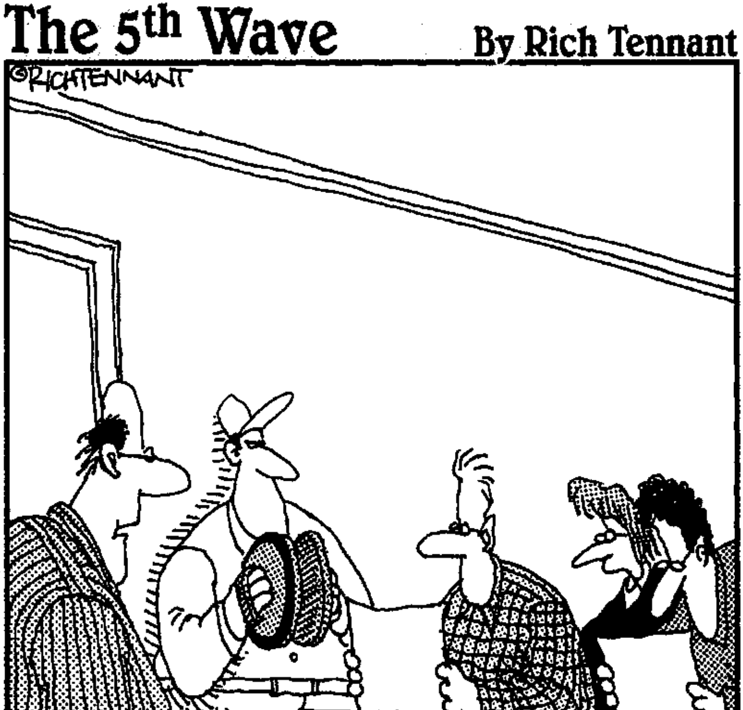
Part II

Blessed Be the Bonds That Tie



"Okay, now that the paramedic is here with the defibrillator and smelling salts, prepare to learn about covalent bonds..."

In this part . . .

Mention chemistry, and most people immediately think of chemical reactions. Scientists use chemical reactions to make new drugs, plastics, cleaners, fabrics — the list is endless. They also use chemical reactions to analyze samples and find out what and how much is in them. Chemical reactions power our bodies, our sun, and our universe. Chemistry is all reactions and the bonding that occurs in them. And that's what this part is all about.

These chapters introduce you to the two main types of bonding found in nature: ionic bonding and covalent bonding. I show you how to predict the formulas of ionic compounds (salts) and how to name them. I explain covalent bonding, how to draw Lewis structural formulas, and how to predict the shapes of simple molecules. I tell you about chemical reactions and show you the various general types. In addition, I cover chemical equilibrium, kinetics, and electrochemistry — batteries, cells, and electroplating.

I think you'll get a charge out of the material in this part. In fact, I don't see how you can fail to react to it.

Chapter 6

Opposites Do Attract: Ionic Bonds

In This Chapter

- Finding out why and how ions are formed
- Discovering how cations and ions are formed
- Understanding polyatomic ions
- Deciphering the formulas of ionic compounds
- Naming ionic compounds
- Clarifying the difference between electrolytes and nonelectrolytes

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.

The Magic of an Ionic Bond: 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 table salt, or $NaCl$, deposited on the inside of the beaker.

Understanding the components

If you really stop and think about it, the process of creating table salt is pretty remarkable. You take two substances that are both very hazardous (chlorine was used by the Germans against Allied troops during World War I), and from them you make a substance that's necessary for life. In this section, I show you what happens during the chemical reaction to create salt and, more importantly, why it occurs.

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 4 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 6-1. (If energy level diagrams are new to you, check out Chapter 3. There are a number of minor variations that are commonly used in writing energy level diagrams, so don't worry if the diagrams in Chapter 3 are slightly different than the ones I show you here.)

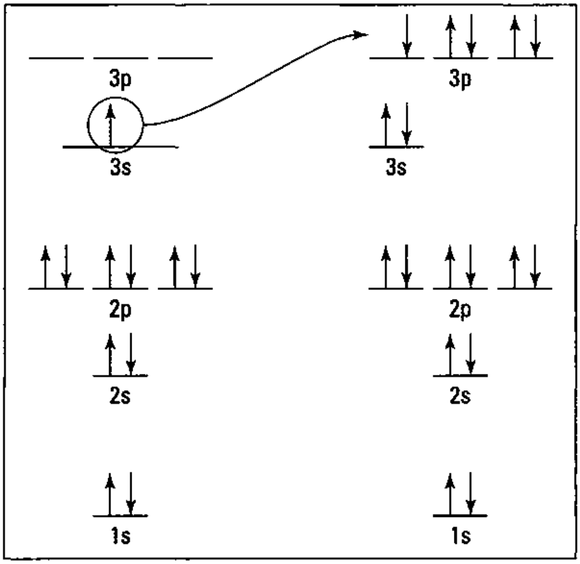


Figure 6-1: Energy level diagram for sodium and chlorine.

[illegible] [illegible]

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 6-1.

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 3.) 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)	$1s^22s^22p^63s^1$
Chlorine (Cl)	$1s^22s^22p^63s^23p^5$

Understanding the reaction

The noble gases are the VIIIA elements on the periodic table. They're extremely unreactive because their 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 "satisfied." 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 satisfied. 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 (8 valence electrons: 2 in the s orbital and 6 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 filled at 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 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:

Na^+ $1s^2 2s^2 2p^6$

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.

There's a difference between the neutral sodium atom and the sodium cation — one electron. In addition, their chemical reactivities are different *and* their sizes are different. The cation is smaller. The filled 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 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

Cl^- $1s^2 2s^2 2p^6 3s^2 3p^6$

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 there are 17 protons attracting 18 electrons. The attractive force 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 6-1, 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 6-2.

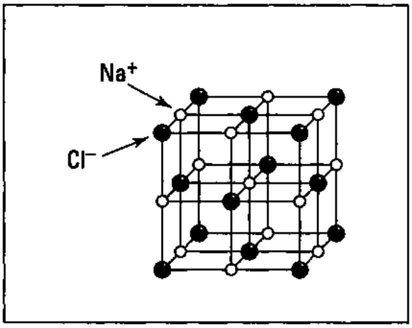


Figure 6-2: Crystal structure of sodium chloride.

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 7. Grasping the concepts involved in ionic bonding makes understanding covalent bonding much easier.

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 6-1 shows the family, element, ion name, and ion symbol for some common monoatomic (one atom) cations, and Table 6-2 gives the same information for some common monoatomic anions.

Table 6-1 Some Common Monoatomic Cations

Family	*Element*	*Ion Name*	*Ion Symbol*
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 6-2 Some Common Monoatomic Anions

Family	*Element*	*Ion Name*	*Ion Symbol*
VA	Nitrogen	Nitride anion	N^{3-}
	Phosphorus	Phosphide anion	P^{3-}

Family	*Element*	*Ion Name*	*Ion Symbol*
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^-

It's more difficult to determine the number of electrons that members of the transition metals (the B families) lose. 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 6-3 shows some common transition metals that have more than one oxidation state.

Table 6-3 Some Common Metals with More than One Oxidation State

Family	*Element*	*Ion Name*	*Ion Symbol*
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+}

(continued)

Table 6-3 *(continued)*

Family	*Element*	*Ion Name*	*Ion Symbol*
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.)

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, take a look at Table 6-3. 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 6-4 lists some important polyatomic ions.

Table 6-4 Some Important Polyatomic Ions

Ion Name	*Ion Symbol*
Sulfate	SO_4^{2-}
Sulfite	SO_3^{2-}
Nitrate	NO_3^-
Nitrite	NO_2^-

Ion Name	*Ion Symbol*
Hypochlorite	ClO^-
Chlorite	ClO_2^-
Chlorate	ClO_3^-
Perchlorate	ClO_4^-
Acetate	$C_2H_3O_2^-$
Chromate	CrO_4^{2-}
Dichromate	$Cr_2O_7^{2-}$
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	$C_2O_4^{2-}$
Thiosulfate	$S_2O_3^{2-}$
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 a salt (see "The Magic of an Ionic Bond: Sodium + Chlorine = Table Salt," earlier in this chapter). An important thing to remember is that the compound must be neutral — have equal numbers of positive and negative charges.

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 6-3 shows this process. (Forget about the crisscrossing lines for now. Well, if you're really curious, they're discussed in the "Using the crisscross rule" section, later in this chapter.)

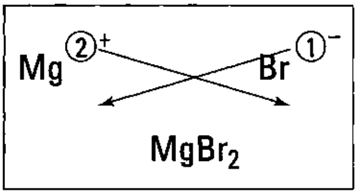


Figure 6-3: Figuring the formula of magnesium bromide.

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

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 form the bromide anion with a 1- charge. The electron configuration for the bromide anion is

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

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+, 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 $MgBr_2$.

Using the crisscross rule

There's a quick way to determine the formula of an ionic compound: Use the *crisscross rule.*

Look at Figure 6-3 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 6-4 shows the crisscross rule used for this reaction.

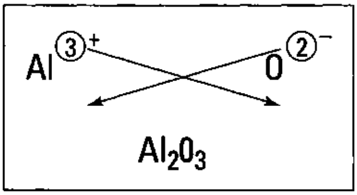


Figure 6-4: Figuring the formula of aluminum oxide.

Compounds involving polyatomic ions work exactly the same way. For example, here's the compound made from the ammonium cation and the sulfide anion:

$(NH_4)_2S$

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 there's a situation where you have to be careful. Suppose that you want to write the compound formed when magnesium 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

Mg_2O_2

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:

MgO

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.*

Li_2S	lithium 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, it is not necessary to add the -ide ending).

$(NH_4)_2CO_3$	Ammonium carbonate
K_3PO_4	Potassium phosphate

When the metal involved is a transition metal with more than one oxidation state (see "Positive and Negative Ions: Cations and Anions," earlier in the chapter, for more info about *that*), there can be more than one way to correctly name the compound. 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, which is still sometimes used (so it's a good idea to know it), is to use *-ous* and *-ic* endings. 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, because

Fe^{3+} has a higher oxidation state than Fe^{2+}, it's called a *ferric ion.* So the compound can be named

$Fe(CN)_3$	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 $FeNH_4(SO_4)_2$.

I show you in Table 6-4 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 6-4 also indicates that the ammonium ion has a 1+ charge, so you can figure out the charge on the iron cation.

Ion	***Charge***
Fe	?
NH_4	1+
$(SO_4)_2$	(2-)×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

$FeNH_4(SO_4)_2$	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

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 6-2) and pull them into the solution. (In Chapter 7, 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. 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 will complete 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 in 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. 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.*

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 7), 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.

Chapter 7

Covalent Bonds: Let's Share Nicely

In This Chapter

- Seeing how one hydrogen atom bonds to another hydrogen atom
- Defining covalent bonding
- Finding out about the different types of chemical formulas
- Taking a look at polar covalent bonding and electronegativity
- Accepting the unusual properties of water

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 6). 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.

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 6.)

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.

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) compound. (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. That's the driving force of hydrogen — 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 can share their electrons. At the atomic level, this sharing is represented by the electron orbitals (sometimes called electron clouds) overlapping. 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 is represented in Figure 7-1(a).

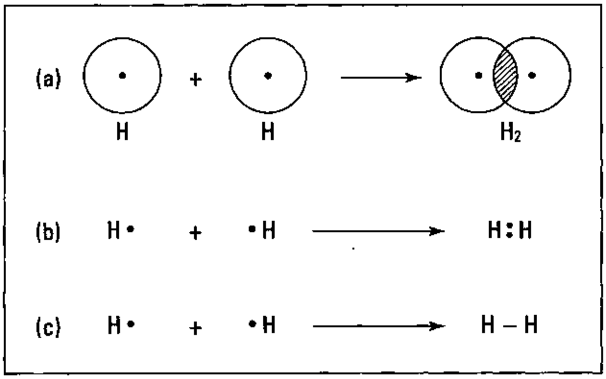


Figure 7-1: The formation of a covalent bond in hydrogen.

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 7-1(b).

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 is shown in Figure 7-1(c). (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 compound (diatomic molecule).

Here's one more example of using the electron-dot formula to represent the shared electron pair of a diatomic compound: This time, look at bromine (Br_2), which is a member of the halogen family (see Figure 7-2). The two halogen atoms, each with seven valence electrons, share an electron pair and fill their octet.

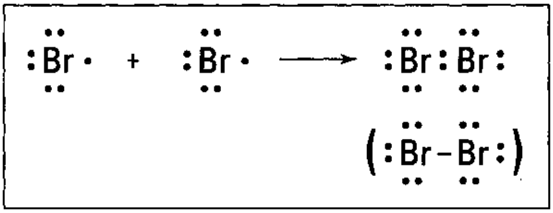


Figure 7-2: The covalent bond formation of Br_2.

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, while 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 6 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, the metals combine to form *alloys,* solutions of one metal in another. But there is such a situation as metallic bonding, and it's present in both alloys and pure metals. In *metallic bonding,* 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.

Understanding multiple bonds

I define covalent bonding as the sharing of one *or more* electron pairs. In hydrogen and the 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.

Nitrogen (N_2) is a diatomic molecule in the *VA family* on the periodic table, meaning that it has five valence electrons (see Chapter 4 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 so-called *triple bond.* The triple bond formation of nitrogen is shown in Figure 7-3.

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 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.

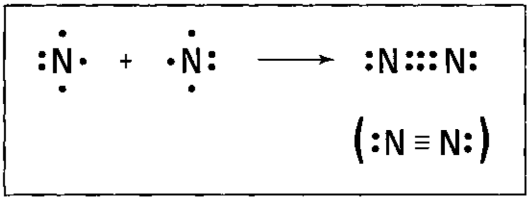


Figure 7-3: Triple bond formation in N_2.

There are no salt molecules!

A *molecule* is a compound that is covalently bonded. It's technically incorrect to refer to sodium chloride, which has ionic bonds, as a molecule, but lots of chemists do it anyway. It's 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*.

Carbon dioxide (CO_2) 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 7-4.

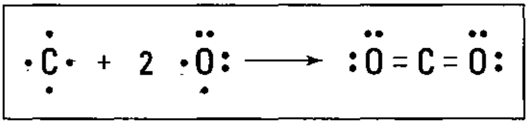


Figure 7-4: Formation of carbon dioxide.

Naming Binary Covalent Compounds

Binary compounds are compounds made up of only two elements, such as carbon dioxide (CO_2). Prefixes are used in the names of binary compounds to indicate the number of atoms of each nonmetal present. Table 7-1 lists the most common prefixes for binary covalent compounds.

Table 7-1 Common Prefixes for Binary Covalent Compounds

Number of Atoms	*Prefix*
1	mono-
2	di-
3	tri-
4	tetra-

(continued)

Table 7-1 *(continued)*

Number of Atoms	*Prefix*
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 **di**oxide
P_4O_{10}	**tetra**phosphorus **dec**oxide (Chemists try to avoid putting an *a* and an *o* together with the oxide name, as in dec**ao**xide, so they normally drop the *a* off the prefix.)
SO_3	sulfur **tri**oxide
N_2O_4	**di**nitrogen **tetr**oxide

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

So Many Formulas, So Little Time

In Chapter 6, 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.

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 that you have a compound with the empirical formula C_2H_6O. 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 C_2H_6O, $C_4H_{12}O_2$, $C_6H_{18}O_3$, $C_8H_{24}O_4$, 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 C_2H_6O is actually the molecular formula, too, meaning that there are actually two carbon atoms, six hydrogen atoms, and one oxygen atom in the compound.

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 7-5. Both compounds have the molecular formula of C_2H_6O.

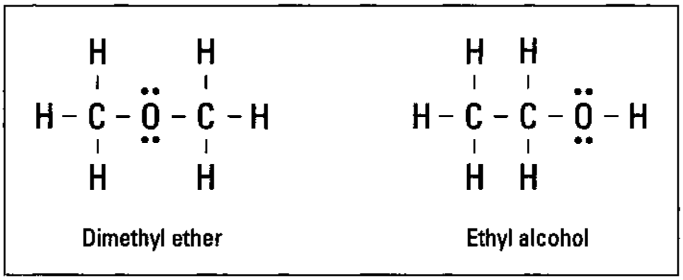


Figure 7-5: Two possible compounds of C_2H_6O.

Both compounds in Figure 7-5 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. These are 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?

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. I point out some examples of compounds that don't obey the octet rule in the section, "What Does Water Really Look Like? The VSEPR Theory," later in this chapter, but 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.

REMEMBER

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.

Structural formula: Add the bonding pattern

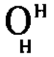
To write a formula that stands for the exact compound you have in mind, you often must write the structural formula instead of the molecular formula. The *structural formula* shows the elements in the compound, the exact number of each atom in the compound, and the bonding pattern for the compound. The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

   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 in filling 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:

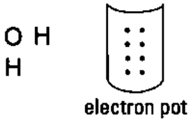


$\mathrm{O}^{\mathrm{H}}_{\;\mathrm{H}}$

It doesn't matter where you put the hydrogen atoms around the oxygen. In the section, "What Does Water Really Look Like? The VSEPR Theory," later in this chapter, you see why 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 one electron, and the oxygen atom has six valence electrons (VIA family), so you have eight electrons in your electron pot. Those are the electrons you use when making your bonds and completing 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 *n*eeded 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* equals the sum of the number of valence electrons *a*vailable 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. *A* is the number of valence electrons in your electron pot.
   >
   > *S* equals the number of electrons *s*hared in the molecule. And if you divide *S* by 2, you have the number of covalent bonds in the molecule.

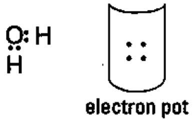
   So in the case of water,

   > $N = 8 + 2(2) = 12$ (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 there are two bonds (two shared pairs of electrons) in water.

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

   You use four electrons from the eight in the pot, which leaves you with four to distribute later. There has to be at least one bond from 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 two electrons to fill its valence energy level. In this case, each hydrogen atom has two electrons, but the oxygen atom has only four electrons, so the remaining four electrons are placed around the oxygen. This empties your electron pot. The completed electron-dot formula for water is shown in Figure 7-6.

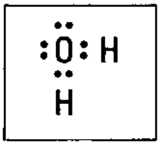


Figure 7-6: Electron-dot formula of H_2O.

Notice that there are actually two types of electrons shown in this structural formula: *bonding electrons,* the electrons that are shared between two atoms, and *nonbonding electrons,* the electrons that are not being shared. The last four electrons (two 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 7-7.

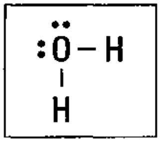
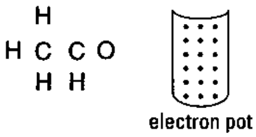


Figure 7-7: The Lewis formula for H_2O.

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:

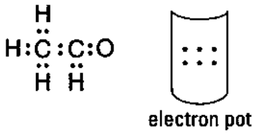


Notice that it has not one but two central atoms — the two carbon atoms. You can put 18 valence electrons into the electron pot: four for each carbon atom, one for each hydrogen atom, and six for the oxygen atom.

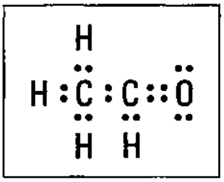
Now apply the $N - A = S$ equation:

> $N = 2(8) + 4(2) + 8 = 32$ (2 carbon atoms with 8 valence electrons each, plus 4 hydrogen atoms with 2 valence electrons each, plus an oxygen atom with 8 electrons)
>
> $A = 2(4) + 4(1) + 6 = 18$ (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)
>
> $S = 32–18 = 14$, and $S/2 = 14/2 = 7$ bonds

Add single bonds between the carbon atoms and the hydrogen atom, between the two carbon atoms, and between the carbon atom and oxygen atom. That's six of your seven bonds.



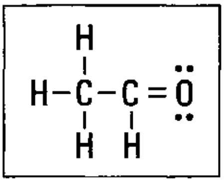
There's only one place that the seventh bond can go, and that's between the carbon atom and the oxygen atom. It can't be between a carbon atom and a hydrogen atom, because that would overfill hydrogen's valence energy level. And it can't be between the two carbon atoms, because that would give the carbon on the left ten electrons instead of eight. So there must be a double bond between the carbon atom and the oxygen atom. The four 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 7-8.



$$\begin{array}{ccccccc} & & \mathrm{H} & & & & \\ & & \cdot\cdot & & & & \cdot\cdot \\ \mathrm{H} & : & \mathrm{C} & : & \mathrm{C} & :: & \mathrm{O} \\ & & \cdot\cdot & & \cdot\cdot & & \cdot\cdot \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

Figure 7-8: Electron-dot formula of C_2H_4O.

If you convert the bonding pairs to dashes, you have the Lewis formula of C_2H_4O, as shown in Figure 7-9.



$$\begin{array}{ccccccc} & & \mathrm{H} & & & & \\ & & | & & & & \cdot\cdot \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & = & \mathrm{O} \\ & & | & & | & & \cdot\cdot \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

Figure 7-9: 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 7-10.

$CH_3-CH=O$

CH_3CHO

Figure 7-10: Condensed structural formulas for C_2H_4O.

Some Atoms Are More Attractive Than Others

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. 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 7-11 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.

Electronegativities are useful because they give information about what will happen to the bonding pair of electrons when two atoms bond. For example, look at the Cl_2 molecule. Chlorine has an electronegativity value of 3.0, as shown in Figure 7-11. 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. A bond in which the electron pair is equally shared is called a *nonpolar covalent bond.* 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.

Now 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. A bond in which the electron pair is shifted toward one atom is called a *polar covalent bond.* 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.

Now look at a case in which the two atoms have extremely different electronegativities — sodium chloride (NaCl). Sodium chloride is ionically bonded (see Chapter 6 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.

Figure 7-11: Electronegativities of the elements.

Increasing →

Decreasing ↓

1 H 2.1																
3 Li 1.0	4 Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0
11 Na 0.9	12 Mg 1.2											13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3.0
19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.9	28 Ni 1.9	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8
37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5
55 Cs 0.7	56 Ba 0.9	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.9	83 Bi 1.9	84 Po 2.0	85 At 2.2
87 Fr 0.7	88 Ra 0.9	89 Ac 1.1														

Electronegativities of the Elements

Electronegativity Difference	*Type of Bond Formed*
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 most cases, the molecule has a positive end and a negative end, called a *dipole* (think of a magnet). Figure 7-12 shows a couple of examples of molecules in which dipoles have formed. (The little Greek symbol by the charges refers to a *partial* charge.)

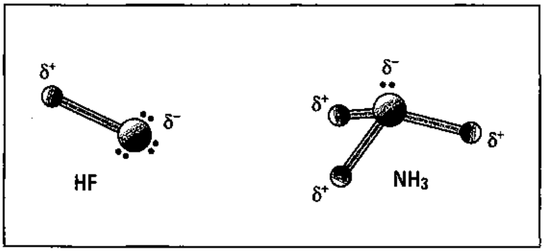


Figure 7-12: Polar covalent bonding in HF and NH_3.

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 (NH_3); 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 would look for a material with as weak a polar covalent bond as possible.

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 this is not true of 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. So 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 7-13.

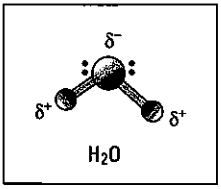


Figure 7-13: Polar covalent bonding in water.

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. The first type is called a *London force* or *dispersion force.* This very weak type of attraction 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.

The second type of intermolecular force is called a *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.

The third type of interaction is really just an extremely strong dipole-dipole interaction that occurs when a hydrogen atom is bonded to one of three extremely electronegative elements — O, N, or F. 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. When the O, N, or F on one molecule attracts the hydrogen of another molecule, the dipole-dipole interaction is very strong. This strong interaction (only about 5 percent of the strength of an ordinary covalent bond but still very strong for an intermolecular force) is called a *hydrogen bond.* The hydrogen bond is the type of interaction that's present in water (see Figure 7-14).

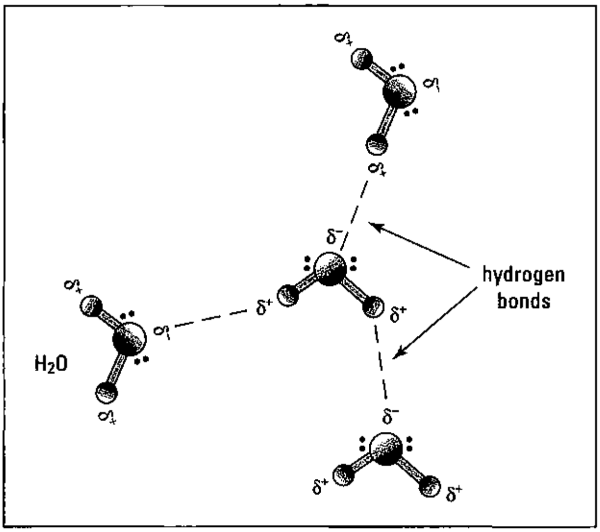


Figure 7-14: Hydrogen bonding in water.

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 7-15, with the hydrogen bond indicated by dotted lines.

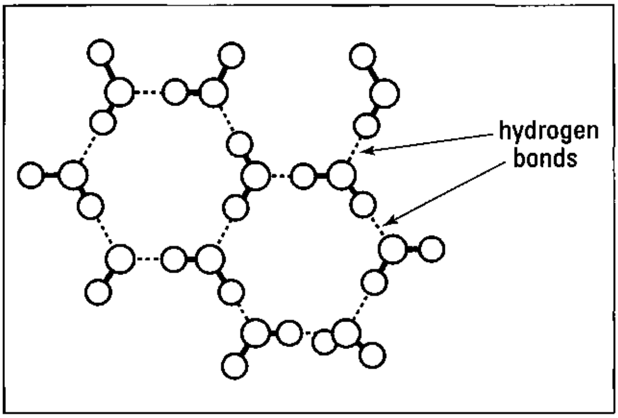


Figure 7-15: The structure of ice.

What Does Water Really Look Like? The VSEPR Theory

The *molecular geometry* of a molecule, how the atoms are arranged in three-dimensional space, is important for chemists to know because it often explains why certain reactions will or won't occur. In the area of medicine, for example, the molecular geometry of a drug may lead to side reactions. Molecular geometry also explains why water is a dipole (a molecule with a positive end and a negative end, like a magnet) and carbon dioxide is not.

The *VSEPR (Valence Shell Electron-Pair Repulsion) theory* allows chemists to predict the molecular geometry of molecules. The VSEPR theory assumes that the electron pairs around an atom, whether they're bonding (shared between two atoms) or nonbonding (not shared), will try to get as far apart from each other in space to minimize the repulsion between themselves. It's like going to a fancy party and seeing someone else wearing the exact same outfit. You're gonna try to stay as far away from that person as possible!

Electron-pair geometry is the arrangement of the electron pairs, bonding and nonbonding, around a central atom. After you determine the electron-pair geometry, you can imagine the nonbonding electrons being invisible and see what's left. What's left is what I call the *molecular geometry,* or *shape,* the arrangement of the other atoms around a central atom.

To determine the molecular geometry, or shape, of a molecule using the VSEPR theory, follow these steps:

1. **Determine the Lewis formula (see "Covalent Bond Basics," earlier in the chapter) of the molecule.**
2. **Determine the total number of electron pairs around the central atom.**
3. **Using Table 7-2, determine the electron-pair geometry.**

   (Table 7-2 relates the number of bonding and nonbonding electron pairs to the electron-pair geometry and molecular shape.)
4. **Imagine that the nonbonding electron pairs are invisible, and use Table 7-2 to determine the molecular shape.**

Table 7-2 Predicting Molecular Shape with the VSEPR Theory

Total Number of Electron Pairs	*Number of Bonding Pairs*	*Electron-pair Geometry*	*Molecular Geometry*
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 (octet rule), I put some of the less common exceptions to the octet rule in Table 7-2. Figure 7-16 shows some of the more common shapes mentioned in the table.

To determine the shapes of water (H_2O) and ammonia (NH_3), the first thing you have to do is determine the Lewis formula for each compound. Follow the rules outlined in the section, "Structural formula: Add the bonding pattern" (the N – A = S rules), and write the Lewis formulas as shown in Figure 7-17.

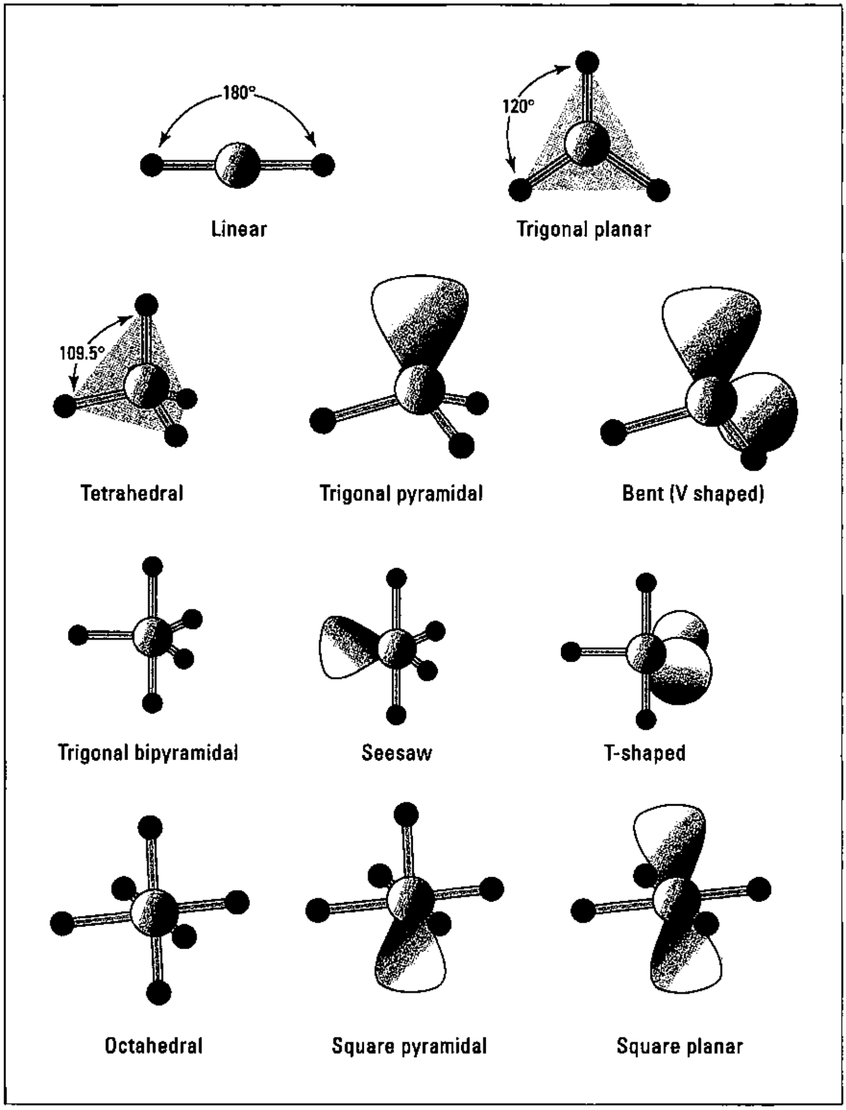


Figure 7-16: Common molecular shapes.

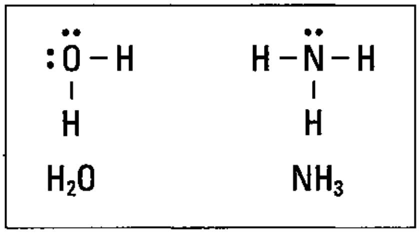


Figure 7-17: Lewis formulas for H_2O and NH_3.

For water, there are four electron pairs around the oxygen atom, so the electron-pair geometry is tetrahedral. 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.

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 lone pair of nonbonding electrons would then stick straight up from the seat. You'd get a surprise if you sat on an ammonia stool!

Chapter 8

Chemical Cooking: Chemical Reactions

In This Chapter

- Differentiating between reactants and products
- Finding out how reactions occur
- Taking a look at the different types of reactions
- Understanding how to balance reactions
- Figuring out chemical equilibrium
- Checking out speeds of reaction

Chemists do a lot of things: They measure the physical properties of substances; they analyze mixtures to find out what they're composed of; and they make new substances. The process of making chemical compounds is called *synthesis*. Synthesis depends on chemical reactions. I always thought that it'd be neat to be a synthetic organic chemist and work on the creation of new and potentially important compounds. I can just imagine the thrill of working for months, or even years, and finally ending up with a little pile of "stuff" that nobody in the world has ever seen. Hey, I am a nerd, after all!

In this chapter, I discuss chemical reactions — how they occur and how to write a balanced chemical equation. I also tell you about chemical equilibrium and explain why chemists can't get the amount of product out of a reaction that they thought they could. And finally, I discuss the speed of reaction and why you shouldn't leave that turkey sitting out on the table after finishing your Thanksgiving feast.

What You Have and What You'll Get: Reactants and Products

In a chemical reaction, substances (elements and/or compounds) are changed into other substances (compounds and/or elements). You can't change one element into another in a chemical reaction — that happens in nuclear reactions, as I describe in Chapter 5. Instead, you create a new substance with chemical reactions.

A number of clues show that a chemical reaction has taken place — something new is visibly produced, a gas is created, heat is given off or taken in, and so on. The chemical substances that are eventually changed are called the *reactants,* and the new substances that are formed are called the *products. Chemical equations* show the reactants and products, as well as other factors such as energy changes, catalysts, and so on. With these equations, an arrow is used to indicate that a chemical reaction has taken place. In general terms, a chemical reaction follows this format:

$$\text{Reactants} \rightarrow \text{Products}$$

For example, take a look at the reaction that occurs when you light your natural gas range in order to fry your breakfast eggs. Methane (natural gas) reacts with the oxygen in the atmosphere to produce carbon dioxide and water vapor. (If your burner isn't properly adjusted to give that nice blue flame, you may also get a significant amount of carbon monoxide along with carbon dioxide.) The chemical equation that represents this reaction is written like this:

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$$

You can read the equation like this: One molecule of methane gas, $CH_4(g)$, reacts with two molecules of oxygen gas, $O_2(g)$, to form one molecule of carbon dioxide gas, $CO_2(g)$, and two molecules of water vapor, $H_2O(g)$. The *2* in front of the oxygen gas and the *2* in front of the water vapor are called the reaction *coefficients.* They indicate the number of each chemical species that reacts or is formed. I show you how to figure out the value of the coefficients in the section "Balancing Chemical Reactions," later in the chapter.

Methane and oxygen (oxygen is a diatomic — two-atom — element) are the reactants, while carbon dioxide and water are the products. All the reactants and products are gases (indicated by the *g*'s in parentheses).

In this reaction, all reactants and products are invisible. The heat being evolved is the clue that tells you a reaction is taking place. By the way, this is a good example of an *exothermic* reaction, a reaction in which heat is given off. A lot of reactions are exothermic. Some reactions, however, absorb energy rather than release it. These reactions are called *endothermic* reactions. Cooking involves a lot of endothermic reactions — frying those eggs, for example. You can't just break the shells and let the eggs lie on the pan and then expect the myriad chemical reactions to take place without heating the pan (except when you're outside in Texas during August; there, the sun will heat the pan just fine).

Thinking about cooking those eggs brings to mind another issue about exothermic reactions. You have to ignite the methane coming out of the burners with a match, lighter, pilot light, or built-in electric igniter. In other words, you have to put in a little energy to get the reaction going. The energy you have to supply to get a reaction going is called the *activation energy* of the reaction. (In the next section, I show you that there's also an activation energy associated with endothermic reactions, but it isn't nearly as obvious.)

But what really happens at the molecular level when the methane and oxygen react? Divert thine eyes to the very next section to find out.

How Do Reactions Occur? Collision Theory

In order for a chemical reaction to take place, the reactants must collide. It's like playing pool. In order to drop the 8-ball into the corner pocket, you must hit it with the cue ball. This collision transfers *kinetic energy* (energy of motion) from one ball to the other, sending the second ball (hopefully) toward the pocket. The collision between the molecules provides the energy needed to break the necessary bonds so that new bonds can be formed.

But wait a minute. When you play pool, not every shot you make causes a ball to go into the pocket. Sometimes you don't hit the ball hard enough, and you don't transfer enough energy to get the ball to the pocket. This is also true with molecular collisions and reactions. Sometimes, even if there is a collision, not enough kinetic energy is available to be transferred — the molecules aren't moving fast enough. You can help the situation somewhat by heating the mixture of reactants. The temperature is a measure of the average kinetic energy of the molecules; raising the temperature increases the kinetic energy available to break bonds during collisions.

Sometimes, even if you hit the ball hard enough, it doesn't go into the pocket because you didn't hit it in the right spot. The same is true during a molecular collision. The molecules must collide in the right orientation, or hit at the right spot, in order for the reaction to occur.

Here's an example: Suppose you have an equation showing molecule *A-B* reacting with *C* to form *C-A* and *B*, like this:

$$\mathrm{A\text{-}B + C \rightarrow C\text{-}A + B}$$

The way this equation is written, the reaction requires that reactant *C* collide with *A-B* on the *A* end of the molecule. (You know this because the product side shows *C* hooked up with *A* — *C-A*.) If it hits the *B* end, nothing will happen. The *A* end of this hypothetical molecule is called the *reactive site,* the place on the molecule that the collision must take place in order for the reaction to occur. If *C* collides at the *A* end of the molecule, then there's a chance that enough energy can be transferred to break the *A-B* bond. After the *A-B* bond is broken, the *C-A* bond can be formed. The equation for this reaction process can be shown in this way (I show the breaking of the *AB* bond and the forming of the *CA* bond as "squiggly" bonds):

$$\mathrm{C{\sim}A{\sim}B \rightarrow C\text{-}A + B}$$

So in order for this reaction to occur, there must be a collision between *C* and *A-B* at the reactive site. The collision between *C* and *A-B* has to transfer enough energy to break the *A-B* bond, allowing the *C-A* bond to form.

Energy is required to break a bond between atoms.

Note that this example is a simple one. I've assumed that only one collision is needed, making this a one-step reaction. Many reactions are one-step, but many others require several steps in going from reactants to final products. In the process, several compounds may be formed that react with each other to give the final products. These compounds are called *intermediates.* They're shown in the reaction *mechanism,* the series of steps that the reaction goes through in going from reactants to products. But in this chapter, I keep it simple and pretty much limit my discussion to one-step reactions.

An exothermic example

Imagine that the hypothetical reaction $\mathrm{A\text{-}B + C \rightarrow C\text{-}A + B}$ is exothermic — a reaction in which heat is given off (released) when going from reactants to products. The reactants start off at a higher energy state than the products, so energy is released in going from reactants to products. Figure 8-1 shows an energy diagram of this reaction.

In Figure 8-1, E_a is the activation energy for the reaction — the energy that you have to put in to get the reaction going. I show the collision of *C* and *A-B* with the breaking of the *A-B* bond and the forming of the *C-A* bond at the top of an activation energy hill. This grouping of reactants at the top of the activation energy hill is sometimes called the *transition state* of the reaction. As I show in Figure 8-1, the difference in the energy level of the reactants and the energy level of the products is the amount of energy (heat) that is released in the reaction.

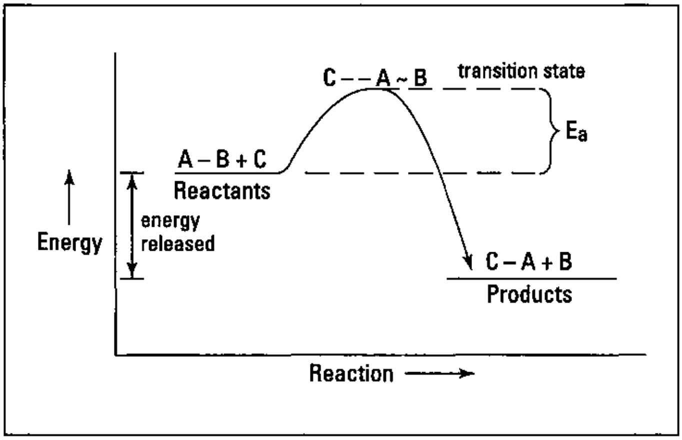


Figure 8-1: Exothermic reaction of A-B + C → C-A + B.

An endothermic example

Suppose that the hypothetical reaction A-B + C → C-A + B is endothermic — a reaction in which heat is absorbed in going from reactants to products — so the reactants are at a lower energy state than the products. Figure 8-2 shows an energy diagram of this reaction.

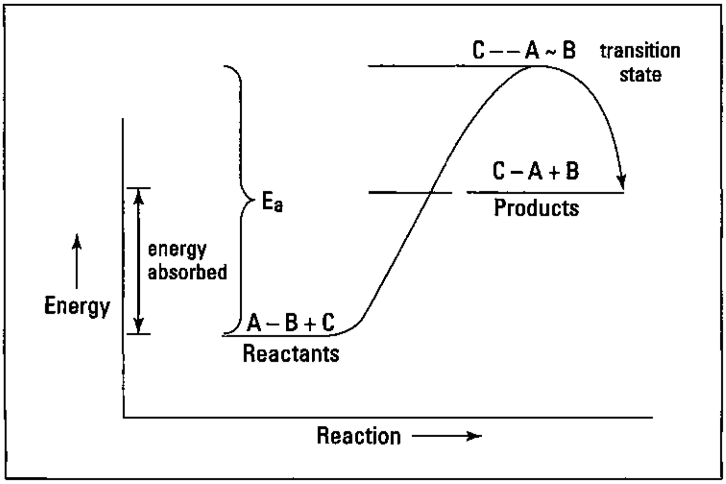


Figure 8-2: Endothermic reaction of A-B + C → C-A + B.

Just as with the exothermic-reaction energy diagram shown in Figure 8-1, this diagram shows that an activation energy is associated with the reaction (represented by E_a). In going from reactants to products, you have to put in more energy initially to get the reaction started, and then you get that energy back out as the reaction proceeds. Notice that the transition state appears at the top of the activation energy hill — just like in the exothermic-reaction energy diagram. The difference is that, in going from reactants to products, energy (heat) must be absorbed in the endothermic example.

What Kind of Reaction Do You Think I Am?

Several general types of chemical reactions can occur based on what happens when going from reactants to products. The more common reactions are

- Combination
- Decomposition
- Single displacement
- Double displacement
- Combustion
- Redox

Combination reactions

In *combination reactions,* two or more reactants form one product. The reaction of sodium and chlorine to form sodium chloride,

$$2\,Na(s) + Cl_2(g) \rightarrow 2\,NaCl(s)$$

and the burning of coal (carbon) to give carbon dioxide,

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

are examples of combination reactions.

Note that, depending on conditions or the relative amounts of the reactants, more than one product can be formed in a combination reaction. Take the burning of coal, for example. If an excess of oxygen is present, the product is carbon dioxide. But if a limited amount of oxygen is available, the product is carbon monoxide:

$2\ C(s) + O_2(g) \rightarrow 2\ CO(g)$ (limited oxygen)

Decomposition reactions

Decomposition reactions are really the opposite of combination reactions. In *decomposition reactions,* a single compound breaks down into two or more simpler substances (elements and/or compounds). The decomposition of water into hydrogen and oxygen gases,

$2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$

and the decomposition of hydrogen peroxide to form oxygen gas and water,

$2\ H_2O_2(l) \rightarrow 2\ H_2O(l) + O_2(g)$

are examples of decomposition reactions.

Single displacement reactions

In *single displacement reactions,* a more active element displaces (kicks out) another less active element from a compound. For example, if you put a piece of zinc metal into a copper(II) sulfate solution (by the way, Chapter 6 explains why copper(II) sulfate is named the way it is — in case you're wondering), the zinc displaces the copper, as shown in this equation:

$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

The notation *(aq)* indicates that the compound is dissolved in water — in an *aq*ueous solution. Because zinc replaces copper in this case, it's said to be more active. If you place a piece of copper in a zinc sulfate solution, nothing will happen. Table 8-1 shows the activity series of some common metals. Notice that because zinc is more active in the table, it will replace copper, just as the preceding equation shows.

Table 8-1 The Activity Series of Some Common Metals

Activity	*Metal*
Most active	Alkali and alkaline earth metals
	Al
	Zn
	Cr
	Fe
	Ni
	Sn
	Pb
	Cu
	Ag
Least Active	Au

Take another look at the reaction between zinc metal and copper(II) sulfate solution:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

I've written this reaction as a molecular equation, showing all species in the neutral form. However, these reactions normally occur in an aqueous (water) solution. When the ionically-bonded $CuSO_4$ is dissolved in water, it breaks apart into *ions* (atoms or groups of atoms that have an electrical charge due to the loss or gain of electrons). The copper ion has a +2 charge because it lost two electrons. It's a *cation,* a positively charged ion. The sulfate ion has a -2 charge because it has two extra electrons. It's an *anion,* a negatively charged ion. (Check out Chapter 6 for a more complete discussion of ionic bonding.)

$$Zn(s) + Cu^{2+} + SO_4^{2-} \rightarrow Zn^{2+} + SO_4^{2-} + Cu(s)$$

Equations written in this form, in which the ions are shown separately, are called *ionic equations* (because they show the reaction and production of ions). Notice that the sulfate ion, SO_4^{2-}, hasn't changed in the reaction. Ions that don't change during the reaction and are found on both sides of the equation in an identical form are called spectator ions. Chemists (a lazy, lazy lot, they are) often omit the spectator ions and write the equation showing only those chemical substances that are changed during the reaction. This is called the net-ionic equation:

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$$

Double displacement reactions

In single displacement reactions, only one chemical species is displaced. In *double displacement reactions,* or *metathesis reactions,* two species (normally ions) are displaced. Most of the time, reactions of this type occur in a solution, and either an insoluble solid (precipitation reactions) or water (neutralization reactions) will be formed.

Precipitation reactions

If you mix a solution of potassium chloride and a solution of silver nitrate, a white insoluble solid is formed in the resulting solution. The formation of an insoluble solid in a solution is called *precipitation.* Here are the molecular, ionic, and net-ionic equations for this double-displacement reaction:

$$KCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + KNO_3(aq)$$

$$K^+ + Cl^- + Ag^+ + NO_3^- \rightarrow AgCl(s) + K^+ + NO_3^-$$

$$Cl^- + Ag^+ \rightarrow AgCl(s)$$

The white insoluble solid that's formed is silver chloride. You can drop out the potassium cation and nitrate anion spectator ions, because they don't change during the reaction and are found on both sides of the equation in an identical form. (If you're totally confused about all those plus and minus symbols in the equations, or don't know what a cation or an anion is, just flip to Chapter 6. It tells all you need to know about this stuff.)

In order to write these equations, you have to know something about the solubility of ionic compounds. Don't fret. Here you go: If a compound is soluble, it will remain in its free ion form, but if it's insoluble, it will precipitate (form a solid). Table 8-2 gives the solubilities of selected ionic compounds.

Table 8-2 Solubilities of Selected Ionic Compounds

Water Soluble	***Water Insoluble***
All chlorides, bromides, iodides	*except those of* Ag^+, Pb^{2+}, Hg_2^{2+}
All compound of NH_4^+	Oxides
All compounds of alkali metals	Sulfides
All acetates	most phosphates
All nitrates	most hydroxides
All chlorates	
All sulfates	*except* $PbSO_4$, $BaSO_4$ and $SrSO_4$

To use Table 8-2, take the cation of one reactant and combine it with the anion of the other reactant, and vice versa (keeping the neutrality of the compounds). This allows you to predict the possible products of the reaction. Then look up the solubilities of the possible products in the table. If the compound is insoluble, it will precipitate. If it is soluble, it will remain in solution.

Neutralization reactions

The other type of double-displacement reaction is the reaction between an acid and a base. This double-displacement reaction, called a *neutralization reaction,* forms water. Take a look at the mixing solutions of sulfuric acid (auto battery acid, H_2SO_4) and sodium hydroxide (lye, NaOH). Here are the molecular, ionic, and net-ionic equations for this reaction:

$$H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$$

$$2\ H^+ + SO_4^{2-} + 2\ Na^+ + 2\ OH^- \rightarrow 2\ Na^+ + SO_4^{2-} + 2\ H_2O(l)$$

$$2\ H^+ + 2\ OH^- \rightarrow 2\ H_2O(l) \text{ or } H^+ + OH^- \rightarrow H_2O(l)$$

To go from the ionic equation to the net-ionic equation, the spectator ions (those that don't really react and that appear in an unchanged form on both sides on the arrow) are dropped out. Then the coefficients in front of the reactants and products are reduced down to the lowest common denominator.

You can find more about acid-base reactions in Chapter 12.

Combustion reactions

Combustion reactions occur when a compound, usually one containing carbon, combines with the oxygen gas in the air. This process is commonly called *burning.* Heat is the most-useful product of most combustion reactions.

Here's the equation that represents the burning of propane:

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$$

Propane belongs to a class of compounds called *hydrocarbons,* compounds composed only of carbon and hydrogen. The product of this reaction is heat. You don't burn propane in your gas grill to add carbon dioxide to the atmosphere — you want the heat for cooking your steaks.

Combustion reactions are also a type of redox reaction.

Redox reactions

Redox reactions, or *reduction-oxidation reactions*, are reactions in which electrons are exchanged:

$2\ Na(s) + Cl_2(g) \rightarrow 2\ NaCl(s)$

$C(s) + O_2(g) \rightarrow CO_2(g)$

$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

The preceding reactions are examples of other types of reactions (such as combination, combustion, and single-replacement reactions), but they're all redox reactions. They all involve the transfer of electrons from one chemical species to another. Redox reactions are involved in combustion, rusting, photosynthesis, respiration, batteries, and more. I talk about redox reactions in some detail in Chapter 9.

Balancing Chemical Reactions

If you carry out a chemical reaction and carefully sum up the masses of all the reactants, and then compare the sum to the sum of the masses of all the products, you see that they're the same. In fact, a law in chemistry, the *Law of Conservation of Mass*, states, "In an ordinary chemical reaction, matter is neither created nor destroyed." This means that you have neither gained nor lost any atoms during the reaction. They may be combined differently, but they're still there.

A chemical equation represents the reaction. That chemical equation is used to calculate how much of each element is needed and how much of each element will be produced. And that chemical equation needs to obey the Law of Conservation of Mass.

You need to have the same number of each kind of element on both sides of the equation. The equation should *balance*. In this section, I show you how to balance chemical equations.

Smell that ammonia

My favorite reaction is called the *Haber process*, a method for preparing ammonia (NH_3) by reacting nitrogen gas with hydrogen gas:

$N_2(g) + H_2(g) \rightarrow NH_3(g)$

This equation shows you what happens in the reaction, but it doesn't show you how much of each element you need to produce the ammonia. To find out how much of each element you need, you have to balance the equation — make sure that the number of atoms on the left side of the equation equals the number of atoms on the right.

You know the reactants and the product for this reaction, and you can't change them. You can't change the compounds, and you can't change the subscripts, because that would change the compounds. So the only thing you can do to balance the equation is add *coefficients,* whole numbers in front of the compounds or elements in the equation. Coefficients tell you how many atoms or molecules you have.

For example, if you write $2\ H_2O$, it means you have two water molecules:

$$2H_2O = \begin{array}{c} H_2O \\ + \\ H_2O \end{array}$$

Each water molecule is composed of two hydrogen atoms and one oxygen atom. So with $2\ H_2O$, you have a total of 4 hydrogen atoms and 2 oxygen atoms:

$$2H_2O = \begin{array}{r} H_2O = 2H + 1O \\ + \qquad\quad + \\ H_2O = 2H + 1O \\ \hline 4H + 2O \end{array}$$

In this chapter, I show you how to balance equations by using a method called *balancing by inspection,* or as I call it, "fiddling with coefficients." You take each atom in turn and balance it by adding appropriate coefficients to one side or the other.

With that in mind, take another look at the equation for preparing ammonia:

$$N_2(g) + H_2(g) \rightarrow NH_3(g)$$

In most cases, it's a good idea to wait until the end to balance hydrogen atoms and oxygen atoms; balance the other atoms first.

So in this example, you need to balance the nitrogen atoms first. You have 2 nitrogen atoms on the left side of the arrow (reactant side) and only 1 nitrogen atom on the right side (product side). In order to balance the nitrogen atoms, use a coefficient of 2 in front of the ammonia on the right.

$$N_2(g) + H_2(g) \rightarrow 2\ NH_3(g)$$

Now you have 2 nitrogen atoms on the left and 2 nitrogen atoms on the right.

Next, tackle the hydrogen atoms. You have 2 hydrogen atoms on the left and 6 hydrogen atoms on the right (2 NH_3 molecules, each with 3 hydrogen atoms, for a total of 6 hydrogen atoms). So put a 3 in front of the H_2 on the left, giving you:

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

That should do it. Do a check to be sure: You have 2 nitrogen atoms on the left and 2 nitrogen atoms on the right. You have 6 hydrogen atoms on the left ($3 \times 2 = 6$) and 6 hydrogen atoms on the right ($2 \times 3 = 6$). The equation is balanced. You can read the equation this way: 1 nitrogen molecule reacts with 3 hydrogen molecules to yield 2 ammonia molecules.

Here's a tidbit for you: This equation would have also balanced with coefficients of 2, 6, and 4 instead of 1, 3, and 2. In fact, any multiple of 1, 3, and 2 would have balanced the equation, but chemists have agreed to always show the lowest whole-number ratio (see the discussion on empirical formulas in Chapter 7 for details).

Flick that bic

Take a look at an equation showing the burning of butane, a hydrocarbon, with excess oxygen available. (This is the reaction that takes place when you light a butane lighter.) The unbalanced reaction is

$$C_4H_{10}(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Because it's always a good idea to wait until the end to balance hydrogen atoms and oxygen atoms, balance the carbon atoms first. You have 4 carbon atoms on the left and one carbon atom on the right, so add a coefficient of 4 in front of the carbon dioxide:

$$C_4H_{10}(g) + O_2(g) \rightarrow 4\ CO_2(g) + H_2O(g)$$

Balance the hydrogen atoms next. You have 10 hydrogen atoms on the left and 2 hydrogen atoms on the right, so use a coefficient of 5 in front of the water on the right:

$$C_4H_{10}(g) + O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(g)$$

Now work on balancing the oxygen atoms. You have 2 oxygen atoms on the left and a total of 13 oxygen atoms on the right [$(4 \times 2) + (5 \times 1) = 13$]. What can you multiply 2 with in order for it to equal 13? How about 6.5?

$$C_4H_{10}(g) + 6.5\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(g)$$

But you're not done. You want the lowest *whole-number* ratio of coefficients. You'll have to multiply the entire equation by 2 in order to generate whole numbers:

$$[C_4H_{10}(g) + 6.5\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(g)] \times 2$$

Multiply every coefficient by 2 (don't touch the subscripts!) to get

$$2\ C_4H_{10}(g) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(g)$$

If you check the atom count on both sides of the equation, you find that the equation is balanced, and the coefficients are in the lowest whole-number ratio.

After balancing an equation, make sure that the same number of each atom is on both sides and that the coefficients are in the lowest whole-number ratio.

Most simple reactions can be balanced in this fashion. But one class of reactions is so complex that this method doesn't work well when applied to them. They're redox reactions. A special method is used for balancing these equations, and I show it to you in Chapter 9.

Chemical Equilibrium

My favorite reaction is the Haber process, the synthesis of ammonia from nitrogen and hydrogen gases. After balancing the reaction (see the section "Smell that ammonia," earlier in this chapter), you end up with

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

Written this way, the reaction says that hydrogen and nitrogen react to form ammonia — and this keeps on happening until you use up one or both of the reactants. But this isn't quite true. (Yep. It's hair-splitting time.)

If this reaction occurs in a closed container (which it has to, with everything being gases), then the nitrogen and hydrogen react and ammonia *is* formed — *but* some of the ammonia soon starts to decompose to nitrogen and hydrogen, like this:

$$2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g)$$

In the container, then, you actually have *two* exactly opposite reactions occurring — nitrogen and hydrogen combine to give ammonia, and ammonia decomposes to give nitrogen and hydrogen.

Instead of showing the two separate reactions, you can show one reaction and use a double arrow like this:

$N_2(g) + 3\ H_2(g) \leftrightarrow 2\ NH_3(g)$

You put the nitrogen and hydrogen on the left because that's what you initially put into the reaction container.

Now these two reactions occur at different speeds, but sooner or later, the two speeds become the same, and the relative amounts of nitrogen, hydrogen, and ammonia become constant. This is an example of a chemical equilibrium. A *dynamic chemical equilibrium* is established when two exactly opposite chemical reactions are occurring at the same place, at the same time, with the same rates (speed) of reaction. I call this example a *dynamic* chemical equilibrium, because when the reactions reach equilibrium, things don't just stop. At any given time, you have nitrogen and hydrogen reacting to form ammonia, and ammonia decomposing to form nitrogen and hydrogen. When the system reaches equilibrium, the amounts of all chemical species become *constant* but not necessarily the same.

Here's an example to help you understand what I mean by this dynamic stuff: I was raised on a farm in North Carolina, and my mother, Grace, *loved* small dogs. Sometimes we'd have close to a dozen dogs running around the house. When Mom opened the door to let them outside, they'd start running out. But some would change their minds after they got outside and would then start running back into the house. They'd then get caught up in the excitement of the other dogs and start running back outside again. There'd be a never-ending cycle of dogs running in and out of the house. Sometimes there'd only be two or three in the house, with the rest outside, or vice versa. The number of dogs inside and outside would be *constant* but not the same. And at any given point, there'd be dogs running out of the house and dogs running into the house. It was a dynamic equilibrium (and a noisy one).

Sometimes there's a lot of product (chemical species on the right-hand side of the double arrow) when the reaction reaches equilibrium, and sometimes there's very little. You can tell the relative amounts of reactants and products at equilibrium if you know the equilibrium constant for the reaction.

Look at a hypothetical equilibrium reaction:

$aA + bB \leftrightarrow cC + dD$

The capital letters stand for the chemical species, and the small letters represent the coefficients in the balanced chemical equation. The *equilibrium constant* (represented as K_{eq}) is mathematically defined as

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The numerator contains the product of the two chemical species on the right-hand side of the equation, with each chemical species raised to the power of its coefficient in the balanced chemical equation. The denominator is the same, but you use the chemical species on the left-hand side of the equation. (It's not important right now, but those brackets stand for something called the molar concentration. You can find out what that is in Chapter 11.) Note that sometimes chemists use the K_c notation instead of the K_{eq} form.

The numerical value of the equilibrium constant gives you a clue as to the relative amounts of products and reactants.

The larger the value of the equilibrium constant (K_{eq}), the more products are present at equilibrium. If, for example, you have a reaction that has an equilibrium constant of 0.001 at room temperature and 0.1 at 100 degrees Celsius, you can say that you will have much more product at the higher temperature.

Now I happen to know that the K_{eq} for the *Haber process* (the ammonia synthesis) is 3.5×10^8 at room temperature. This large value indicates that, at equilibrium, there's a lot of ammonia produced from the nitrogen and hydrogen, but there's still hydrogen and nitrogen left at equilibrium. If you're, say, an industrial chemist making ammonia, you want as much of the reactants as possible to be converted to product. You'd like the reaction to go to completion (meaning you'd like the reactants to keep creating the product until they're all used up), but you know that it's an equilibrium reaction, and you can't change that. But it would be nice if you could, in some way, manipulate the system to get a little bit more product formed. There is such a way — through Le Chatelier's Principle.

Le Chatelier's Principle

A French chemist, Henri Le Chatelier, discovered that if you apply a change of condition (called *stress*) to a chemical system that's at equilibrium, the reaction will return to equilibrium by shifting in such a way as to counteract the change (the stress). This is called *Le Chatelier's Principle.*

You can stress an equilibrium system in three ways:

- Change the concentration of a reactant or product.
- Change the temperature.
- Change the pressure on a system that contains gases.

Now if you're a chemist who's looking for a way to make as much ammonia (money) as possible for a chemical company, you can use Le Chatelier's Principle to help you along. In this section, I show you how.

But first, I want to show you a quick, useful analogy. A reaction at equilibrium is like one of my favorite pieces of playground equipment, a teeter-totter. Everything is well balanced, as shown in Figure 8-3.

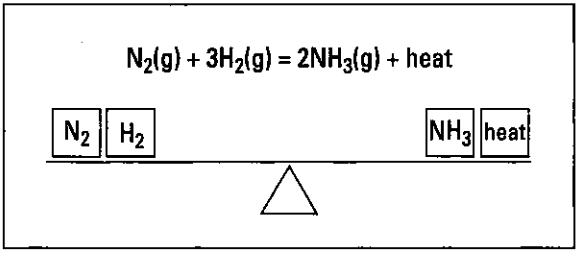


Figure 8-3: The Haber ammonia system at equilibrium.

The Haber process, the synthesis of ammonia from nitrogen and hydrogen gases, is exothermic: It gives off heat. I show that heat on the right-hand side of the teeter-totter in the figure.

Changing the concentration

Suppose that you have the ammonia system at equilibrium (see Figure 8-3, as well as the section, "Chemical Equilibrium," earlier in this chapter), and you then put in some more nitrogen gas. Figure 8-4 shows what happens to the teeter-totter when you add more nitrogen gas.

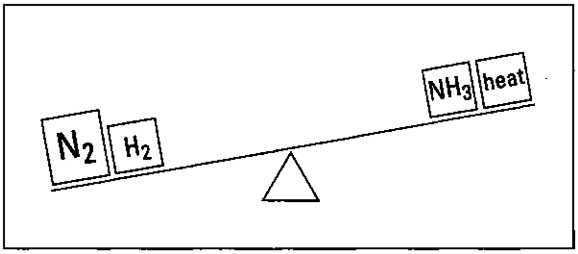


Figure 8-4: Increasing the concentration of a reactant.

In order to reestablish the balance (equilibrium), weight has to be shifted from the left to the right, using up some nitrogen and hydrogen, and forming more ammonia and heat. Figure 8-5 shows this shifting of weight.

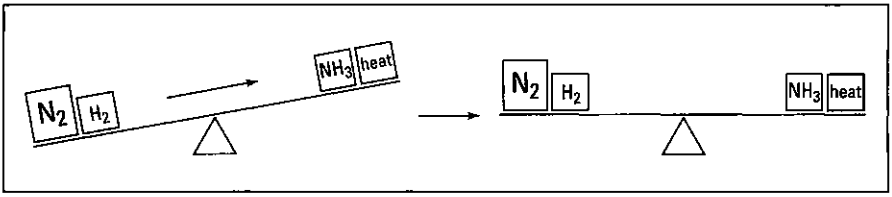


Figure 8-5: Reestablishing the equilibrium.

The equilibrium has been reestablished. There is less hydrogen and more nitrogen, ammonia, and heat than you had before you added the additional nitrogen. The same thing would happen if you had a way of removing ammonia as it was formed. The right-hand side of the teeter-totter would again be lighter, and weight would be shifted to the right in order to reestablish the equilibrium. Again, more ammonia would be formed. In general, if you add more of a reactant or product, the reaction will shift to the other side to use it up. If you remove some reactant or product, the reaction shifts to that side in order to replace it.

Changing the temperature

Suppose that you heat the reaction mixture. You know that the reaction is exothermic — heat is given off, showing up on the right-hand side of the equation. So if you heat the reaction mixture, the right side of the teeter-totter gets heavier, and weight must be shifted to the left in order to reestablish the equilibrium. This weight shift uses up ammonia and produces more nitrogen and hydrogen. And as the reaction shifts, the amount of heat also decreases, lowering the temperature of the reaction mixture. Figure 8-6 shows this shift in weight.

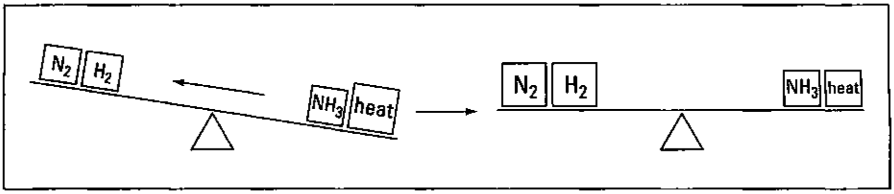


Figure 8-6: Increasing the temperature on an exothermic reaction and reestablishing the equilibrium.

That's not what you want! You want more ammonia, not more nitrogen and hydrogen. So you have to cool the reaction mixture, using up heat, and then the equilibrium shifts to the right in order to replace it. This process helps you make more ammonia and more profit. That's more like it.

In general, heating a reaction causes it to shift to the endothermic side. (If you have an exothermic reaction where heat is produced on the right side, then the left side is the endothermic side.) Cooling a reaction mixture causes the equilibrium to shift to the exothermic side.

Changing the pressure

Changing the pressure only affects the equilibrium if there are reactants and/or products that are gases. In the Haber process, all species are gases, so there is a pressure effect.

My teeter-totter analogy of equilibrium systems begins to break down when I explain pressure effects, so I have to take another approach. Think about the sealed container where your ammonia reaction is occurring. (The reaction has to occur in a sealed container with everything being gases.) You have nitrogen, hydrogen, and ammonia gases inside. There is pressure in the sealed container, and that pressure is due to the gas molecules hitting the inside walls of the container.

Now suppose that the system is at equilibrium, and you want to increase the pressure. You can do so by making the container smaller (with a piston type of arrangement) or by putting in an unreactive gas, such as neon. You get more collisions on the inside walls of the container, and, therefore, you have more pressure. Increasing the pressure stresses the equilibrium; in order to remove that stress and reestablish the equilibrium, the pressure must be reduced.

Take another look at the Haber reaction and see if there may be some clues as to how this may happen.

$$N_2(g) + 3\,H_2(g) \leftrightarrow 2\,NH_3(g)$$

Every time the forward (left to right) reaction takes place, four molecules of gas (one nitrogen and three hydrogen) form two molecules of ammonia gas. This reaction reduces the number of molecules of gas in the container. The reverse reaction (right to left) takes two ammonia gas molecules and makes four gas molecules (nitrogen and hydrogen). This reaction increases the number of gas molecules in the container.

The equilibrium has been stressed by an increase in pressure; reducing the pressure will relieve the stress. Reducing the number of gas molecules in the container will reduce the pressure (fewer collisions on the inside walls of the container), so the forward (left to right) reaction is favored because four gas molecules are consumed and only two are formed. As a result of the forward reaction, more ammonia is produced!

In general, increasing the pressure on an equilibrium mixture causes the reaction to shift to the side containing the *fewest* number of gas molecules.

Reacting Fast and Reacting Slow: Chemical Kinetics

Say that you're a chemist who wants to make as much ammonia as possible from a given amount of hydrogen and nitrogen. Manipulating the equilibrium (see the preceding section) isn't your total solution. You want to produce as much as possible, *as fast as possible.* So there's something else you must consider — the kinetics of the reaction.

Kinetics is the study of the speed of a reaction. Some reactions are fast; others are slow. Sometimes chemists want to speed the slow ones up and slow the fast ones down. There are several factors that affect the speed of a reaction:

- ✓ Nature of the reactants
- ✓ Particle size of the reactants
- ✓ Concentration of the reactants
- ✓ Pressure of gaseous reactants
- ✓ Temperature
- ✓ Catalysts

Nature of the reactants

In order for a reaction to occur, there must be a collision between the reactants at the reactive site of the molecule (see "How Do Reactions Occur? Collision Theory," earlier in this chapter). The larger and more complex the reactant molecules, the less chance there is of a collision at the reactive site. Sometimes, in very complex molecules, the reactive site is totally blocked off by other parts of the molecule, so no reaction occurs. There may be a lot of collisions, but only the ones that occur at the reactive site have any chance of leading to chemical reaction.

In general, the reaction rate is slower when the reactants are large and complex molecules.

Particle size of the reactants

Reaction depends on collisions. The more surface area on which collisions can occur, the faster the reaction. You can hold a burning match to a large chunk of coal and nothing will happen. But if you take that same piece of coal, grind it up very, very fine, throw it up into the air, and strike a match, you'll get an explosion because of the increased surface area of the coal.

Concentration of the reactants

Increasing the number of collisions speeds up the reaction rate. The more reactant molecules there are colliding, the faster the reaction will be. For example, a wood splint burns okay in air (20 percent oxygen), but it burns *much* faster in pure oxygen.

In most simple cases, increasing the concentration of the reactants increases the speed of the reaction. However, if the reaction is complex and has a complex *mechanism* (series of steps in the reaction), this may not be the case. In fact, determining the concentration effect on the rate of reaction can give you clues as to which reactant is involved in the rate-determining step of the mechanism. (This information can then be used to help figure out the reaction mechanism.) You can do this by running the reaction at several different concentrations and observing the effect on the rate of reaction. If, for example, changing the concentration of one reactant has no effect on the rate of reaction, then you know that reactant is not involved in the slowest step (the rate-determining step) in the mechanism.

Pressure of gaseous reactants

The pressure of gaseous reactants has basically the same effect as concentration. The higher the reactant pressure, the faster the reaction rate. This is due to (you guessed it!) the increased number of collisions. But if there's a complex mechanism involved, changing the pressure may not have the expected result.

Temperature

Okay, why did mom tell you to put that turkey in the refrigerator after Thanksgiving dinner? Because it would've spoiled if you didn't. And what is spoilage? It's increased bacterial growth. So when you put the turkey in the refrigerator, the cold temperature inside the fridge slowed down the rate of bacterial growth.

Bacterial growth is simply a *biochemical reaction,* a chemical reaction involving living organisms. In most cases, increasing the temperature causes the reaction rate to increase. In organic chemistry, there's a general rule that says increasing the temperature 10 degrees Celsius will cause the reaction rate to double.

But why is this true? Part of the answer is (you guessed it!) an increased number of collisions. Increasing the temperature causes the molecules to move faster, so there's an increased chance of them colliding with each other and reacting. But this is only part of the story. Increasing the temperature also increases the average kinetic energy of the molecules. Look at Figure 8-7 for an example of how increasing the temperature affects the kinetic energy of the reactants and increases the reaction rate.

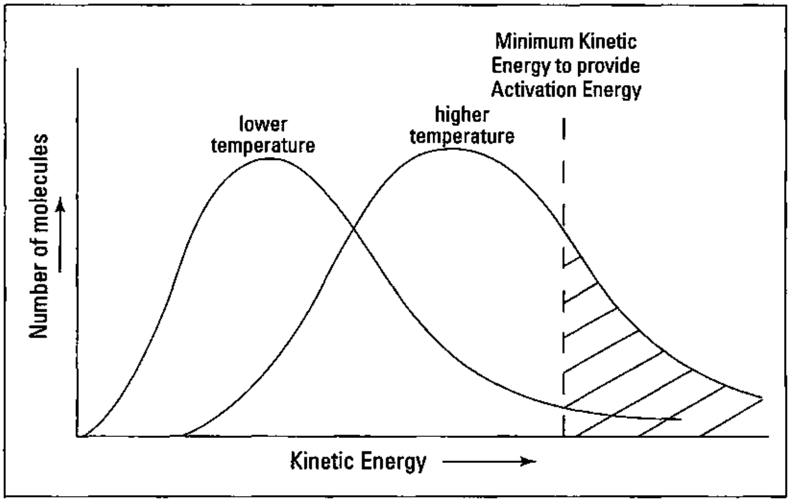


Figure 8-7: The effect of temperature on the kinetic energy of reactants.

At a given temperature, not all the molecules are moving with the same kinetic energy. A small number of molecules are moving very slow (low kinetic energy), while a few are moving very fast (high kinetic energy). A vast majority of the molecules are somewhere in between these two extremes.

In fact, temperature is a measure of the average kinetic energy of the molecules. As you can see in Figure 8-7, increasing the temperature increases the average kinetic energy of the reactants, essentially shifting the curve to the right toward higher kinetic energies. But also notice that I've marked the minimum amount of kinetic energy needed by the reactants to provide the activation energy (the energy required to get a reaction going) during collision. The reactants have to collide at the reactive site, but they also have to transfer *enough* energy to break bonds so that new bonds can be formed. If the reactants don't have enough energy, a reaction won't occur even if the reactants do collide at the reactive site.

Notice that at the lower temperature, very few of the reactant molecules have the minimum amount of kinetic energy needed to provide the activation energy. At the higher temperature, many more molecules possess the minimum amount of kinetic energy needed, which means a lot more collisions will be energetic enough to lead to reaction.

Increasing the temperature not only increases the number of collisions but also increases the number of collisions that are effective — that transfer enough energy to cause a reaction to take place.

Catalysts

Catalysts are substances that increase the reaction rate without themselves being changed at the end of the reaction. They increase the reaction rate by lowering the activation energy for the reaction.

Look at Figure 8-1, for example. If the activation energy hill were lower, it'd be easier for the reaction to occur and the reaction rate would be faster. You can see the same thing in Figure 8-7. If you shift to the left that dotted line representing the minimum amount of kinetic energy needed to provide the activation energy, then many more molecules will have the minimum energy needed, and the reaction will be faster.

Catalysts lower the activation energy of a reaction in one of two ways:

- Providing a surface and orientation
- Providing an alternative mechanism (series of steps for the reaction to go through) with a lower activation energy

Surface and orientation — heterogeneous catalysis

In the section "How Do Reactions Occur? Collision Theory," I describe how molecules react, using this generalized example:

$$C\text{-}A\text{-}B \rightarrow C\text{-}A + B$$

Reactant *C* must hit the reactive site on the *A* end of molecule *A-B* in order to break the *A-B* bond and form the *C-A* bond shown in the equation. The probability of the collision occurring in the proper orientation is pretty much driven by chance. The reactants are moving around, running into each other, and sooner or later the collision may occur at the reactive site. But what would happen if you could tie the *A-B* molecule down with the *A* end exposed? It'd be much easier and more probable for *C* to hit *A* with this scenario.

This is what a heterogeneous catalyst accomplishes: It ties one molecule to a surface while providing proper orientation to make the reaction easier. The process of heterogeneous catalysis is shown in Figure 8-8.

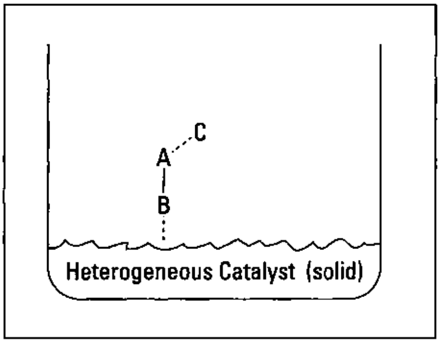


Figure 8-8: An example of heterogeneous catalysis.

The catalyst is called a *heterogeneous* catalyst because it's in a different phase than the reactants. This catalyst is commonly a finely divided solid metal or metal oxide, while the reactants are gases or in solution. This heterogeneous catalyst tends to attract one part of a reactant molecule due to rather complex interactions that are not fully understood. After the reaction takes place, the forces that bound the *B* part of the molecule to the surface of the catalyst are no longer there. So *B* can drift off, and the catalyst can be ready to do it again.

Most of us sit very close to a heterogeneous catalyst every day — the catalytic converter in our automobile. It contains finely divided platinum and/or palladium metal and speeds up the reaction that causes harmful gases from gasoline (such as carbon monoxide and unburned hydrocarbons) to decompose into mostly harmless products (such as water and carbon dioxide).

Alternative mechanism — homogeneous catalysis

The second type of catalyst is a *homogeneous catalyst* — one that's in the same phase as the reactants. It provides an alternative mechanism, or reaction pathway, that has a lower activation energy than the original reaction.

For an example, check out the decomposition reaction of hydrogen peroxide:

$$2\,H_2O_2(l) \rightarrow 2\,H_2O(l) + O_2(g)$$

This is a slow reaction, especially if it's kept cool in a dark bottle. It may take years for that bottle of hydrogen peroxide in your medicine cabinet to decompose. But if you put a little bit of a solution containing the ferric ion in the bottle, the reaction will be much faster, even though it will be a two-step mechanism instead of a one-step mechanism:

(Step 1) $2\,Fe^{3+} + H_2O_2(l) \rightarrow 2\,Fe^{2+} + O_2(g) + 2\,H^+$

(Step 2) $2\,Fe^{2+} + H_2O_2(l) + 2\,H^+ \rightarrow 2\,Fe^{3+} + 2\,H_2O(l)$

If you add the two preceding reactions together and cancel the species that are identical on both sides, you get the original, uncatalyzed reaction:

$\mathbf{2\,Fe^{3+}} + H_2O_2(l) + \mathbf{2\,Fe^{2+}} + H_2O_2(l) + \mathbf{2\,H^+} \rightarrow \mathbf{2\,Fe^{2+}} + O_2(g) + \mathbf{2\,H^+} + \mathbf{2\,Fe^{3+}} + 2\,H_2O(l)$ (species to be cancelled are bolded)

$2\,H_2O_2(l) \rightarrow 2\,H_2O(l) + O_2(g)$

The ferric ion catalyst was changed in the first step and then changed back in the second step. This two-step catalyzed pathway has a lower activation energy and is faster.

Chapter 9

Electrochemistry: Batteries to Teapots

In This Chapter

- Finding out about redox reactions
- Figuring out how to balance redox equations
- Taking a look at electrochemical cells
- Checking out electroplating
- Discovering how burning fuels and burning foods are similar

Many of the things we deal with in real life are related either directly or indirectly to electrochemical reactions. Think of all the things around you that contain batteries — flashlights, watches, automobiles, calculators, PDAs, pacemakers, cell phones, toys, garage door openers, and so on.

Do you drink from an aluminum can? The aluminum was extracted by an electrochemical reaction. Do you have a car with a chrome bumper? That chrome is electroplated onto the bumper, just like the silver on Grandmother Grace's tea service or the gold on that five-dollar gold chain. Do you watch television, use electric lights or an electric blender, or have a desktop computer? There's a good chance that the electricity you use for these things is generated from the combustion of some fossil fuel. Combustion is a redox reaction. So are respiration, photosynthesis, and many other biochemical processes that we depend upon for life. Electrochemical and redox reactions surround us.

In this chapter, I explain redox reactions, go through the balancing of this type of equation, and then show you some applications of redox reactions in an area of chemistry called electrochemistry.

There Go Those Pesky Electrons: Redox Reactions

Redox reactions — reactions in which there's a simultaneous transfer of electrons from one chemical species to another — are really composed of two different reactions: *oxidation* (a loss of electrons) and *reduction* (a gain of electrons). These reactions are coupled, as the electrons that are lost in the oxidation reaction are the same electrons that are gained in the reduction reaction. In fact, these two reactions (reduction and oxidation) are commonly called *half-reactions,* because it takes these two halves to make a whole reaction, and the overall reaction is called a *redox* (*red*uction/*ox*idation) reaction. In Chapter 8, I describe a redox reaction that occurs between zinc metal and the cupric (Cu^{2+}) ion. The zinc metal loses electrons and the cupric ion gains them.

Now where did I put those electrons? Oxidation

There are three definitions you can use for oxidation:

- ✓ The loss of electrons
- ✓ The gain of oxygen
- ✓ The loss of hydrogen

Because I typically deal with electrochemical cells, I normally use the definition that describes the loss of the electrons. The other definitions are useful in processes such as combustion and photosynthesis.

Loss of electrons

One way to define oxidation is with the reaction in which a chemical substance loses electrons in going from reactant to product. For example, when sodium metal reacts with chlorine gas to form sodium chloride (NaCl), the sodium metal loses an electron, which is then gained by chlorine. The following equation shows sodium losing the electron:

$$Na(s) \rightarrow Na^{+} + e^{-}$$

When it loses the electron, chemists say that the sodium metal has been oxidized to the sodium cation. (A *cation* is an ion with a positive charge due to the loss of electrons — see Chapter 6.)

Reactions of this type are quite common in *electrochemical reactions,* reactions that produce or use electricity. (For more info about electrochemical reactions, flip to the section, "Power On the Go: Electrochemical Cells," later in this chapter.)

Gain of oxygen

Sometimes, in certain oxidation reactions, it's obvious that oxygen has been gained in going from reactant to product. Reactions where the gain of oxygen is more obvious than the gain of electrons include combustion reactions (*burning*) and the *rusting* of iron. Here are two examples:

$C(s) + O_2(g) \rightarrow CO_2(g)$ (burning of coal)

$2\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$ (rusting of iron)

In these cases, chemists say that the carbon and the iron metal have been oxidized to carbon dioxide and rust, respectively.

Loss of hydrogen

In other reactions, oxidation can best be seen as the loss of hydrogen. Methyl alcohol (wood alcohol) can be oxidized to formaldehyde:

$CH_3OH(l) \rightarrow CH_2O(l) + H_2(g)$

In going from methanol to formaldehyde, the compound went from having four hydrogen atoms to having two hydrogen atoms.

Look what I found! Reduction

Like oxidation, there are three definitions you can use to describe reduction:

- The gain of electrons
- The loss of oxygen
- The gain of hydrogen

Gain of electrons

Reduction is often seen as the gain of electrons. In the process of electroplating silver onto a teapot (see the section, "Five Dollars for a Gold Chain? Electroplating," later in this chapter), for example, the silver cation is reduced to silver metal by the gain of an electron. The following equation shows the silver cation gaining the electron:

$Ag^+ + e^- \rightarrow Ag$

When it gains the electron, chemists say that the silver cation has been reduced to silver metal.

Loss of oxygen

In other reactions, it's easier to see reduction as the loss of oxygen in going from reactant to product. For example, iron ore (primarily rust, Fe_2O_3) is reduced to iron metal in a blast furnace by a reaction with carbon monoxide:

$$Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$$

The iron has lost oxygen, so chemists say that the iron ion has been reduced to iron metal.

Gain of hydrogen

In certain cases, a reduction can also be described as the gain of hydrogen atoms in going from reactant to product. For example, carbon monoxide and hydrogen gas can be reduced to methyl alcohol:

$$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(l)$$

In this reduction process, the CO has gained the hydrogen atoms.

One's loss is the other's gain

Neither oxidation nor reduction can take place without the other. When those electrons are lost, something has to gain them.

Consider, for example, the *net-ionic equation* (the equation showing just the chemical substances that are changed during a reaction — see Chapter 8) for a reaction with zinc metal and an aqueous copper(II) sulfate solution:

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

This overall reaction is really composed of two half-reactions:

$Zn(s) \rightarrow Zn^{2+} + 2e^-$ (oxidation half-reaction — the loss of electrons)

$Cu^{2+} + 2e^- \rightarrow Cu(s)$ (reduction half-reaction — the gain of electrons)

To help yourself remember which is oxidation and which is reduction in terms of electrons, memorize the phrase "LEO goes GER" (*L*ose *E*lectrons *O*xidation; *G*ain *E*lectrons *R*eduction).

Zinc loses two electrons; the copper(II) cation gains those same two electrons. Zn is being oxidized. But without Cu^{2+} present, nothing will happen. That copper cation is the *oxidizing agent.* It's a necessary agent for the oxidation process to proceed. The oxidizing agent accepts the electrons from the chemical species that is being oxidized.

Cu^{2+} is reduced as it gains electrons. The species that furnishes the electrons is called the *reducing agent.* In this case, the reducing agent is zinc metal.

The oxidizing agent is the species that's being reduced, and the reducing agent is the species that's being oxidized. Both the oxidizing and reducing agents are on the left (reactant) side of the redox equation.

Playing the numbers: Oxidation numbers, that is

Oxidation numbers are bookkeeping numbers. They allow chemists to do things such as balance redox equations. Oxidation numbers are positive or negative numbers, but don't confuse them with charges on ions or valences. Oxidation numbers are assigned to elements using these rules:

- **Rule 1:** The oxidation number of an element in its free (uncombined) state is zero (for example, Al(s) or Zn(s)). This is also true for elements found in nature as *diatomic* (two-atom) elements (H_2, O_2, N_2, F_2, Cl_2, Br_2, or I_2) and for sulfur, found as S_8.
- **Rule 2:** The oxidation number of a *monatomic* (one-atom) ion is the same as the charge on the ion (for example, $Na^+ = +1$, $S^{2-} = -2$).
- **Rule 3:** The sum of all oxidation numbers in a neutral compound is zero. The sum of all oxidation numbers in a *polyatomic* (many-atom) ion is equal to the charge on the ion. This rule often allows chemists to calculate the oxidation number of an atom that may have multiple oxidation states, if the other atoms in the ion have known oxidation numbers. (See Chapter 6 for examples of atoms with multiple oxidation states.)
- **Rule 4:** The oxidation number of an alkali metal (IA family) in a compound is +1; the oxidation number of an alkaline earth metal (IIA family) in a compound is +2.
- **Rule 5:** The oxidation number of oxygen in a compound is usually –2. If, however, the oxygen is in a class of compounds called *peroxides* (for example, hydrogen peroxide, or H_2O_2), then the oxygen has an oxidation number of –1. If the oxygen is bonded to fluorine, the number is +1.
- **Rule 6:** The oxidation state of hydrogen in a compound is usually +1. If the hydrogen is part of a *binary metal hydride* (compound of hydrogen and some metal), then the oxidation state of hydrogen is –1.
- **Rule 7:** The oxidation number of fluorine is always –1. Chlorine, bromine, and iodine usually have an oxidation number of –1, unless they're in combination with an oxygen or fluorine. (For example, in ClO^-, the oxidation number of oxygen is –2 and the oxidation number of chlorine is +1; remember that the sum of all the oxidation numbers in ClO^- have to equal –1.)

These rules give you another way to define oxidation and reduction — in terms of oxidation numbers. For example, consider this reaction, which shows oxidation by the loss of electrons:

$$Zn(s) \rightarrow Zn^{2+} + 2e^-$$

Notice that the zinc metal (the reactant) has an oxidation number of zero (rule 1), and the zinc cation (the product) has an oxidation number of +2 (rule 2). In general, you can say that a substance is oxidized when there's an *increase* in its oxidation number.

Reduction works the same way. Consider this reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

The copper is going from an oxidation number of +2 to zero. A substance is reduced if there's a *decrease* in its oxidation number.

Balancing redox equations

Redox equations are often so complex that the inspection method (the fiddling with coefficients method) of balancing chemical equations doesn't work well with them (see Chapter 8 for a discussion of this balancing method). So chemists have developed two different methods of balancing redox equations. One method is called the *oxidation number method.* It's based on the changes in oxidation numbers that take place during the reaction. Personally, I don't think this method works nearly as well as the second method, the *ion-electron* (half-reaction) method, because it's sometimes difficult to determine the exact change in the numerical value of the oxidation numbers. So I'm just going to show you the second method.

Here's an overview of the ion-electron method: The unbalanced redox equation is converted to the ionic equation and then broken down into two half-reactions — oxidation and reduction. Each of these half-reactions is balanced separately and then combined to give the balanced ionic equation. Finally, the spectator ions are put into the balanced ionic equation, converting the reaction back to the molecular form. (Buzzword-o-rama, eh? For a discussion of molecular, ionic, and net-ionic equations, see Chapter 8.) It's important to follow the steps precisely and in the order listed. Otherwise, you may not be successful in balancing redox equations.

Now how about an example? I'm going to show you how to balance this redox equation with the ion-electron method:

$$Cu(s) + HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + NO(g) + H_2O(l)$$

Follow these steps:

1. **Convert the unbalanced redox reaction to the ionic form.**

   In this reaction, you show the nitric acid in the ionic form, because it's a strong acid (for a discussion of strong acids, see Chapter 12). Copper(II) nitrate is soluble (indicated by *(aq)*), so it's shown in its ionic form (see Chapter 8). Because NO(g) and water are molecular compounds, they remain shown in the molecular form:

   $Cu(s) + H^+ + NO_3^- \rightarrow Cu^{2+} + 2\ NO_3^- + NO(g) + H_2O(l)$

2. **If necessary, assign oxidation numbers and then write two half-reactions (oxidation and reduction) showing the chemical species that have had their oxidation numbers changed.**

   In some cases, it's easy to tell what has been oxidized and reduced; but in other cases, it isn't as easy. Start by going through the example reaction and assigning oxidation numbers. You can then use the chemical species that have had their oxidation numbers changed to write your unbalanced half-reactions:

   $Cu(s) + H^+ + NO_3^- \rightarrow Cu^{2+} + 2\ NO_3^- + NO(g) + H_2O(l)$

   0 +1 +5(-2)3 +2 +5(-2)3 +2 -2 (+1)2 -2

   Look closely. Copper changed its oxidation number (from 0 to 2) and so has nitrogen (from –2 to +2). Your unbalanced half-reactions are

   $Cu(s) \rightarrow Cu^{2+}$

   $NO_3^- \rightarrow NO$

3. **Balance all atoms, with the exception of oxygen and hydrogen.**

   It's a good idea to wait until the end to balance hydrogen and oxygen atoms, so always balance the other atoms first. You can balance them by inspection — fiddling with the coefficients. (You can't change subscripts; you can only add coefficients.) However, in this particular case, both the copper and nitrogen atoms already balance, with one each on both sides:

   $Cu(s) \rightarrow Cu^{2+}$

   $NO_3^- \rightarrow NO$

4. **Balance the oxygen atoms.**

   How you balance these atoms depends on whether you're dealing with acid or basic solutions:

   - In acid solutions, take the number of oxygen atoms needed and add that same number of water molecules to the side that needs oxygen.
   - In basic solutions, add 2 OH^- to the side that needs oxygen for every oxygen atom that is needed. Then, to the other side of the equation, add half as many water molecules as OH^- anions used.

An acidic solution will have some acid or H^+ shown; a basic solution will have an OH^- present. The example equation is in acidic conditions (nitric acid, HNO_3, which, in ionic form, is $H^+ + NO_3^-$). There's nothing to do on the half-reaction involving the copper, because there are no oxygen atoms present. But you do need to balance the oxygen atoms in the second half-reaction:

$Cu(s) \rightarrow Cu^{2+}$

$NO_3^- \rightarrow NO + 2\ H_2O$

5. **Balance the hydrogen atoms.**

   Again, how you balance these atoms depends on whether you're dealing with acid or basic solutions:

   - In acid solutions, take the number of hydrogen atoms needed and add that same number of H^+ to the side that needs hydrogen.
   - In basic solutions, add one water molecule to the side that needs hydrogen for every hydrogen atom that's needed. Then, to the other side of the equation, add as many OH^- anions as water molecules used.

   The example equation is in acidic conditions. You need to balance the hydrogen atoms in the second half-reaction:

   $Cu(s) \rightarrow Cu^{2+}$

   $4\ H^+ + NO_3^- \rightarrow NO + 2\ H_2O$

6. **Balance the ionic charge on each half-reaction by adding electrons.**

   $Cu(s) \rightarrow Cu^{2+} + 2\ e^-$ (oxidation)

   $3\ e^- + 4\ H^+ + NO_3^- \rightarrow NO + 2\ H_2O$ (reduction)

   The electrons should end up on opposite sides of the equation in the two half-reactions. Remember that you're using ionic charge, not oxidation numbers.

7. **Balance electron loss with electron gain between the two half-reactions.**

   The electrons that are lost in the oxidation half-reaction are the same electrons that are gained in the reduction half-reaction. The number of electrons lost and gained must be the same. But Step 6 shows a loss of 2 electrons and a gain of 3. So you must adjust the numbers using appropriate multipliers for both half-reactions. In this case, you have to find the lowest common denominator between 2 and 3. It's 6, so multiply the first half-reaction by 3 and the second half-reaction by 2.

   $3 \times [Cu(s) \rightarrow Cu^{2+} + 2\ e^-] = 3\ Cu(s) \rightarrow 3\ Cu^{2+} + 6\ e^-$

   $2 \times [3\ e^- + 4\ H^+ + NO_3^- \rightarrow NO + 2\ H_2O] = 6\ e^- + 8\ H^+ + 2\ NO_3^- \rightarrow 2\ NO + 4\ H_2O$

8. **Add the two half-reactions together and cancel anything common to both sides. The electrons should always cancel (the number of electrons should be the same on both sides).**

   $3\ Cu \cancel{+} 6\ e^- + 8\ H^+ + 2\ NO_3^- \rightarrow 3\ Cu^{2+} + 6\ e^- \cancel{+} 2\ NO + 4\ H_2O$

9. **Convert the equation back to the molecular form by adding the spectator ions.**

   If it's necessary to add spectator ions to one side of the equation, add the same number to the other side of the equation. For example, there are 8 H^+ on the left side of the equation. In the original equation, the H^+ was in the molecular form of HNO_3. You need to add the NO_3^- spectator ions back to it. You already have 2 on the left, so you simply add 6 more. You then add 6 NO_3^- to the right-hand side to keep things balanced. Those are the spectator ions that you need for the Cu^{2+} cation to convert it back to the molecular form that you want.

   $3\ Cu(s) + 8\ HNO_3(aq) \rightarrow 3\ Cu(NO_3)_2(aq) + 2\ NO(g) + 4\ H_2O(l)$

10. **Check to make sure that all the atoms are balanced, all the charges are balanced (if working with an ionic equation at the beginning), and all the coefficients are in the lowest whole-number ratio.**

That's how it's done. Reactions that take place in base are just as easy, as long as you follow the rules.

Power On the Go: Electrochemical Cells

In the section, "One's loss is the other's gain," I discuss a reaction in which I put a piece of zinc metal into a copper(II) sulfate solution. The copper metal begins spontaneously plating out on the surface of the zinc. The equation for this reaction is

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

This is an example of *direct* electron transfer. Zinc gives up two electrons (becomes oxidized) to the Cu^{2+} ion that accepts the electrons (reducing it to copper metal). In Chapter 8, I show you that nothing happens if you place a piece of copper metal into a solution containing Zn^{2+}, because zinc gives up electrons more easily than copper. I also show you the activity series of metals that allows you to predict whether or not a displacement (redox) reaction will take place.

Now this is a useful reaction if you want to plate out copper onto zinc. However, not many of us have a burning desire to do this! But if you were able to separate those two half-reactions so that when the zinc is oxidized, the electrons it releases are forced to travel through a wire to get to the Cu^{2+}, you'd have something useful. You'd have a *galvanic* or *voltaic cell,* a redox reaction that produces electricity. In this section, I show you how that Zn/Cu^{2+} reaction may be separated out so that you have an *indirect* electron transfer and can produce some useable electricity.

Galvanic cells are commonly called batteries, but sometimes this name is somewhat incorrect. A battery is composed of two or more cells connected together. You put a battery in your car, but you put a cell into your flashlight.

Nice cell there, Daniell

Take a look at Figure 9-1, which shows a Daniell cell that uses the Zn/Cu^{2+} reaction to produce electricity. (This cell is named after John Frederic Daniell, the British chemist who invented it in 1836.)

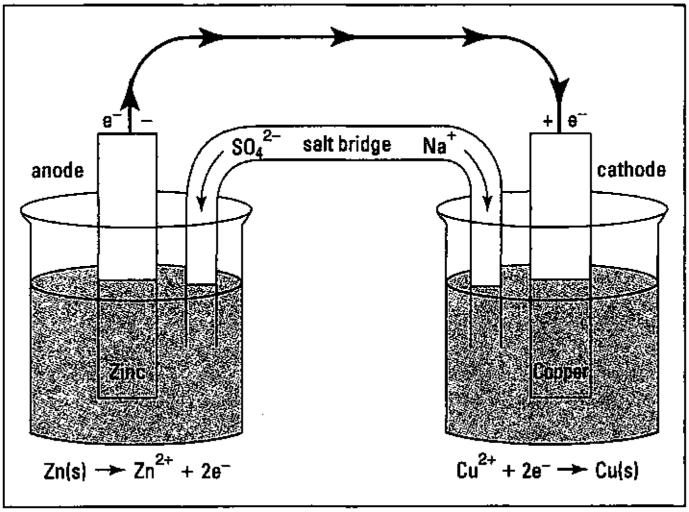


Figure 9-1: A Daniell cell.

In the Daniell cell, a piece of zinc metal is placed in a solution of zinc sulfate in one container, and a piece of copper metal is placed in a solution of copper(II) sulfate in another container. These strips of metal are called the cell's *electrodes*. They act as a terminal, or a holding place, for electrons. A wire connects the electrodes, but nothing happens until you put a salt bridge between the two containers. The *salt bridge*, normally a U-shaped hollow tube filled with a concentrated salt solution, provides a way for ions to move from one container to the other to keep the solutions electrically neutral. It's like running only one wire up to a ceiling light; the light won't work unless you put in a second wire to complete the circuit.

With the salt bridge in place, electrons can start to flow. It's the same basic redox reaction as the one I show you at the beginning of this section. Zinc is being oxidized, releasing electrons that flow through the wire to the copper electrode, where they're available for the Cu^{2+} ions to use in forming copper metal. Copper ions from the copper(II) sulfate solution are being plated out on the copper electrode, while the zinc electrode is being consumed. The cations in the salt bridge migrate to the container containing the copper electrode to replace the copper ions being consumed, while the anions in the salt bridge migrate toward the zinc side, where they keep the solution containing the newly formed Zn^{2+} cations electrically neutral.

The zinc electrode is called the *anode,* the electrode at which oxidation takes place, and is labeled with a "–" sign. The copper electrode is called the *cathode,* the electrode at which reduction takes place, and is labeled with a "+" sign.

This cell will produce a little over one volt. You can get just a little more voltage if you make the solutions that the electrodes are in very concentrated. But what can you do if you want, for example, two volts? You have a couple of choices. You can hook two of these cells up together and produce two volts, or you can choose two different metals from the activity series chart in Chapter 8 that are farther apart than zinc and copper. The farther apart the metals are on the activity series, the more voltage the cell will produce.

Let the light shine: Flashlight cells

The common flashlight cell (see Figure 9-2), a dry cell (it's not in a solution like a Daniell cell), is contained in a zinc housing that acts as the anode. The other electrode, the cathode, is a graphite rod in the middle of the cell. A layer of manganese oxide and carbon black (one of the many forms of carbon) surrounds the graphite rod, and a thick paste of ammonium chloride and zinc chloride serves as the electrolyte. The cell reactions are

$Zn(s) \rightarrow Zn^{2+} + 2\ e^-$ (anode reaction/oxidation)

$2\ MnO_2(s) + 2\ NH_4^+ + 2\ e^- \rightarrow Mn_2O_3(s) + 2\ NH_3(aq) + H_2O(l)$ (cathode reaction/reduction)

Note that the case is actually one of the electrodes; it's being used up in the reaction. If there's a thin spot in the case, a hole could form, and the cell could leak the corrosive contents. In addition, the ammonium chloride tends to corrode the metal case, again allowing for the possibility of leakage.

In the alkaline dry cell (alkaline battery), the acidic ammonium chloride of the regular dry cell is replaced by basic (alkaline) potassium hydroxide. With this chemical, corrosion of the zinc case is greatly reduced.

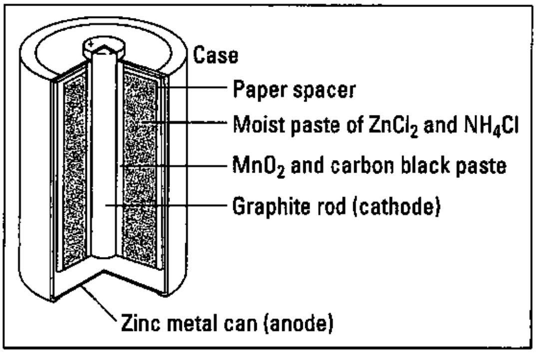


Figure 9-2: A dry cell.

Another cell with the same basic construction is the small mercury battery commonly used in watches, pacemakers, and so on. With this battery, the anode is zinc, as in the regular dry cell, but the cathode is steel. Mercury(II) oxide (HgO) and some alkaline paste form the electrolyte. You should dispose of this type of battery carefully, to keep the mercury from being released into the environment.

All these galvanic cells produce electricity until they run out of a reactant. Then they must be discarded. However, there are cells (batteries) that can be recharged, as the redox reaction can be reversed to regenerate the original reactants. Nickel-cadmium (Ni-Cad) and lithium batteries fall into this category. The most familiar type of rechargeable battery is probably the automobile battery.

Gentlemen, start your engines: Automobile batteries

The ordinary automobile battery, or lead storage battery, consists of six cells connected in series (see Figure 9-3). The anode of each cell is lead, while the cathode is lead dioxide (PbO_2). The electrodes are immersed in a sulfuric acid (H_2SO_4) solution. When you start your car, the following cell reactions take place:

$Pb(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2\,H^+ + 2\,e^-$ (anode)

$2\,e^- + 2\,H^+ + PbO_2(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2\,H_2O(l)$ (cathode)

$Pb(s) + PbO_2(s) + 2\,H_2SO_4(aq) \rightarrow 2\,PbSO_4 + 2\,H_2O(l)$ (overall reaction)

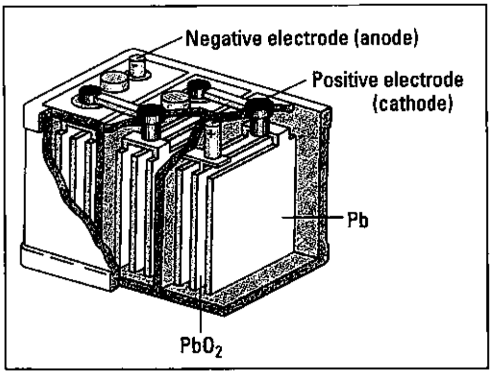


Figure 9-3: The lead storage battery.

When this reaction takes place, both electrodes become coated with solid lead (II) sulfate, and the sulfuric acid is used up.

After the automobile has been started, the alternator or generator takes over the job of producing electricity (for spark plugs, lights, and so on) and also recharges the battery. The alternator reverses both the flow of electrons into the battery and the original redox reactions, and regenerates the lead and lead dioxide:

$$2\ PbSO_4(s) + 2\ H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2\ H_2SO_4(aq)$$

The lead storage battery can be discharged and charged many times. But the shock of running over bumps in the road (or dead armadillos in Texas) or into the curb flakes off a little of the lead (II) sulfate and eventually causes the battery to fail.

During charging, the automobile battery acts like a second type of electrochemical cell, an *electrolytic cell,* which uses electricity to produce a desired redox reaction. This reaction may be the recharging of a battery, or it may be involved in the plating of Grandmother Grace's teapot.

Five Dollars for a Gold Chain? Electroplating

Electrolytic cells, cells that use electricity to produce a desired redox reaction, are used extensively in our society. Rechargeable batteries are a primary example of this type of cell, but there are many other applications. Ever wonder how the aluminum in that aluminum can is mined? Aluminum ore is primarily aluminum oxide (Al_2O_3). Aluminum metal is produced by reducing the aluminum oxide in a high temperature electrolytic cell using approximately 250,000 amps. That's a lot of electricity. It's far cheaper to take old aluminum cans, melt them down, and reform them into new cans than it is to extract the metal from the ore. That's why the aluminum industry is strongly behind the recycling of aluminum. It's just good business.

Water can be decomposed by the use of electricity in an electrolytic cell. This process of producing chemical changes by passing an electric current through an electrolytic cell is called *electrolysis* (yes, just like the permanent removal of hair). The overall cell reaction is

$$2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$$

In a similar fashion, sodium metal and chlorine gas can be produced by the electrolysis of molten sodium chloride.

Electrolytic cells are also used in a process called *electroplating*. In electroplating, a more-expensive metal is plated (deposited in a thin layer) onto the surface of a cheaper metal by electrolysis. Back before plastic auto bumpers became popular, chromium metal was electroplated onto steel bumpers. Those five-dollar gold chains you can buy are really made of some cheap metal with an electroplated surface of gold. Figure 9-4 shows the electroplating of silver onto a teapot.

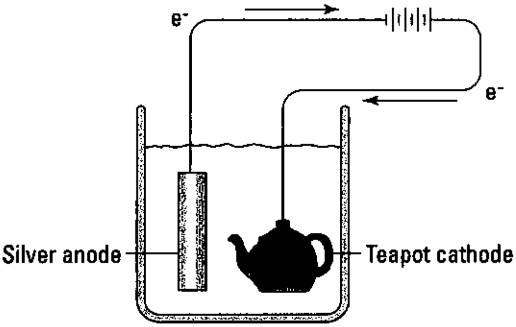


Figure 9-4: Electroplating silver onto a teapot.

A battery is commonly used to furnish the electricity for the process. The teapot acts as the cathode and a bar of silver acts as the anode. The silver bar furnishes the silver ions that are reduced onto the surface of the teapot. Many metals and even some alloys can be plated out in this fashion. Everybody loves those plated surfaces, especially without the high cost of the pure metal. (Reminds me of an Olympic athlete who was so proud of his gold metal that he had it bronzed!)

This Burns Me Up! Combustion of Fuels and Foods

Combustion reactions are types of redox reactions that are absolutely essential for life and civilization — because heat is the most important product of these reactions. The burning of coal, wood, natural gas, and petroleum heats our homes and provides the majority of our electricity. The combustion of gasoline, jet fuel, and diesel fuel powers our transportation systems. And the combustion of food powers our bodies.

Have you ever wondered how the energy content of a fuel or food is measured? An instrument called a *bomb calorimeter* is used to measure energy content. Figure 9-5 shows the major components of a bomb calorimeter.

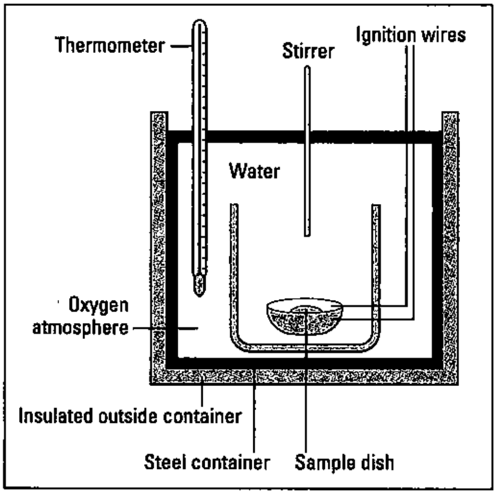


Figure 9-5: A bomb calorimeter.

To measure the energy content of fuels, a known mass of the material to be measured is placed into a sample cup and sealed. The air is removed from the sample cup and replaced with pure oxygen. The cup is then placed in the calorimeter with a known amount of water covering it. The initial temperature of the water is measured, and then the sample is ignited electrically. The rise in the temperature is measured, and the number of calories of energy that is released is calculated. A *calorie* is the amount of energy needed to raise the temperature of 1 gram of water 1 degree Celsius. The complete combustion of a large kitchen match, for example, gives you about one kilocalorie of heat. (See Chapter 2 for the basics of calories and measuring energy.)

The caloric content of foods can be determined in exactly the same fashion. Chemists report the results in calories or kilocalories, while nutritionists report the results in nutritional Calories. A nutritional Calorie is equal to a chemist's kilocalorie (1,000 calories). A 300 Calorie candy bar produces 300,000 calories of energy. Unfortunately, not all that energy is required immediately, so some is stored in compounds such as fats. I'm carrying around the result of *many* candy bars.