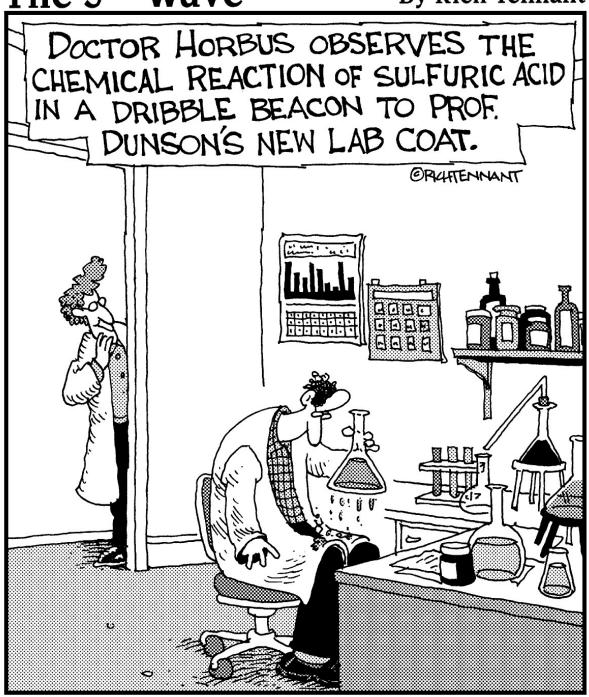
# Part II A Cornucopia of Chemical Concepts



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 those reactions and bonds are what this part is all about.

These chapters introduce you to chemical reactions. I then introduce you to the mole. No, not the small furry animal that burrows holes in your backyard, but the concept that unites the microscopic world of atoms and molecules with the macroscopic world of grams and metric tons. In this part I also show you solutions, how to make them and how to calculate their concentrations. To heat things up, I introduce you to thermochemistry. Chemical reactions either give off energy or absorb energy, and in the thermochemistry chapter I show you how to calculate how much heat is given off or absorbed. Finally, I cover acids and bases, discussing their properties, including their sour and bitter tastes, along with the concept of pH. I don't think this part will leave a sour taste in your mouth. In fact, I don't see how you can fail to react to it.

#### <u>Chapter 7</u>

## Chemical Cooking: Chemical Reactions

#### In This Chapter

- Differentiating between reactants and products
- Applying energy to set off reactions
- Taking a look at different kinds of reactions
- Keeping track of atoms with balanced reactions

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*, and it depends on chemical reactions. I always thought that being a synthetic organic chemist and working on the creation of new and potentially important compounds would be neat. 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, the different types of chemical reactions, and how to write a balanced chemical equation.

# Knowing 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 20. Instead, you create new substances 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:

#### Reactants $\rightarrow$ 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. This is not a good thing!) 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.

# **Understanding How Reactions Occur: The 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. Energy is required to break a bond between atoms and energy is released when a bond is made. The *collision theory* states that the collision between the molecules can provide the energy needed to break the necessary bonds so that new bonds can be formed. The collision takes place at the right spot and transfers sufficient energy. The following sections provide three examples of what can happen during a collision.

#### Eyeing a one-step collision example

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 situation also occurs with molecular collisions and reactions. Sometimes, even if a collision takes place, 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.

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

$$A-B + C \rightarrow C-A + B$$

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 happens. 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 enough energy may 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 A-B bond and the forming of the C-A bond as "squiggly" bonds):

$$C \sim A \sim B \rightarrow C - A + B$$

So in order for this reaction to occur, a collision between C and A-B must occur 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.

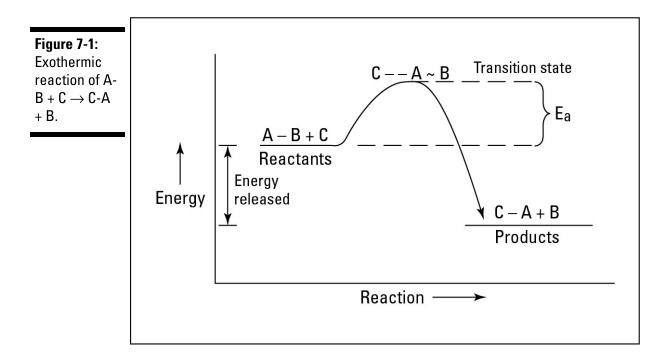
If instead of having a simple *A-B* molecule, you have a large complex molecule, like a protein or a polymer, then the likelihood of *C* colliding at the reactive site is much smaller. You may have a lot of collisions, but few at the reactive site. This reaction will probably be much slower than the simple case.

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 before the reactants become the 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.

#### Considering an exothermic example

Imagine that the hypothetical reaction A-B + C  $\rightarrow$  C-A + B is *exothermic* — a reaction in which thermal energy 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 7-1 shows an energy diagram of this reaction.

In Figure 7-1, E<sub>a</sub> 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 7-1, 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.



Some reactions may give off energy but not thermal energy. An example is light sticks. You mix two chemical solutions by flexing the light stick, and the resulting product glows — it gives off light but not heat. Another example is fireflies, which mix two chemicals in their bodies and give off light. (I remember catching fireflies in a jar for a nightlight many evenings in North Carolina. Ah, the good old days!) These reactions that give off energy are *exergonic*. If that energy is in the form of heat, the reaction is subclassified as exothermic.

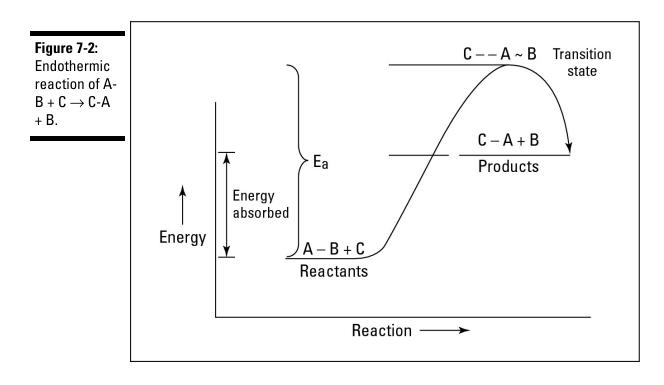
#### Looking at an endothermic example

Suppose that the hypothetical reaction A-B + C  $\rightarrow$  C-A + B is endothermic — a reaction in which heat is absorbed — so the reactants are at a lower energy state than the products. Figure 7-2 shows an energy diagram of this reaction.

Just as in the exothermic-reaction energy diagram shown in Figure 7-1, 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 some of 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. But although both endothermic and exothermic reactions require activation energy, exothermic reactions release thermal energy, and endothermic reactions absorb it.

Cooking is a great example of an endothermic reaction. That ground beef isn't going to be a delicious hamburger unless you cook it. You have to continually supply energy in order for the chemical reactions called cooking to take place. Cold packs that athletic trainers use to treat injuries are another example of an endothermic reaction. Two solutions in the pack are mixed, and the pack absorbs thermal energy from the surroundings. The surroundings therefore become colder.



Other reactions may absorb energy but not necessarily heat. For example, some reactions absorb light energy in order to react. The general term that chemists use to describe reactions

that absorb energy (heat or otherwise) is *endergonic*. Endothermic reactions are a subset of endergonic reactions.

### Identifying Different Types of Reactions

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

The following sections provide more insight into these types of reactions.

#### **Combination reactions**

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

$$2 \operatorname{Na}(s) + \operatorname{Cl}_2(g) \rightarrow 2 \operatorname{NaCl}(s)$$

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 13 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 aqueous 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 happens. But how do you know which metal is the most active? An activity table lists the activity of metals. Table 7-1 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 7-1 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:

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

I've written this reaction as a molecular equation, showing all species in the molecular/atomic 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 13 for a more complete discussion of ionic bonding.)

To show the reaction and production of ions in a reaction, you can write an *ionic equation*, like the following:

$$\operatorname{Zn}(s) + \operatorname{Cu}^{2+}(aq) + \operatorname{SO}_4^{2-}(aq) \to \operatorname{Zn}^{2+}(aq) + \operatorname{SO}_4^{2-}(aq) + \operatorname{Cu}(s)$$
 (ionic equation)

Notice that the sulfate ion,  $SO_4^{2-}$ , doesn't change 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 format is called the *net-ionic equation*:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
 (net-ionic equation)

#### **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) is 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:

$$\text{KCl}(aq) + \text{AgNO}_3(aq) \rightarrow \text{AgCl}(s) + \text{KNO}_3(aq)$$
 (molecular equation)   
 $\text{K}^*(aq) + \text{Cl}^-(aq) + \text{Ag}^*(aq) + \text{NO}_3^-(aq) \rightarrow \text{AgCl}(s) + \text{K}^*(aq) + \text{NO}_3^-(aq)$  (ionic equation)   
 $\text{Cl}^-(aq) + \text{Ag}^*(aq) \rightarrow \text{AgCl}(s)$  (net-ionic equation)

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 13. It tells you 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 7-2 gives the solubility of selected ionic compounds.

#### **Table 7-2 Solubility of Selected Ionic Compounds**

Water Soluble	Water Insoluble
All chlorides, bromides, iodides	Except those of Ag <sup>+</sup> , Pb <sup>2+</sup> , Hg <sub>2</sub> <sup>2+</sup>
All compounds of NH <sub>4</sub> <sup>+</sup>	Oxides
All compounds of alkali metals	Sulfides
All acetates	Most phosphates
All nitrates	Most hydroxides
All chlorates	-
All sulfates	Except PbSO <sub>4</sub> , BaSO <sub>4</sub> and SrSO <sub>4</sub>

To use Table 7-2, 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 solubility of the possible products in the table. If the compound is insoluble, it precipitates. If it is soluble, it remains 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:

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

$$2 \text{ H}^+(aq) + \text{SO}_4^{\ 2-}(aq) + 2 \text{ Na}^+(aq) + 2 \text{ OH}^-(aq) \rightarrow 2 \text{ Na}^+(aq) + \text{SO}_4^{\ 2-}(aq) + 2 \text{ H}_2\text{O}(l) \text{ (ionic equation)}$$

$$2 \text{ H}^+(aq) + 2 \text{ OH}^-(aq) \rightarrow 2 \text{ H}_2\text{O}(l) \text{ or } \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$$
 (net-ionic equation)

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 11.

#### **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 molecular 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, which I discuss in the following section.

#### **Redox reactions**

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

$$2 \text{ Na}(s) + \text{Cl}_2(g) \rightarrow 2 \text{ NaCl}(s)$$

$$C(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$$

$$Zn(s) + \text{CuSO}_4(aq) \rightarrow \text{ZnSO}_4(aq) + \text{Cu}(s)$$

The preceding reactions are examples of other types of reactions (such as combination, combustion, and single-replacement reactions), but they're all also 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.

#### **Balancing Chemical Reactions**

If you carry out a chemical reaction, carefully sum up the masses of all the reactants, and compare that 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 must 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.

#### **Balancing ammonia production**

My favorite reaction is called the *Haber process*, a method for preparing ammonia (NH<sub>3</sub>) by reacting nitrogen gas with hydrogen gas. This reaction is my favorite because it helps to feed the world. The ammonia that's produced is used to produce ammonium nitrate and ammonium phosphate, both of which are synthetic fertilizers that have allowed the increased production of food. Here's the equation:

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

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  $2 H_2 O_2$ , it means you have two water molecules:

$$2 H_2O = H_2O + H_2O$$

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:

$$2 H_2O$$
 =  $H_2O + H_2O$   
=  $2 H + 1 O + 2 H + 1 O$   
=  $4 H + 2 O$ 

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, waiting until the end to balance hydrogen atoms or oxygen atoms is a good idea based on many years of experience; 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.

This equation also balances with coefficients of 2, 6, and 4 instead of 1, 3, and 2. In fact, any multiple of 1, 3, and 2 balances the equation, but chemists always show the lowest whole-number ratio (see the discussion on empirical formulas in Chapter 14 for details).

#### Flicking the lighter

In this section, follow the steps to balance the 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.)

#### 1. Start with the unbalanced reaction written in a molecular equation.

The equation of burning butane with excess oxygen available is

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

#### 2. Balance the carbon atoms first.

You want to wait until the end to balance hydrogen and oxygen atoms.

You have 4 carbon atoms on the left and 1 carbon atom on the right, so add a coefficient of 4 in front of the carbon dioxide:

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

#### 3. When all non-hydrogen and non-oxygen atoms are balanced, balance the hydrogen atoms.

Carbon is the only other atom in this example, so you can move on to hydrogen now. 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:

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

#### 4. Balance 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?

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

#### 5. Multiple all coefficients in the equation to get the lowest whole-number ratio of coefficients.

For this example, multiply the entire equation by 2 (just the coefficients, please) in order to generate whole numbers:

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

Multiplying every coefficient by 2 (don't touch the subscripts!) gives:

$$2 C_4 H_{10}(g) + 13 O_2(g) \rightarrow 8 CO_2(g) + 10 H_2O(g)$$

### 6. Check the atom count on both sides of the equation to ensure that the equation is balanced and 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, but I'll save that for another time (or another book).

#### **Chapter 8**

#### The Mole: Can You Dig It?

#### In This Chapter

- Figuring out how to count atoms and molecules by their weight
- ► Understanding how moles help you with chemical calculations
- Working with moles in practical applications

One of the many things chemists do is make new substances, a process called *synthesis*. And a logical question they ask is "How much?"

"How much of this reactant do I need to make this much product?" "How much product can I make with this much reactant?" In order to answer these questions, chemists must be able to take a balanced chemical equation, expressed in terms of atoms and molecules, and convert it to grams or pounds or tons — some type of unit they can actually weigh out in the lab. The mole concept enables chemists to move from the microscopic world of atoms and molecules to the real world of grams and kilograms and is one of the most important central concepts in chemistry. In this chapter, I introduce you to Mr. Mole.

#### **Counting Particles by Massing**

Suppose that you have a job packing 1,000 nuts and 1,000 bolts in big bags, and you get paid for each bag you fill. So what's the most efficient and quickest way of counting out nuts and bolts? Determine the mass of a hundred, or even ten, of each, and then figure out the mass of a thousand of each. Fill up the bag with nuts until it equals the mass you figured for 1,000 nuts. After you have the correct amount of nuts, use the same process to fill the bag with bolts. In other words, count by massing; that's one of the most efficient ways of counting large numbers of objects.

In chemistry, you count very large numbers of particles, such as atoms and molecules. To count them efficiently and quickly, you need to use the count-by-massing method, which means you need to know the masses of individual atoms and molecules. You can get the mass of the individual atoms on the periodic table, but what about the mass of the compounds? Well, you can simply add together the masses of the individual atoms in the compound to figure the molecular mass or formula mass. (Molecular masses refer to covalently bonded compounds, and formula masses refer to both ionic and covalent compounds. Check out Chapters 13 and 14 for details on ionic and covalent bonds.)

Water, H<sub>2</sub>O, is composed of two hydrogen atoms and one oxygen atom. By looking on the periodic table, you can find that one hydrogen atom equals 1.0079 amu and one oxygen atom weighs 15.999 amu (*amu* stands for *atomic mass units* — see Chapter 4 for details). To calculate the molecular mass of water, you simply add together the atomic masses of two hydrogen atoms and one oxygen atom:

 $2 \times 1.0079$  amu = 2.016 amu (two hydrogen atoms)

 $1 \times 15.999$  amu = 15.999 amu (one oxygen atom)

2.016 amu + 15.999 amu = 18.015 amu (the mass of a water molecule)

Now try a little harder one. Calculate the formula mass of aluminum sulfate,  $Al_2(SO_4)_3$ . In this salt, you have 2 aluminum atoms, 3 sulfur atoms, and 12 oxygen atoms. After you find the individual masses of the atoms on the periodic table, you can calculate the formula mass like this:

 $(2 \text{ Al} \times 26.982 \text{ amu/Al}) + (3 \text{ S} \times 32.066 \text{ amu/S}) + (12 \text{ O} \times 15.999 \text{ amu/O})$ 

= 342.150 amu for  $Al_2(SO_4)_3$ 

#### **Using Moles to Count**

When people deal with objects, they often think in terms of a convenient amount. For example, when a woman buys earrings, she normally buys a pair of them. When a man goes to the grocery store, he buys eggs by the dozen. And when I go the office supply store, I buy copy paper by the ream.

People use words to represent numbers all the time — a pair is 2, a dozen is 12, and a ream is 500. All these words are units of measure, and they're convenient for the objects they're used to measure. Rarely would you buy a ream of earrings or a pair of paper.

Likewise, when chemists deal with atoms and molecules, they need a convenient unit that takes into consideration the very small size of atoms and molecules. The *mole* is just such a unit. The following sections dive deeper into how to count with a mole.

### Looking up Avogadro's number: Not in the phone book

The word *mole* stands for a number —  $6.022 \times 10^{23}$ . It's commonly called *Avogadro's number*, named for Amedeo Avogadro, the scientist who laid the groundwork for the mole principle.

Now a mole —  $6.022 \times 10^{23}$  — is a really *big* number. When written in longhand notation, it's

602,200,000,000,000,000,000,000

And *that* is why chemists like scientific notation.

If you had a mole of marshmallows, it would cover the United States to a depth of about 600 miles. A mole of rice grains would cover the land area of the world to a depth of about 75 meters. And a mole of moles . . . no, I don't even want to think about that!

Avogadro's number stands for a certain number of *things*. Normally, those things are atoms and molecules. So the mole relates to the microscopic world of atoms and molecules. But how does it relate to the macroscopic world where I work?

The answer is that a *mole* (abbreviated as *mol*) is also the number of particles in exactly 12 grams of a particular isotope of carbon (C-12). So if you have exactly 12 grams of  $^{12}$ C, you have  $6.022 \times 10^{23}$  carbon atoms, which is also a mole of  $^{12}$ C

atoms. For any other element, a mole is the atomic mass expressed in grams. And for a compound, a mole is the formula (or molecular) mass in grams.

#### **Putting moles to work**

The weight of a water molecule is 18.015 amu (see the section "Counting Particles by Massing" for how to calculate the mass of compounds). Because a mole is the formula (or molecular) mass in grams of a compound, you can now say that the mass of a mole of water is 18.015 grams. You can also say that 18.015 grams of water contains  $6.022 \times 10^{23} \, \text{H}_2\text{O}$  molecules, or a mole of water. And the mole of water is composed of two moles of hydrogen and one mole of oxygen.

The mole is the bridge between the microscopic and macroscopic worlds.

 $6.022\times10^{23}$  particles  $\leftrightarrow$  mole  $\leftrightarrow$  atomic/formula/molecular mass in grams

If you have any one of the three things — particles, moles, or grams — then you can calculate the other two.

Suppose you want to know how many water molecules are in 5.50 moles of water. You can set up a problem like this:

$$\frac{5.50 \text{ mol}}{1} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = 3.31 \times 10^{24} \text{molecules}$$

Or suppose that you want to know how many moles are in 25.0 grams of water. You can set up the problem like this:

$$\frac{25.0 \text{ g H}_2\text{O}}{1} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} = 1.39 \text{ moles H}_2\text{O}$$

You can even go from grams to particles by going through the mole.

For example, how many molecules are there in 100.0 grams of carbon dioxide?

To solve this question, do the following:

#### 1. Determine the molecular mass of $CO_2$ by looking at the periodic table.

The periodic table shows that one carbon atom equals 12.011 amu and one oxygen atom weighs 15.999 amu.

2. Figure the molecular mass.

For this example, your calculations look like this:  $[(1~C\times12.011~g/mol~C) + (2~O\times15.999~g/mol~O)] = 44.01~g/mol~CO_2$ 

3. Work the problem and solve.

$$\frac{100.0 \text{ g CO}_2}{1} \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol}} = 1.368 \times 10^{24} \text{ CO}_2 \text{ molecules}$$

And it's just as easy to go from particles to moles to grams.

#### **Calculating empirical formulas**

You can use the mole concept to calculate the empirical formula of a compound using the *percentage composition* data for that compound — the percentage by mass of each element in the compound. (The *empirical formula* indicates the different types of elements in a molecule and the lowest whole-number ration of each kind of atom in the molecule. See Chapter 14 for details.)

When I try to determine the empirical formula of a compound, I often have percentage data available. The determination of the percentage composition is one of the first analyses that a chemist does in learning about a new compound. For example, suppose I determine that a particular compound has the following weight percentage of elements present:

26.4% Na

36.8% S

36.8% O

Because I'm dealing with percentage data (amount per hundred), I assume that I have 100 grams of the compound so that my percentages can be used as masses. I then convert each mass to moles, like this:

$$\frac{26.4 \text{ g Na}}{1} \times \frac{1 \text{ mol Na}}{22.99 \text{ g}} = 1.15 \text{ mol Na}$$

$$\frac{36.8 \text{ g S}}{1} \times \frac{1 \text{ mol S}}{32.07 \text{ g}} = 1.15 \text{ mol S}$$

$$\frac{36.8 \text{ g O}}{1} \times \frac{1 \text{ mol O}}{16.00 \text{ g}} = 2.30 \text{ mol O}$$

Now I can write an empirical formula:

$$Na_{1.15}S_{1.15}O_{2.30}$$

I know that my subscripts have to be whole numbers, so I divide each of these by the smallest common factor, 1.15:

$$\frac{1.15 \text{ Na}}{1.15} = 1 \text{ Na}$$
  $\frac{1.15 \text{ S}}{1.15} = 1 \text{ S}$   $\frac{2.30 \text{ O}}{1.15} = 2 \text{ O}$ 

I end up with an empirical formula of NaSO<sub>2</sub>. (If a subscript is 1, it's not shown.)

I can then calculate a mass for the empirical formula by adding together the atomic masses on the periodic table of 1 sodium (Na), 1 sulfur (S), and 2 oxygen (O). The sum gives me an empirical formula mass of 87.056 grams.

Suppose, however, that in another experiment I determined the actual molecular mass of this compound to be 174.1112 grams. By dividing 174.1112 grams by 87.056 grams (actual molecular mass by the empirical formula mass), I get 2. That number means the molecular formula is twice the empirical formula, so the compound is actually  $Na_2S_2O_4$ .

## **Understanding the Role of Moles in Chemical Reactions**

I think one of the reasons I enjoy being a chemist is that I like to cook. I see a lot of similarities between cooking and chemistry (except that chemists shouldn't lick the spoon). A chemist takes certain things called *reactants* and makes something new from them. A cook does the same thing. He or she takes certain things called ingredients and makes something new from them. And both the chemist and the cook follow a set of directions: The cook follows a recipe while the chemist follows the balanced chemical reaction. And both can scale up or down to produce more or less product. In the following sections I show you how.

#### Making the calculations

If you know the formula weight of the reactants and product, you can calculate how much you need and how much you'll get. For example, check out the *Haber reaction*, which is a method of preparing ammonia (NH<sub>3</sub>) by reacting nitrogen gas with hydrogen gas:

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

1 mole + 3 moles  $\rightarrow$  2 moles

All you need to do is figure the molecular weights of each reactant and product and then incorporate the weights into the equation. Use the periodic table to find the weights of the atoms and the compound (see the section "Counting Particles by Massing," earlier in this chapter, for the directions) and multiply those numbers by the number of moles, like this:

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

 $1~\text{mol} \times 28.014~\text{g/mol} + 3~\text{mol} \times 2.016~\text{g/mol} \rightarrow 2~\text{mol} \times 17.031~\text{g/mol}$ 

In Chapter 7, I use this reaction for various examples (like I said, it's my *favorite* reaction) and explain that you can read the reaction like this: 1 molecule of nitrogen gas reacts with 3 molecules of hydrogen gas to yield 2 molecules of ammonia.

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

1 molecule + 3 molecules  $\rightarrow$  2 molecules

Now you can scale everything up by a factor of 12:

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

1 dozen molecules + 3 dozen molecules  $\rightarrow$  2 dozen molecules

You can even scale it up by 1,000:

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

1,000 molecules + 3,000 molecules  $\rightarrow$  2,000 molecules

Or how about a factor of  $6.022 \times 10^{23}$ :

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

 $6.022\times 10^{23}$  molecules +  $3(6.022\times 10^{23}$  molecules)  $\rightarrow 2(6.022\times 10^{23}$  molecules)

Wait a minute! Isn't  $6.022 \times 10^{23}$  a mole? So you can write the equation like this:

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

1 mole + 3 moles  $\rightarrow$  2 moles

That's right — not only can those coefficients in the balanced chemical equation represent atoms and molecules, but they can also represent the number of moles.

Suppose you want to figure out how many grams of ammonia you can produce if you react 60.0 g of hydrogen gas with excess nitrogen.

Remember that the balanced chemical equation gives the mole relationship of the reactants and products, and if you have moles you have grams.

1. Take the grams of hydrogen gas (recall that it is diatomic) and convert it to moles using its molar mass (mass of 1 mole):

$$\frac{60.0 \text{ g H}_2}{1} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g}}$$

2. Convert the mole of hydrogen gas to moles of ammonia, using the coefficients in the balanced chemical equation:

$$\frac{60.0 \text{ g H}_2}{1} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g}} \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2}$$

3. Convert from moles of ammonia to grams of ammonia using the molar mass and solve the equation.

$$\frac{60.0 \text{ g H}_2}{1} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g}} \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} \times \frac{17.031 \text{ g NH}_3}{1 \text{ mol}} = 338 \text{ g NH}_3$$

### Determining what you need and what you'll get: Reaction stoichiometry

After you have the weight relationships in place, you can do some stoichiometry problems. *Stoichiometry* refers to the mass relationship in balanced chemical equations.

Look at my favorite reaction — you guessed it — the Haber process:

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

Suppose that you want to know how many grams of diatomic hydrogen gas will be needed to fully react with 75.00 grams of nitrogen.

The mole concept is the key. The coefficients in the balanced equation are not only the number of individual atoms or molecules but also the number of moles.

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

1 mole + 3 moles  $\rightarrow$  2 moles

1. Convert the 75.00 grams of nitrogen to moles of nitrogen.

$$\frac{75.00 \text{ g N}_2}{1} \times \frac{1 \text{ mol N}_2}{28.014 \text{ g}}$$

2. Use the ratio of the moles of hydrogen to the moles of nitrogen from the balanced equation to convert to moles of hydrogen.

$$\frac{75.00 \text{ g N}_2}{1} \times \frac{1 \text{ mol N}_2}{28.014 \text{ g}} \times \frac{3 \text{ mol H}_2}{1 \text{ mol N}_2}$$

3. Take the moles of hydrogen and convert to grams, and then solve the equation.

$$\frac{75.00 \text{ g N}_2}{1} \times \frac{1 \text{ mol N}_2}{28.014 \text{ g}} \times \frac{3 \text{ mol H}_2}{1 \text{ mol N}_2} \times \frac{2.016 \text{ g H}_2}{1 \text{ mol}} = 16.19 \text{ g H}_2$$

The ratio of the moles  $H_2/\text{mol }N_2$  is called a *stoichiometric ratio*. This ratio enables you to convert from the moles of one substance in a balanced chemical equation to the moles of another substance.

By the way, can you figure out how much ammonia is produced? One way is to construct a set-up similar to the preceding one, but convert from moles of nitrogen to moles of ammonia and then to grams of ammonia. The stoichiometric ratio will be different (along with the molar mass used). Another way is to reason that 75.00 grams of nitrogen reacted with 16.19 grams of hydrogen to produce 91.19 grams of ammonia (75.00 g + 16.19 g = 91.19 g).

Getting tired of the Haber process? (Me? *Never.*) Take a look at another reaction — the reduction of rust  $(Fe_2O_3)$  to iron metal by treatment with carbon (coke — a fuel, not the drink). The balanced chemical reaction looks like this:

$$2 \text{ Fe}_2\text{O}_3(s) + 3 \text{ C}(s) \rightarrow 4 \text{ Fe}(s) + 3 \text{ CO2}(g)$$

When you get ready to work stoichiometry problems, you *must* start with a balanced chemical equation. If you don't have it to start with, you've got to go ahead and balance the equation.

In this example, the formula weights you need are

- **Fe₂O₃:** 159.70 g/mol
- **✓ C:** 12.01 g/mol
- **✓ Fe:** 55.85 g/mol
- **CO₂:** 44.01 g/mol

Suppose that you want to know how many grams of carbon it takes to react with 1.000 kilogram of rust.

You need to convert the kilogram of rust to grams and convert the grams to moles of rust. Then you can use a stoichiometric ratio to convert from moles of rust to moles of carbon and finally to grams. The equation looks like this:

$$\frac{1.000 \text{ kg Fe}_2\text{O}_3}{1} \times \frac{1,000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{159.70 \text{ g}} \times \frac{3 \text{ mol C}}{2 \text{ mol Fe}_2\text{O}_3} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 112.8 \text{ g C}$$

You can even calculate the number of carbon atoms it takes to react with that 1.000 kilogram of rust. Basically, you use the same conversions, but instead of converting from moles of carbon to grams, you convert from moles of carbon atoms using Avogadro's number:

$$\frac{1.000 \text{ kg Fe}_2\text{O}_3}{1} \times \frac{1,000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Fe}_2\text{O}_3}{159.70 \text{ g}} \times \frac{3 \text{ mol C}}{2 \text{ mol Fe}_2\text{O}_3} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol C}} = 5.656 \times 10^{24} \text{ atoms of C}$$

Now I want to show you how to calculate the number of grams of iron produced from reacting 1.000 kilogram of rust with excess carbon. It's the same basic process as before — kilograms of rust to grams of rust to moles of iron to grams of iron:

$$\frac{1.000~kg~Fe_{2}O_{3}}{1}\times\frac{1,000~g}{1~kg}\times\frac{1~mol~Fe_{2}O_{3}}{159.70~g}\times\frac{4~mol~Fe}{2~mol~Fe_{2}O_{3}}\times\frac{55.85~g~Fe}{1~mol~Fe}=699.5~g~Fe$$

So you predict that you'll get 699.5 grams of iron metal formed. What if, however, you carry out this reaction and only get 525.0 grams of iron metal formed? Several reasons may cause you to produce less than you expect, such as sloppy technique or impure reactants. It may also be quite likely that the reaction is an equilibrium reaction, and you'll never get 100 percent conversion from reactant to products. (Equilibrium reactions don't use up all the reactants — topic for a new book.) Wouldn't it be nice if you had a way to label the efficiency of a particular reaction? You do. It's called the percent yield.

# Figuring out the bang for your buck: Percent yield

In almost any reaction, you're going to produce less than expected. You may produce less because most reactions are equilibrium reactions or because some other conditions come into play. Chemists can get an idea of the efficiency of a reaction by calculating the *percent yield* for the reaction using this equation:

% yield = 
$$\frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

The *actual yield* is how much of the product you get when you carry out the reaction. The *theoretical yield* is how much of the

product you *calculate* you'll get. The ratio of these two yields gives you an idea about how efficient the reaction is. For the reaction of rust to iron (see preceding section), your theoretical yield is 699.5 grams of iron; your actual yield is 525.0 grams. Therefore, the percent yield is

% yield = 
$$\frac{525.0 \text{ g}}{699.5 \text{ g}} \times 100\% = 75.05\%$$

A percent yield of about 75 percent isn't too bad, but chemist and chemical engineers would rather see 90+ percent. One plant using the Haber reaction has a percent yield of better than 99 percent. Now that's efficiency!

# Running out of something and leaving something behind: Limiting reactants

I love to cook, and I'm always hungry. So I want to talk about making some ham sandwiches. Because I'm a chemist, I can write an equation for a ham sandwich lunch:

2 pieces of bread + 1 ham slice + 1 cheese slice  $\rightarrow$  1 ham sandwich

Suppose I check my supplies and find that I have 12 pieces of bread, 5 slices of ham, and 10 slices of cheese. How many sandwiches can I make? I can make 5, of course. I have enough bread for 6 sandwiches, enough ham for 5, and enough cheese for 10. But I'm going to run out of ham first — I'll have bread and cheese left over. And the ingredient I run out of first really limits the amount of product (sandwiches) I'll be able to make; it can be called the *limiting ingredient*.

The same is true of chemical reactions. Normally, you run out of one of the reactants and have some others left over. (In some of the problems sprinkled throughout this chapter, I tell you which reactant is the limiting one by saying you have *an excess* of the other reactant(s).)

In this section, I show you how to calculate which reactant is the limiting reactant.

Here is a reaction between ammonia and oxygen:

$$4 \text{ NH}_3(g) + 5 \text{ O}_2(g) \rightarrow 4 \text{ NO}(g) + 6 \text{ H}_2\text{O}(l)$$

Suppose that you start out with 100.0 grams of both ammonia and oxygen, and you want to know how many grams of NO (nitrogen monoxide, sometimes called nitric oxide) you can produce.

You must determine the limiting reactant and base your stoichiometric calculations on it.

A sure way to know that you have a limiting reactant problem is when you're given amounts of more than one reactant. In order to figure out which reactant is the limiting reactant, you can calculate the mole-to-coefficient ratio: You can calculate the number of moles of both ammonia and oxygen, and then you divide each by their coefficient in the balanced chemical equation. The one with the smallest mole-to-coefficient ratio is the limiting reactant. For the reaction of ammonia to nitric oxide, you can calculate the mole-to-coefficient ratio for the ammonia and oxygen like this:

$$\frac{100.0 \text{ g NH}_3}{1} \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g}} = 5.87 \text{ mol} \div 4 = 1.47$$

$$\frac{100.0 \text{ g O}_2}{1} \times \frac{1 \text{ mol O}_2}{32.00 \text{ g}} = 3.13 \text{ mol} \div 5 = 0.625$$

Ammonia has a mole-to-coefficient ratio of 1.47, and oxygen has a ratio of 0.625. Because oxygen has the lowest ratio, oxygen is the limiting reactant and will determine how much NO(g) will be produced. You'll need to base your calculations on the limiting reactant, the oxygen. Now it's just another stoichiometry problem. You convert grams of oxygen to moles, to moles of NO, and to grams NO:

$$\frac{100.0 \text{ g O}_2}{1} \times \frac{1 \text{ mol O}_2}{32.00 \text{ g}} \times \frac{4 \text{ mol NO}}{5 \text{ mol O}_2} \times \frac{30.01 \text{ g NO}}{1 \text{ mol NO}} = 75.03 \text{ g NO}$$

That 75.03 grams NO is your theoretical yield. But you can even calculate the amount of ammonia left over. With the following equation, you can figure the amount of ammonia consumed:

$$\frac{100.0 \text{ g O}_2}{1} \times \frac{1 \text{ mol O}_2}{32.00 \text{ g}} \times \frac{4 \text{ mol NH}_3}{5 \text{ mol O}_2} \times \frac{17.03 \text{ g NH}_3}{1 \text{ mol NH}_3} = 42.58 \text{ g NH}_3$$

In this equation, convert from grams of oxygen gas to moles of oxygen gas and then to moles of ammonia and finally to grams of ammonia.

You started with 100.0 grams of ammonia, and you used 42.58 grams of it. The difference (100 grams – 42.58 grams = 57.42 grams) is the amount of ammonia left over.

## **Chapter 9**

## **Mixing Matter Up: Solutions**

#### In This Chapter

- ▶ Differentiating between solutes, solvents, and solutions
- Working with the different kinds of solution concentration units
- Discovering how particle quantities can make all the difference
- ► Meeting the middle child of the solutions family: Colloids

You encounter solutions all the time in everyday life. The air you breathe is a solution. That sports drink you use to replenish your electrolytes is a solution. That soft drink *and* that hard drink are both solutions. Your tap water is most likely a solution, too. In this chapter, I show you some of the properties of solutions. I introduce you to the different ways chemists represent a solution's concentration, and I tell you about the *colligative* properties of solutions (the properties of solutions that depend only on the number of particles present, not their type) and relate them to ice-cream making and antifreeze. So sit back, sip on your solution of choice, and read all about solutions.

# Getting Your Definitions Straight: Solutes, Solvents, and Solutions

A *solution* is a homogeneous mixture, meaning that its properties are the same throughout. If you dissolve sugar in water and mix it really well, for example, your mixture is basically the same no matter where you sample it.

A solution is composed of a solvent and one or more solutes. The *solvent* is the substance that doesn't change state and is present in the largest amount, and the *solute* is the substance that changes state and is present in the lesser amount. You can determine which is which based on the quantities most of the time, but in a few cases of extremely soluble salts, such as lithium chloride, more than 5 grams of salt can be dissolved in 5 milliliters of water. However, water is still considered the solvent, because it's the species that has not changed state.

A solution can have more than one solute. If you dissolve salt in water to make a brine solution and then dissolve some sugar in the same solution, you have two solutes, salt and sugar. You still have only one solvent, though — water.

When I talk about solutions, most people think of liquids. But there can also be solutions of gases. Our atmosphere, for example, is a solution. Because air is almost 79 percent nitrogen, nitrogen is considered the solvent, and the oxygen, carbon dioxide, and other gases are considered the solutes. Solids can also make solutions. Alloys, for example, are solutions of one metal in another metal. Brass is a solution of zinc in copper.

## Discussing solubility: How much solute will dissolve

Why do some things dissolve in one solvent and not in another? For example, oil and water don't mix to form a solution, but oil dissolves in gasoline. A general rule of solubility says that *like-dissolves-like* in regards to polarity of both the solvent and

solutes. Water, for example, is a polar material; it's composed of polar covalent bonds with the positive and negative ends of the molecule. (For a rousing discussion of water and its polar covalent bonds, see Chapter 14.) Water dissolves polar solutes, such as salts and alcohols. Oil, however, is composed of largely nonpolar bonds. So water doesn't act as a suitable solvent for oil.

You know from your own experiences, I'm sure, that only so much solute can be dissolved in a given amount of solvent. You probably have been guilty of putting far too much sugar in iced tea. No matter how much you stir, there's some undissolved sugar at the bottom of the glass. The reason is that the sugar has reached its maximum solubility in water at that temperature. *Solubility* is the maximum amount of solute that will dissolve in a given amount of a solvent at a specified temperature. Solubility normally has the units of grams solute per 100 milliliters of solvent (g/100 mL).

The solubility is related to the temperature of the solvent. For solids dissolving in liquids, solubility normally increases with increasing temperature. So if you heat that iced tea, the sugar at the bottom readily dissolves. However, for gases dissolving in liquids, such as oxygen dissolving in lake water, the solubility goes down as the temperature increases. This is the basis of *thermal pollution*, the addition of heat to water that decreases the solubility of the oxygen and affects the aquatic life.

### **Exploring saturation**

A *saturated* solution contains the maximum amount of dissolved solute possible at a given temperature. If the solution has less than the maximum amount, it's called an *unsaturated* solution. Sometimes, under unusual circumstances, the solvent may

actually dissolve more than its maximum amount and become *supersaturated*. This supersaturated solution is unstable, though, and sooner or later solute will precipitate (form a solid) until the saturation point has been reached.

If a solution is unsaturated, then the amount of solute that is dissolved may vary over a wide range. A couple of rather indefinite terms describe the relative amount of solute and solvent that you can use:

- You can say that the solution is *dilute*, meaning that, relatively speaking, it contains very little solute per given amount of solvent. If you dissolve 0.01 grams of sodium chloride in a liter of water, for example, the solution is dilute. I once asked some students to give me an example of a dilute solution, and one replied "A \$1 margarita." She was right a lot of solvent (water) and a very little solute (tequila) are used in her example.
- A solution may be *concentrated*, containing a large amount of solute per the given amount of solvent. If you dissolve 200 grams of sodium chloride in a liter of water, for example, the solution is concentrated.

But suppose you dissolve 25 grams or 50 grams of sodium chloride in a liter of water? Is the solution dilute or concentrated? These terms don't hold up very well for most cases. And consider the case of IV solutions — they *must* have a very precise amount of solute in them, or the patient is in danger. So you must have a quantitative method to describe the relative amount of solute and solvent in a solution. Such a method exists — solution concentration units.

# Focusing on Solution Concentration Units

You can use a variety of solution concentration units to quantitatively describe the relative amounts of the solute(s) and the solvent. In everyday life, percentage is commonly used. In chemistry, *molarity* (the moles of solute per liter of solution) is the solution concentration unit of choice. In certain circumstances, though, another unit, *molality* (the moles of solute per kilogram of solvent), is used. And I use parts per million or parts per billion when I discuss pollution control. The following sections cover some of these concentration units.

## **Percent composition: Three different ratios**

You probably have looked at a bottle of vinegar and seen "5% acetic acid," a bottle of hydrogen peroxide and seen "3% hydrogen peroxide," or a bottle of bleach and seen "5% sodium hypochlorite." Those percentages are expressing the concentration of that particular solute in each solution. *Percentage* is the amount per one hundred. Depending on the way you choose to express the percentage, the units of amount per one hundred vary. Three different percentages are commonly used:

- ✓ Mass/mass (m/m) percentage
- ✓ Mass/volume (m/v) percentage
- ✓ Volume/volume (v/v) percentage

Unfortunately, although the percentage of solute is often listed, the method (m/m, m/v, v/v) is not. I normally assume that the

method is weight/weight, but I'm sure you know about assumptions.

In the following sections I give some examples of solutions with these percentages. Most of the solutions are *aqueous*, solutions in which water is the solvent.

#### Mass/mass percentage

In *mass/mass percentage*, or *mass percentage*, the mass of the solute is divided by the mass of the solution and then multiplied by 100 to get the percentage. Another term that is sometimes used is *mass percentage* (*mass/mass percentage*). Normally the weight unit is grams. Mathematically, it looks like this:

$$m_m\% = \frac{grams\ solute}{grams\ solution} \times 100\%$$

If, for example, you dissolve 5.0 grams of sodium chloride in 50 grams of water, the mass percent is

$$\frac{m}{m}$$
% =  $\frac{5.0 \text{ g NaCl}}{55 \text{ g water}} \times 100\% = 9.1\%$ 

Therefore, the solution is a 9.1 percent (m/m) solution.

Suppose that you want to make 350.0 grams of a 5 percent (w/w) sucrose, or table sugar, solution. You know that 5 percent of the weight of the solution is sugar, so you can multiply the 350.0 grams by 0.05 to get the weight of the sugar:

 $350.0 \text{ grams} \times 0.05 = 17.5 \text{ grams of sugar}$ 

The rest of the solution (350.0 grams - 17.5 grams = 332.5 grams) is water. You can simply weigh out 17.5 grams of sugar and add it to 332.5 grams of water to get your 5 percent (w/w) solution.

Mass percentage is the easiest percentage solution to make, but sometimes you may need to know the volume of the solution. In this case, you can use the mass/volume percentage.

#### Mass/volume percentage

*Mass/volume percentage* is very similar to mass/mass percentage, but instead of using grams of solution in the denominator, it uses milliliters of solution:

$$\frac{m}{v}\% = \frac{\text{grams solute}}{\text{mL solution}} \times 100\%$$

Suppose that you want to make 100 milliliters of a 15 percent (m/v) potassium nitrate solution.

Because you're making 100 milliliters, you already know that you're going to weigh out 15 grams of potassium nitrate (commonly called saltpeter —  $KNO_3$ ). Now, here comes something that's a little different: You dissolve the 15 grams of  $KNO_3$  in a little bit of water and dilute it to exactly 100 milliliters in a volumetric flask. In other words, you dissolve and dilute 15 grams of  $KNO_3$  to 100 milliliters. (I tend to abbreviate *dissolve* and *dilute* by writing d & d, but sometimes it gets confused with Dungeons & Dragons. Yes, chemists are really, *really* nerdy.) You won't know exactly how much water you put in, but it's not important as long as the final volume is 100 milliliters.

You can also use the percentage and volume to calculate the grams of solute present. You may want to know how many grams of sodium hypochlorite are in 500 milliliters of a 5 percent (m/v) solution of household bleach. Because it is a 5 percent (m/v) solution, it has 5 grams of potassium nitrate per 100 milliliters of solution. You can set up the problem like this:

$$\frac{5 \text{ g NaOCl}}{100 \text{ mL solution}} \times \frac{500 \text{ mL solution}}{1} = 25 \text{ g NaOCl}$$

You now know that you have 25 grams of sodium hypochlorite in the 500 milliliters of solution. Sometimes both the solute and solvent are liquids. In this case, using a volume/volume percentage is more convenient.

#### Volume/volume percentage

With *volume/volume percentages*, both the solute and solution are expressed in milliliters:

$$\frac{v}{v}$$
% =  $\frac{mL \text{ solute}}{mL \text{ solution}} \times 100\%$ 

## **Proof reading**

When it comes to ethyl alcohol solutions, another concentration unit, called proof, is commonly used to measure the relative amount of alcohol and water. The proof is simply twice the percentage. A 50 percent ethyl alcohol solution is 100 proof. Pure ethyl alcohol (100 percent) is 200 proof. This term dates back to earlier times, when the production of ethyl alcohol for human consumption was a cottage industry. (In the part of North Carolina where I grew up, it still is a cottage industry.) There was no quality control back then, so the buyer had to be sure that the alcohol he was buying was concentrated enough (or "strong" enough) for the desired purpose. Some of the alcohol solution was poured over gunpowder and then lit. If enough alcohol was present, the gunpowder would ignite, giving "proof" that the solution was strong enough.

Ethyl alcohol (drinking alcohol) solutions are commonly made using volume/volume percentages. If you want to make 100 milliliters of a 50 percent ethyl alcohol solution, you take 50 milliliters of ethyl alcohol and dilute it to 100 milliliters with water. Again, it's a case of dissolving and diluting to the required volume. You can't simply add 50 milliliters of alcohol to 50 milliliters of water — you'd get less than 100 milliliters of solution. The polar water molecules attract the polar alcohol molecules, which tends to fill in the open framework of water molecules and prevents the volumes from simply being added together.

#### Molarity: It's number one!

Molarity is the concentration unit most often used by chemists, because it utilizes moles. The mole concept is central to chemistry, and molarity lets chemists easily work solutions into reaction stoichiometry. (If you're cussing me out right now because you have no idea what burrowing mammals have to do with chemistry, let alone what stoichiometry is, just flip to Chapter 8 for the scoop. Your mother would probably recommend washing your mouth out with soap first.)

*Molarity (M)* is defined as the moles of solute per liter of solution. Mathematically, it looks like this:

 $M = \frac{\text{mol solute}}{\text{L solution}}$ 

For example, you can take 1 mole (abbreviated as *mol*) of KCl (formula mass of 74.55 g/mol — you can get the scoop on formula and molecular masses in Chapter 8, too) and dissolve and dilute the 74.55 grams to 1 liter of solution in a volumetric flask. You then have a 1-molar solution of KCl. You can label that solution as 1 M KCl. You don't add the 74.55 grams to 1 liter of water. You want to end up with a final volume of 1 liter. When

preparing molar solutions, always dissolve and dilute to the required volume. This process is shown in Figure 9-1.

If 25.0 grams of KCl are dissolved and diluted to 350.0 milliliters, how would you calculate the molarity of the solution?

You know that molarity is moles of solute per liter of solution. To solve this problem, start by taking the grams and converting them to moles using the formula weight of KCl (74.55 g/mol). Divide the moles by 0.350 liters (350.0 milliliters). You can set up the equation like this:

$$\frac{25.0 \text{ g KCl}}{1} \times \frac{1 \text{ mol KCl}}{74.55 \text{ g}} \times \frac{1}{0.350 \text{ L}} = 0.958 \text{ M}$$

Now suppose that you want to prepare 2.00 liters of a 0.550 M KCl solution.

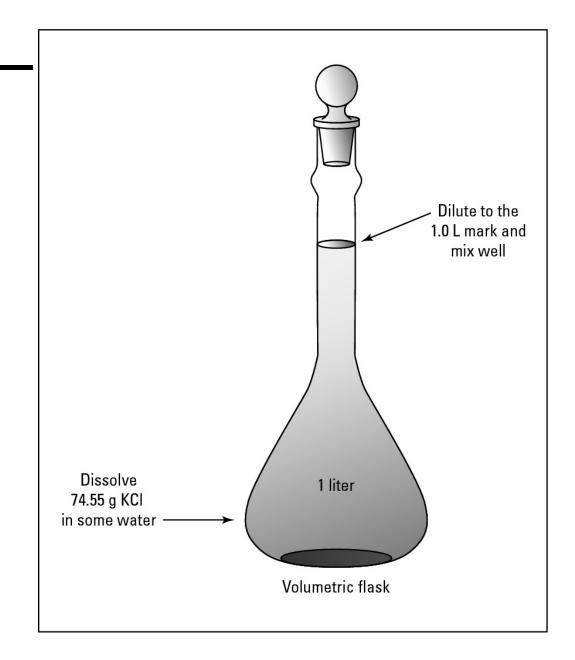
#### 1. Calculate how much KCl you need to weigh.

The solution must have 0.550 moles of potassium chloride per liter. If you convert from moles of KCl to grams of KCl, you get the number of grams of KCl per liter. You are preparing 2.00 liters, so multiplying by 2.00 liters gives you the number of grams of KCl.

$$\frac{0.550 \text{ mol KCl}}{1 \text{ L}} \times \frac{74.55 \text{ g KCl}}{1 \text{ mol}} \times \frac{2.00 \text{ L}}{1} = 82.0 \text{ g KCl}$$

2. Take that 82.0 grams of KCl and dissolve and dilute it to 2.00 liters.

molar KCl solution.



You have another option for preparing solutions — the dilution of a more concentrated solution to a less concentrated one. For example, you can buy hydrochloric acid from the manufacturer as a concentrated solution of 12.0 M.

Suppose you want to prepare 500 milliliters of 2.0 M HCl. You can dilute some of the 12.0 M to 2.0 M, but how

#### much of the 12.0 M HCl is needed?

To figure out the volume you need, follow these simple steps:

#### 1. Use the following formula:

$$V_{old} \times M_{old} = V_{new} \times M_{new}$$

In the preceding equation,  $V_{old}$  is the old volume, or the volume of the original solution,  $M_{old}$  is the molarity of the original solution,  $V_{new}$  is the volume of the new solution, and  $M_{new}$  is the molarity of the new solution.

#### 2. Substitute the values in the equation.

$$V_{old} \times 12.0 \text{ M} = 500.0 \text{ mL} \times 2.0 \text{ M}$$

$$V_{old}$$
 = (500.0 mL  $\times$  2.0 M)/12.0 M = 83.3 milliliters

## 3. Take 83.3 milliliters of the 12.0 M HCl solution and dilute it to exactly 500.0 milliliters.

Put about 400 milliliters of water into a 500.0 mL volumetric flask, slowly add the 83.3 milliliters of the concentrated HCl as you stir, and then dilute to the final 500 milliliters with water.

If you're actually doing a dilution of concentrated acids, be sure to *add the acid to the water* instead of the other way around! If the water is added to the concentrated acid, then so much heat will be generated that the solution will quite likely splatter all over you.

The usefulness of the molarity concentration unit is readily apparent when dealing with reaction stoichiometry.

Suppose that you want to know how many milliliters of 2.50 M sulfuric acid it takes to neutralize a solution

containing 100.0 grams of sodium hydroxide.

1. Write the balanced chemical equation for the reaction:

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

2. Convert the weight of sodium hydroxide to moles (using the formula weight of NaOH, 40.00 g/mol).

$$\frac{100.0 \text{ g NaOH}}{1} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}}$$

3. Convert from moles of NaOH to moles of H<sub>2</sub>SO<sub>4</sub>.

$$\frac{100.0 \text{ g NaOH}}{1} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}}$$

4. Calculate the volume using the molarity of the acid solution and convert the volume to milliliters.

$$\frac{100.0\text{ g NaOH}}{1}\times\frac{1\text{ mol NaOH}}{40.00\text{ g NaOH}}\times\frac{1\text{ mol H}_2\text{SO}_4}{2\text{ mol NaOH}}\times\frac{1\text{ L}}{2.50\text{ mol H}_2\text{SO}_4}\times\frac{1\text{ L}}{2.50\text{ mol H}_2\text{SO}_4}\times\frac{1,000\text{ mL}}{1\text{ L}}=500.0\text{ mL}$$

500.0 milliliters of the 2.50 M  $H_2SO_4$  solution is needed to completely react with the solution that contains 100.0 grams of NaOH.

### Molality: Another use for the mole

Molality is another concentration term that involves moles of solute. It isn't used very much except in dealing with colligative properties, but I want to tell you a little about it, just in case you happen to run across it. *Molality* (*m*) is defined as the moles of solute per kilogram of solvent. It's one of the few concentration units that doesn't use the solution's weight or volume. Mathematically, it looks like this:

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

Suppose you want to dissolve 15.0 grams of NaCl in 50.0 grams of water.

To calculate the molality, you need to convert the 50.0 grams of water to kilograms (0.0500 kg). Then convert the grams of NaCl to moles of NaCl and divide by the kilograms of water, as in the following equation:

$$\frac{15.0 \text{ g NaCl}}{1} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \times \frac{1}{0.0500 \text{ kg}} = 5.13 \text{ m}$$

#### Parts per million: The pollution unit

Percentage and molarity, and even molality, are convenient units for the solutions that chemists routinely make in the lab or the solutions that are commonly found in nature. However, if you begin to examine the concentrations of certain pollutants in the environment, you find that those concentrations are very, very small. Percentage and molarity work when you're measuring very dilute solutions found in the environment, but they're not very convenient. In order to express the concentrations of very dilute solutions, scientists have developed another concentration unit — parts per million.

Percentage is parts per hundred, or grams solute per 100 grams of solution. *Parts per million (ppm)* is grams solute per one million grams of solution. It's most commonly expressed as milligrams solute per kilogram solution, which is the same ratio. The reason it's expressed this way is that chemists can easily weigh out milligrams or even tenths of milligrams, and, if you're talking about aqueous solutions, a kilogram of solution is the same as a liter of solution. (The density of water is 1 gram per milliliter, or 1 kilogram per liter. The weight of the solute in these solutions is so very small that it's negligible when converting from the mass of the solution to the volume.)

By law, the maximum contamination level of lead in drinking water is 0.05 ppm. This number corresponds to 0.05 milligrams of lead per liter of water. That's pretty dilute. But mercury is regulated at the 0.002 ppm level. Sometimes, even this unit isn't sensitive enough, so environmentalists have resorted to the parts per billion (ppb) or parts per trillion (ppt) concentration units. Some neurotoxins are deadly at the parts per billion level.

# Comprehending Colligative Properties of Solutions

Some properties of solutions depend on the specific nature of the solute. In other words, an effect you can record about the solution depends on the specific identity of the solute. For example, salt solutions taste salty, whereas sugar solutions taste sweet. Salt solutions conduct electricity (they're electrolytes — see Chapter 13), but sugar solutions don't (they're nonelectrolytes). Solutions containing the nickel cation are commonly green, and those containing the copper cation are blue.

Some properties of solution don't depend on the specific type of solute — just the *number* of solute particles. Properties that simply depend on the relative number of solute particles are called *colligative properties*. The effect you can record about the solution depends on the number of solute particles present. The following sections discuss in greater detail these colligative properties — these effects — including

- ✓ Vapor-pressure lowering
- ✓ Boiling-point elevation
- ✓ Freezing-point depression



# Reducing the pressure: Vapor-pressure lowering

If a liquid is contained in a closed container, the liquid eventually evaporates, and the gaseous molecules contribute to the pressure above the liquid. The pressure due to the gaseous molecules of the evaporated liquid is called the liquid's *vapor pressure*.

If you make that same liquid the solvent in a solution, the vapor pressure due to the solvent evaporation is lower because the solute particles in the liquid take up space at the surface and the solvent can't evaporate as easily. And many times, the solute and solvent may have an attraction that also makes it more difficult for the solvent to evaporate. That lowered vapor pressure is independent of what kind of solute you use. Instead, it depends on the number of solute particles.

For example, if you add one mole of sucrose to a liter of water and add one mole of dextrose to another liter of water, the amount that the pressure lowers is the same, because you're adding the same *number* of solute particles. If, however, you add a mole of sodium chloride to a liter of water, the vapor pressure lowers by twice the amount of the sucrose or glucose solutions. Sodium chloride breaks apart into two ions, so adding a mole of sodium chloride yields two moles of particles (ions), and the greater number of solute particles leads to lower pressure.

This lowering of vapor pressure partially explains why the Great Salt Lake has a lower evaporation rate than you may expect. The salt concentration is so high that the vapor pressure (and evaporation) has been significantly lowered.

## Using antifreeze in summer: Boilingpoint elevation

Each individual liquid has a specific temperature at which it boils (at a given atmospheric pressure). This temperature is the liquid's *boiling point*. If you use a particular liquid as a solvent in a solution, you find that the boiling point of the solution is always higher than the pure liquid. This is called the *boiling-point elevation*.

Boiling-point elevation explains why you don't replace your antifreeze with pure water in the summer. You want the coolant to boil at a higher temperature so that it absorbs as much engine heat as possible *without* boiling. You also use a pressure cap on your radiator, because the higher the pressure, the higher the boiling point. This concept also explains why a pinch of salt in the cooking water causes foods to cook a little faster. The salt raises the boiling point so that more energy can be transferred to cooking the food during a given amount of time.

You can actually calculate the amount of boiling-point elevation by using this formula:

$$\Delta T_{\rm b} = K_{\rm b} m$$

 $\Delta T_{\rm b}$  is the *increase* in the boiling point,  $K_{\rm b}$  is the boiling-point elevation constant (0.512°C/m for water), and m is the molality of particles. (For molecular substances, the molality of particles is the same as the molality of the substance; for ionic compounds, you have to take into consideration the formation of ions and calculate the molality of the ion particles.) Solvents other than water have a different boiling point elevation constant ( $K_{\rm b}$ ).

Suppose you want to know the boiling point of 2.0 m aqueous KNO<sub>3</sub> solution.

 $KNO_3$  is a salt, a strong electrolyte. In a 2.0 m solution you have 4.0 m in particles, because  $KNO_3$  dissociates completely into  $K^+$  and  $NO_3^-$ . Therefore:

$$\Delta T_{\rm b} = K_{\rm b} m$$

$$\Delta T_{\rm b} = (0.512^{\circ} \text{C/m}) \times (4.0 \text{ m})$$

$$\Delta T_{\rm b} = 2.0^{\circ} \text{C}$$

The change in boiling point is 2.0 degrees Celsius. You know that the boiling point of a solution is always *higher* that the pure solvent, so the solution's boiling point is:

$$100.0^{\circ}\text{C} + 2.0^{\circ}\text{C} = 102.0^{\circ}\text{C}$$

# Making ice cream: Freezing-point depression

Each individual liquid has a specific temperature at which it freezes. If you use a particular liquid as a solvent in a solution, though, you find that the freezing point of the solution is always lower than the pure liquid. This is called the *freezing-point depression*, and it's a colligative property of a solution, meaning that it depends on the number of solute particles.

The depression of the freezing point of a solution relative to the pure solvent explains why you put rock salt in the ice/water mix when making homemade ice cream. The rock salt forms a solution with a lower freezing point than water (or the ice cream mix that's to be frozen). The freezing-point depression

effect also explains why a salt (normally calcium chloride,  $CaCl_2$ ) is spread on ice to melt it. The dissolving of calcium chloride is highly exothermic (it gives off a lot of heat). As the calcium chloride dissolves, it melts the ice and forms a solution in the resulting water. The salt solution that's formed when the ice melts has a lowered freezing point that keeps the solution from refreezing. Freezing-point depression also explains the use of antifreeze in your cooling system during the winter. The more you use (up to a concentration of 50/50), the lower the freezing point.

In case you're interested, you can actually calculate the amount the freezing point will be depressed:

$$\Delta T_{\rm f} = K_{\rm f} m$$

 $\Delta T_{\rm f}$  is the amount the freezing point will be lowered,  $K_{\rm f}$  is the freezing point depression constant (1.86°C/m for water), and m is the molality of the particles.

Suppose you want to calculate the freezing point of that 2.0 m aqueous KNO<sub>3</sub> solution used in the previous section.

You know that the solution is 4.0 m in particles, so

$$\Delta T_{\rm f} = {\rm K_f m}$$
  
 $\Delta T_{\rm f} = (1.86^{\circ}{\rm C/m}) \times 4.0 {\rm m}$   
 $\Delta T_{\rm f} = 7.4^{\circ}{\rm C}$ 

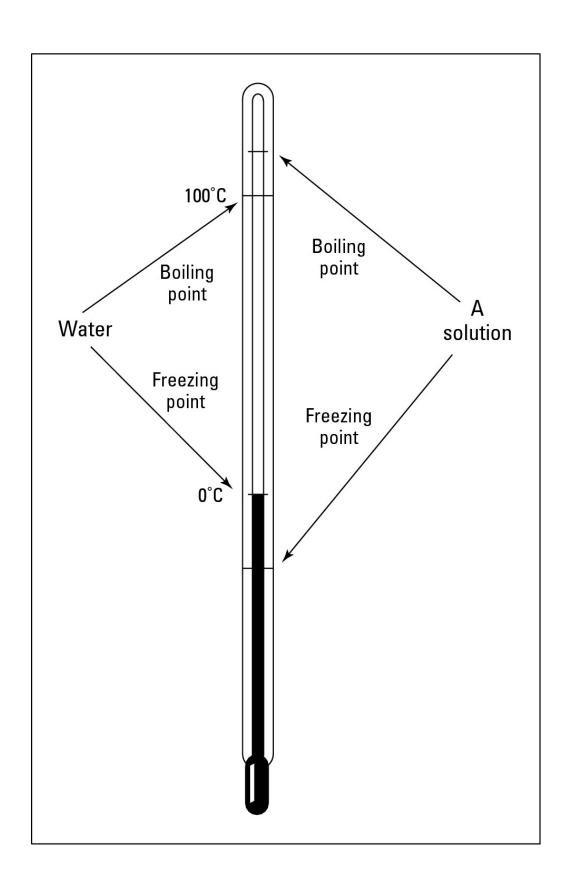
You know that the freezing point of the solution is lower that the freezing point of water (the solvent), so the freezing point of the solution is

$$0.0^{\circ}\text{C} - 7.4^{\circ}\text{C} = -7.4^{\circ}\text{C}$$

Figure 9-2 shows the effect of a solute on both the freezing point and the boiling point of a solvent.

#### Figure 9-2: Boiling-point elevation and freezing-point depression of

a solution.

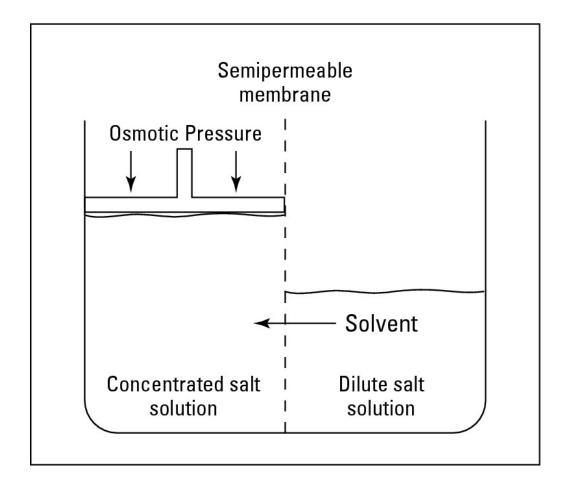


# Keeping blood cells alive and well: Osmotic pressure

Suppose that you take a container and divide it into two compartments with a thin membrane containing microscopic pores large enough to allow water molecules but not solute particles to pass through. This membrane type is called a *semipermeable membrane;* it lets only some small particles pass through.

You then add a concentrated salt solution to one compartment and a more dilute salt solution to the other. Initially, the two solution levels start out the same. But after a while, you notice that the level on the more concentrated side has risen, and the level on the more dilute side has dropped. This change in levels is due to the passage of water molecules from the more dilute side to the more concentrated side through the semipermeable membrane. This process is called *osmosis*, the passage of a solvent through a semipermeable membrane into a solution of higher solute concentration. The pressure that you have to exert on the more concentrated side in order to stop this process is called *osmotic pressure*. This process is shown in Figure 9-3.

Figure 9-3: Osmotic pressure.



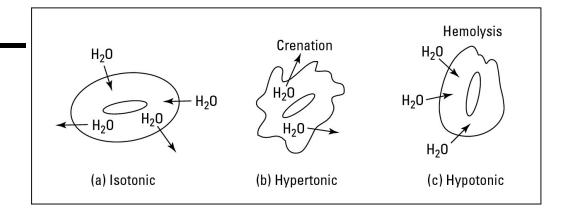
The solvent always flows through the semipermeable membrane from the more dilute side to the more concentrated side. In fact, you can have pure water on one side and any salt solution on the other, and water always goes from the pure-water side to the salt-solution side. The more concentrated the salt solution, the more pressure it takes to stop the osmosis (the higher the osmotic pressure).

But what if you apply more pressure than is necessary to stop the osmotic process, exceeding the osmotic pressure? Water is forced through the semipermeable membrane from the more concentrated side to the more dilute side, a process called *reverse osmosis*. Reverse osmosis is a good, relatively inexpensive way of purifying water. My local "water store" uses this process to purify drinking water (so-called "RO water"). The world has many reverse osmosis plants that extract drinking water from seawater. Navy pilots even carry small reverse osmosis units with them in case they have to eject at sea.

Cell walls often act as semipermeable membranes. Do you ever eat pickles? Cucumbers are soaked in a brine solution in order to make pickles. The concentration of the solution inside the cucumber is less than the concentration of the brine solution, so water migrates through the cell walls into the brine, causing the cucumber to shrink.

One of the most biologically important consequences of osmotic pressure involves the cells within our own bodies. You can look at red blood cells as an example. Inside the blood cell is an aqueous solution, and outside the cell is another aqueous solution (intercellular fluid). When the solution outside the cell has the same osmotic pressure as the solution inside the cell, it's said to be *isotonic*. Water can be exchanged in both directions, helping to keep the cell healthy. However, if the intercellular fluid becomes more concentrated and has a higher osmotic pressure (hypertonic), water flows primarily out of the blood cell, causing it to shrink and become irregular in shape. This is a process called *crenation*. The process may occur if the person becomes seriously dehydrated, and the crenated cells are not as efficient in carrying oxygen. If, on the other hand, the intercellular fluid is more dilute than the solution inside the cells and has a lower osmotic pressure (hypotonic), the water flows mostly into the cell. This process, called *hemolysis*, causes the cell to swell and eventually rupture. Figure 9-4 shows crenation and hemolysis.





The processes of crenation and hemolysis explain why the concentration of IV solutions is so very critical. If they're too dilute, then hemolysis can take place, and if they're too concentrated, crenation is a possibility.

You can calculate the osmotic pressure  $(\pi)$  by using the following equation:

$$\pi = (nRT/V)i = iMRT$$

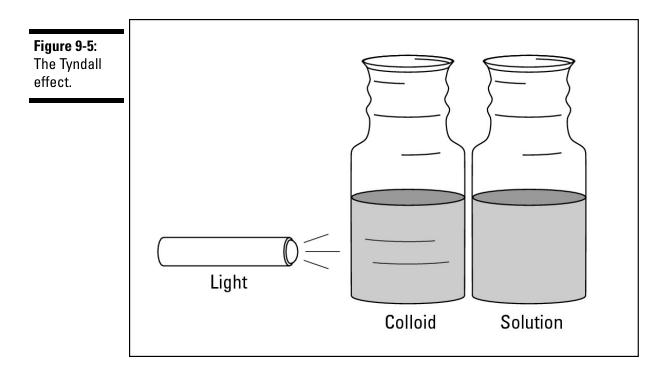
In this equation  $\pi$  is the osmotic pressure in atmospheres, n is the number of moles of solute, R is the ideal gas law constant (0.0821 L atm/K mol), T is the Kelvin temperature, V is the volume of the solution, and i is the van 't Hoff factor (the number of moles of particles that will be formed from 1 mole of solute). n/V may be replaced by M, the molarity of the solution.

## **Clearing the Air on Colloids**

If you dissolve table salt in water, you form an aqueous solution. The solute particle size is very small — around 1 nanometer (nm), which is  $1\times 10^{-9}$  meters. This solute doesn't settle to the bottom of a glass, and it can't be filtered out of the solution.

If, however, you go down to your local stream and dip out a glass of water, you'll notice that there's a lot of material in it. Many of the solute particles are larger than 1,000 nm. They quickly settle to the bottom of the glass and can be filtered out. In this case, you have a *suspension* and not a solution. Whether you have one or the other depends on the size of the solute particles.

But an intermediate range exists between solutions and suspensions. When the solute particle size is 1 to 1,000 nanometers, you have a *colloid*. Solutes in colloids don't settle out like they do in suspensions. In fact, distinguishing colloids from true solutions is sometimes difficult. One of the few ways to distinguish between them is to shine a light through the suspected liquid. If it's a true solution, with very small solute particles, the light beam will be invisible. If you have a colloid, however, you'll be able to see the light beam as it reflects off the relatively large solute particles. This is called the *Tyndall effect*, and it's shown in Figure 9-5.



Colloids come in many varieties. Have you ever eaten a marshmallow? It's a colloid of a gas in a solid. Whipped cream is a colloid of a gas in a liquid. Have you ever driven through the fog and seen your headlight beams? You were experiencing the Tyndall effect of a liquid-in-a-gas colloid. Smoke is a colloid of a solid (ash or soot) in a gas (air). Air pollution problems are often caused by the stability of this type of colloid.

## **Chapter 10**

## **Thermochemistry: Hot Stuff**

#### In This Chapter

- Checking out how energy changes during reactions
- Reacting under constant pressure: Enthalpy
- Determining how much heat occurs in reaction
- Seeing how temperature stays the same during phase transitions

Reactants form products, but something else goes on as well during a chemical reaction — energy changes. In this chapter, I focus on one type of energy change that takes place — changes in heat.

Many chemical reactions that you may be able to mention are *exothermic reactions*, reactions that release energy. Burning natural gas to run the stove when you fry chicken, burning wood in a campfire to keep warm, and the combustion of gasoline in your automobile's engine are all example of exothermic reactions. In many cases, the energy produced is the reaction product that's desired.

In other reactions, energy is absorbed as the reaction takes place. These reactions are *endothermic*, and energy appears on the reactants' side at the start. Cooking is a great example of endothermic reactions. Crack a couple of eggs into a hot frying pan, and energy from the pan is absorbed into the eggs during the myriad chemical reactions called cooking.

Thermochemistry is the study of the energy changes that take place during a chemical reaction. In this chapter, you investigate the concepts associated with thermochemistry. You discover how to calculate the amount of heat produced during a specific chemical reaction and how much heat is needed to cause a desired reaction to take place. So turn on the air conditioning and grab a glass of cold tea — this chapter may heat things up a bit.

## Looking at Reactions and Energy Changes

Thermochemistry is concerned with the heat changes that occur during a chemical reaction (or a physical change such as melting). It's part of a wider field of chemistry called *thermodynamics*, the general study of energy transfers. But before you can study these energy changes, I first have to define a few terms. The following sections give you an overview of some important concepts you need to understand before delving deeper into thermochemistry.

#### **Systems and surroundings**

In thermochemistry, thermal (heat) energy changes occur between the system and surroundings. The *system* is that part of the universe being studied (the place in which the chemical reaction takes place), and the *surroundings* are the rest of the universe that is being affected by the system. Suppose you're carrying out a reaction in a beaker in the chemistry lab. The beaker is the system, and the surroundings are the lab. Although some scientists may say the rest of the universe is the surroundings, for practical purposes, the beaker is the system.

You can feel energy changes in the beaker, but I doubt that some alien millions of light years away will be able to ever detect it.

#### Heat

Heat (normally represented as q) is the energy that flows when a system and surroundings are at different temperatures. The energy always flows from the area of higher temperature to the area of lower temperature. If q has a positive value (+q), the system has absorbed energy via heat transfer from the surroundings (an *endothermic* process). If q has a negative value (-q), the system has transferred heat to the surroundings (an *exothermic* process).

The transferred heat is an *extensive property*, which means its amount depends on the amount of matter involved. For example, more fire means more heat, so you get more heat from a large fire than from a small fire, even if the large fire isn't hotter. *Temperature* (the average kinetic energy of matter) is an *intensive property*, a property that's not affected by the amount of matter involved. The temperature of your latte may be the same as the temperature of your bath water, but much more energy (heat) was required to warm up the bath water.

### **Units of energy**

The two units that you use in thermochemistry calculations are the *joule* and the *calorie*.

- **Joule (J)** is the SI unit of energy. It has the units of kg  $m^2/s^2$ . Remember that  $1 J = 1 \text{ kg m}^2/s^2$ .
- **Calorie (cal)** is the amount of energy needed to raise the temperature of 1 gram of water 1 degree Celsius. By definition a calorie is exactly 4.184 J.

Although both units may be used, most older textbooks (and older teachers) tend to use calories, while newer text tend to use joules. I tend to use both, just so you're familiar with both.

I'm sure you've heard the term *calories* before. Who hasn't talked about cutting back on calories or wondering how many calories that triple bacon cheeseburger contains? But those calories are different — they're nutritional Calories (notice the capital *C*). Nutritional Calories are really kilocalories, 1,000 calories. So that 300-Calorie candy bar really contains 300,000 calories of energy that must either be used up or, more likely, stored as fat. Now that's sticker shock! Food sellers count on 300 Calories sounding better than 300,000 calories.

You can usually tell from the context which type of calorie is being discussed. In general chemistry, calories are used much more often than nutritional Calories.

Engineers often use the British thermal unit (BTU). A BTU was originally defined as the amount of heat required to raise the temperature of 1 pound (0.454 kg) of liquid water by 1 degree Fahrenheit (0.556°C) at a constant pressure of 1 atmosphere. It's equivalent to 1,054 joules and is commonly used when referring to the power output of steam engines and air-conditioning units.

#### **Heat capacities**

If you heat a substance, whether it's water, copper, or mercury, the temperature of the substance increases, but the magnitude of that temperature change varies from substance to substance. The *specific heat capacity, s* (sometimes simply called the *specific heat*), of a substance is the amount of heat that's

required to raise the temperature of 1 gram of that substance 1 degree Celsius and can be measured in units of J/°C or cal/°C.

To calculate heat capacity, take the heat absorbed or released by a certain mass of that substance during a chemical process and divide it by the mass (in grams) times the temperature change ( $/(\text{mass})\Delta T$ ), as in the following equation:

 $s = q/(\text{mass})\Delta T$ 

The specific heats of substances vary somewhat with temperature, so you need to know the specific temperature of the substance before trying to calculate s. The temperature variance isn't very great, so you normally can use the tabulated values of specific heats that have been measured at around 25 degrees Celsius. For example, one gram of  $H_2O$ , water, absorbs 4.184 J or exactly 1 calorie when increasing its temperature from 25 to 26 degrees Celsius. It also loses that same amount of energy when cooling from 26 to 25 degrees. The units of specific heat capacity are  $J/g^{\circ}C$  or cal/ $g^{\circ}C$ .

Because units of Celsius and Kelvin have the same magnitude, you may use a Kelvin temperature change in place of a Celsius temperature change when calculating specific heat capacities.

If you know the specific heat of a substance, its mass, and the change in temperature, you can use the following equation to calculate the amount of heat, *q*, that was involved in the process:

 $q = s(mass)(\Delta T)$ 

An even more useful heat capacity quantity is the molar heat capacity. The *molar heat capacity*, *S*, is the amount of heat needed to raise the temperature of one mole of a substance one degree Celsius (or Kelvin). It has units of J/mole°C or cal/mole°C. Table 10-1 lists the specific heat capacities and molar heat capacities of some common substances.

Table 10-1 Specific and Molar Heat Capacities of Selected Substances at 25 Degrees Celsius

Substance	Specific Heat Capacity (J/g°C)	Molar Heat Capacity (J/mole°C)
Al (solid)	0.90	24.3
C (diamond)	0.50	6.0
C (graphite)	0.72	8.6
Cu (solid)	0.39	24.5
Fe (solid)	0.44	24.8
H <sub>2</sub> O (solid)	2.09	37.7
H <sub>2</sub> O (liquid)	4.18	75.3
H <sub>2</sub> O (gas)	2.03	36.4

You can see in the table that liquid water has a relatively high heat capacity. This capacity allows the oceans and other bodies of water to absorb large amounts of heat, helping to keep the earth's temperature moderate. But the table also shows that water's three states of matter have different heat capacities. Be careful when pulling a heat capacity value from this or any other table that you use the heat capacity value for the correct state.

The different allotropes of an element also have different heat capacities. (*Allotropes* are different forms of an element where the atoms of the element are bonded together in different

ways.) Table 10-1 includes the heat capacities of graphite and diamond, two allotropic forms of carbon.

Here is a typical thermochemical problem you may encounter that addresses the points in this section:

How much heat does it take to raise the temperature of 50.0 grams of solid iron from 20.0 to 35.0 degrees Celsius?

Looking at Table 10-1, you see that the specific heat capacity of iron (Fe) is  $0.44 \text{ J/g}^{\circ}\text{C}$ . And you know that  $s = q/(\text{mass})(\Delta T)$ , so  $q = s(\text{mass})(\Delta T)$ .

Substitute the given values to get this answer:

$$q = (0.44 \text{ J/g}^{\circ}\text{C})(50.0 \text{ g})(35.0 - 20.0^{\circ}\text{C}) = 330 \text{ J}$$

#### **Calorimetry**

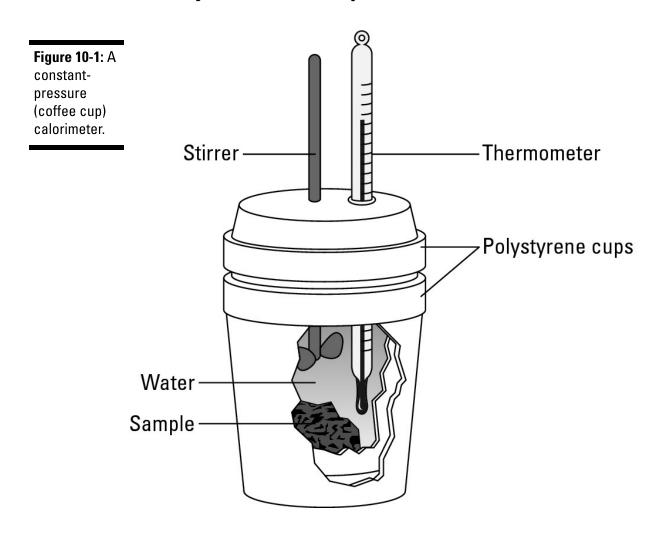
In order to measure the energy change that takes place during a chemical process (the study of *calorimetry*), chemists use an instrument called a *calorimeter*. The following sections take a look at the two general types of calorimeters used by chemists: constant-pressure and constant-volume.

#### **Constant-pressure calorimeters**

The constant-pressure calorimeter is the simpler of the two types. It's used to measure the energy changes taking place at a constant pressure  $(q_p)$ , which is useful when studying processes involving solutions, such as in acid-base neutralization reactions and dilution, or in measuring the specific heats of

materials. The calorimeter holds the pressure constant by exposing the reaction container to the atmosphere, which keeps the pressure of the reaction at atmospheric pressure.

You can make a constant-pressure calorimeter easily by stacking two Styrofoam coffee cups together. Using two stacked cups really insulates the system from the surroundings. In addition, you need to provide some way to stir the solution, and you need a thermometer to measure the temperature change. You can run the thermometer and stirrer through a lid which helps to provide additional insulation. Figure 10-1 illustrates how a coffee cup calorimeter may be constructed.



Styrofoam has a very low thermal conductivity, so hardly any of the heat of the reaction in absorbed by the cups. Therefore, the heat changes that occur are contained within the solution and recorded by the thermometer.

The heat lost or gained by the process is equal to the heat lost or gained by the solution. Knowing the heat capacity of the solution, its mass, and the temperature change allows you to calculate the heat of reaction  $(q_{rxn})$ .

You can use this same method to measure the heat capacity of a substance: Heat a known mass of a substance to a certain temperature, and then add it to the calorimeter containing a known mass of water at a known temperature. You know that the heat lost by the substance equals the heat gained by the water:

$$-q_{\rm solid} = q_{\rm water}$$

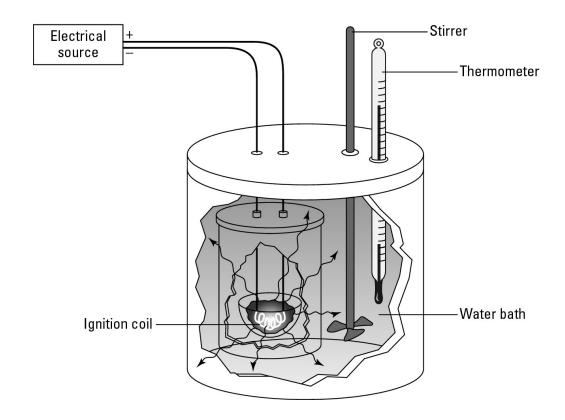
If you then substitute the mathematical relationship for the heat capacities, you get the following equation. Because you know everything except the specific heat of the solid, you can solve for it.

$$-(s_{\text{solid}})(\text{mass}_{\text{solid}})(\Delta T_{\text{solid}}) = (s_{\text{water}})(\text{mass}_{\text{water}})(\Delta T_{\text{water}})$$

#### **Constant-volume (bomb) calorimeter**

Constant-volume calorimeters (commonly called *bomb* calorimeters) are used to measure energy changes that occur during combustion reactions. Figure 10-2 is a diagram of a typical bomb calorimeter.

Figure 10-2: A constant-volume (bomb) calorimeter.



To use this type of calorimeter, follow these steps:

1. Place a weighed sample of the substance to be tested into a cup and place it into a heavy-walled reaction vessel called the bomb.

An electrical ignition apparatus is in contact with the sample.

- 2. Evacuate the air in the bomb and replace it with oxygen.
- 3. Place the bomb in an insulated container filled with a known amount of water.
- 4. Insert a thermometer in the water to measure temperature changes while a stirrer circulates the water around the bomb.
- 5. After giving everything an opportunity to stabilize, ignite the sample electrically.

The sample burns in the oxygen gas. The energy given off by the combustion of the sample is absorbed by the water inside the calorimeter and by the calorimeter itself.

### 6. Compare the temperature of the water before the combustion occurs to the temperature after combustion.

The heat absorbed by the water  $(q_{\text{water}})$  is the specific heat capacity of the water (in J/g°C) times the mass of water (in g) times the change in temperature (final temperature [°C<sub>final</sub>] minus initial temperature [°C<sub>initial</sub>]):

$$q_{\text{water}} = (J/g^{\circ}C)(g)(^{\circ}C_{\text{final}} - ^{\circ}C_{\text{initial}})$$

The amount of energy absorbed by the calorimeter is equal to the heat capacity of the calorimeter times the change in temperature (final temperature – initial temperature):

$$q_{cal} = (J/^{\circ}C)(^{\circ}C_{final} - ^{\circ}C_{initial})$$

The heat of reaction,  $q_{\rm rxn}$ , is equal to the energy absorbed by the water plus the energy absorbed by the calorimeter:

$$q_{\rm rxn}$$
 =  $q_{\rm water}$  +  $q_{\rm cal}$ 

### 7. Calculate the specific heat capacity or the molar heat capacity of the substance.

Use the equation you used in the previous section "Heat capacities" and solve for *s*:

$$q = s(mass)(\Delta T)$$
  
 $s = q/(mass)(\Delta T)$ 

If you know the molar mass of the substance, you can then convert the grams to moles and calculate the molar heat capacity.

### **Understanding Enthalpy Changes**

A vast majority of the reactions that chemists study are reactions at constant pressure, because the pressure can be held constant at atmospheric pressure by simply having the reaction vessel (the beaker or flask, for example) open to the atmosphere. Because these reactions are so common, the

energy change at constant pressure has a special name, enthalpy. The enthalpy change ( $\Delta H$ ) is the heat lost or gained by the system during a chemical reaction while under constant pressure conditions. The following conventions apply to  $\Delta H$ :

- If  $\Delta H < 0$ , then energy is released and the reaction is *exothermic*.
- ✓ If  $\Delta H > 0$ , then energy is absorbed and the reaction is *endothermic*.

For example, consider the reaction of hydrogen and oxygen gases to form a mole of water under constant pressure conditions. The state of gas is indicated by (g).

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)\Delta H = -241.8 \text{ kJ}$$

Although this enthalpy change is somewhat difficult to measure under constant pressure conditions, it can be calculated in other ways, as you see later in this chapter.

The negative sign on the enthalpy indicates that this reaction is exothermic; energy is released. (I used to do this reaction as part of my chemical magic show, and I can testify that a lot of energy is released!) This energy change is many times called the enthalpy (heat) of reaction,  $\Delta H_{\rm reaction}$  or  $\Delta H_{\rm rxn}$ .

A thermochemical equation is a balanced chemical equation that shows not only the mole relationship between reactants and products but also the enthalpy change associated with that specific reaction. Note that in a thermochemical equation, having fractional coefficients is perfectly okay (unlike in ordinary chemical reactions), and the coefficients always refer to moles of reactants or products, not individual molecules.

Be sure to pay attention to the states of the reactants and products. You also want to remember two other conventions that apply to thermochemical equations:

Because the enthalpy change is an extensive property, if you use a multiplier on the equation, you use that same multiplier on the  $\Delta H$ .

For example, if you want to write the thermochemical equation for the production of 2 moles of water, you have to multiply the entire equation above, including the  $\Delta H$ , by 2.

$$2 \left[ H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2 O(g) \Delta H = -241.8 \text{ kJ} \right]$$

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(g) \Delta H = -483.6 \text{ kJ}$$

If you reverse a thermochemical equation, you reverse the sign on the enthalpy change. For example, if you want to write the thermochemical equation for the decomposition of a mole of water, simply reverse the initial equation for the formation of a mole of water and change the sign of the  $\Delta H$ .

$$H_2O(g) \to H_2(g) + \frac{1}{2}O_2(g)\Delta H = +241.8 \text{ kJ}$$

This equation tells you that if you want to decompose a mole of water (about 18 grams), you must supply 241.8 kJ of energy.

### **Finding Heats of Reaction**

To the industrial chemist, the balanced chemical equation allows her to calculate amounts of reactants needed and

amounts of products formed. A chemistry student has to determine the same kinds of calculations when running a chemical reaction in the lab (or on paper in the middle of an exam). But the energy changes that take place are just as important. When doing experiments (either in the instructional lab or the industrial lab), you want to know whether you have to continuously supply heat during the reaction or get rid of heat being produced and how much heat will need to be supplied or disposed of. The answers to these questions can be found with the thermochemical equation and the associated  $\Delta H$  (enthalpy change — see the preceding section). The following sections explain the four main ways of determining heats of reactions.

#### **Doing it yourself**

You can go into the lab and determine the heats of reactions  $(\Delta H_{\rm rxn})$  yourself. That way, you can set the conditions of temperature, pressure, and so on to exactly what you want. For uncommon reactions that aren't well documented, taking the necessary steps to determine the heats works fine, but it's a time-consuming and costly process. Wouldn't it be nice if you were able to find a tabulated value or calculate the enthalpy of reaction from known values, instead of doing all that messy lab work? In fact, most of the time you can do just that, as the next three methods show.

#### **Referring to tables**

If you're fortunate, you can find the specific reaction you're looking for in a table (maybe in the back of your chemistry textbook) and use the data provided there. Earlier in this chapter I identified and used several thermochemical equations, such as in the decomposition reaction for liquid water:

$$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)\Delta H = +241.8 \text{ kJ}$$

Simply referring to a table is a great procedure if you can find the reaction you want, but many times this quick fix isn't possible.

#### **Relying on Hess's law**

If you can find some related reactions and their heat changes  $(\Delta H)$ , you have the option of a method called *Hess's law calculations*. Enthalpy is a *state function*, which means the path taken during the reaction doesn't matter; all that matters are the initial and final states. The enthalpy change is the same whether the reaction occurs in one step or in a series of steps. The basis of Hess's law is that you can calculate the enthalpy change for a desired reaction by manipulating associated reactions until you reach the desired reaction. Hess's law states that if you can write a desired reaction as the sum of two or more known reactions, then the enthalpy change for the desired reaction is simply the sum of the enthalpy changes for the known reactions.

Suppose you want to determine the enthalpy change in kJ for the following reaction, where (*s*) indicates a solid state and (*g*) means gas:

$$2 C(s) + H_2(g) \rightarrow C_2H_2(g) \Delta H = ?$$

 $\Delta H$  can be determined experimentally with a great deal of difficulty, but the easier option is to use the following known reactions:

$$(1)C(s) + O_2(g) \rightarrow CO_2(g)\Delta H = -393.5 \text{ kJ}$$

$$(2)H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)\Delta H = -285.8 \text{ kJ}$$

$$(3)C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)\Delta H = -1299.8 \text{ kJ}$$

Because the coefficient in front of the carbon is 2 in the desired reaction, you multiply reaction (1) by 2.  $C_2H_2(g)$  is the product in the desired reaction, so reverse reaction (3), changing the sign of its  $\Delta H$ . Keep reaction (2) unchanged, because you need one  $H_2$  on the left. If you add together these three reactions, you get the desired reaction, and simply adding together the enthalpy changes of the three reactions gives you the enthalpy change for the desired reaction:

$$2[C(s)+O_{2}(g) \to CO_{2}(g)]\Delta H = 2(-393.5 \text{ kJ})$$

$$+H_{2}(g)+\frac{1}{2}O_{2}(g) \to H_{2}O(l)\Delta H = -285.8 \text{ kJ}$$

$$+2CO_{2}+H_{2}O(l) \to C_{2}H_{2}(g)+\frac{5}{2}O_{2}(g)\Delta H = +1299.8 \text{ kJ}$$

$$=2C(s)+H_{2}(g) \to C_{2}H_{2}(g)\Delta H = 227.0 \text{ kJ}$$

You can save time and effort by calculating the  $\Delta H$  for the reaction you want from other thermochemical reactions. But what if those other thermochemical reactions are not available? That's where the fourth method comes in, using standard heats of formation.

#### Using standard heats of formation

If you can't find appropriate equations, you can calculate heats of reaction using standard enthalpies of formation. Standard enthalpies of formation,  $\Delta H_f^*$  (where the superscript  $^{\circ}$  indicates standard conditions and the subscript f indicates a formation

reaction), are the enthalpy changes associated with the formation of one mole of a substance from its elements with all materials in their standard states. The standard state for thermodynamic properties is the state (form) in which the substance is found at 1 bar of pressure (approximately atmospheric pressure at sea level).

The standard heat of formation for an element in its standard state is exactly 0. Table 10-2 lists the standard enthalpies of formation for a number of chemical substances, and you can normally find a more complete table in the back of your chemistry text.

Table 10-2 Standard Enthalpies of Formation at 25°C (298K)

$\Delta H_{f}^{\circ}(kJ/mole)$
0
1.896
<del>-74.87</del>
227
52.47
-393.5
-825.5
-241.826
-285.840
<del>-45.9</del>
-80.83
82.05
90.29

These tabulated standard enthalpies of formation may be used to calculate the standard enthalpy (heat) of reaction,  $\Delta H_{\rm rxn}$ , the enthalpy of reaction at standard conditions.

Calculate the standard heat of reaction by taking the sum of the standard heats of formation of all products (taking into consideration the number of moles of each) minus the standard heats of formation of all reactants (again taking into consideration the number of moles of each reactant):

$$\Delta H_{\rm rxn} = \Sigma \Delta H_{\rm f}({\rm products}) - \Sigma \Delta H_{\rm f}({\rm reactants})$$

The symbol  $\Sigma$  means "the sum of." If a substance has more than one mole present, you must use the coefficient in the balanced chemical equation as a multiplier.

Consider the following reaction, used in the previous example:

$$2 CO_2 + H_2O(l) \rightarrow C_2H_2(g) + \frac{5}{2} O_2(g)$$

Use standard enthalpies of formation to calculate the standard enthalpy of reaction. Be sure when using Table 10-2 to choose the substance in the right physical state. For example, in this problem you use the enthalpy of formation for liquid water, not gaseous water.

$$\Delta H_{\text{rxn}} = \Sigma \Delta H_f \left( \text{products} \right) - \Sigma \Delta H_f \left( \text{reactants} \right)$$

$$= \left[ 1 \operatorname{mole} \left( \Delta H_f^{\circ} \left( C_2 H_2(g) \right) \right) + \frac{5}{2} \operatorname{moles} \left( \Delta H_f^{\circ} \left( O_2(g) \right) \right) \right] -$$

$$\left[ 2 \operatorname{moles} \left( \Delta H_f^{\circ} \left( CO_2(g) \right) \right) + 1 \operatorname{mole} \left( \Delta H_f^{\circ} \left( H_2 O(l) \right) \right) \right]$$

$$= \left[1 \text{ mole}\left(227 \frac{\text{kJ}}{\text{mole}}\right) + \frac{5}{2} \text{ moles}\left(0 \frac{\text{kJ}}{\text{mole}}\right)\right] - \left[2 \text{ moles}\left(-393.5 \frac{\text{kJ}}{\text{mole}}\right) + 1 \text{ mole}\left(-285.840 \frac{\text{kJ}}{\text{mole}}\right)\right]$$
$$= 1299.8 \text{ kJ}$$

Notice that this result agrees with the enthalpy of reaction used previously in this chapter.

# Uncovering Enthalpies and Phase Transitions

Any time that a substance changes phase, whether melting or boiling or subliming, the temperature remains constant, but an enthalpy (energy change at constant pressure) value is associated with that phase change. If your teacher wants you to calculate the total energy change that takes place between two temperatures that include one or more phase changes, then the following discussion should help.

For example, when ice is melting, the temperature remains constant at 0 degrees Celsius until all the ice is converted to water. The heat that is absorbed during this phase change overcomes the strong intermolecular forces in the solid ice and breaks down the crystalline structure of the water. The heat required to convert one mole of a substance from a solid at its melting point to a liquid at its melting point is the *molar* enthalpy (heat) of fusion ( $\Delta H_{\rm fus}$ ). Water has a heat of fusion of 6.01 kJ/mole.

The process of going from a liquid to a solid at constant temperature, the opposite of melting (fusion), is *solidification* (*crystallization*). The enthalpy change is the *molar enthalpy of* 

solidification,  $\Delta H_{\rm sol}$ , and is equal in magnitude but opposite in sign to the molar heat of fusion, making it -6.01 kJ/mole for water.

When water starts to boil, converting from a liquid to a gas, the same temperature stability occurs. The energy heating the water is used to overcome the intermolecular forces in the liquid, but from the time that water reaches 100 degrees Celsius as  $H_2O(l)$  until it has all been converted to  $H_2O(g)$ , the temperature remains constant. The heat required to vaporize one mole of a substance at its boiling point is the *molar enthalpy* (heat) of vaporization ( $\Delta H_{\rm vap}$ ). For water, the molar enthalpy of vaporization is  $40.7 \, {\rm kJ/mole}$ .

What happens if you start with steam,  $H_2O(g)$ , and cool it until it begins to condense? The process of going from a gas to a liquid at constant temperature, *condensation*, is the opposite of vaporization. Water's molar enthalpy of vaporization,  $\Delta H_{\rm vap}$ , is  $40.7 \, \rm kJ/mole$ . Therefore, the molar enthalpy of condensation,  $\Delta H_{\rm con}$ , is  $-40.7 \, \rm kJ/mole$  for water.

Most substances change from solid to liquid to gas as temperature rises. However, some substances, such as dry ice,  $CO_2(s)$ , undergo *sublimation*, changing directly from the solid state to the gaseous state without becoming a liquid. *Molar enthalpy of sublimation*,  $\Delta H_{\rm sub}$ , is the enthalpy change when one mole of a solid substance sublimes. The enthalpy of sublimation is simply the sum of the molar heats of fusion and vaporization:

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

*Deposition*, the opposite of sublimation, is going directly from the gaseous state to the solid state without first becoming a liquid. The *molar enthalpy of deposition*,  $\Delta H_{\rm dep}$ , is equal in magnitude but opposite in sign from the molar heat of sublimation.

#### Chapter 11

#### **Sour and Bitter: Acids and Bases**

#### In This Chapter

- Discovering the properties of acids and bases
- Finding out about the two acid-base theories
- Determining what makes acids and bases strong
- Using indicators to quickly identify bases and acids
- Taking a look at the pH scale
- Figuring out buffers

Acids and bases are indicators of pH, and if you walk into any kitchen or bathroom, you find a multitude of each. In the refrigerator you find soft drinks full of carbonic acid. The pantry holds vinegar and baking soda, an acid and a base. Peek under the sink, and you notice the ammonia and other cleaners, most of which are bases. Check out that can of lye-based drain opener — it's highly basic. In the medicine cabinet, you find aspirin, an acid, and antacids, bases. The everyday world is full of acids and bases, and so is the everyday world of the industrial chemist. In this chapter, I cover acids and bases and some good basic chemistry.

# Getting to Know the Properties of Acids and Bases: Macroscopic

#### View

Before you can fully grasp an appreciation for acids and bases, you first need a basic understanding of what they are. The following lists look at the properties of acids and bases that you can observe in everyday life.

#### Acids:

- ✓ Taste sour (but remember, in the lab, you test, not taste)
- ✓ Produce a painful sensation on the skin
- React with certain metals (magnesium, zinc, and iron) to produce hydrogen gas
- ✓ React with limestone and baking soda to produce carbon dioxide
- ✓ React with litmus paper and turn it red

#### Bases:

- ✓ Taste bitter (again, in the lab, you test, not taste)
- Feel slippery on the skin
- ✓ React with oils and greases
- React with acids to produce a salt and water
- React with litmus paper and turn it blue

Tables 11-1 and 11-2 show some common acids and bases found around the home.

Table 11-1 Common Acids Found in the Home

Hydrochloric acid	HCI	Muratic acid
Acetic acid	CH <sub>3</sub> COOH	Vinegar
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	Auto battery acid
Carbonic acid	H <sub>2</sub> CO <sub>3</sub>	Carbonated water
Boric acid	$H_3BO_3$	Antiseptic; eye drops
Acetylsalicylic acid	C <sub>16</sub> H <sub>12</sub> O <sub>6</sub>	Aspirin

**Table 11-2 Common Bases Found in the Home** 

Chemical Name	Formula	Common Name or Use
Ammonia	NH <sub>3</sub>	Cleaner
Sodium hydroxide	NaOH	Lye
Sodium bicarbonate	NaHCO <sub>3</sub>	Baking soda
Magnesium hydroxide	Mg(OH) <sub>2</sub>	Milk of magnesia
Calcium carbonate	CaCO <sub>3</sub>	Antacid
Aluminum hydroxide	AI(OH) <sub>3</sub>	Antacid

# Recognizing Acids and Bases: Microscopic View

If you look at Tables 11-1 and 11-2 closely, you may notice that all the acids contain hydrogen, and most of the bases contain the hydroxide ion (OH<sup>-</sup>). Two main theories of the structure of acids and bases use these facts in their descriptions of acids and bases and their reactions:

✓ Arrhenius theory

#### ✓ Bronsted-Lowry theory

The following sections take a closer look at these two theories to help you gain a firmer understanding of acids and bases.

#### The Arrhenius theory: Must have water

The Arrhenius theory was the first modern acid-base theory developed. In this theory, an acid is a substance that yields H<sup>+</sup> (hydrogen) ions when dissolved in water, and a base is a substance that yields OH<sup>-</sup> (hydroxide) ions when dissolved in water. HCl(*g*) can be considered a typical Arrhenius acid, because when this gas dissolves in water, it *ionizes* (forms ions) to give the H<sup>+</sup> ion. (Chapter 13 is where you need to go for the riveting details about ions.)

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

According to the Arrhenius theory, sodium hydroxide is classified as a base, because when it dissolves, it yields the hydroxide ion:

$$NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq)$$

Arrhenius also classified the reaction between an acid and a base as a *neutralization* reaction, because if you mix an acidic solution with a basic solution, you end up with a neutral solution composed of water and a salt.

$$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$$

Look at the ionic form of this equation (the form showing the reaction and production of ions) to see where the water comes from:

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow H_2O(l) + Na^+(aq) + Cl^-(aq)$$

As you can see, the water is formed from combining the hydrogen and hydroxide ions. In fact, the net-ionic equation (the equation showing only those chemical substances that are changed during the reaction) is the same for all Arrhenius acid-base reactions:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The Arrhenius theory is still used quite a bit. But, like all theories, it has some limitations. It specifies that the reactions must take place in water and that bases must contain hydroxide ions, but many reactions that do not meet these stipulations resemble acid-base reactions. For example, look at the gas phase reaction between ammonia and hydrogen chloride gases:

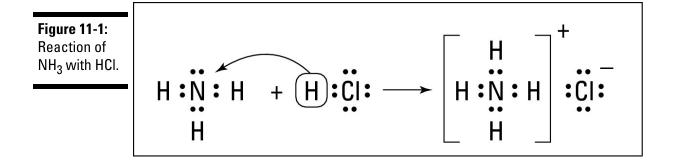
$$NH_3(g) + HCl(g) \rightarrow NH_4^+(aq) + Cl^-(aq) \rightarrow NH_4Cl(s)$$

The two clear, colorless gases mix, and a white solid of ammonium chloride forms. I show the intermediate formation of the ions in the equation so that you can better see what's actually happening. The HCl transfers one H<sup>+</sup> to the ammonia. That's basically the same thing that happens in the HCl/NaOH reaction, but the reaction involving the ammonia can't be classified as an acid-base reaction, because it doesn't occur in water and it doesn't involve the hydroxide ion. But again, the same basic process is taking place in both cases. In order to account for these similarities, a new acid-base theory was developed, the Bronsted-Lowry theory.

## The Bronsted-Lowry acid-base theory: Giving and accepting

The Bronsted-Lowry theory attempts to overcome the limitations of the Arrhenius theory by defining an acid as a proton (H<sup>+</sup>) donor and a base as a proton (H<sup>+</sup>) acceptor. The base accepts the H<sup>+</sup> by furnishing a lone pair of electrons for a *coordinate-covalent* bond, which is a covalent bond (shared pair of electrons) in which one atom furnishes both of the electrons for the bond. Normally, one atom furnishes one electron for the bond and the other atom furnishes the second electron (see Chapter 14). In the coordinate-covalent bond, one atom furnishes both bonding electrons.

Figure 11-1 shows the NH<sub>3</sub>/HCl reaction using the electron-dot structures of the reactants and products. (Electron-dot structures are covered in Chapter 14, too.)



HCl is the acid, so it's the proton donor, and ammonia is the base, the proton acceptor. Ammonia has a lone pair of nonbonding electrons that it can furnish for the coordinate-covalent bond.

I discuss acid-base reactions under the Bronsted-Lowry theory in the section "Competing for protons: Bronsted-Lowry acidbase reactions," later in this chapter.

# Distinguishing between Strong and Weak Acids and Bases

I want to introduce you to a couple different categories of acids and bases — strong and weak. However, remember that acid-base strength is not the same as concentration. *Strength* refers to the amount of ionization or breaking apart that a particular acid or base undergoes. *Concentration* refers to the amount of acid or base that you initially have. You can have a concentrated solution of a weak acid, or a dilute solution of a strong acid, or a concentrated solution of a strong acid, or . . . well, I'm sure you get the idea. The following sections point out the main differences between strong and weak acids and bases.

#### **Ionizing completely: Strong acids**

Acids that ionize completely are considered strong. If you dissolve hydrogen chloride gas in water, the HCl reacts with the water molecules and donates a proton to them:

$$HCl(g) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

The  $H_3O^+$  ion is called the *hydronium ion*. This reaction goes essentially to completion, meaning the reactants keep creating the product until they're all used up. In this case, all the HCl ionizes to  $H_3O^+$  and  $Cl^-$ ; no more HCl is present. Note that water, in this case, acts as a base, accepting the proton from the hydrogen chloride.

Because strong acids ionize completely, calculating the concentration of the hydronium ion and chloride ion in solution is easy if you know the initial concentration of the strong acid. For example, suppose that you bubble 0.1 moles (see Chapter 8 to get a firm grip on moles) of HCl gas into a liter of water. You can say that the initial concentration of HCl is 0.1 M (0.1 mol/L). *M* stands for molarity, and *mol/L* stands for moles of solute per liter. (For a detailed discussion of molarity and other concentration units, see Chapter 9.)

You can represent this 0.1 M concentration for the HCl in this fashion: [HCl] = 0.1. The brackets around the compound indicate molar concentration, or mol/L. Because the HCl completely ionizes, you see from the balanced equation that for every HCl that ionizes, you get one hydronium ion and one chloride ion. So the concentration of ions in that 0.1 M HCl solution is

$$[H_3O^+] = 0.1 \text{ M} \text{ and } [Cl^-] = 0.1 \text{ M}$$

This idea is valuable when you calculate the pH of a solution. (And you can do just that in the section "Putting Coffee and Other Substances on the pH Scale," later in this chapter.) Table 11-3 lists the most common strong acids you're likely to encounter.

**Table 11-3 Common Strong Acids** 

Name	Formula
Hydrochloric acid	HCI
Hydrobromic acid	HBr
Hydroiodic acid	HI
Nitric acid	HNO <sub>3</sub>
Perchloric acid	HCIO <sub>4</sub>
Sulfuric acid (first ionization	on only) H <sub>2</sub> SO <sub>4</sub>

Sulfuric acid is called a *diprotic* acid. It can donate 2 protons, but only the first ionization goes 100 percent. The other acids listed in Table 11-3 are *monoprotic* acids, because they donate only one proton.

#### Falling to pieces: Strong bases

A strong base *dissociates* (breaks apart) completely in water. You normally see only one strong base, the hydroxide ion, OH<sup>-</sup>. Calculating the hydroxide ion concentration is really straightforward. Suppose that you have a 1.5 M (1.5 mol/L) NaOH solution. The sodium hydroxide, a salt, completely dissociates into ions:

$$NaOH \rightarrow Na^{+}(aq) + OH^{-}(aq)$$

If you start with 1.5 mol/L NaOH, then you have the same concentration of ions:

$$[Na^+] = 1.5 \text{ M} \text{ and } [OH^-] = 1.5 \text{ M}$$

#### **Ionizing partway: Weak acids**

Acids that only partially ionize are called *weak acids*. One example is acetic acid ( $\mathrm{CH_3COOH}$ ). If you dissolve acetic acid in water, it reacts with the water molecules, donating a proton and forming hydronium ions. It also establishes an equilibrium in which you have a significant amount of unionized acetic acid. (In reactions that go to completion, the reactants are completely used up creating the products. But in equilibrium systems, two exactly opposite chemical reactions — one on each side of the reaction arrow — are occurring at the same place, at the same time, with the same speed of reaction.)

The acetic acid reaction with water looks like this:

$$CH_3COOH(l) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

The acetic acid that you added to the water is only partially ionized, so it's a weak acid. In the case of acetic acid, about 5 percent ionizes, and 95 percent remains in the molecular form. The amount of hydronium ion that you get in solutions of acids

that don't ionize completely is much less than it is with a strong acid.

Calculating the hydronium ion concentration in weak acid solutions isn't as straightforward as it is in strong solutions, because not all the weak acid that dissolves initially has ionized. In order to calculate the hydronium ion concentration, you must use the equilibrium constant expression for the weak acid. For weak acid solutions, you use a mathematical expression called the K<sub>a</sub> — the *acid ionization constant*.

Take a look at the generalized ionization of some weak acid HA (hypothetical acid):

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

The K<sub>a</sub> expression for this weak acid is

$$K_a = \frac{\left[H_3O^+\right]\left[A^-\right]}{\left[HA\right]}$$

Note that the [HA] represents the molar concentration of HA *at equilibrium*, not initially. Also, note that the concentration of water doesn't appear in the  $K_a$  expression, because there's so much water that it actually becomes a constant incorporated into the  $K_a$  expression.

Now go back to that acetic acid equilibrium. The  $K_a$  for acetic acid is  $1.8\times10^{-5}$ . The  $K_a$  expression for the acetic acid ionization is

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

## Use this K<sub>a</sub> to calculate the hydronium ion concentration in a 2.0 M solution of acetic acid.

1. Start by considering what information you have about the initial concentration and the products.

The initial concentration of acetic acid is 2.0 M, and you know that a little bit has ionized, forming a little hydronium ion and acetate ion. You also can see from the balanced reaction that for every hydronium ion that's formed, an acetate ion is also formed — so their concentrations are the same.

2. Using the information you've gathered from the balanced reaction, represent the amount of  $[H_3O^+]$  and  $[CH_3COO^-]$  as x:

$$[H_3O^+] = [CH_3COO^-] = x$$

3. In order to produce the x amount of hydronium and acetate ion, the same amount of ionizing acetic acid is required. Represent the amount of acetic acid remaining at equilibrium as the amount you started with.

In this example, you started with 2.0 M, minus the amount that ionizes, *x*:

$$[CH_3COOH] = 2.0 - x$$

4. For the vast majority of situations, you can say that x is very small in comparison to the initial concentration of the weak acid. Therefore, you can often approximate the equilibrium concentration of the weak acid with its initial concentration.

In this case, you can say that 2.0 - x is approximately equal to 2.0. The equilibrium constant expression now looks like this:

$$K_a = 1.8 \times 10^{-5} = \frac{[x][x]}{[2.0]} = \frac{[x]^2}{[2.0]}$$

#### 5. Solve for x, which is the $[H_3O^+]$ :

$$(1.8 \times 10^{-5})[2.0] = [x]^{2}$$
  
 $\sqrt{3.6 \times 10^{-5}} = [x] = [H_{3}O^{+}]$   
 $6.0 \times 10^{-3} = [H_{3}O^{+}]$ 

Refer to Table 11-3 to see some common strong acids. Most of the other acids you encounter are weak.

One way to distinguish between strong and weak acids is to look for an acid ionization constant (K<sub>a</sub>) value. If the acid has a K<sub>a</sub> value, then it's weak.

## Finding equilibrium with water: Weak bases

Weak bases also react with water to establish an equilibrium system. Ammonia is a typical weak base. It reacts with water to form the ammonium ion and the hydroxide ion:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+ + OH^-$$

Like a weak acid, a weak base is only partially ionized. The modified equilibrium constant expression for weak bases is  $K_b$ . You use it exactly the same way you use the  $K_a$  (see "Ionizing partway: Weak acids" for the details) except you solve for the  $[OH^-]$ .

## Competing for protons: Bronsted-Lowry acid-base reactions

With the Arrhenius theory, acid-base reactions are neutralization reactions. With the Bronsted-Lowry theory, acidbase reactions are a competition for a proton. For example, take a look at the reaction of ammonia with water:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Ammonia is a base (it accepts the proton), and water is an acid (it donates the proton) in the forward (left to right) reaction. But in the reverse reaction (right to left), the ammonium ion is an acid and the hydroxide ion is a base. If water is a stronger acid than the ammonium ion, then a relatively large concentration of ammonium and hydroxide ions are at equilibrium. If, however, the ammonium ion is a stronger acid, much more ammonia than ammonium ion is present at equilibrium.

Bronsted and Lowry said that an acid reacts with a base to form conjugate acid-base pairs, which differ by a single  $H^+$ .  $NH_3$  is a base, for example, and  $NH_4^+$  is its conjugate acid.  $H_2O$  is an acid in the reaction between ammonia and water, and  $OH^-$  is its conjugate base. In this reaction, the hydroxide ion is a strong base and ammonia is a weak base, so the equilibrium is shifted to the left — not much hydroxide is present at equilibrium.

#### Playing both parts: Amphoteric water

Water can act as either an acid or a base, depending on what it's combined with. When an acid reacts with water, water acts as a base, or a proton acceptor. But in reactions with a base (like ammonia; see the preceding section), water acts as an acid, or a proton donor. Substances that can act as either an acid or a base are called *amphoteric*.

But can water react with itself? Yes, it can. When two water molecules react with each other, one donates a proton and the other accepts it:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This reaction is an *equilibrium reaction*. A modified equilibrium constant, called the  $K_w$  (which stands for *water dissociation constant*), is associated with this reaction. The  $K_w$  has a value of  $1.0 \times 10^{-14}$  and has the following form:

$$1.0 \times 10^{-14} = K_w = [H_3O^+] [OH^-]$$

In pure water, the  $[H_3O^+]$  equals the  $[OH^-]$  from the balanced equation, so  $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ . The  $K_w$  value is a constant. This value allows you to convert from  $[H^+]$  to  $[OH^-]$ , and vice versa, in *any* aqueous solution, not just pure water. In aqueous solutions, the hydronium ion and hydroxide ion concentrations are rarely going to be equal. But if you know one of them, the  $K_w$  allows you to figure out the other one.

Take a look at the 2.0 M acetic acid solution problem in the section "lonizing partway: Weak acids," earlier in this chapter. You find that the  $[H_3O^+]$  is  $6.0\times 10^{-3}$ . Now you have a way to calculate the  $[OH^-]$  in the solution by using the  $K_w$  relationship:

$$\begin{split} \text{K}_{\text{w}} &= \ 1.0 \times 10^{-14} = & \quad \text{[H}_{3}\text{O}^{+}\text{] [OH^{-}]} \\ &1.0 \times 10^{-14} = & \quad \text{[6.0} \times 10^{-3}\text{] [OH^{-}]} \\ &1.0 \times 10^{-14}/6.0 \times 10^{-3} = & \quad \text{[OH^{-}]} \\ &1.7 \times 10^{-12} = & \quad \text{[OH^{-}]} \end{split}$$

# Identifying Acids and Bases with Indicators

Indicators are substances (organic dyes) that change color in the presence of an acid or base. You may be familiar with an acid-base indicator plant — the hydrangea. If it's grown in acidic soil, it turns pink; if it's grown in alkaline soil, it turns blue. Another common substance that acts as a good acid-base indicator is red cabbage. I have my students chop some up and boil it (most of them really love this part). They then use the leftover liquid to test substances. When mixed with an acid, the liquid turns pink; when mixed with a base, it turns green. In fact, if you take some of this liquid, make it slightly basic, and then exhale your breath into it through a straw, the solution eventually turns pink, indicating that the solution has turned slightly acidic. The carbon dioxide in your breath reacts with the water, forming carbonic acid:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Carbonated beverages are slightly acidic due to this reaction. Carbon dioxide is injected into the liquid to give it fizz. A little of this carbon dioxide reacts with the water to form carbonic acid. This reaction also explains why rainwater is slightly acidic. It absorbs carbon dioxide from the atmosphere as it falls to earth.

In chemistry, indicators are used to indicate the presence of an acid or a base. Chemists have many indicators that change at slightly different pH levels. (You've probably heard the term *pH* used in various contexts. Me, I even remember it being used to sell deodorant and shampoo on TV. If you want to know what it actually stands for, check out the section "Putting Coffee and Other Substances on the pH Scale.") The two most commonly used indicators, which I discuss in the following sections, are

Litmus paper

Phenolphthalein

#### Taking a quick dip with litmus paper

*Litmus* is a substance that is extracted from a type of lichen and absorbed into porous paper. (In case you're scheduled for a hot game of Trivial Pursuit this weekend, *lichen* is a plant that's made up of an alga and a fungus that live intimately together and mutually benefit from the relationship. Sounds kind of sordid to me.)

There are three different types of litmus:

- Red litmus is used to test for bases.
- ✓ Blue litmus is used to test for acids.
- ✓ Neutral litmus can be used to test for both.

If a solution is acidic, both blue and neutral litmus turn red. If a solution is basic, both red and neutral litmus turn blue. Litmus paper is a good, quick test for acids and bases. And you don't have to put up with the smell of boiling cabbage.

#### Titrating with phenolphthalein

Phenolphthalein (pronounced fe-nul-tha-leen) is another commonly used indicator. Until a few years ago, phenolphthalein was used as the active ingredient in a popular laxative. In fact, I used to extract the phenolphthalein from the laxative by soaking it in either rubbing alcohol or gin (being careful not to drink it). I'd then use this solution as an indicator.

Phenolphthalein is clear and colorless in an acid solution and pink in a basic solution. It's commonly used in a procedure called a *titration*, where the concentration of an acid or base is determined by its reaction with a base or acid of known concentration.

### Determine the molar concentration of an HCl solution.

To calculate, following these steps:

1. Place a known volume (say, 25.00 milliliters measured accurately with a pipette) in an Erlenmeyer flask and add a couple drops of phenolphthalein solution.

An *Erlenmeyer flask* is a flat-bottomed, conical-shaped container.

Because you're adding the indicator to an acidic solution, the solution in the flask remains clear and colorless.

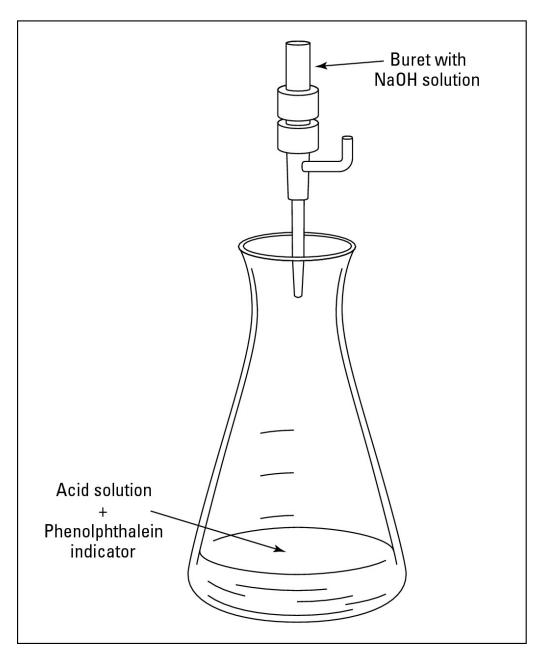
2. Add small amounts of a standardized sodium hydroxide solution of known molarity (for example, 0.100 M) with a buret.

A *buret* is a graduated glass tube with a small opening and a stopcock, which helps you measure precise volumes of a solution.

3. Keep adding the base until the solution turns the faintest shade of pink.

I call this the *endpoint* of the titration, the point in which the indicator shows that the acid has been exactly neutralized by the base. Figure 11-2 shows the titration setup.

Figure 11-2: Titration of an acid with a base.



Suppose that it takes 35.50 milliliters of the 0.100 M NaOH to reach the endpoint of the titration of the 25.00 milliliters of the HCl solution. Here's the reaction:

$$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$$

From the balanced equation, you can see that the acid and base react in a 1:1 mole ratio. So if you can calculate the moles of bases added, you'll also know the number of moles of HCl present. Knowing the volume of the acid solution then allows

you to calculate the molarity (note that you convert the milliliters to liters so that your units cancel nicely):

$$\frac{0.100 \text{ mol NaOH}}{1} \times \frac{0.03550 \text{ L}}{1} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1}{0.02500 \text{ L}} = 0.142 \text{ M HCl}$$

You can calculate the titration of a base with a standard acid solution (one of known concentration) in exactly the same way, except the endpoint is the first disappearance of the pink color.

# Putting Coffee and Other Substances on the pH Scale

The amount of acidity in a solution is related to the concentration of the hydronium ion in the solution. The more acidic the solution is, the larger the concentration of the hydronium ion. In other words, a solution in which the  $[H_3O^+]$  equals  $1.0 \times 10^{-2}$  is more acidic than a solution in which the  $[H_3O^+]$  equals  $1.0 \times 10^{-7}$ . The *pH scale*, a scale based on the  $[H_3O^+]$ , was developed to more easily tell at a glance the relative acidity of a solution. *pH* is defined as the negative logarithm (abbreviated as log) of the  $[H_3O^+]$ . Mathematically, it looks like this:

$$pH = -log [H_3O^+]$$

Based on the water dissociation constant,  $K_w$  (see "Playing both parts: Amphoteric water," earlier in this chapter), in pure water the  $[H_3O^+]$  equals  $1.0\times 10^{-7}$ . Using this mathematical relationship, you can calculate the pH of pure water:

```
pH = -\log [H_3O^+]

pH = -\log [1.0 \times 10^{-7}]

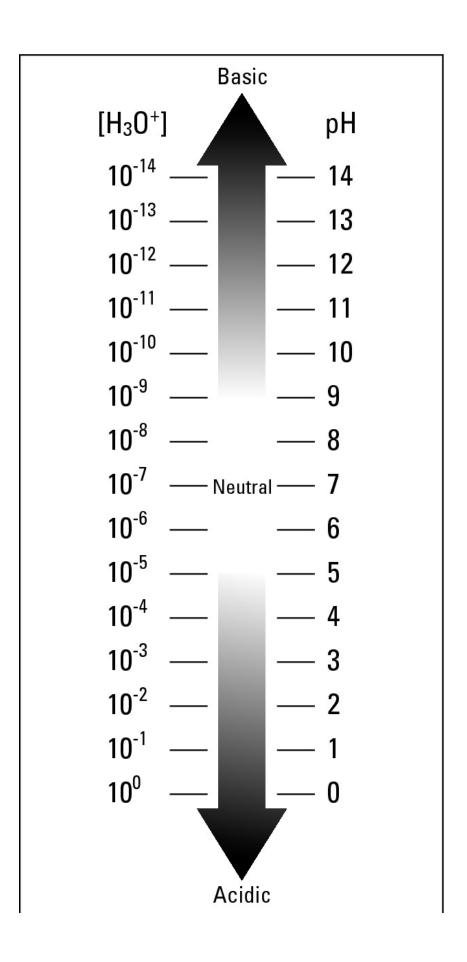
pH = -[-7]

pH = 7
```

The pH of pure water is 7. Chemists call this point on the pH scale *neutral*. A solution is called *acidic* if it has a larger  $[H_3O^+]$  than water and a smaller pH value than 7. A *basic* solution has a smaller  $[H_3O^+]$  than water and a larger pH value than 7.

The pH scale really has no end. You can have a solution of pH that registers less than 0. (A 10 M HCl solution, for example, has a pH of –1.) However, the 0 to 14 range is a convenient range to use for weak acids and bases and for dilute solutions of strong acids and bases. Figure 11-3 shows the pH scale.

Figure 11-3: The pH scale.



The  $[H_3O^+]$  of a 2.0 M acetic acid solution is  $6.0 \times 10^{-3}$ . Looking at the pH scale, you see that this solution is acidic. Now calculate the pH of this solution:

pH = 
$$-\log [H_3O^+]$$
  
pH =  $-\log [6.0 \times 10^{-3}]$   
pH =  $-[-2.22]$   
pH =  $2.22$ 

In the section "Playing both parts: Amphoteric water," I explain that the  $K_w$  expression enables you to calculate the  $[H_3O^+]$  if you have the  $[OH^-]$ . Another equation, called the pOH, can be useful in calculating the pH of a solution. The pOH is the negative logarithm of the  $[OH^-]$ . You can calculate the pOH of a solution just like the pH by taking the negative log of the hydroxide ion concentration. If you use the  $K_w$  expression and take the negative log of both sides, you get 14 = pH + pOH. This equation makes going from pOH to pH quite easy.

Just as you can convert from  $[H_3O^+]$  to pH, you can also go from pH to  $[H_3O^+]$ . To do this, you use what's called the *antilog relationship*, which is

$$[H_3O^+] = 10^{-pH}$$

Human blood, for example, has a pH of 7.3. Here's how you calculate the [H<sub>3</sub>O<sup>+</sup>] from the pH of blood:

$$[H_3O^+] = 10^{-pH}$$
 
$$[H_3O^+] = 10^{-7.3}$$
 
$$[H_3O^+] = 5.01 \times 10^{-8}$$

The same procedure can be used to calculate the [OH<sup>-</sup>] from the pOH.

#### **Antacids: Good, basic chemistry**

Go to any drugstore or grocery store and look at the shelves upon shelves of antacids. They represent acid-base chemistry in action!

The stomach secretes hydrochloric acid in order to activate certain enzymes (biological catalysts) in the digestion process. But sometimes the stomach produces too much acid, or the acid makes its way up into the esophagus (leading to heartburn or acid reflux), and you need to neutralize the excess acid with — you guessed it — a base. The basic formulations that are sold to neutralize this acid are called *antacids*. Antacids include the following compounds as active ingredients:

- ✓ Bicarbonates NaHCO₃ and KHCO₃
- ✓ Carbonates CaCO₃ and MgCO₃
- Hydroxides Al(OH)<sub>3</sub> and Mg(OH)<sub>2</sub>

Trying to select the "best" antacid for occasional use can be complicated. Certainly price is a factor, but the chemical nature of the bases can also be a factor. For example, individuals with high blood pressure may want to avoid antacids containing sodium bicarbonate because the sodium ion tends to increase blood pressure. Individuals concerned about loss of calcium from the bones, or *osteoporosis*, may want to use an antacid containing calcium carbonate. However, both calcium carbonate and aluminum hydroxide can cause constipation if used in large doses. On the other hand, large doses of both magnesium carbonate and magnesium hydroxide can act as laxatives. Selecting an antacid can really be a balancing act!

Substances commonly found in everyday life cover a wide range of pH values. Table 11-4 lists some common substances and

their pH values.

**Table 11-4 Average pH Values of Some Common Substances** 

Substance	рН
Oven cleaner	13.8
Hair remover	12.8
Household ammonia	11.0
Milk of magnesia	10.5
Chlorine bleach	9.5
Seawater	8.0
Human blood	7.3
Pure water	7.0
Milk	6.5
Black coffee	5.5
Soft drinks	3.5
Aspirin	2.9
Vinegar	2.8
Lemon juice	2.3
Auto battery acid	8.0

To sustain life, human blood must stay within about +/-0.2 pH units of 7.3, a narrow range. Many things in our environment, such as foods and hyperventilation, can act to change the pH of our blood. Buffers help to regulate blood pH and keep it in the 7.1 to 7.5 range.

### **Controlling pH with Buffers**

Buffers, or buffer solutions as they're sometimes called, resist a change in pH caused by the addition of acids or bases. Obviously, the buffer solution must contain something that reacts with an acid — a base. Something else in the buffer solution reacts with a base — an acid. In general, buffers come in two types:

✓ **Mixtures of weak acids and bases:** The mixtures of weak acids and bases may be conjugate acid-base pairs (such as H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub><sup>-</sup>) or nonconjugate acid-base pairs (such as NH<sub>4</sub><sup>+</sup>/CH<sub>3</sub>COO<sup>-</sup>). (For more info about conjugate acid-base pairs, see "Competing for protons: Bronsted-Lowry acid-base reactions," earlier in this chapter.)

In the body, conjugate acid-base pairs are more common. In the blood, for example, the carbonic acid/bicarbonate pair helps to control the pH. This buffer can be overcome, though, and some potentially dangerous situations can arise. If a person exercises strenuously, lactic acid from the muscles is released into the bloodstream. If there's not enough bicarbonate ion to neutralize the lactic acid, the blood pH drops, and the person is said to be in *acidosis*. Diabetes may also cause acidosis. On the other hand, if a person hyperventilates (breathes too fast), she breathes out too much carbon dioxide. The carbonic acid level in the blood is reduced, causing the blood to become too basic. This condition, called *alkalosis*, can be very serious.

✓ **Amphoteric species:** Amphoteric species may also act as buffers by reacting with an acid or a base. (For an example of an amphoteric species, see "Playing both parts: Amphoteric water," earlier in this chapter.) The bicarbonate ion (HCO<sub>3</sub>⁻) and the monohydrogen

phosphate ion  $(HPO_4^{-2})$  are amphoteric species that neutralize both acids and bases. Both of these ions are also important in controlling the blood's pH.

## Acids with bad press: An introduction to acid rain

Over the past decade or so, acid rain has emerged as a great environmental problem. Natural rainwater is somewhat acidic (around pH 5.6) due to the absorption of carbon dioxide from the atmosphere and the creation of carbonic acid. However, when acid rain is mentioned in the press, it usually refers to rain in the pH 3 to 3.5 range.

The two major causes of acid rain are automotive and industrial pollution. In the automobile's internal combustion engine, nitrogen in the air is oxidized to various oxides of nitrogen. These nitrogen oxides, when released into the atmosphere, react with water vapor to form nitric acid (HNO<sub>3</sub>).

In fossil fuel power plants, oxides of sulfur are formed from the burning of the sulfur impurities commonly found in coal and petroleum. These oxides of sulfur, if released into the atmosphere, combine with water vapor to form both sulfuric and sulfurous acids  $(H_2SO_4$  and  $H_2SO_3)$ . Oxides of nitrogen are also produced in these power plants.

These acids fall to earth in the rain and cause a multitude of problems. They dissolve the calcium carbonate of marble statues and monuments. They decrease the pH of lake water to such a degree that fish can no longer live in the lakes. They cause whole forests to die or become stunted. They react with the metals in cars and buildings.

Industrial controls have been somewhat effective in reducing the problem, but acid rain is still a major environmental issue. (See Chapter 18 for more info about acid rain.)