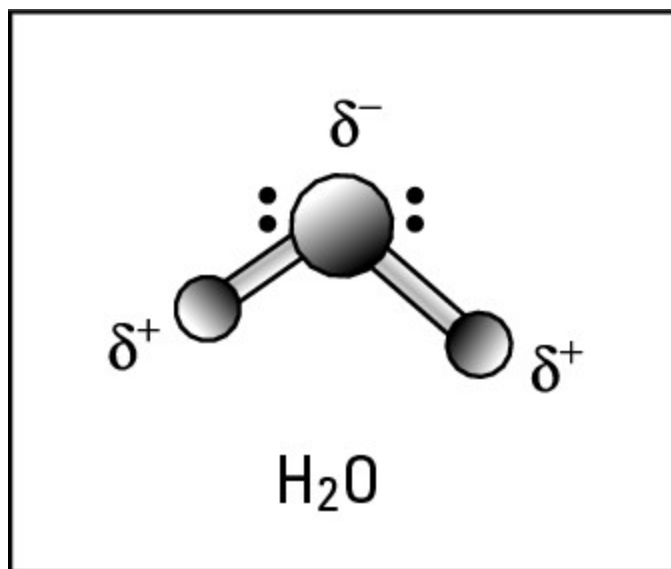
And those ice cubes are floating! In the solid state, the particles of matter are usually much closer together than they are in the liquid state. So if you put a solid into its corresponding liquid, it sinks — but not for water. Its solid state is less dense than its liquid state, so it floats. Imagine what would happen if ice sank. In the winter, the lakes would freeze, and the ice would sink to the bottom, exposing more water. The extra exposed water would then freeze and sink, and so on, until the entire lake was frozen solid. This would destroy the aquatic life in the lake in no time. Fortunately, instead, the ice floats and insulates the water underneath it, protecting aquatic life. And water's boiling point is unusually high. Other compounds similar in weight to water have a *much* lower boiling point.

Another unique property of water is its ability to dissolve a large variety of chemical substances. It dissolves salts and other ionic compounds, as well as polar covalent compounds such as alcohols and organic acids. In fact, water is sometimes called the universal solvent because it can dissolve so many things. It can also absorb a large amount of heat, which allows large bodies of water to help moderate the temperature on earth.

Water has many unusual properties because of its polar covalent bonds. Oxygen has a larger electronegativity than hydrogen, so the electron pairs are pulled in closer to the

oxygen atom, giving it a partial negative charge. Subsequently, both of the hydrogen atoms take on a partial positive charge. The partial charges on the atoms created by the polar covalent bonds in water are shown in Figure 14-13.

Figure 14-13:
Polar
covalent
bonding in
water.



Water is a dipole and acts like a magnet, with the oxygen end having a negative charge and the hydrogen end having a positive charge. These charged ends can attract other water molecules. The partially negatively charged oxygen atom of one water molecule can attract the partially positively charged hydrogen atom of another water molecule. This attraction between the molecules occurs frequently and is a type of *intermolecular force* (force between different molecules).

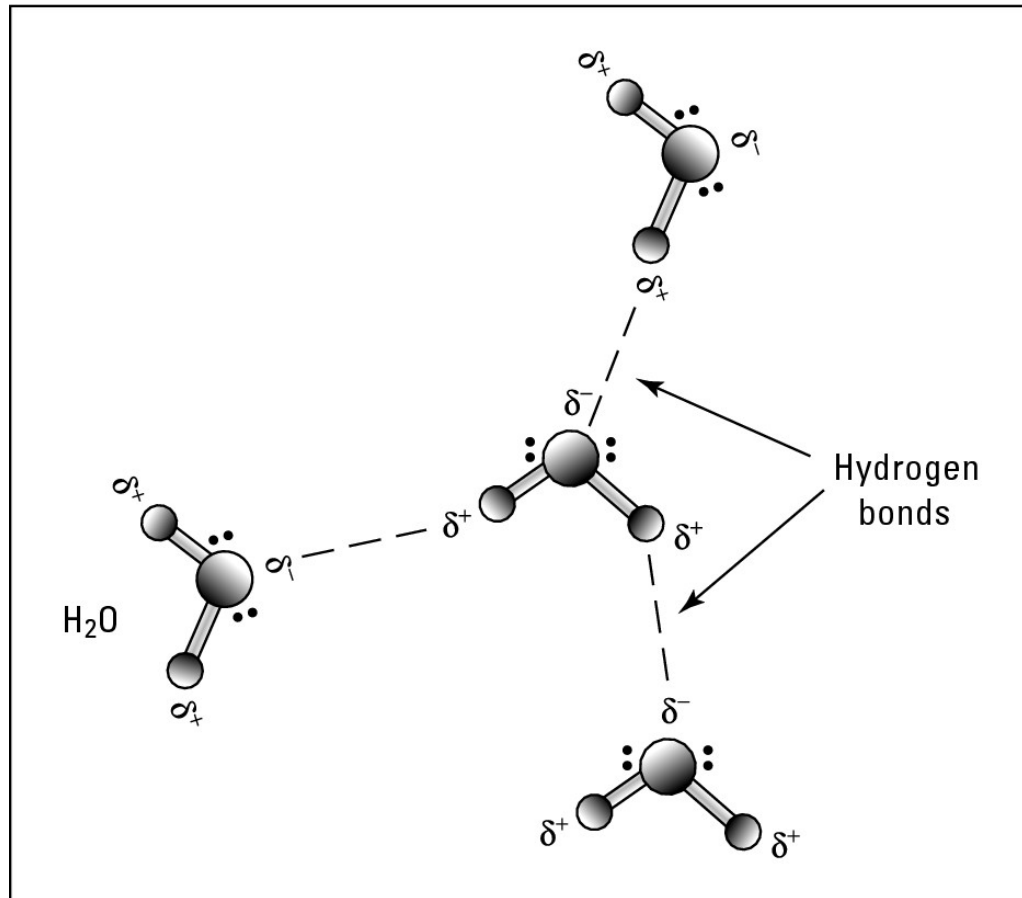
Intermolecular forces can be of three different types:

- ✓ **London force:** Also called the *dispersion force*, this force is a very weak type of attraction that generally occurs between nonpolar covalent molecules, such as nitrogen (N_2), hydrogen (H_2), or methane (CH_4). It results from the

ebb and flow of the electron orbitals, giving a very weak and very brief charge separation around the bond.

- ✓ **Dipole-dipole interaction:** This intermolecular force occurs when the positive end of one dipole molecule is attracted to the negative end of another dipole molecule. It's much stronger than a London force, but it's still pretty weak.
- ✓ **Hydrogen bond:** The third type of interaction is really just an extremely strong dipole-dipole interaction that occurs when a hydrogen atom on one molecule is bonded to one of three extremely electronegative elements — O, N, or F — on another molecule. These three elements have a very strong attraction for the bonding pair of electrons, so the atoms involved in the bond take on a large amount of partial charge. This bond turns out to be highly polar — and the higher the polarity, the more effective the bond. It's only about 5 percent of the strength of an ordinary covalent bond, but still very strong for an intermolecular force. The hydrogen bond is the type of interaction that's present in water (see Figure 14-14). For a more complete discussion of intermolecular forces, check out Chapter 17.

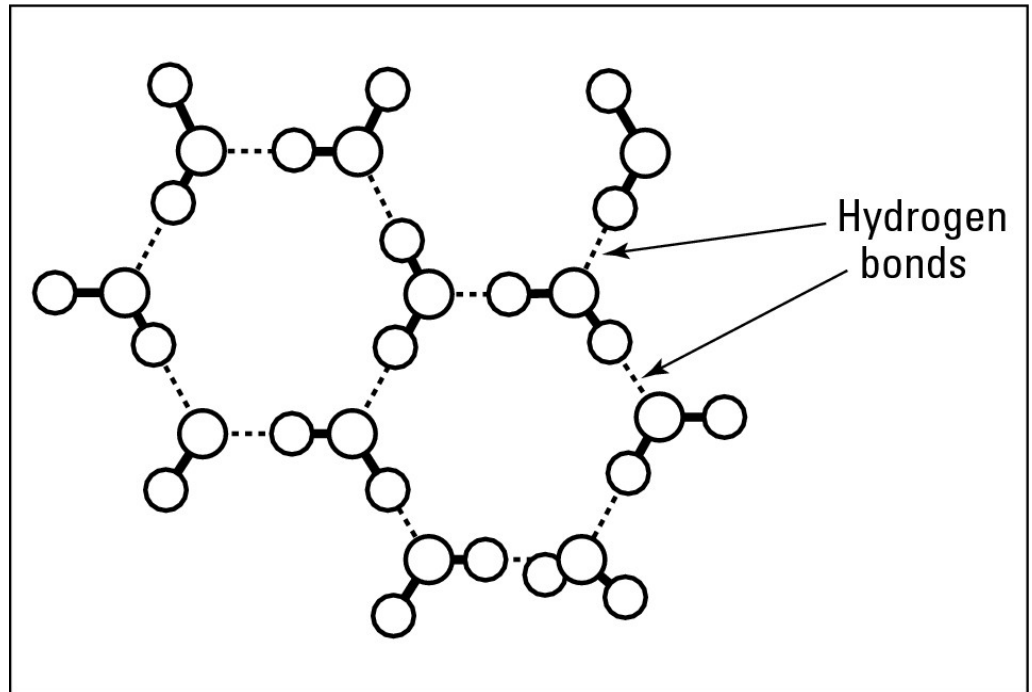
Figure 14-14:
Hydrogen
bonding in
water.



Water molecules are stabilized by these hydrogen bonds, so breaking up (separating) the molecules is very hard. The hydrogen bonds account for water's high boiling point and ability to absorb heat. When water freezes, the hydrogen bonds lock water into an open framework that includes a lot of empty space. In liquid water, the molecules can get a little closer to each other, but when the solid forms, the hydrogen bonds result in a structure that contains large holes. The holes increase the volume and decrease the density. This process explains why the density of ice is less than that of liquid water (the reason ice floats). The structure of ice is shown in Figure 14-15, with the hydrogen bonds indicated by dotted lines.

Figure 14-15:
The structure

of ice.



Chapter 15

What Do Molecules Really Look Like? Molecular Geometry and Hybridization

In This Chapter

- ▶ Sizing up the importance of shape
 - ▶ Delving into electron and molecular geometry
 - ▶ Finding out what the valence bond theory reveals about covalent bonds
 - ▶ Bonding with the molecular orbital theory
-

Atoms come together to make compounds with ionic bonding or covalent bonding. Ionic compounds are held together in a type of crystal lattice. You can describe the shape of the lattice but not the individual ion. In covalent bonding, the atoms combine to make a molecule, which has a shape that can be described. This chapter is about determining the shape of molecules created by covalent bonding.

The shape of a molecule can be predicted in two ways:

- ✓ **The VSEPR method:** This method, which stands for *valence-shell electron-pair repulsion*, relies on the Lewis structure of the molecule.
- ✓ **The valence bond method:** This approach relies on the electron configuration of the central atom.

So why use two methods when they both give the same result? The VSEPR method tends to be simpler to apply, but the valence bond approach allows you to determine and rationalize other properties of molecules. I discuss both methods of determining shape in this chapter. I also throw in a discussion on the molecular orbital theory, which can also be used to predict the shape of molecules, for no additional charge.

Seeing How Shape Matters

The *shape* (orientation in space of the atoms in a molecule) of a molecule may determine a great deal of its properties. For example, the shape of many organic molecules determines whether they're reactive in certain circumstances. The shape is especially indicative of reactivity for *enzymes*, biological catalysts, that are found in the human body. If the shape of a particular enzyme is altered, that enzyme becomes useless in helping a certain biochemical reaction occur. Shape is also important in the complex molecules of drugs; it makes the drugs active but also leads to side effects. The following sections examine the importance of shape and the role polarity plays in an atom's shape.

Getting charged with polarity

One of the important consequences of the shape of a molecule is the *polarity* (separation of charge) of the molecule. Some molecules are *polar*; they have charged regions that can attract oppositely charged regions in other molecules. Other molecules are *nonpolar*; they have no charged regions to attract other molecules. Whether or not a molecule is polar is related to the presence of charge separation in the bonds and also on the shape of the molecule. You can have polar bonds, but if they're

symmetrically distributed in the molecule, the molecule itself won't be polar.



A polar molecule has a partially positive charge at one end and a partially negative charge at the opposite end. The partial charge on one molecule attracts the opposite partial charge on another molecule. This attraction is less than the attraction between ions because these molecules only have partial (slight) charges. This attraction, even if less than in an ionic situation, is a significant factor in the physical properties of these molecules.

To explore an example of polarity, start by looking at Figure 15-1, which shows the Lewis structures of two diatomic molecules, the hydrogen molecule, H_2 , and the chlorine fluoride molecule, ClF . (The Lewis structure is a way of showing the structural formula of a molecule; refer to Chapter 14 for more information.)

Figure 15-1:
Lewis
structures of
hydrogen and
chlorine
fluoride.



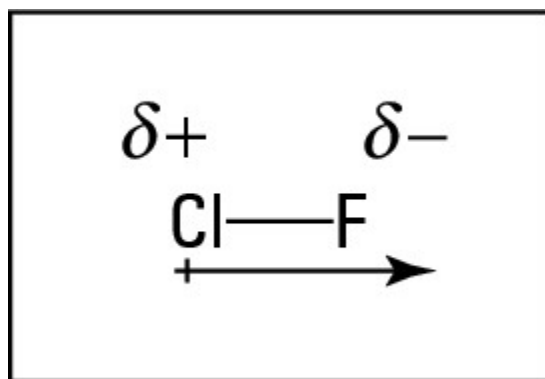
The arrows beneath the two structures illustrate the relative electronegativities of the elements. In the hydrogen molecule, the two arrows are the same length because both atoms have equal electronegativities. In the chlorine fluoride molecule, the arrows are of different lengths because the electronegativities are different. The electronegativity of fluorine is greater than that of chlorine, so the arrow pointing to the fluorine is longer than the arrow pointing to the chlorine.

If you combine the two equal arrows in the hydrogen molecule, they cancel. Hydrogen atoms, due to their identical electronegativities, pull equally on the shared electrons, resulting in an equal sharing of the electrons. Therefore, H_2 is nonpolar, because the charges on either end of the molecule are the same and equal.

However, if you combine the unequal arrows in chlorine fluoride, you're left with a net arrow pointing toward the fluorine end of the molecule. This remaining arrow indicates that the shared negative electrons are pulled closer toward the fluorine. The unequal sharing of the electrons leads to a slight (partial) negative charge on the fluorine, leaving a slight (partial) positive charge on the chlorine. Thus, ClF is a polar molecule. (If the difference in electronegativities were greater, the more electronegative element would strip the electron from the less electronegative element to form an ionic bond.)

A lowercase Greek letter delta, δ , indicates the presence of a partial charge. If you add the partial charges to the picture of the chlorine fluoride molecule, you get the structure shown in Figure 15-2.

Figure 15-2:
The Lewis structure of chlorine fluoride shows partial charges.



The arrow below the molecule is an alternative to the partial charges. The arrow has a cross at the positive end and points toward the more negative end.

Predicting polarity

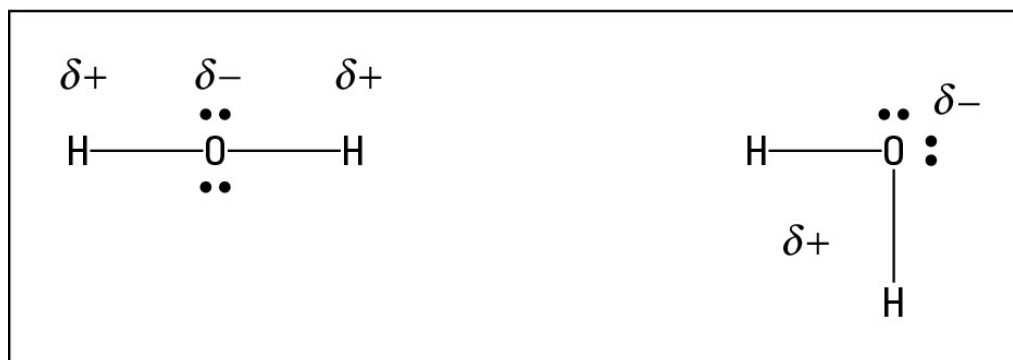
Predicting the polarity of diatomic molecules is simple. A diatomic molecule is polar if the bond is a polar covalent bond, and it is nonpolar if the covalent bond is nonpolar. Thus, molecules such as HCl, NO, and ClF are polar, and molecules such as H₂, Cl₂, and N₂ are nonpolar. Refer to Chapter 14 for a discussion of electronegativities and polar covalent bonding.



A polar molecule is a dipole. *Dipole* refers to the two poles, the partially positive pole and the partially negative pole. The magnitude of the dipole is related to the difference in the electronegativities (and, to a lesser degree, to the distance between the two atoms). The *dipole moment* is a measure of the magnitude of the dipole. Nonpolar molecules have a zero dipole moment, and all polar molecules have a nonzero dipole moment.

Although the prediction of the polarity of a diatomic molecule is relatively simple, what happens when there are more than two atoms? I use water to illustrate this problem because water clearly demonstrates that, if you want to know about the polarity of a molecule, you must first know the *molecular geometry*, the arrangement of the atoms and electrons in three-dimensional space. Figure 15-3 shows the correct Lewis structures for the water molecule.

Figure 15-3:
Two possible
Lewis
structures of
water.



Due to the difference in electronegativities between the hydrogen and the oxygen, all the bonds are polar covalent. The oxygen atom, being more electronegative than the hydrogens, has a partial negative charge, leaving a partial positive charge on each hydrogen atom. The linear arrangement in the Lewis structure on the left has a partial positive charge at each end and a partial negative charge in the center. Because the molecule does not have a partial positive end and a partial negative end, this molecule is nonpolar. The bent molecule, however, is polar because it has a partial negative oxygen on one end of the molecule and two hydrogens with partial positives at the other end.

The properties of water indicate which structure is more likely. A nonpolar water molecule would have properties similar to other nonpolar molecules of approximately the same molecular mass, such as methane. For example, it should boil at about – 100 degrees Celsius. Because water boils 200 degrees higher (+100 degrees Celsius), you can reasonably assume that water must be polar instead of nonpolar.

Delving Into Electron and Molecular Geometry (VSEPR)

One method to predict the shape of molecules is the *valence-shell electron-pair repulsion (VSEPR) theory*. The basis of this theory is that the valence-shell electron pairs around a central atom try to move as far away from each other as possible (like two supermodels showing up at a party wearing the same dress). Electrons spread out to minimize the repulsion between their like (negative) charges. This theory includes both electrons in bonds and nonbonding or lone-pair electrons.

With this VSEPR method, I show you how to actually determine two geometries. The two geometries are as follows:

- ✓ **Electron-pair geometry:** Sometimes called the *electron-group geometry*, it considers all electron pairs surrounding a nucleus.
- ✓ **Molecular geometry:** The nonbonding electrons become “invisible,” and you consider only the arrangement of the atomic nuclei.

In determining geometry, double and triple bonds count the same as single bonds.



In order to determine the electron-group and molecular geometry, follow these steps:

1. Write the Lewis electron-dot formula of the compound.

Refer to Chapter 14 for the rules of writing Lewis structures.

2. Determine the number of electron pair groups surrounding the central atom(s).

Remember that double and triple bonds count the same as a single bond.

3. Determine the geometric shape that maximizes the distance between the electron groups.

Check out Table 15-1 for electron-pair geometry, the shapes associated with the number of electron pairs.

4. Mentally allow the nonbonding electrons to become invisible.

They are still present and are still repelling the other electron pairs. However, you just don't “see” them.

5. Determine the molecular geometry from the arrangement of bonding pairs around the central atom by referring to Table 15-1.

Table 15-1		Predicting Molecular Shape with the VSEPR Theory	
<i>Total Number of Electron Pairs</i>	<i>Number of Bonding Pairs</i>	<i>Electron-Pair Geometry</i>	<i>Molecular Geometry</i>
2	2	Linear	Linear
3	3	Trigonal planar	Trigonal planar
3	2	Trigonal planar	Bent, V shaped
3	1	Trigonal planar	Linear
4	4	Tetrahedral	Tetrahedral
4	3	Tetrahedral	Trigonal pyramidal
4	2	Tetrahedral	Bent, V shaped
5	5	Trigonal bipyramidal	Trigonal bipyramidal
5	4	Trigonal bipyramidal	Seesaw
5	3	Trigonal bipyramidal	T shaped
5	2	Trigonal bipyramidal	Linear
6	6	Octahedral	Octahedral
6	5	Octahedral	Square pyramidal
6	4	Octahedral	Square planar

Even though you normally don't have to worry about more than four electron pairs around the central atom (because of the octet rule), I put some of the less common exceptions to the octet rule in Table 15-1. Figure 15-4 shows some of the more common shapes mentioned in the table.



Determine the shapes of water (H_2O) and ammonia (NH_3).

To do so, the first thing you have to do is determine the Lewis formula for each compound. Follow the rules outlined in Chapter 14 and write the Lewis formulas as shown in Figure 15-5.

For water, four electron pairs are around the oxygen atom, so the electron-pair geometry is *tetrahedral* (refer to Figure 15-4). Only two of these four electron pairs are involved in bonding, so the molecular shape is bent or V shaped. Because the molecular shape for water is V shaped, I always show water with the hydrogen atoms at about a 90-degree angle to each other — it's a good approximation of the actual shape.

Figure 15-4:
Common
molecular
shapes.

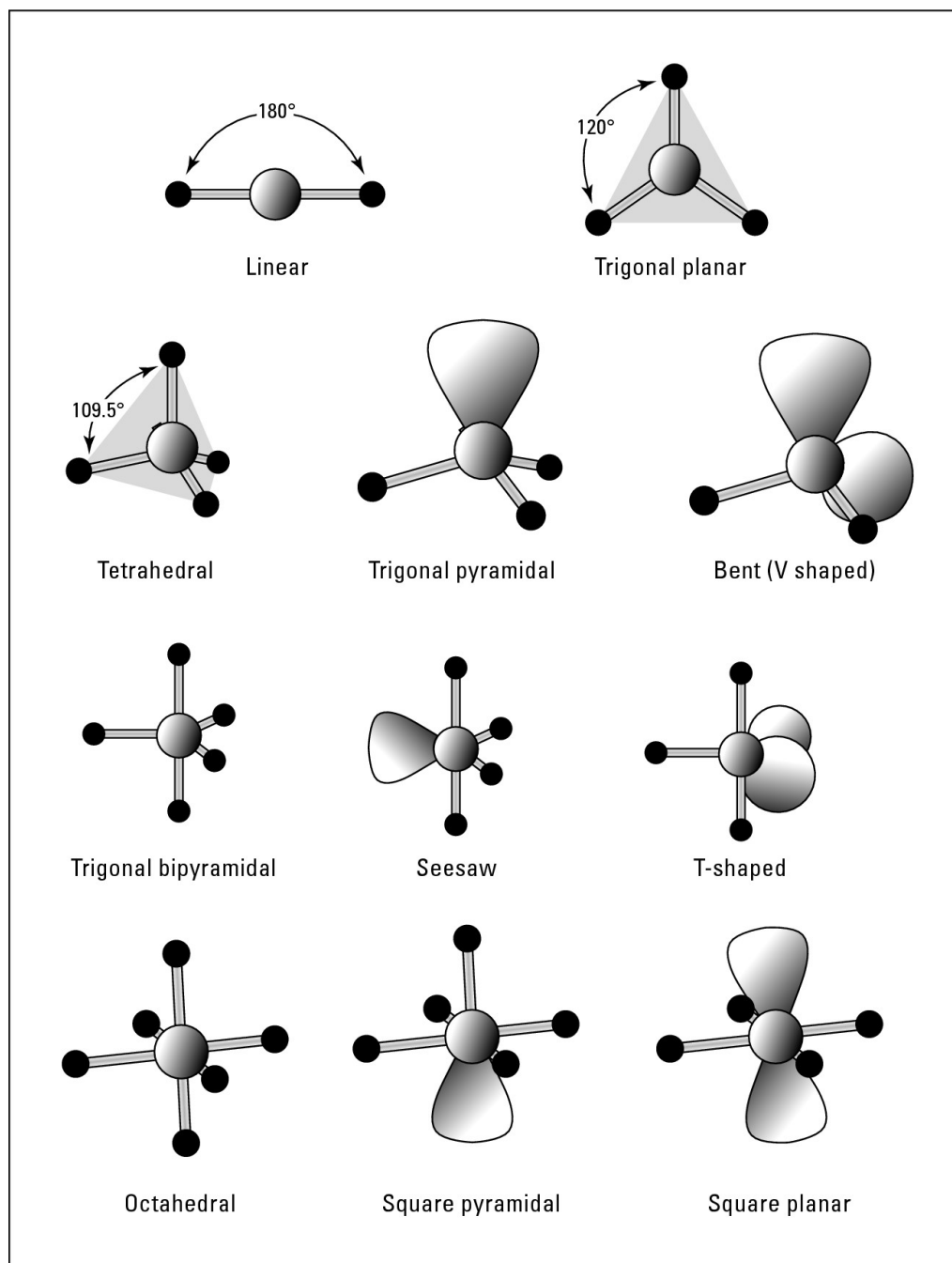
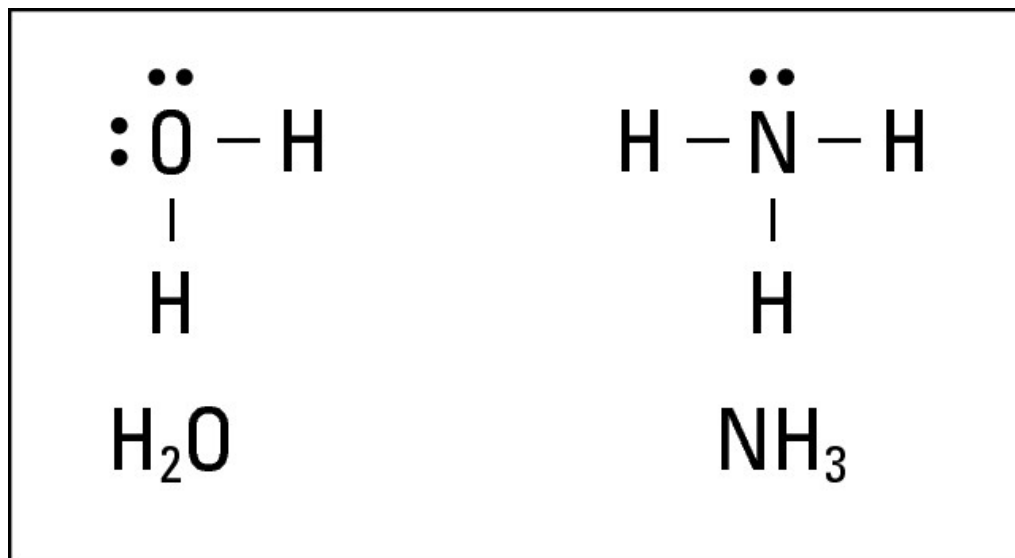


Figure 15-5:
Lewis
formulas for
 H_2O and NH_3 .



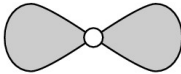
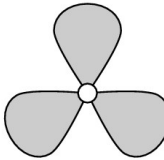
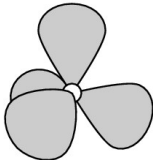
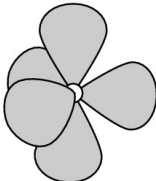
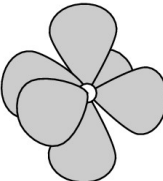
Ammonia also has four electron pairs around the nitrogen central atom, so its electron-pair geometry is tetrahedral as well. Only one of the four electron pairs is nonbonding, however, so its molecular shape is *trigonal pyramidal*. This shape is like a three-legged milk stool, with the nitrogen being the seat, the three bonding pairs of electrons being the legs, and the “invisible” lone pair of nonbonding electrons sticking straight up from the seat. You’d get a surprise if you sat on an ammonia stool!

Comprehending the Valence Bond Theory (Hybridization)

Another method to determine molecular geometry involves using the valence bond theory. *Valence bond theory* explains covalent bonding in terms of the blending of atomic orbitals to form new types of orbitals, hybrid orbitals. *Hybrid orbitals* are orbitals formed when the atomic orbitals of the central atom combine when forming a compound. However, the total number of orbitals doesn’t change; the number of hybrid orbitals equals

the number of atomic orbitals used. The number and type of atomic orbitals used determine what type of hybrid orbitals form. Figure 15-6 shows the hybrid orbitals resulting from the mixing of s, p, and d orbitals. The atoms share electrons through the overlapping of their orbitals.

Figure 15-6:
Hybridization
involving the
s, p, and d
orbitals.

	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Atomic orbitals mixed	one s one p	one s two p	one s three p	one s three p one d	one s three p two d
Hybrid orbitals formed	two sp	three sp^2	four sp^3	five sp^2d	six sp^3d^2
Unhybridized orbitals remaining	two p	one p	none	four d	three d
Orientation					

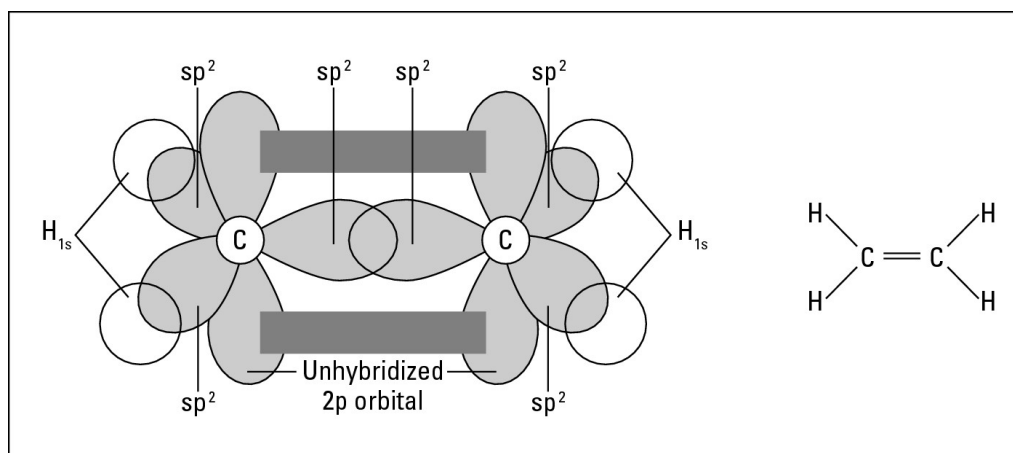
The type of hybridization formed depends on the type and number of atomic orbitals that are involved, and this in turn affects the shape of the resulting molecule:

- ✓ *sp hybridization* results from the overlap of one s orbital with one p orbital. Two sp-hybrid orbitals form with a bond angle of 180 degrees, which is called a *linear orientation*.
- ✓ *sp² hybridization* results from the overlap of one s orbital with two p orbitals. Three sp²-hybrid orbitals form with a trigonal planar orientation and a bond angle of 120 degrees. This type of bonding occurs in the formation of the C-to-C double bond, as in CH₂=CH₂.
- ✓ *sp³ hybridization* results from the combination of one s orbital and three p orbitals, resulting in four sp³-hybrid orbitals with a tetrahedral geometric orientation. You find this sp³ hybridization in carbon when it forms four single bonds.

- ✓ sp^3d hybridization results from the blending of one s orbital, three p orbitals, and one d orbital. The result is five sp^3d orbitals with a trigonal bipyramidal orientation. This type of bonding occurs in compounds like PCl_5 , an exception to the octet rule.
- ✓ sp^3d^2 hybridization occurs when one s orbital, three p orbitals, and two d orbitals come together to create an octahedral arrangement. SF_6 is an example. As you have seen before, SF_6 is an exception to the octet rule. If one of the bonding pairs in an sp^3d^2 hybridization becomes a lone pair, a square pyramidal shape results; two lone pairs results in a square planar shape.

Figure 15-7 shows the hybridization found in ethylene, $H_2C=CH_2$. Each carbon has sp^2 hybridization. On each carbon, two of the hybrid orbitals overlap with an s orbital on a hydrogen atom to form a carbon-to-hydrogen covalent bond. The third sp^2 -hybrid orbital overlaps with the sp^2 hybrid on the other carbon to form a carbon-to-carbon covalent bond. Note that each carbon has a remaining p orbital that has not undergone hybridization. These p orbitals also overlap above and below a line joining the carbons.

Figure 15-7:
Hybridization
in ethylene.



Ethylene has two types of bonds. *Sigma* (σ) *bonds* have the overlap of the orbitals on a line between the two atoms involved in the covalent bond. In ethylene, the C-H bonds and one of the C-C bonds are sigma bonds. *Pi* (π) *bonds* have the overlap of orbitals above and below a line through the two nuclei of the atoms involved in the bond. A double bond is always composed of one sigma bond and one pi bond. A carbon-to-carbon triple bond results from the overlap of one sp-hybrid orbital and two p orbitals on one carbon and the same overlap on the other carbon, resulting in one sigma bond (overlap of the sp-hybrid orbitals) and two pi bonds (overlap of two sets of p orbitals).



In a multiple bond, one of the bonds must always be a sigma bond and the others are pi.

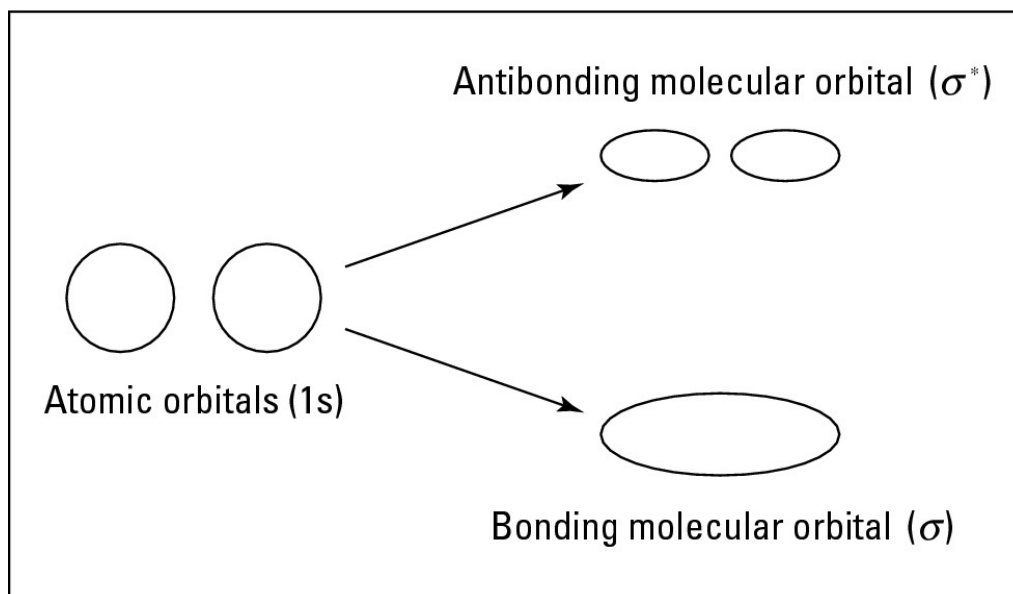
Breaking Down the Molecular Orbital (MO) Theory

Another covalent bonding model is molecular orbital theory. In *molecular orbital (MO) theory*, atomic orbitals on the individual atoms combine to form molecular orbitals (MOs), which aren't hybrid orbitals. A molecular orbital covers the entire molecule and has a definite shape and energy. The combination of two atomic orbitals produces two molecular orbitals. (Like in hybridization, the total number of orbitals never changes.)

- ✓ **Bonding molecular orbital:** The bonding MO has a lower energy than the original atomic orbitals.
- ✓ **Antibonding molecular orbital:** The antibonding molecular orbital has a higher energy than the original atomic orbitals.

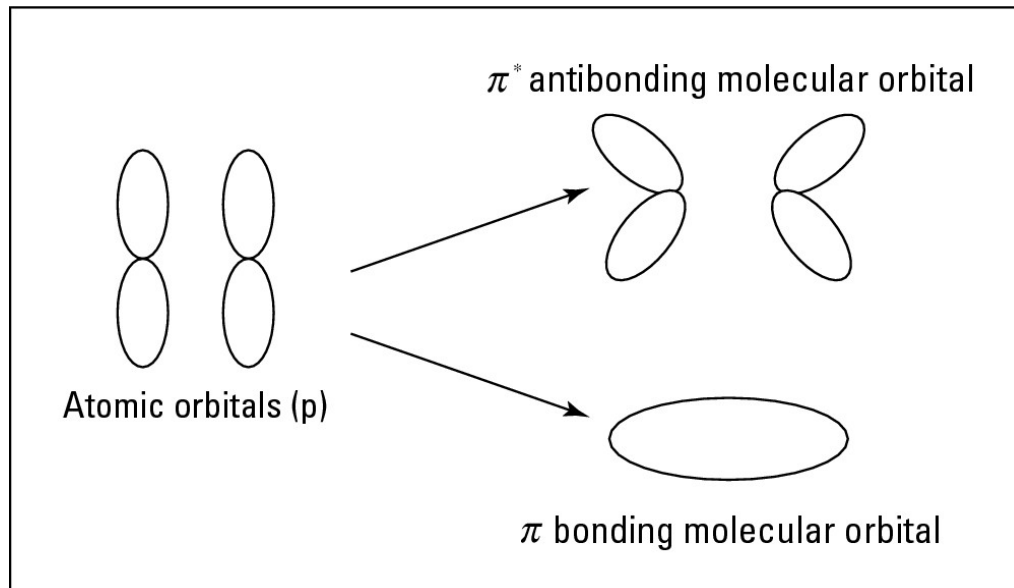
As shown in Figure 15-8, lower-energy orbitals are more stable than higher-energy orbitals. Notice that the bonding molecular orbital, because it's of lower energy than the original atomic orbitals, strengthens the bond.

Figure 15-8:
Formation of
bonding and
antibonding
molecular
orbitals from
the overlap of
two atomic
orbitals.



The end-to-end overlap of two p orbitals yields a σ bonding and a σ^* antibonding molecular orbital. The side-by-side overlapping of p orbitals yields a π bond composed of one π bonding molecular orbital and one π^* antibonding molecular orbital, as you can see in Figure 15-9.

Figure 15-9:
Formation of
 π and π^*
molecular
orbitals.

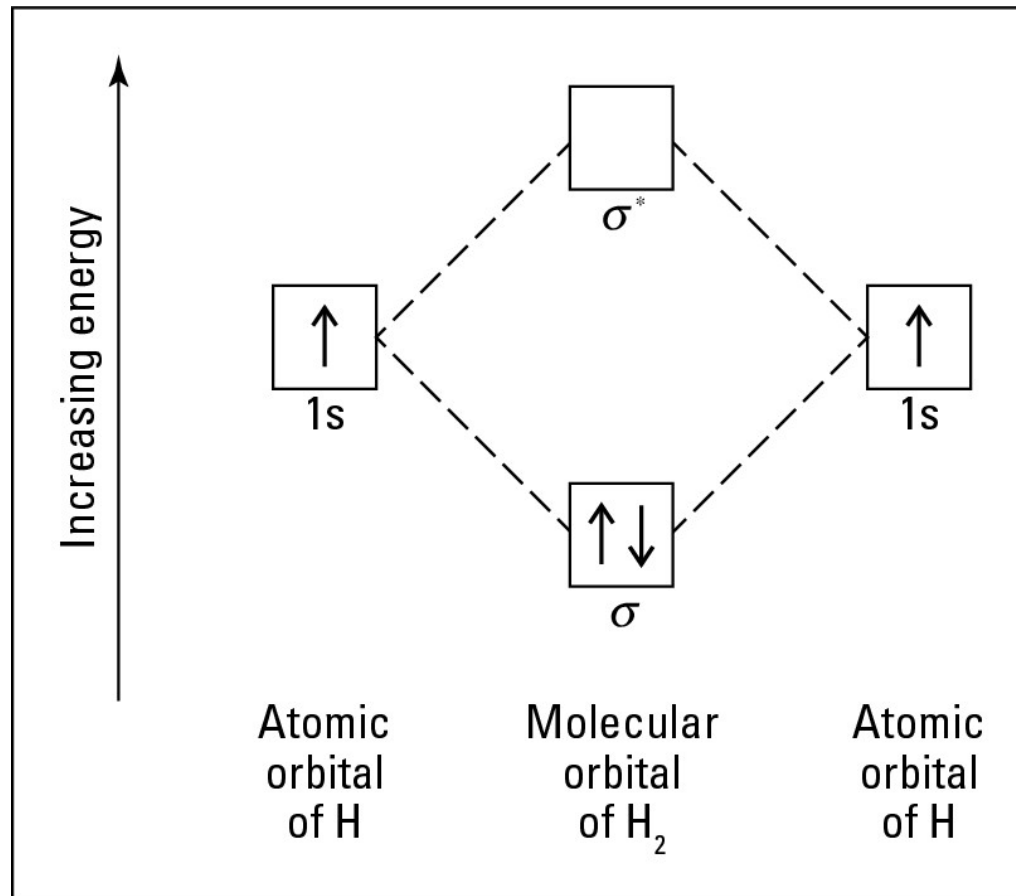


After the molecular orbitals form, you put electrons in. You add electrons using the same rules you used for electron configurations (see Chapter 12).

- ✓ The lower-energy orbitals fill first.
- ✓ Each orbital has a maximum of two electrons.
- ✓ Orbitals of equal energy half-fill orbitals before pairing electrons.
- ✓ When two s atomic orbitals combine, two sigma (σ) molecular orbitals form. One is sigma bonding (σ), and the other is sigma antibonding (σ^*).

Figure 15-10 shows the molecular orbital diagram for H_2 .

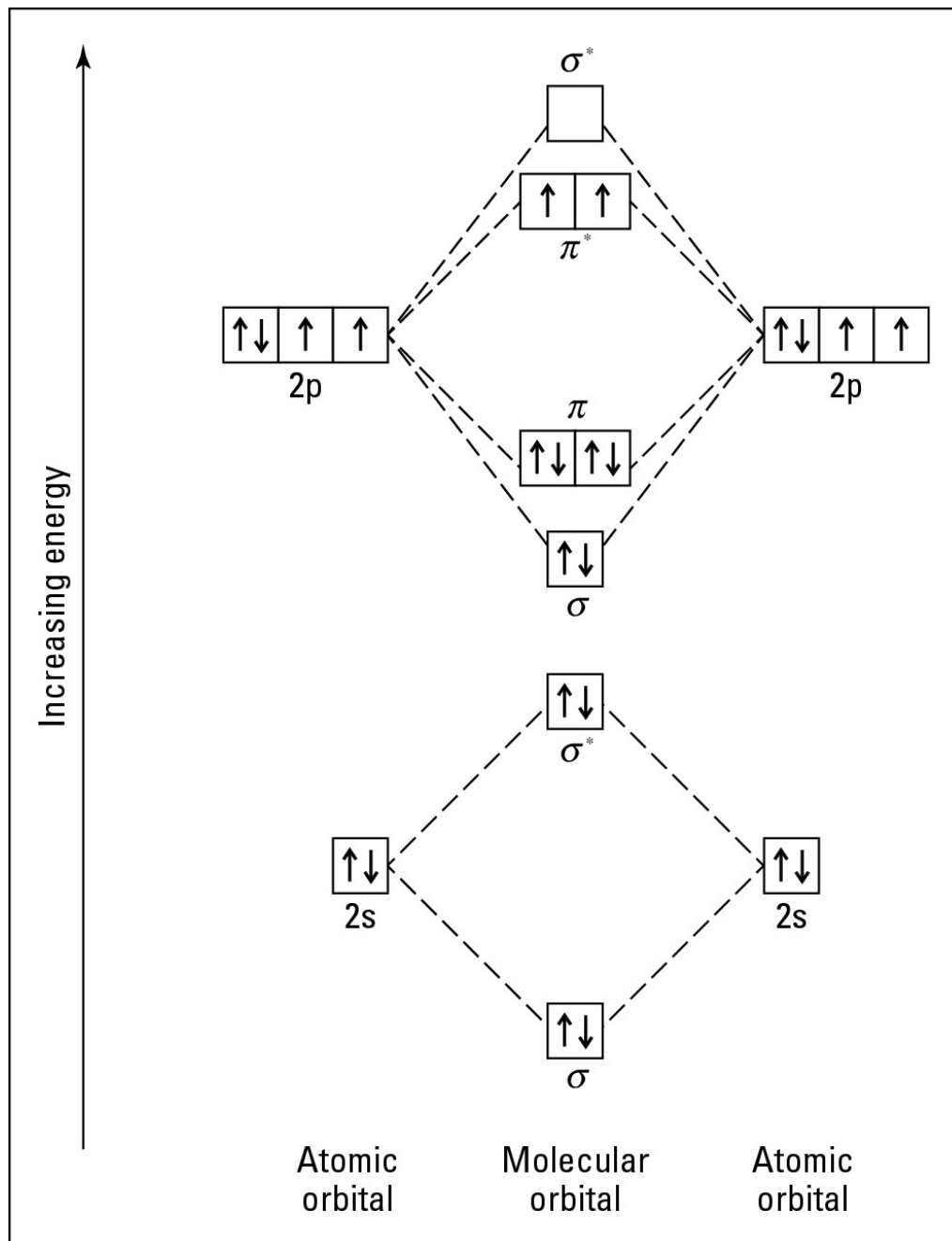
Figure 15-10:
Molecular
orbital
diagram for
 H_2 .



Notice that the two electrons (one from each hydrogen atom) have both gone into the sigma bonding MO. You can determine the bonding situation in the molecular orbital theory by calculating the MO bond order. The *MO bond order* is the number of electrons in bonding MOs minus the number of electrons in antibonding MOs, divided by 2. A stable bonding situation exists between two atoms when the bond order is greater than zero. The larger the bond order, the stronger the bond. For H₂ in Figure 15-10, the bond order is $(2 - 0)/2 = 1$.

When two sets of p orbitals combine, one sigma bonding and one sigma antibonding MO are formed along with two pi bonding MOs and two pi antibonding MOs. Figure 15-11 shows the MO diagram for O₂. For the sake of simplicity, I don't show the 1s orbitals of each oxygen or MOs here, just the valence-electron orbitals.

Figure 15-11:
MO diagram
for O_2
(valence-shell
electrons
only).



The bond order for O_2 is $(10 - 6)/2 = 2$. (Don't forget to count the bonding and antibonding electrons at energy level 1.)

Chapter 16

Tackling Periodic Trends

In This Chapter

- ▶ Tracing trends in the size of atoms and ions
 - ▶ Dealing with ionization energy of cations
 - ▶ Taking a look at anions' electron affinity
-

In Chapter 5, I explain a lot of information concerning the periodic table. I show you a number of ways to classify elements on the periodic table — by groups or families (the vertical columns); by periods (the horizontal rows); by metals, nonmetals and metalloids; and so on. I also explain how the arrangement of electrons determines an element's position on the periodic table and how those outermost electrons, the valence electrons, determine the chemical properties of the elements.

In this chapter, I show you some trends in the properties of elements on the periodic table. I know, when you think of trends you think of fashion — bell-bottom pants and platform shoes. (Oops, did I just give you a clue as to my age?) The periodic table has trends, too, and although they may not be very stylish, these periodic trends can be useful in predicting speeds of reaction, size of atoms and ions, and other characteristics. So sit back and get trendy.

Checking Out the Importance of Size

When working with atoms and their parts, understanding the different sizes and their relationship to each other is essential. The occupied energy levels of the atom basically determine the atom's size. The nucleus is tiny; the electrons in their energy levels around the nucleus really determine the boundaries of the atom. Some additional factors, especially the effective nuclear charge, have an effect on the electron and thus on the size of the atom. I discuss these factors in the following sections.

Comprehending effective nuclear charge

The nucleus of an atom contains protons and neutrons. As I discuss in Chapter 4, the number of protons in a nucleus is the *atomic number*. Neutrons have no charge, whereas protons have a positive charge. If you add together the positive charges of all those protons, you have what's called the *nuclear charge*. This positive charge in the nucleus attracts electrons, which are negatively charged. (Unlike charges attract, and like charges repel.) If the atom contains only a single electron, the attraction force is straightforward. However, when more than one electron is present, the situation becomes more complicated.

The negative charge of one electron interferes with the attractive force of the nucleus to other electrons. Electrons occupy "energy levels" that form a sort of layered shell around the nucleus. When electrons closer to the nucleus come between another electron and the nucleus, they cause a greater interference. Therefore, electrons that are contained in the same energy level produce a minimum interference on each other, but the core electrons (inner-shell electrons) partially

shield the outer electrons from the attraction of the positive charge in the nucleus, the nuclear charge. This shielding affects all electrons in an atom, but for trends in size, the shielding of the valence electrons (outermost electrons) is the key. Those outermost electrons are contained in the orbital with the highest value of the principal quantum number, n , and are the electrons that determine the size of the atomic radius. If shielding lessens the attractive force of the nucleus to the valence electrons, they're free to move a little bit farther from the nucleus, and the atomic diameter increases.



The core electrons screen the nuclear charge from the valence electrons. The actual charge attracting the valence electrons is called the effective nuclear charge. The *effective nuclear charge* is the nuclear charge minus the shielding effect of the core electrons. The shielding effect is essentially the same for any period on the periodic table, but when going down a family (group), the effect increases as you move toward the bottom of the column. The greater the shielding, the less the effective nuclear charge, allowing the valence electrons to move a little farther away from the nucleus. This increases the size of the atom.

Explaining changes in atomic radii

The atomic *radius* is the distance from the center of the nucleus to the valence energy level. It's how chemists describe the size of the atom or ion. It's important in determining the type of crystal lattice formed, solubility, and so on. On the periodic table, atomic *radii* (the plural of radius) increase from top to bottom within a family and decrease from left to right within a period.

When you move down a family, the atomic radii of the atoms increase, making each atom significantly larger than the one

above it. This increase in size is the result of electrons occupying energy levels of increasing distance from the nucleus, increasing n values. The nuclear charge increases as you go down a family (increased numbers of protons in the nucleus), but an increasing number of core electrons shield the valence electrons from the charge in the nucleus. The effective nuclear charge on the valence electrons is thus decreased, allowing the electrons to move slightly away from the nucleus and countering the nuclear charge. Therefore, simply adding an energy level predominates in determining the size of the atomic radii.

Understanding the size changes as you move across a period isn't so simple. Unlike atoms in families, which add energy levels, atoms in periods add electrons to the same energy level. Because the added electrons don't come between other electrons and the nucleus, causing interference, you may think that the size of the atoms would remain basically constant. However, as you go from one element to the next, more protons are added to the nucleus, increasing the nuclear charge. The shielding effect of the core electrons is essentially constant as you move from left to right within a period, so the effective nuclear charge increases slightly with each move. This increased effective nuclear charge pulls the atom's electrons, especially the valence electrons, slightly closer to the nucleus, causing the atomic radii (size) of the atoms to slightly decrease when moving from left to right in a period.

Tracing tendencies of ionic radii

Atoms are neutral, but they may gain or lose electrons to form *ions* (atoms or groups of atoms that have an overall charge). To keep things simple, in this chapter I discuss only *monatomic ions*, ions that have only one atom.

If an atom loses electrons, the chemical species that is left has more protons (more positive charges) than electrons (negative charges) and therefore has an overall positive charge. An ion with a positive charge is a *cation*. (I would have preferred the name *dogion*, but they didn't ask my opinion.) A cation has one positive charge for each electron lost.



A cation's radius size (its *ionic radii*) is smaller than a unionized atom. The loss of electrons leads to a decrease in the size when compared to the neutral atom because, at least for a representative element, the ion loses an entire energy level. Thus, a potassium ion, K^+ , is smaller than a potassium atom. The more electrons removed, the greater the decrease in radius becomes. Therefore, you observe the trend in radii of $Fe > Fe^{2+} > Fe^{3+}$.



When an atom gains electrons, it produces an *anion*, which has a larger ionic radius than the original atom. You observe this trend because the effective nuclear charge (determined by the number of protons) is the same in both the atom and the anion but is spread over an increasing number of electrons. The more electrons added, the greater the increase in size. For oxygen and a couple of its anions, you see the following trend in radii: $O < O^- < O^{2-}$.

For a set of isoelectronic anions (anions with the same number of electrons), such as the anions of nitrogen, oxygen, and fluorine, the number of protons in the nucleus increases as you move across the period from N to O to F. This increase means that the effective nuclear charge also increases, pulling the electrons closer to the nucleus. Therefore, the trend in ionic radii is $F^- < O^{2-} < N^{3-}$.

Eyeing Trends in Ionization Energies

The ease of forming a cation, an ion with a positive charge, varies with the position of the element on the periodic table. To understand the trend in ability to form cations, you must use the concept of ionization energies of the elements. The *ionization energy* is the energy required to remove an electron from a gaseous atom in its ground state. This definition is demonstrated by the thermochemical equation for the formation of a cation from some atom (A) in a gaseous state (*g*):



In this equation, e^- is the electron being lost and ΔH is the enthalpy (energy) needed to accomplish the removal of the electron.



Removing an electron from an atom always takes energy, so the ionization energy is always *endothermic* (requiring energy). The removal of a second electron requires even more energy (the second ionization energy), the removal of a third electron requires the third ionization energy, and so forth.

The following sections describe some of the trends in ionization energies that you may encounter.

Noting an increase in sequential energy

The amount of energy required for sequential ionization energies (removing more than one electron from an atom) increases with the number of electrons removed. You encounter

this in the formation of cations of a +2 or +3 charge, corresponding to the loss of 2 and 3 electrons, respectively. This increase is due to the attractive force between the increasing positive charge of the cation and the electron that is in the process of being removed. Unfortunately, this increase isn't simply linear.



The general relationship between the value of an element's ionization energy and the position of the element on the periodic table is essentially the reverse of the atomic radii (which I discuss in the earlier section "Checking Out the Importance of Size"). Small atoms have high ionization energies, and large atoms have low ionization energies. The size increase of an atom near the bottom of a column on the periodic table means that its outer electrons are further from the nucleus. The greater the distance between the positively charged protons and the negatively charged electrons, the weaker the attraction of the nucleus for the electrons (something physicists call the *inverse square law*). A weaker attraction holding electrons in an energy level means that you can use less energy to overcome the attractive force, which results in a lower ionization energy for the electron. For example, much more energy is required to remove an electron from lithium than from cesium (both alkali metals), because the electron being removed from lithium is much closer to the nucleus and therefore is held more strongly.

Within a period (a row on the periodic table), the ionization energy increases from left to right because the effective nuclear charge is increasing and therefore a greater attractive force must be overcome. However, this trend in ionization energy is more complicated than a simple increase in the effective nuclear charge.

The trends in ionization energy suggest that elements on the left side of the periodic table, especially the lower left, form cations (lose electrons) more readily than the elements on the right. The elements with lower ionization energies are the metals, and the elements with higher ionization energies are the nonmetals. And as I indicate in the chapter on ionic bonding (Chapter 13), metals do lose electrons to form cations.

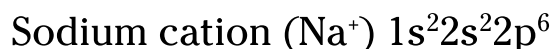
For example, if you examine the elements from lithium, Li, to neon, Ne, you can see the expected increase in ionization energies from left to right on the periodic table. However, the trend isn't linear; peaks occur at beryllium (Be) and nitrogen (N). Why are the ionization energy values for beryllium and nitrogen higher than expected? If you examine the electron configuration of beryllium, you can see that it is $1s^2 2s^2$ (see Chapter 4 for a discussion of electron configurations). The valence shell of beryllium has a filled 2s subshell. The filling of a subshell leads to additional stability and therefore requires more energy to pull the electron away.

In the case of nitrogen, the 2p sublevel is half-filled. The electrons are in different orbitals and are as widely separated as possible for electrons in the same sublevel. This wide separation minimizes repulsion among the negative charges and stabilizes the half-filled sublevel arrangement of electrons in nitrogen. This kind of stability also leads to an increase in the ionization energy.

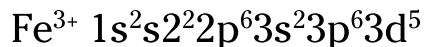
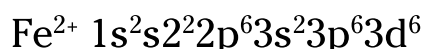
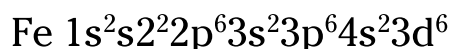
Taking stability into consideration

The stability of certain electron configurations affects the general trend in the ionization energies based on size and effective nuclear charge. As I note in the preceding section, stability increases anytime a sublevel is either half-filled or filled.

You can write electronic configurations of cations. For example, a sodium atom loses a single electron to form a Na^+ cation. The electron configuration of Na^+ is



Because of quantum mechanical considerations coupled with the effective nuclear charge, the electrons are always lost from the level with the highest principal quantum number. For the representative elements, the last electron to enter is the first electron lost. In the case of the transition metals, the first electron lost is not the last electron to enter. If you use iron, Fe, for example, you can examine the electron configuration of the element and the configurations of the two common iron cations, Fe^{2+} and Fe^{3+} .

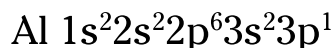
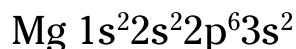
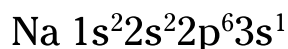


The formation of the iron(II) cation, Fe^{2+} , involves the loss of the two 4s electrons because these two electrons have a higher principal quantum number than the last electrons to enter (the 3d electrons). This factor explains why many of the transition metals have a stable 2^+ ion. The iron 3d electrons are not affected until after the removal of the 4s electrons. And this removal deletes energy level 4, making the ions more stable because they have a lower overall energy.

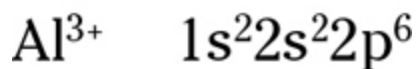
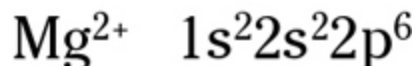
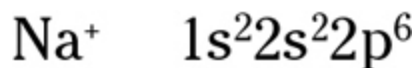
Considering a few exceptions to the rule

For any element, ionization energy increases as an increasing number of electrons are removed. However, some elements do react differently in certain levels. The second ionization energy of sodium, the third ionization energy of magnesium, and the

fourth ionization energy of aluminum are significantly higher than you would expect based on their preceding ionization energies. Apparently something else is going on. If you examine the electron configurations of these three elements, you find



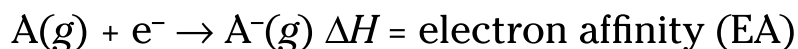
The first ionization energy of sodium, the first two ionization energies of magnesium, and the first three ionization energies of aluminum leave you with the following electron configurations:



For these three elements, removal of an *additional* electron involves removal from the electron configuration $1s^2 2s^2 2p^6$, which contains only core electrons (the valence electrons having been already removed in the formation of the cation). This factor is at the root of all three high ionization energy values for the preceding stable ions: The removal of a core electron requires significantly more energy than the removal of valence electrons. In normal chemical reactions, sufficient energy is available to remove valence electrons but not core electrons. Thus, the simple removal of the valence electrons forms common cations of the representative elements.

Considering Trends in Electron Affinities

Although ionization energies describe the formation of cations, chemists use a different term to describe the formation of anions. *Electron affinity* is the energy change accompanying the addition of an electron to a gaseous atom in its ground state. Following is the thermochemical equation for this process, where A is an atom, (g) represents the gaseous state, e^- is an electron, and ΔH represents the enthalpy (energy) needed to accomplish the addition of the electron.



Unlike the ionization energies, which are always *endothermic* (requiring energy), the first electron affinity of an atom may be endothermic, *exothermic* (producing energy), or even zero. Adding additional electrons, though, is always endothermic. The second and higher electron affinities require energy because, after adding the first electron, the ion is negatively charged and subsequent electrons must overcome the repulsion. Electron affinity values are more difficult to measure than ionization energies; many times they're calculated from thermochemical data.



The general trend of electron affinities is about the same as the trend for ionization energies (discussed in the previous section “Eyeing Trends in Ionization Energies”). Small atoms having a vacancy in the valence shell teamed with a high effective nuclear charge have high electron affinities. Therefore, electron affinities tend to increase going up a column (increasing effective nuclear charge) and moving from left to right in a period (which also increases the effective nuclear charge).

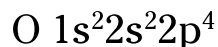
However, electron configurations complicate this trend even more than they complicate the trend for ionization energies. The noble gases have ionization energies, but because of their filled valence shells, they don't have electron affinities. In addition, the alkaline earth metals with their s^2 configurations (no vacancy in the lowest shell of the valence shell) have essentially no electron affinity. Additional complications appear when you consider elements other than the representative elements. For example, the electron affinity of gold is higher than every element other than the halogens. The electron affinity of fluorine is lower than expected because the fluoride ion is too small to accommodate the additional negative charge without a significant amount of repulsion. Because fluorine has a lower than expected electron affinity, the highest electron affinity of all the elements belongs to chlorine. Large positive electron affinities indicated that the negative ion is very stable.

As for the representative elements, the nonmetals have high electron affinities and tend to form anions. The metals have low electron affinities and tend not to form anions.

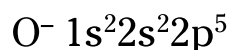


You can write electron configuration and orbital diagrams for anions, just as you can do so for atoms and cations. The extra electrons are added according to the aufbau principle, which means that they enter the lowest possible orbital (see Chapter 4).

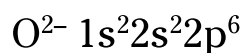
As an example, use oxygen. You find that the atom has the following electron configuration:



When an oxygen atom gains one electron (corresponding to the electron affinity), you get this configuration:



The addition of a second electron (corresponding to the second electron affinity) gives you the following:



The oxide ion, O^{2-} , is now *isoelectronic* (having the same number of electrons) with the noble gas neon, Ne, and like the noble gases, it will not accommodate any additional electrons. It has a filled valence shell, and this situation is extremely stable. The representative elements will only gain electrons until they fill their valence shells (attain an electron arrangement isoelectronic with the next noble gas).

Chapter 17

Examining the Link between Intermolecular Forces and Condensed States

In This Chapter

- ▶ Understanding the types of intermolecular forces
 - ▶ Grasping the properties of liquids
 - ▶ Figuring out solids
 - ▶ Making sense of phase diagrams
-

In this chapter, I tell you about *intermolecular forces* (the forces between atoms and/or ions and/or molecules) and *condensed states* (by which I mean liquids and solids). You may think these two topics seem unrelated, but in fact they are related. The state of matter in which a substance is found is dependent on the kinetic energy of the particles of the substance and the strength of the forces between those particles, the intermolecular forces.

Here I show you the different types of intermolecular forces and then discuss the properties of liquids and solids. (I'm not going to talk much about gases; they're pretty well covered in Chapter 6.) So off you go, and may the (intermolecular) forces be with you.

Understanding Types of Intermolecular Forces

Intermolecular forces are those attractive or repulsive forces (interactions) that take place between atoms, molecules, and ions. They are all related to charge, whether a full charge in the case of ions or a partial charge in the case of atoms or molecules. **Remember:** Unlike charges attract; like charges repel.



Being able to recognize whether or not a molecule is polar is important in order to determine which intermolecular forces are important in a particular situation. *Polar* molecules have a partial positive and a partial negative end and thus are dipoles. You may want to glance over Chapters 14 and 15 on covalent bonding and molecular geometry.

Many of the properties of chemical substances, such as solubility, are related to intermolecular forces. Being able to recognize the intermolecular forces present will many times allow you to predict some physical properties and even reactivities.

The following intermolecular forces are listed in order of decreasing strength of interaction.

Bringing ions and dipoles together

Sometimes an ion is attracted to a molecule that is a dipole. If the ion is a *cation* (positive charge), it's attracted to the negative end of the dipole, and if the ion is an *anion* (negative charge), it's attracted to the positive end of the dipole. This

interaction occurs quite commonly in aqueous solution in which an ion attracts water molecules.

Suppose, for example, you dissolve some white, crystalline AlCl_3 in water. The Al^{3+} cation attracts water molecules because it is a small ion with a large amount of positive charge. (Chemists say it has a large charge density.) Because of its high charge density, it attracts the partial negative end of the water molecule, the oxygen. In fact, it attracts a total of six water molecules, creating the hydrated aluminum ion, $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

The chloride ions attract the partial positive ends of water molecules, the hydrogens. However, because chloride ions are large ions with only a single negative charge, their charge density is low and so the attractive force is much weaker.

If you carefully evaporate the solution to dryness, you can recover $\text{Al}(\text{H}_2\text{O})_6\text{Cl}_3$, the hexahydrated aluminum chloride. This substance is a hydrate; it has six waters of hydration incorporated into its crystalline structure. Careful heating of most hydrates results in the waters being driven out of the crystalline structure, leaving the anhydrous form.

Mutually attracting dipoles

Dipole-to-dipole attraction is important when dipoles are present. The positive end of one dipole is attracted to the negative end of another. For example, in the extremely reactive chlorine monofluoride gas, the chlorine has a partial positive charge, and the more electronegative fluorine has a partial negative charge, allowing a dipole-dipole intermolecular attraction between two of the molecules:





Dipole-dipole forces tend to be especially important in polar liquids and are considered a strong intermolecular force, but not as strong as ion-dipole.

Drawing close to hydrogen

Hydrogen bonding is a subset of dipole-dipole interaction, but one in which a hydrogen is bonded to an extremely electronegative element (N, O, F). The covalent bond between the hydrogen and these three elements is extremely polar. The hydrogen on one molecule can interact with the O, N, or F on another molecule. This intermolecular force is much stronger than other dipole-dipole forces and so therefore is given its own special name. The strength of this interaction explains a number of unusual properties of substances such as water. As I discuss in Chapter 14, the reason that water has such relatively high boiling and melting points, among other properties, is related to its hydrogen bonding.



In order for an intermolecular force to be hydrogen bonding, a hydrogen atom must be bonded to an N, O, or F, and this hydrogen must interact with an O, N, or F on another molecule.

Uniting through the cloud

Induced dipole intermolecular forces occur when the charge on an ion or a dipole distorts the electron cloud of a nonpolar molecule. A cation attracts the electron cloud, whereas an anion repels it. Either force induces a temporary dipole in the nonpolar molecule. These interactions are fairly weak and tend to occur in solution.

Bonding temporarily with London (dispersion) forces

This intermolecular attraction occurs in all substances but is usually only significant for nonpolar substances. It is created from the momentary distortion of the electron cloud in which the electron density flows to one side of the atom/molecule. That electron cloud is not fixed; I like to compare it to a ball of cotton candy, easily pushed around (but not as tasty).

This distortion causes a very weak temporary dipole. This weak dipole induces a dipole in another molecule. These weak dipoles lead to an attraction. The more electrons present, the larger the cloud and the greater the London force. This interaction is extremely weak and an individual one does not last very long. However, it is strong enough to allow chemists to liquefy nonpolar gases such as hydrogen, H_2 , which would be impossible if intermolecular forces didn't attract these molecules.

Grasping the Properties of Liquids

A liquid is a phase in which the randomly orientated particles are in contact. The particles may clump together to exhibit short-range areas of order, but they usually don't last very long. The random orientation allows the liquid to change shape to match that of the container, and because the particles are in contact, a liquid isn't very compressible. In this section, I show you a few important macroscopic properties of liquids. The strength of the intermolecular forces is the key to these different properties.

Resisting an increase: Surface tension

Within the body of a liquid, intermolecular forces pull the molecules in all directions. However, at the liquid's surface, the molecules are pulled down into the body of the liquid and from the sides. As a result, neither molecules nor an attractive force above the surface pulls in that direction. The effect of these unbalanced attractive forces is that the liquid tries to minimize its surface area. The *surface tension* is the resistance of a liquid to an increase in its surface area.

The minimum surface area for a given quantity of matter is a sphere. You may have seen video or pictures of a liquid, usually water, being released in zero gravity. The droplets form little spheres. In a large pool of liquid, where sphere formation is not possible, the surface behaves as if it had a thin, stretched elastic membrane or skin over it. Surface tension requires force to break these attractive forces at the surface. The greater the intermolecular force, the greater the surface tension. Polar liquids, especially those that utilize hydrogen bonding, have a much higher surface tension than nonpolar liquids.

Surface tension is what allows a bug to walk over water. It also allows you to add more water to a glass than its volume. Try it. Carefully add water to a glass and see the water dome at the top. Now touch a toothpick that has been dipped into dishwashing liquid to that dome and see it break. That happens because the dishwashing liquid is a *surfactant*, which disrupts surface tension.

Resisting to flow: Viscosity

Viscosity is the resistance to flow. Suppose you have a glass of paint thinner (nonpolar molecules) and a glass of molasses (polar molecules). Try pouring each into another container. The molasses pours much more slowly than the paint thinner. The two important factors influencing the viscosity of a liquid are as follows:

- ✓ **Intermolecular forces:** The stronger the intermolecular force, the greater the viscosity. This is the factor in the paint thinner and molasses situation. The mixture of polar molecules that make up molasses attract each other, and the result is a resistance to flow. The size of the molecules also affects intermolecular forces (and molasses). Large and complex molecules have difficulty moving past one another, so the viscosity is high.
- ✓ **Temperature:** Heat and cold also affect viscosity. If you heat the glass of molasses, it pours more easily because you reduce its viscosity by increasing the kinetic energy of the particles. The higher kinetic energy overcomes the intermolecular attractive forces, causing a lower viscosity. Putting the molasses in the refrigerator causes the opposite effect. The kinetic energy is reduced and the viscosity is increased; hence the phrase, “Slower than molasses in wintertime.”

Some liquids have very high viscosities. If the viscosity is high enough, the liquid may not appear to flow at all and may be mistaken for a solid. A high viscosity liquid that appears to be a solid is commonly referred to as an *amorphous* solid. Sometimes scientists refer to these amorphous solids as *glasses* because glass is the most common example. Rubber and charcoal are other examples of amorphous solids.

Climbing the walls: Capillary action

Another property of liquids that's related to intermolecular forces is capillary action. *Capillary action* is the rising of a liquid through a narrow tube against the force of gravity. It's a result of the competition of intermolecular forces within the liquid and the attractive forces between the liquid and the wall of the tube. The stronger the attraction between the liquid and the wall, the higher the level rises.

Mercury has a weak attraction to the walls of a glass tube and so has low capillary action. Water has a strong attraction to the walls of a glass tube and therefore has high capillary action. This capillary action explains why you observe a meniscus with water contained in a thin tube. A *meniscus* is a concave water surface due to the attraction of the water molecules adjacent to the glass walls. Because of mercury's weak attraction to the glass walls, no meniscus is present. However, if you replace the glass tube with a plastic one, water behaves much more like the mercury did in the glass tube because very little attraction exists between the polar water molecules and the nonpolar plastic.

Only the liquid near the walls of the tube is attracted to the walls. The particles farther away from the walls pull the other molecules back. The narrower the tube, the fewer central molecules and the higher the liquid raises in the tube. This property is one of the ways in which water reaches the top of a tall tree.

Warming up: Heat capacity

Heat capacity is the amount of energy needed to cause the temperature of a substance to rise 1K. (See Chapter 10 for a more complete discussion of heat capacity.) The stronger the intermolecular forces between the molecules of a liquid, the more energy that's required to break the forces and the greater the heat capacity. The same reason explains why liquids that have strong intermolecular forces have higher boiling points and vapor pressures than those that do not.

Working with Solids

At the macroscopic level, a *solid* is a substance that has both a definite shape and volume. At the microscopic level, solids are structures in which the particles are very close to each other. The intermolecular forces have overcome the kinetic energy of the particles, which exhibit no real motion, just vibration.

Solids may be amorphous or crystalline:

- ✓ **Amorphous:** *Amorphous solids* lack extensive ordering of the particles, so the structure has a lack of regularity. Small regions of order may be separated by large areas of disordered particles. Amorphous solids have no distinct melting point; they simply become softer and softer as the temperature rises.

As noted in “Resisting to flow: Viscosity” earlier in this chapter, liquids with high viscosity that appear to be solid are referred to as amorphous solids. Glass, rubber, and charcoal are examples.

- ✓ **Crystalline:** *Crystalline solids* display a very regular ordering of the particles in a three-dimensional structure called a *crystal lattice*. In this crystal lattice are repeating units called *unit cells*. Think of a brick wall that is very long, high, and deep. The wall is like the crystal lattice, and each individual brick is like a unit cell.

You can find several types of unit cells in solids. One of the most common is the cubic unit cell, in which all angles are 90 degrees. However, particles can be arranged in this cubic cell in three ways:

- ✓ **Simple unit:** Also called the *primitive* unit cell, the particles are located at the corners of a simple cube.
- ✓ **Body-centered unit:** The particles are located at the corners and another particle is in the center of the cube.

- ✓ **Face-centered unit:** The particles are in the corners of the cell and in the center of each face but not in the center of the unit cell.

The crystalline solids can be further divided into a number of different types based on the type of bonding or intermolecular force that holds the individual particles in the crystal lattice. Scientists know of five types of crystalline solids:

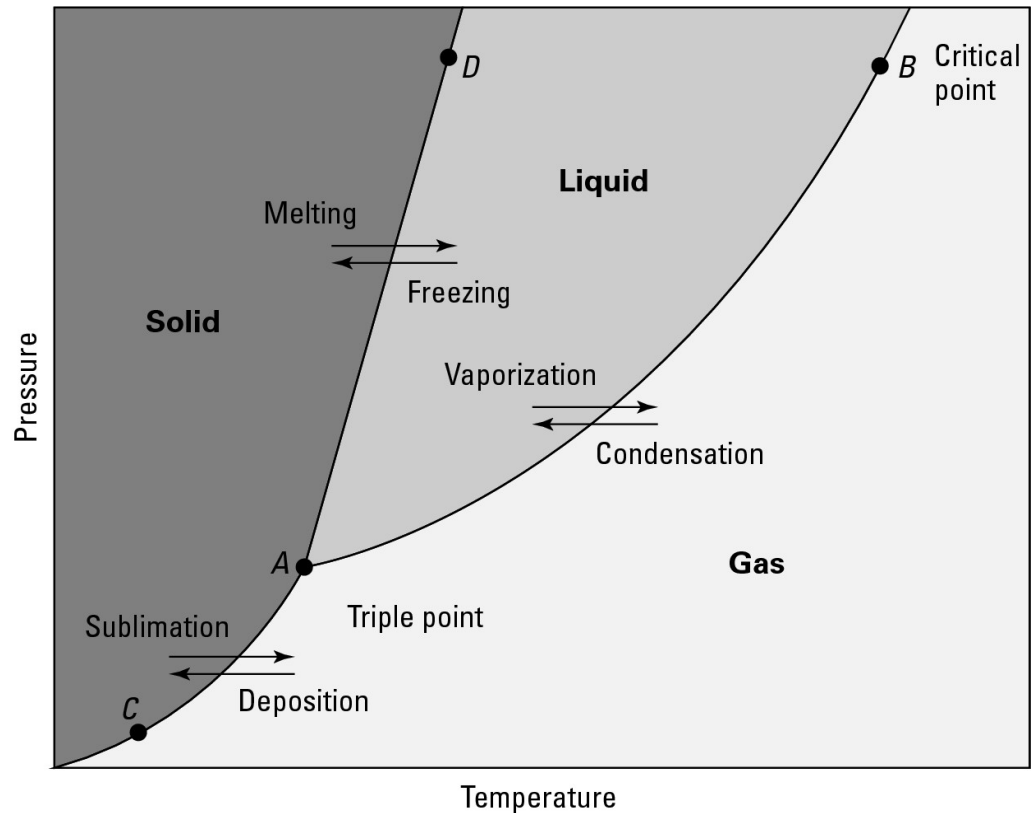
- ✓ **Atomic solids:** In these solids, the particles are held together in a crystal lattice by London forces. The noble gases are the only known examples of atomic solids.
- ✓ **Molecular solids:** In these solids, the particles in their crystal lattices are held in place by London, dipole-dipole, and hydrogen-bonding intermolecular forces. Water and solid methane are examples of molecular solids.
- ✓ **Ionic solids:** In this type, the particles in the crystal lattice are held together by the attraction of cations and anions. This type of crystal lattice tends to be very strong with high melting points, due to the strong attractive forces between the oppositely charged ions. Sodium chloride (NaCl) is an example of an ionic solid. (Have you ever tried to melt salt?)
- ✓ **Metallic solids:** Metal atoms are in a crystal lattice held together by *metallic bonding*, a type of bonding in which the electrons of the metal atoms are delocalized and donated to a “sea of electrons.” The electrons are free to move throughout the entire solid, which explains why metals are such good conductors of both electricity and heat. This metallic bonding is also responsible for the luster of metals.
- ✓ **Network (covalent) solids:** These solids have their atoms in the crystal lattice held together by covalent

bonds. They tend to have a very extensive structure, and, in fact, you can think of a network solid as one large molecule. Diamonds are examples of network solids. That Hope diamond is a single large molecule! Graphite and silicon dioxide are also examples of network solids.

Deciphering Phase Diagrams

A *phase diagram* is a graph representing the relationship of all the states of matter of a specific substance. The most common type of phase diagram relates the states to temperature and pressure. The pressure is the vertical axis and the temperature is the horizontal axis. Different substances have different ranges of temperature and/or pressure. The lines may be longer or shorter, and the angles may vary, but the solid (S), liquid (L), and gas (G), regions always have the same basic relationship to each other. The phase diagram allows you to predict which state of matter exists at a certain temperature and pressure combination. Figure 17-1 shows a general form of a phase diagram.

Figure 17-1: A
general
phase
diagram.



You should be able to sketch a simple phase diagram, but knowing how to read the phase diagram for a particular substance is really useful. With a phase diagram you can predict the type of phase change a substance may undergo if the temperature is changed at constant pressure and vice versa.

Notice that the phase diagram has the following three general areas corresponding to the three states of matter (solid, liquid, and gas). The lines separating each area correspond to phase changes:

- ✓ **A to C:** This line represents the change in vapor pressure of the solid with temperature for *sublimation* (going directly from a solid to a gas without first becoming a liquid). Crossing the solid-gas line from left to right is sublimation, and the reverse process is deposition. The heat of sublimation or deposition is applicable for changes in this region.

- ✓ **A to B:** This line represents the relationship of the vapor pressure of a liquid with pressure. Crossing the liquid-gas line in the diagram from left to right represents vaporization and from right to left represents condensation. Crossing this line involves the heat of vaporization or the heat of condensation.
- ✓ **A to D:** This line represents the relationship of the melting point with pressure. Crossing the solid-liquid line in the diagram from left to right is melting (fusion) and from right to left is freezing (solidification). The heats of fusion or solidification are related to these types of changes.

The B point shown in this phase diagram is the *critical point* of the substance, the point beyond which the liquid and gas phases are indistinguishable from each other. Both liquids and gases contain randomly arranged particles; the real difference between liquids and gases is that in a liquid, the particles are in contact, while in a gas the particles are widely separated. Increasing the pressure on a gas pushes its particles closer together. As the pressure continues to increase, the particles eventually come into contact and there is no longer any difference between the gas and a liquid. The two phases become identical in appearance.

At or beyond this critical point, no matter how much pressure is applied, the gas cannot be condensed into a liquid. The temperature at the critical point is the *critical temperature*, and the pressure at the critical point is the *critical pressure*.

Point A is the *triple point* of the substance, the combination of temperature and pressure at which all three states of matter can exist. At the triple point, all phases are present. Any type of change is possible, because melting, boiling, and sublimation (and their reverses) occur simultaneously.

The incredible strength of water

Quite a few activities illustrate the strength of hydrogen bonding in water. One way is to take a clean penny, place it on the table, and carefully add drops of water. You'll be amazed to see how many drops you can add without breaking the surface tension. (This little experiment is also a neat way to check out the magnifying effect of the water dome.)

The other demonstration that I really like that illustrates surface tension is the paperclip experiment. Fill a glass totally full of water and then start adding paperclips slowly. Take a guess how many you can add. In most cases you will greatly underestimate the number of paperclips that you can add to that "full" glass.

Speaking of paperclips, you can float a paperclip on the surface of water if you place it on the surface very carefully. The paperclip is made of steel, which has a density much greater than the density of water, so it should sink, but the hydrogen bonding creates the surface tension that supports the weight of the paperclip. The same phenomenon is also how some insects are able to walk across the surface of a puddle or pond.