

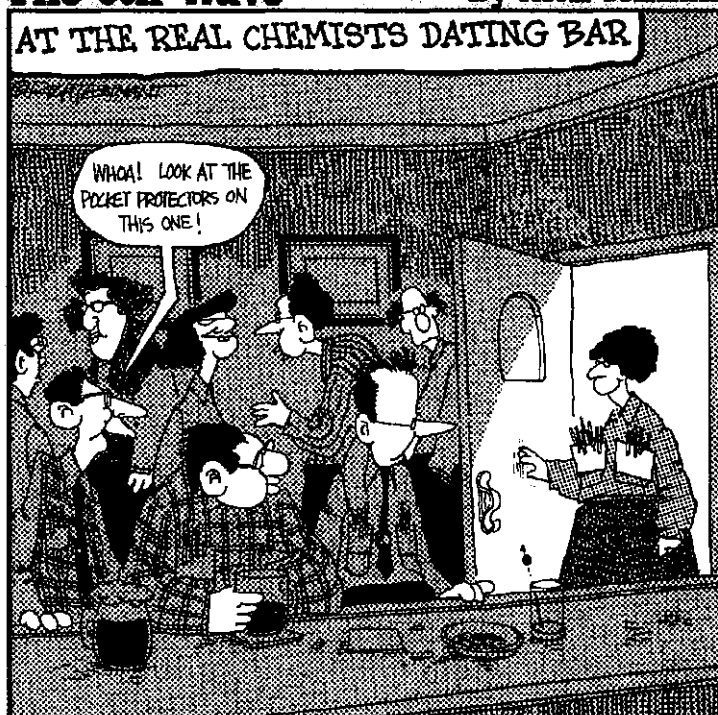
Part IV

Chemistry in Everyday Life: Benefits and Problems

The 5th Wave

By Rich Tennant

AT THE REAL CHEMISTS DATING BAR.



In this part . . .

Chemistry isn't just something that's done in an academic or industrial lab. Professional chemists aren't the only individuals who do chemistry. *You* do chemistry, too. Chemistry touches your life each and every day.

Chemistry gives us great benefits, but it can also give us great problems. Our modern society is complex. Chemistry holds the promise of solving many of the problems facing society, making our lives easier and more meaningful.

In the chapters of this part, I show you some applications of chemistry. I cover the chemistry of carbon and show you how it applies to petroleum and the process of making gasoline. I show you how that very same petroleum can be used to make plastics and synthetic fibers. I zip you home to look at the chemistry behind cleaners and detergents, medicines, and cosmetics of all kinds. And I show you some problems that society, technology, and science have created — air and water pollution.

Chapter 14

The Chemistry of Carbon: Organic Chemistry

In This Chapter

- ▶ Taking a look at hydrocarbons
 - ▶ Seeing how to name some simple hydrocarbons
 - ▶ Checking out the different functional groups
 - ▶ Discovering organic chemistry's place in society
-

The largest and most systematic area of chemistry is *organic chemistry*, the chemistry of carbon. Of the 11 to 12 million chemical compounds known, about 90 percent are organic compounds. We burn organic compounds as fuel. We eat organic compounds. We wear organic compounds. We're made of organic compounds. Our whole world is built of organic compounds.

In this chapter, I give you a brief introduction to organic chemistry. I spend some time showing you the *hydrocarbons*, compounds of carbon and hydrogen, as well as some other classes of organic compounds and their uses in everyday life. As you read this chapter, you'll find that a lot of chemistry can be found in carbon.

Organic synthesis: Where it all began

In the early years of chemistry, it was thought that organic compounds could only be produced from living organisms. People thought that there had to be a "vital force" involved. But in 1828, the German scientist Friedrich Wohler changed

the field of chemistry forever by developing an organic compound, urea, by accident while trying to make an inorganic compound. This was the beginning of our modern field of organic synthesis.

Hydrocarbons: From Simple to Complex

A natural question chemistry students ask is “Why are there so many compounds of carbon?” The answer: Carbon contains four valence electrons and so can form four covalent bonds to other carbons or elements. (A common mistake organic chemistry students make when drawing structures is not ensuring that every carbon has four bonds attached to it.) The bonds that carbon forms are strong covalent bonds (Chapter 7 covers covalent bonds), and carbon has the ability to bond to itself in long chains and rings. It can form double and triple bonds to another carbon or to another element. No other element, with the possible exception of silicon, has this ability. (And the bonds silicon makes aren’t nearly as strong as carbon’s.) These properties allow carbon to form the vast multitude of compounds needed to make an amoeba or a butterfly or a baby.

The simplest organic compounds are called the *hydrocarbons*, compounds composed of carbon and hydrogen. Economically, the hydrocarbons are extremely important to us — primarily as fuels. Gasoline is a mixture of hydrocarbons. We use methane (natural gas) and propane and butane, all hydrocarbons, for their ability to burn and release a large amount of energy. Hydrocarbons may contain only single bonds (the alkanes) or double bonds (the alkenes) or triple bonds (the alkynes). And they may form rings containing single or double bonds (cycloalkanes, cycloalkenes, and aromatics).

Even compounds containing only carbon and hydrogen have a great deal of diversity; imagine what can happen when a few more elements are mixed in!

From gas grills to gasoline: Alkanes

The simplest of the hydrocarbons are the *alkanes*. Alkanes are called *saturated* hydrocarbons — that is, each carbon is bonded to four other atoms. Carbon can form a maximum of four covalent bonds. If those four covalent bonds are to different atoms, then chemists say that the carbon is saturated. There are no double or triple bonds in the alkanes.

Alkanes have the general formula of C_nH_{2n+2} , where n is a whole number. If $n = 1$, then there are four hydrogen atoms, and the result is CH_4 , methane.

Table 14-1 lists the names of the first ten *normal*, or *straight-chained*, alkanes. They really aren’t straight; that’s just what they’re called. When I draw the structures, though, I often show them in a straight line. (Technically, they’re carbon bonds in a tetrahedral fashion with bond angles of 109.5 degrees. See Chapter 7 for a discussion of this stuff, called *molecular geometry*.) Every carbon, except the end ones, is bonded to two other carbons. Figure 14-1 shows models of the first four listed in the table.

<i>n</i>	<i>Formula</i>	<i>Name</i>
1	CH ₄	Methane
2	C ₂ H ₆	Ethane
3	C ₃ H ₈	Propane
4	C ₄ H ₁₀	Butane
5	C ₅ H ₁₂	Pentane
6	C ₆ H ₁₄	Hexane
7	C ₇ H ₁₆	Heptane
8	C ₈ H ₁₈	Octane
9	C ₉ H ₂₀	Nonane
10	C ₁₀ H ₂₂	Decane

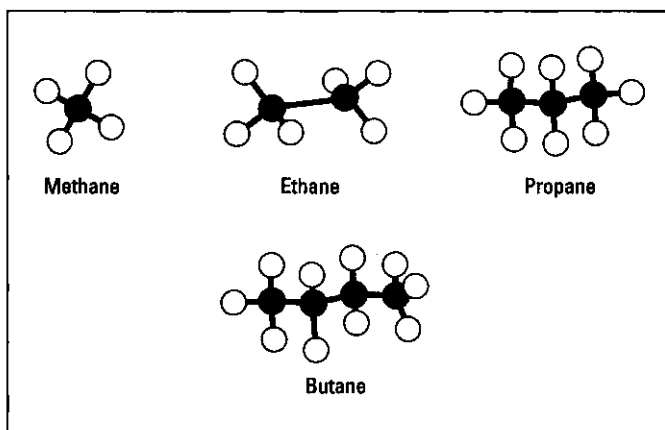


Figure 14-1:
The first
four
alkanes.

Molecular and structural formulas

Table 14-1 shows the molecular formula of some of the alkanes. The *molecular formula* shows what atoms are present in the compound and the actual number of each. They're all normal, or straight-chained, hydrocarbons, but the bonding pattern can be illustrated better by using a structural formula. The *structural formula* shows the atoms present, the actual number of each, and the bonding pattern, or what is bonded to what.

The structural formula can be shown in a number of different ways. One is called the *expanded structural formula*, which basically shows each covalent

bond as a line. With organic compounds such as the hydrocarbons, if you're really just interested in showing the way the carbons are bonded, you can omit the hydrogen atoms on the expanded form and just indicate them by the covalent-bond line. You can also use a condensed form, which groups parts of the molecule and still indicates the bonding pattern. The condensed form can be done several ways. Figure 14-2 shows a couple of expanded and three condensed forms of the structural formula of butane, C_4H_{10} .

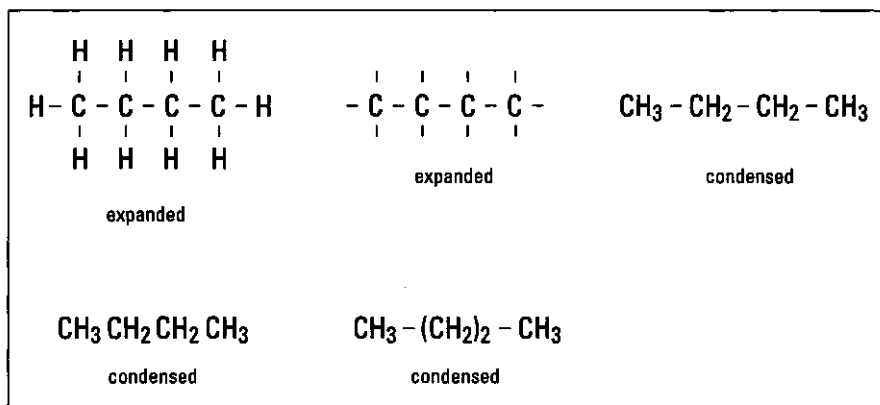


Figure 14-2:
Structural
formulas
of butane.

Naming problems

Sometimes two entirely different compounds — with two entirely different sets of properties — have the same molecular structure. The difference is in the way the atoms are bonded — what's bonded to what. These types of compounds are called *isomers*, compounds that have the same molecular formula but different structural formulas. Simply knowing the molecular formula isn't enough to distinguish between them.

An isomer of butane, for example, has the same molecular formula as the straight-chained compound shown in Figure 14-2, C_4H_{10} , but a different bonding pattern. This isomer is mostly referred to by the common name *isobutane* and is what I call a branched hydrocarbon. Check out Figure 14-3 to see it shown in a variety of ways.

So how do you differentiate which butane you're talking about when faced with the formula C_4H_{10} ? Use a unique name that stands only for that one compound. For the straight-chained compound, you can say butane or normal-butane or, better yet, *n*-butane. The *n*- makes it perfectly clear to a chemist that you're talking about the straight-chained isomer.

But what about the other isomer, isobutane? You can use the common name, but it isn't really accepted everywhere. Chemists all over the world need to agree on the name to help communication among scientists of all nations.

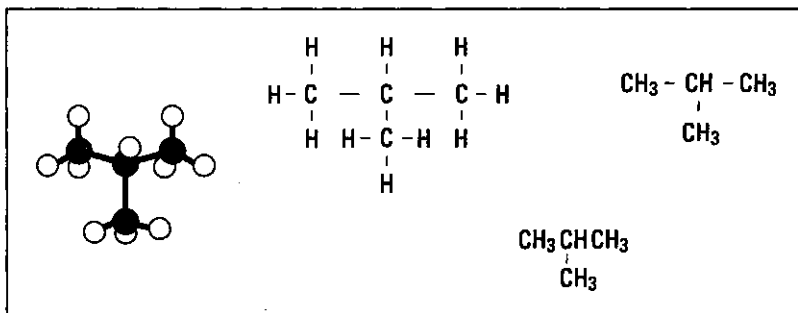


Figure 14-3:
Isobutane.

An international group of chemists sets rules for things such as the naming of organic compounds. This group is called IUPAC, the International Union of Pure and Applied Chemistry. These chemists have developed an extremely systematic set of rules for the naming of compounds, and they meet regularly to decide how to name new types of compounds discovered in nature or made in the laboratory.

Systematically naming all the various types of organic compounds would probably take another book, *IUPAC Nomenclature For Dummies*. Here, I just show you the rules for naming simple alkanes (even the naming of alkanes can get complicated, so it's important to use the KISS Rule — Keep It Simple, Silly):

- ✓ **Rule 1:** Locate the longest continuous carbon chain in the alkane (*longest* means the greatest number of carbon atoms, and *continuous* means starting at one end of the chain and connecting the carbons with your pencil without picking it up or backtracking). The straight-chained hydrocarbon that has the greatest number of carbons is the parent, or base, name of the alkane. The parent name ends in the suffix *-ane*.
- ✓ **Rule 2:** The parent name is modified by adding the names of substituent groups that are attached as branches to the parent compound. *Substituent groups* are those groups that have been substituted for a hydrogen atom in the alkane parent. For alkane hydrocarbons, these substituent groups are alkane branches that attach to the parent. They are named by taking the alkane name, dropping the *-ane*, and substituting *-yl*. So, for example, methane becomes methyl, ethane becomes ethyl, and so on.
- ✓ **Rule 3:** The position of a particular substituent group on the parent carbon chain is indicated by location numbers. They're assigned by consecutively numbering the carbons of the parent carbon chain from one end to the other so that the sum of the location numbers of all substituent groups will be as small as possible. (If this doesn't make any sense — and I feel your pain here — see “Naming examples” for, well, some examples. They make this stuff pretty clear.) The location number of the carbon to which the group is attached is placed in front of the substituent group name and separated from the name by a hyphen.

- ✓ **Rule 4:** The names of the substituent groups are placed in front of the parent name in alphabetical order. If there are a number of identical substituent groups, then the numbers of all the carbons to which these groups are attached — separated by commas — are used, and the common Greek prefixes — such as *di-*, *tri-*, *tetra-*, *penta-* — are used. These prefix names are not used to determine alphabetical order.
- ✓ **Rule 5:** The last substituent alkyl group is used as a prefix to the parent alkane name.

Naming examples

Okay. You're ready to throw down this book in disgust, aren't you? I know the alkane naming system sounds ridiculous, but it's really much easier than it looks. In fact, most of my students find that naming organic compounds is one of the most fun things to do in organic chemistry.

To show you how easy it can be, I'm going to walk you through the process of naming the compound shown in Figure 14-4 (cross-referencing the rule numbers as I go along).

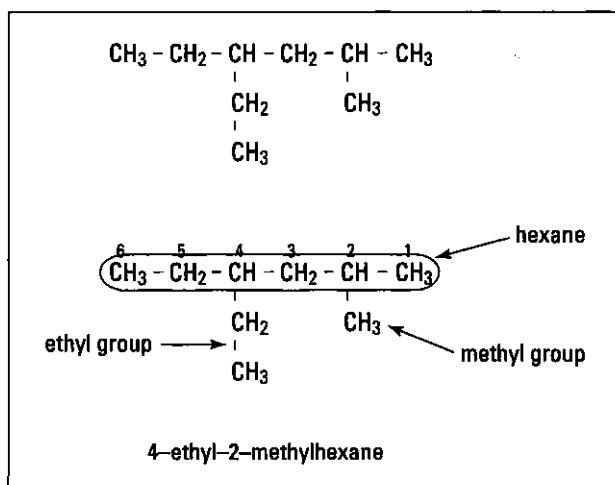


Figure 14-4:
Naming of
an alkane.

Using the condensed structural formula, the longest continuous carbon chain is composed of six carbons. Three different 6-carbon chains can actually be used (with the same name resulting eventually), but start with the horizontal one. The chain has six carbons, so the parent name is hexane (Rule 1). You have two substituent groups, one composed of two carbons (ethyl) and another with one carbon (methyl) (Rule 2). Number the parent chain from right to left, giving you alkyl groups at carbons 2 and 4 (sum of 6). Now do the same thing numbering from left to right on the parent chain, giving you groups at carbons 3 and 5 (sum of 8). Compare the right-to-left sum with the

left-to-right sum and go with the smallest sum's numbers. So you have a 4-ethyl and a 2-methyl (Rule 3). Placing them alphabetically and with the last substituent alkyl group used as a prefix to the parent alkane name, the result is 4-ethyl-2-methylhexane (Rules 4 and 5).

Got it?

Now you try one: Name the alkane shown in Figure 14-5.

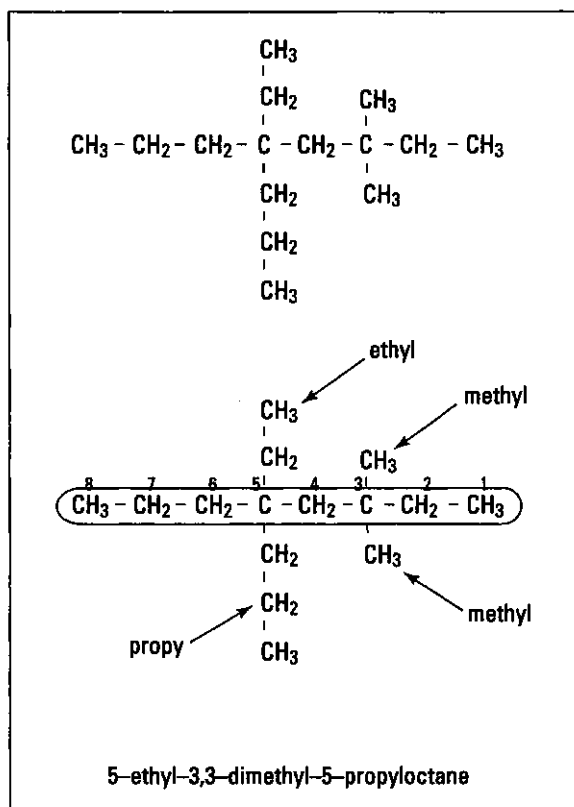


Figure 14-5:
Naming
another
alkane.

The longest carbon chain has eight carbon atoms, so you have an octane parent name. You have two methyl groups (dimethyl), an ethyl group, and a propyl group. Again, number right to left ($3+3+5=16$) instead of left to right ($4+4+6+6=20$) so that you have 3,3-dimethyl (remember that if you have identical substituent groups, then you include the numbers of all the carbons to which these groups are attached, separated by commas), 5-ethyl, and 5-propyl groups. Then arrange them alphabetically, remembering that the *di-* of dimethyl doesn't count: 5-ethyl-3,3-dimethyl-5-propyloctane.

Now, that wasn't as hard as you thought it'd be, was it?

As you may figure, the more carbons you have, the more isomers are possible. For an alkane with the formula $C_{20}H_{42}$, there are over 300,000 possible isomers, and for $C_{40}H_{82}$, there are about 62 *trillion* possible isomers!

Ring in the cycloalkanes

Alkanes may also form ring systems to make compounds called *cycloalkanes*. The naming of these compounds is very similar to the branched alkanes, except the *cyclo-* prefix is used on the parent name. In the condensed structural formula, the ring is often drawn as lines where the intersection of two straight lines indicates a carbon atom, and the hydrogen atoms aren't shown at all. Figure 14-6 shows both the expanded and condensed form of 1,3-dimethyl cyclohexane.

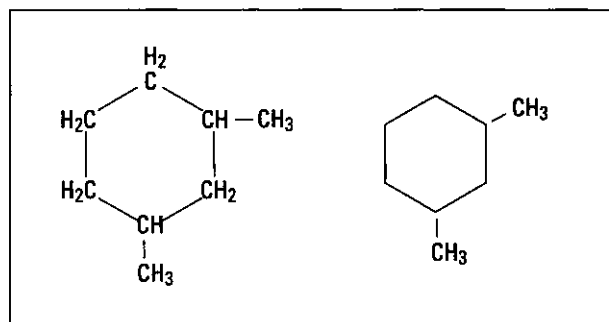


Figure 14-6:
1,3-dimethyl
cyclohexane.

Straight-chained alkanes and some cycloalkanes are primarily used as fuels. Methane is the primary component in natural gas and, like most hydrocarbons, is odorless. The gas companies add a stinky organic compound containing sulfur, called a *mercaptan*, to the natural gas to help alert you to gas leaks. Butane is used in lighters, and propane is used in gas grills. Some of the heavier hydrocarbons are found in petroleum. Combustion is the primary reaction of alkanes.

Say hello to halogenated hydrocarbons

The *halogenated hydrocarbons* are a related class of compounds. These are hydrocarbons, including alkanes, in which one or more of the hydrogen atoms have been replaced by some halogen — normally chlorine or bromine. Halogen substituents are named as *chloro-*, *bromo-*, and so on. Members of this class of compound include chloroform, once used as an anesthetic; carbon tetrachloride, used at one time in dry cleaning solvent; and freons (chlorofluorocarbons, CFCs), elements that have played a major role in the depletion of the ozone layer. See Chapter 18 for a discussion of CFCs and ozone.

Unsaturated hydrocarbons: Alkenes

Alkenes are hydrocarbons that have at least one carbon-to-carbon double bond (C=C). Alkenes that have only one double bond have the general formula C_nH_{2n} . For every additional double bond, subtract two hydrogen atoms.

These compounds are called *unsaturated hydrocarbons* because they don't have the maximum possible number of hydrogen atoms attached to the carbons. (I'm sure that you've heard the terms *saturated* and *unsaturated* used in regard to fats and oils in nutrition discussions. They mean exactly the same thing there — saturated fats and oils contain no carbon-to-carbon double bonds, unsaturated fats and oils do, and polyunsaturated fats and oils have more than one C=C per molecule.)

Naming alkenes

Alkenes have a parent name ending with the *-ene* suffix. You find the longest carbon chain containing the double bond and number it so that the carbon atoms involved in the double bond have the lowest location numbers.

Ethene, written as $H_2C=CH_2$ or $CH_2=CH_2$, and *propene*, $CH_3CH=CH_2$, are the first two members of the alkene family. These two alkenes are often called by their common names, ethylene and propylene, respectively. They are two of the most important chemicals produced by the chemical industry in the United States. Ethylene is used in the production of *polyethylene*, one of the most useful plastics produced, and in the production of *ethylene glycol*, the principal ingredient in most antifreeze. Propylene is used in the production of *isopropyl alcohol* (rubbing alcohol) and some plastics. Figure 14-7 shows a couple of ways to represent the structural formula of ethene (ethylene).

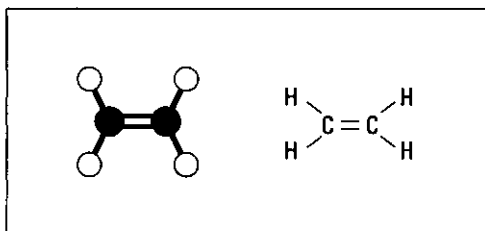


Figure 14-7:
Ethene.

Alkene reactions

Although the alkenes will readily undergo combustion, their primary reaction is *addition reactions*. A double bond is very reactive. One of the bonds can easily be broken, and the two carbons can then form new single bonds to other atoms. One of the most economically important addition reactions is

the process of *hydrogenation*, in which hydrogen is added across the double bond. Here's the hydrogenation of propene: $\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$

This hydrogenation reaction is used in the food industry to convert unsaturated vegetable oils to solid fats (vegetable oil to margarine, for example) and requires the use of a nickel metal catalyst.

Another important addition reaction of alkenes is *hydration*, the addition of a water molecule across the double bonding, yielding an alcohol. Here's the hydration of ethylene that gives ethyl alcohol (notice that I show the water molecule in a slightly different way so you can tell where the -OH ends up):



The ethyl alcohol produced in this way is identical to the ethyl alcohol produced by the fermentation process, but, by federal law, it can't be sold for human consumption in alcoholic beverages.

Undoubtedly, the most important reaction of the alkenes is *polymerization*, in which the double bond reacts to produce long chains of the once-alkenes bonded together. This is the process used to produce plastics (see Chapter 16).

It takes alkynes to make the world

Alkynes are hydrocarbons that have at least one carbon-to-carbon triple bond. These compounds have the IUPAC suffix *-yne*. Hydrocarbons with only a single triple bond have the general formula of $\text{C}_n\text{H}_{2n-2}$. The simplest alkyne is ethyne, commonly called *acetylene*. Figure 14-8 shows the structure of acetylene.

Figure 14-8:
Ethyne
(Acetylene).



Acetylene is produced in a variety of ways. One way is to react coal with calcium oxide to produce calcium carbide, CaC_2 . Calcium carbide is then reacted with water to produce acetylene. Miners' lamps used to be powered by this reaction. Water was dripped on calcium carbide, and the acetylene burned to produce light. Today, most of the acetylene produced is either used in oxyacetylene torches in cutting and welding or to make a variety of polymers (plastics).

Aromatic compounds: Benzene and other smelly compounds

Aromatic hydrocarbons are hydrocarbons that contain a cyclohexene type of ring system that has alternating single and double bonds. The simplest aromatic compound is *benzene*, C_6H_6 . Benzene is far less reactive than you'd imagine, having those three sets of double bonds. In the current model for benzene, six electrons, two from each of the three double bonds, are donated to an electron cloud associated with the entire benzene molecule. These electrons are *delocalized* over the entire ring instead of simply located between two carbon atoms. This electron cloud is above and below the planar ring system. Figure 14-9 shows a couple of traditional ways to represent the benzene molecule and a couple of ways to represent the delocalized structure.

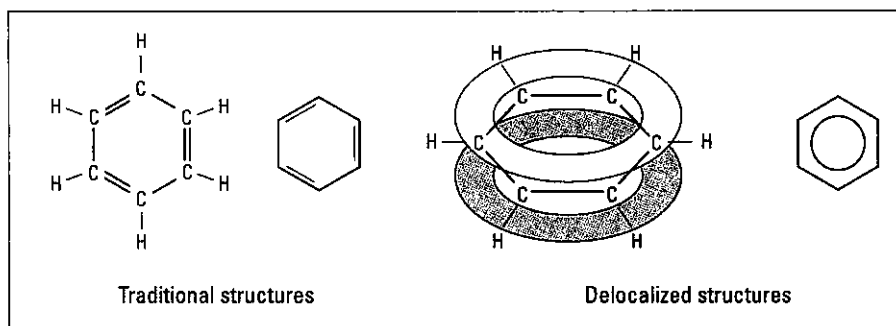


Figure 14-9:
Benzene.

Many groups may be attached to this benzene ring, making many new aromatic compounds. For example, an $-OH$ may replace a hydrogen atom. The resulting compound is called *phenol*. Phenol is used as a disinfectant and in the manufacture of plastics, drugs, and dyes. Two benzene rings fused together make *naphthalene*, which is commonly called mothballs.

Benzene and its related compounds burn, but they burn with a sooty flame. It's also been shown that benzene and some of its related compounds are either known or suspected carcinogens.

Functional Groups: That Special Spot

The preceding section covers hydrocarbons, or compounds of just carbon and hydrogen. Can you imagine how many new organic compounds can be

generated if a nitrogen atom, halogen atom, sulfur atom, or some other element is thrown in?

Consider some alcohols. Ethyl alcohol (drinking alcohol), methyl alcohol (wood alcohol), and isopropyl alcohol (rubbing alcohol) are quite different and yet remarkably the same in terms of the kinds of chemical reactions they undergo. The reactions all involve the -OH group on the molecule, the part of the molecule that really defines the identity of an alcohol, just as the double bond really defines the identity of an alkene. In many cases, it doesn't really matter what the rest of the molecule turns out to be. In reactions, one alcohol is pretty much the same as another.

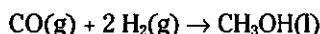
The atom or group of atoms that defines the reactivity of the molecule is called the *functional group*. For alcohols, it's the -OH; for alkenes, it's the C=C; and so on. This makes it much easier to study and classify the properties of compounds. You can learn the general properties of all alcohols instead of the properties of every individual one, for example. The use of functional groups makes the study of organic chemistry *much* easier.

This section places a spotlight on a few functional groups. What can really make things complex in the lab is that a molecule may have two, three, or more functional groups present, which leads to a wide array of reactions. But this is one of the things that makes organic chemistry challenging — and fun.

Alcohols (rubbing to drinking): R-OH

Alcohols are a group of organic compounds that contain the -OH functional group. In fact, alcohols are often generalized as *R-OH*, where the *R* stands for the *Rest* of the molecule (like that radio newscaster's "rest of the story"). Alcohols are named using the *-ol* suffix replacing the *-ane* of the corresponding alkane.

Methanol, methyl alcohol, is sometimes called wood alcohol because years ago, its primary synthesis involved heating wood in the absence of air. The more current method of synthesis of methanol involves reacting carbon monoxide and hydrogen with a special catalyst at elevated temperatures:



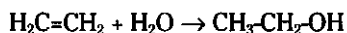
About half of the methanol produced in the United States is used in the production of *formaldehyde*, which is used as embalming fluid and in the plastics industry. It's also sometimes added to ethanol to make it unfit for human consumption, a process called *denaturing*. Methanol is also being considered as a replacement to gasoline, but some major problems still need to be overcome. A process that uses methanol in the production of gasoline does exist. New Zealand currently has such a plant that produces about a third of its gasoline.

Ethanol, ethyl alcohol or grain alcohol, is produced primarily in one of two ways. If the ethanol is to be used in alcoholic beverages, it's produced by the fermentation of carbohydrates and sugars by the enzymes in yeast:



As a brewer of beer and mead, I can attest that the yeast beasties certainly know how to make good alcohol!

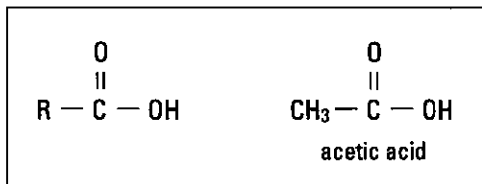
If the ethanol is to be used for industrial purposes, such as a solvent in perfumes and medicines or as an additive to gasoline (making it *gasohol*), it's produced by the hydration of ethylene using an acid catalyst:



Carboxylic acids (smelly things): R-COOH

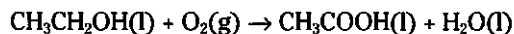
Figure 14-10 shows the structure of the carboxylic acid functional group.

Figure 14-10:
The carboxylic acid functional group and acetic acid.



Chemists often use -COOH or -CO₂H to indicate this functional group. These compounds are named with an *-oic acid* suffix. Acetic acid, shown in Figure 14-10, is also called *ethanoic acid*.

Carboxylic acids can be prepared by the oxidation of an alcohol. For example, leave a bottle of wine in contact with the air or some other oxidizing agent, and the ethanol oxidizes to acetic acid:



This is something that really breaks my heart, especially if I paid a lot for that particular bottle.

Formic acid, or methanoic acid, can be isolated by the distillation of ants. Yes, as in the critters that make mountainous sand piles in the cracks of the sidewalk in front of your house. The sting resulting from the bite of an ant is due to formic acid. That's why applying some base, such as baking soda,

helps to neutralize the acid and relieve the pain. (Chapter 12 is a lively read about acids and bases, if you're interested.)

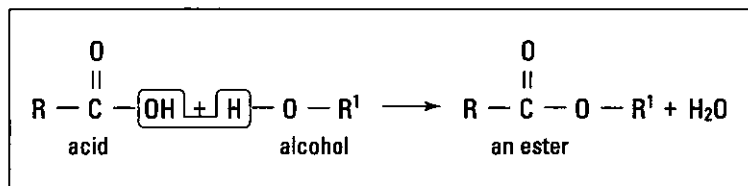
Many of these organic acids have a distinct odor associated with them. I'm sure you're familiar with the odor of vinegar, or acetic acid, but other acids have distinct odors, such as those mentioned in Table 14-2.

Table 14-2	Nasty Smells and What They Are	
$\text{CH}_3(\text{CH}_2)_2\text{COOH}$	Butyric acid	Odor of rancid butter
$\text{CH}_3(\text{CH}_2)_3\text{COOH}$	Pentanoic acid	Odor of manure
$\text{CH}_3(\text{CH}_2)_4\text{COOH}$	Hexanoic acid	Odor of goats

Esters (more smelly things, but mostly good odors): R-COOR'

The ester functional group is very similar to the carboxylic acid functional group except that another -R group has replaced the hydrogen atom. Esters are made by reacting a carboxylic acid with an alcohol, producing an ester and water. Figure 14-11 shows the synthesis of an ester.

Figure 14-11:
Synthesis of
an ester.



Although many of the carboxylic acids that esters are made from have foul odors, many esters have pleasant odors. Oil of wintergreen is an ester. Other esters have the odor of bananas, apples, rum, roses, and pineapples. Esters are often used in the flavoring and perfume industry.

Aldehydes and ketones: Related to alcohols

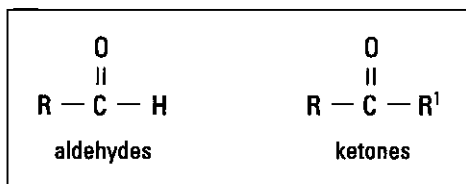
Both aldehydes and ketones are produced by the oxidation of alcohols. These functional groups are shown in Figure 14-12.

Eewww — what's that smell?

I liked organic chemistry when I was in college and enjoyed the lab experiments a bunch — especially the synthesis labs where I got to build complex molecules from simpler ones. I

wasn't really wild about the odors, though. Organic chemistry is one of the main reasons chemistry has the reputation for being stinky.

Figure 14-12:
Aldehyde
and ketone
functional
groups.



Formaldehyde, HCHO, is an economically important aldehyde. It's used as a solvent and for preservation of biological specimens. Formaldehyde is also used in the synthesis of certain polymers, such as Bakelite and *Melmac* (used in melamine dishes). Other aldehydes, especially those with a benzene ring in their structure, have pleasing odors and, like esters, are used in the perfume and flavoring industry.

Acetone, CH₃-CO-CH₃, is the simplest ketone and has many uses as a solvent, especially for paint. Many of us are familiar with acetone-based fingernail polish remover. And methyl ethyl ketone is the solvent in model airplane glue.

Ethers (sleepy time): R-O-R

Ethers contain an oxygen atom bonded to two hydrocarbon groups, R-O-R. This reminds me of a corny joke that chemists are wont to tell: Did you hear about the ether that was found in the Playboy Mansion? She was an ether bunny!

Diethyl ether was once used as an anesthetic, but its high flammability has caused it to be largely replaced in operating rooms. Because ethers are fairly unreactive (except for combustion), they're commonly used as solvents in organic reactions. They will, however, slowly react with the oxygen in the atmosphere to form explosive compounds called *peroxides*.

You can synthesize ethers by the reaction of alcohols with the loss of water (a *dehydration* reaction). Diethyl ether can be made by reacting ethyl alcohol in the presence of sulfuric acid:

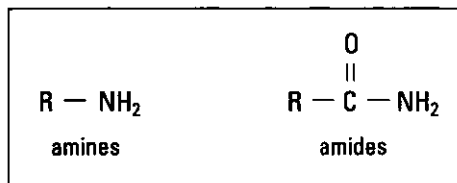


If you use two different alcohols, you get what's called a mixed ether, where the two R groups are not the same.

Amines and amides: Organic bases

Amines and amides are derived from ammonia and contain nitrogen in their functional groups. Figure 14-13 shows the amine and amide functional groups.

Figure 14-13:
Amine and
amide
functional
groups.



Take another look at the figure. Any of the hydrogen atoms attached to the nitrogen on both the amine and amide can be replaced by some other R group.

Amines and amides, like ammonia, tend to be weak bases (see Chapter 12). Amines are used in the synthesis of disinfectants, insecticides, and dyes. They're in many drugs, both naturally occurring and synthetic. *Alkaloids* are naturally occurring amines found in plants. Most amphetamines are amines.

Chapter 15

Petroleum: Chemicals for Burning or Building

.....

In This Chapter

- ▶ Discovering how petroleum is refined
 - ▶ Taking a look at gasoline
-

Petroleum is the basis of our modern society. Our automobiles run on gasoline, which is produced in part from petroleum, and many of our homes are heated with petroleum. It provides the feedstock for the expansive petrochemical industry. It's used to make plastics, paints, medicines, textiles, herbicides, and pesticides. The list is almost endless. Every year, the United States consumes over six billion barrels of petroleum. States and whole nations have risen to prosperity thanks to petroleum.

In this chapter, I show you how petroleum is refined and converted into useful products. I concentrate on the production of gasoline, because it's one of the most economically important uses of petroleum. I show you some of the problems that have been caused by our reliance on the internal combustion engine. This is one chapter in which I can talk crude — oil, that is.

Don't Be Crude, Get Refined

Petroleum, or crude oil (sometimes referred to as “Black Gold” or “Texas Tea”), as it comes out of the ground, is a complex mixture of hydrocarbons (see Chapter 14) of varying molecular weights. The lighter hydrocarbons are gases dissolved in the liquid mixture, while the heavier hydrocarbons are higher molecular weight solids that are also dissolved in the liquid mixture. The mixture was formed from decaying animal and plant material that was in the earth's crust for a very long time. Because it takes an extremely long time for petroleum to form (many millions of years), it's called a *nonrenewable resource*.

Before the hydrocarbon mixture can really be of much economic value, it must be *refined*, freed from impurities or unwanted material. The mixture is separated into groups of hydrocarbons, and in some cases, the molecular structure of the hydrocarbons is changed. The refining process occurs at a plant called a *refinery*, which produces the refined mixtures and individual compounds that are used for gasoline and feedstock for the vast petrochemical industry. A number of processes occur at the refinery, starting with the fractional distillation of the crude petroleum.

Fractional distillation: Separating chemicals

You've probably simmered a liquid in a covered pot on the stove. And you've probably noticed that when you remove the lid, water is on the inside of the lid. The heat has caused the water to evaporate from the liquid, and the vapors have condensed back into a liquid on the inside of the cooler lid. This is the most basic example of a process called *distillation*.

In the laboratory, you can take a mixture of liquids and carefully heat them. The liquid with the lowest boiling point boils first. You can then condense this vapor back to a liquid and collect it. The substance with the next highest boiling point then begins to boil, and so on. You can use this process of distillation as a means for separating the components of a mixture and purifying them. Distillation is an important procedure in organic chemistry, and it's the first step in the refining process. The distillation process that's commonly used in the refining industry is called *fractional distillation*. In this process, the petroleum mixture is heated and different *fractions* (groups of hydrocarbons with similar boiling points) are collected. Figure 15-1 shows the fractional distillation of crude oil.

The crude oil is brought into the refinery by pipeline and is initially heated and vaporized in a furnace. The hot vapors are then allowed to enter a huge distillation column, called a *fractional distillation tower*. The vapors containing the lightest molecular weight hydrocarbons rise to the top of the tower. The higher the molecular weight of the hydrocarbons, the lower the level to which they rise. The various fractions are then collected as each hydrocarbon reaches its distinct boiling point. The hydrocarbons within a fraction are all somewhat similar in size and complexity and can be used for the same purposes in the chemical industry. Six fractions are commonly collected:

➤ The first fraction is composed of the lightest hydrocarbons, which are gases with a boiling point of less than 40 degrees Celsius. A major component of this fraction is methane (CH_4), a gas that's sometimes called "marsh gas" because it was first found in marshes. Its primary use is as a fuel, *natural gas*, because it's a very clean-burning gas. Propane (C_3H_8) and butane (C_4H_{10}) are also found in this fraction. These two gases are normally collected and put under pressure, a process that causes them

to liquefy. They can then be transported by truck as liquefied petroleum (LP) gas and used as fuel. This fraction is also used as starting materials in the synthesis of plastics.

- ✔ The second fraction is composed of hydrocarbons of C_5H_{12} (pentane) to $C_{12}H_{26}$ (dodecane), with boiling points below the 200 degrees Celsius range. This fraction is commonly called *natural gasoline* or *straight-run gasoline*, because it can be used in automobile engines with little additional refining. With each barrel (42 gallons) of crude oil that starts out in the tower, less than a quarter of a barrel of straight-run gasoline is produced.
- ✔ The third fraction is composed of hydrocarbons of 12 to 16 carbon atoms in the boiling range of 150 to 275 degrees Celsius. This fraction is used as *kerosene* and *jet fuel*. In the next section, I tell you how this fraction is also used to make additional gasoline.
- ✔ The fourth fraction is composed of hydrocarbons in the 12 to 20 carbon-atom chains, with a boiling range of 250 to 400 degrees Celsius. This fraction is used for *heating oil* and *diesel fuel*. Again, it can be used in the production of additional gasoline.
- ✔ The fifth fraction is composed of hydrocarbons in the 20 to 36 carbon-atom range, with boiling points of 350 to 550 degrees Celsius. They're used as *greases*, *lubricating oils*, and *paraffin-based waxes*.
- ✔ The sixth fraction is composed of the residue of semisolid and solid materials that has a boiling point well above 550 degrees Celsius. It's used as *asphalt* and *tar*.

This cracks me up: Catalytic cracking

A barrel of crude oil yields a wide variety of products, but they don't all have the same value to us. Gasoline is the product of petroleum that's in the highest demand. The straight-run gasoline fraction that comes directly from the crude oil can't keep pace with the demand for gasoline.

With the high demand for gasoline, somebody got the bright idea that if you take a fraction of higher molecular weight hydrocarbons and break it down into smaller chains, the lower molecular weight hydrocarbons can be used for gasoline. The idea of *catalytic cracking* was born.

In a catalytic cracking plant ("cat crackers," as they're called in Texas), fractions in the C_{12} to C_{20} range are heated in the absence of air with a catalyst. This process causes the long *alkanes* (compounds of carbon and hydrogen with only carbon-to-carbon single bonds, which are covered in glorious detail in Chapter 14) to break apart into smaller alkanes and *alkenes* (hydrocarbons with at least one carbon-to-carbon double bond, covered in equally glorious detail in Chapter 14).

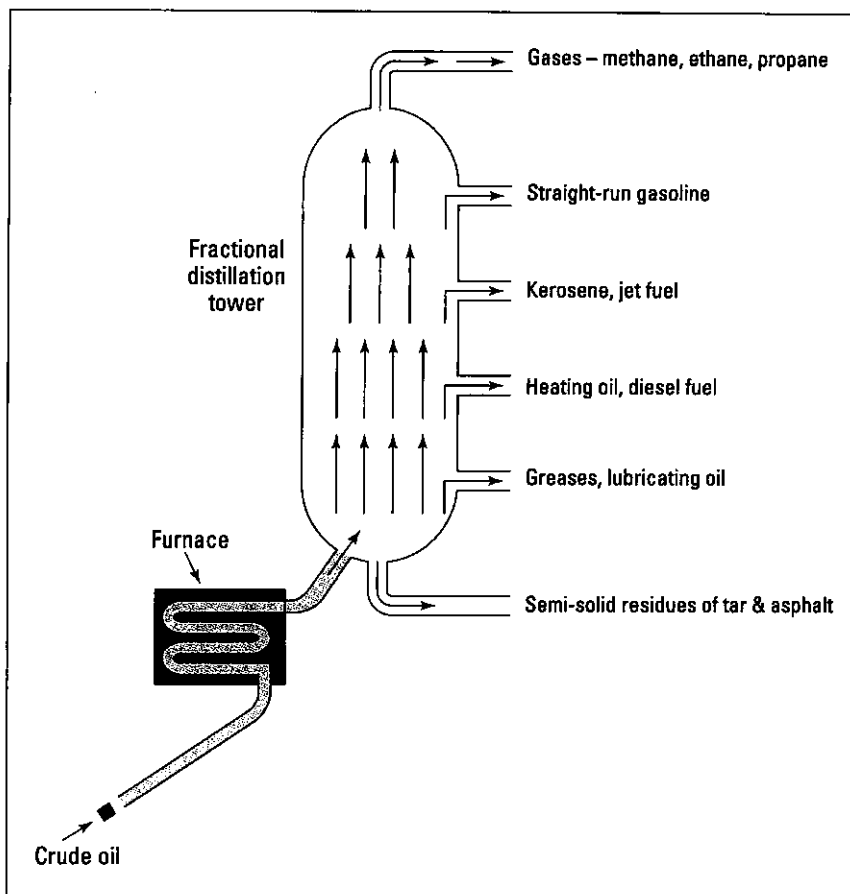
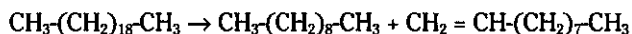


Figure 15-1:
Fractional distillation of petroleum.

For example, suppose that you take $C_{20}H_{42}$ and “crack it”:



This process yields hydrocarbons that are useful in the production of gasoline. In fact, the double bonds actually give it a higher octane rating, as I explain in “The Gasoline Story,” later in this chapter.

Catalytic cracking is done on the fraction that’s used for kerosene and jet fuel. But in order to produce even more gasoline, catalytic cracking is also done on the fraction used for heating oil. Using this fraction can present a problem, though, if a severe winter hits and the demand for heating oil skyrockets. Oil companies watch the long-range weather forecasts closely. In the summer, when the demand for gasoline is high, fractions that can be

used for heating oil are converted to gasoline to meet the demand. Then, as fall arrives, refineries shift their production schedule somewhat. They reduce the amount of gasoline they produce and increase the amount of heating oil so that the winter demand for heating oil can be met. But the refineries don't want to overproduce heating oil and have to store large amounts, so they try to second-guess the weather to develop a supply that will meet the demand. It's a real balancing act.

Moving molecular parts around: Catalytic reforming

As the internal combustion engine gained popularity as a mode of transportation, chemists noted that if the gasoline contained only straight-chained hydrocarbons, it didn't burn properly; it had a tendency to knock or ping. They found that hydrocarbons with branched structures burned much better. In order to increase the amount of branching in the petroleum hydrocarbon fraction being used for gasoline, a process called *catalytic reforming* was developed. In this process, the hydrocarbon vapors are passed over a metal catalyst such as platinum, and the molecule is rearranged into one with a branched structure or even a cyclic structure. Figure 15-2 shows the catalytic reforming of n-hexane to 2-methylpentane and to cyclohexane.

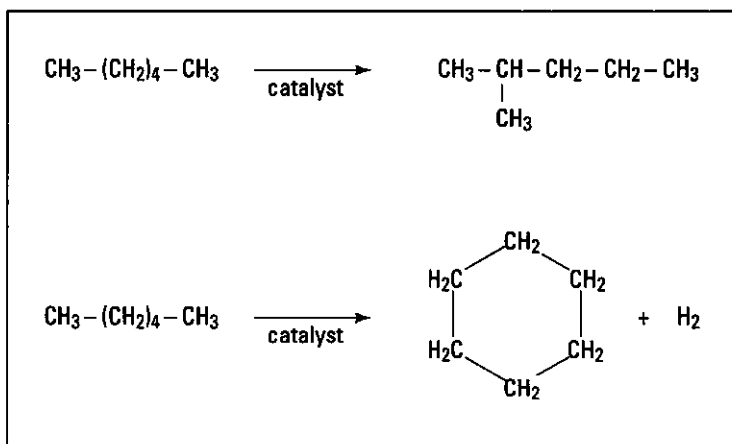


Figure 15-2:
Catalytic
reforming of
n-hexane.

This same process is used extensively to produce benzene and other aromatic compounds for use in the manufacture of plastics, medicines, and synthetic materials. (For a discussion of aromatic compounds, as well as branched and cyclic structures, see Chapter 14. What a treasure trove it is.)

The Gasoline Story

In order for you to better understand the properties of gasoline, I want to tell you a little about how gasoline is reacted in an internal combustion engine. The gasoline is mixed with air (a mixture of nitrogen, oxygen, and so on) and injected into the cylinder as the piston moves to the bottom of the cylinder. The piston then begins to move upward, compressing the gasoline-air mixture. At just the right moment, the spark plug fires, igniting the mixture. The hydrocarbons react with the oxygen in the cylinder, producing water vapor, carbon dioxide, and, unfortunately, large amounts of carbon monoxide.

This reaction is an example of converting the potential energy contained in the hydrocarbon bonds to the kinetic energy of the hot gas molecules. The increase in the number of gas molecules boosts the pressure tremendously, shoving the piston down. The linear motion is then converted to a rotary motion, which powers the wheels. And off you go!

The gasoline-air mixture must ignite at exactly the right moment in order for the engine to operate properly. This process is largely a property of the gasoline and not the engine itself (assuming the timing is set correctly, the spark plugs are good, the compression ratio is okay, and so on). The *volatility* of the hydrocarbon fuel (that is, how easily it's converted into a vapor) is important. Volatility is related to the boiling point of the hydrocarbon. In fact, manufacturers *blend* (adjust the hydrocarbon mixture) their gasoline to match the climate. (They don't do that in the part of Texas I live in — it's summer almost year-round.) Winter gas is more volatile than summer gas. Some fuels are prone to produce knocking or pinging in an engine. This propensity to cause knocking or pinging may be a result of *preignition*, where the igniting of the gasoline occurs before the compression of the fuel-air mixture is complete, or *spotty ignition*, where combustion starts taking place at a number of sites in the cylinder instead of right around the spark plug electrode. Again, this is a property of the gasoline and not the engine. The energy content of the fuel is important, but how efficiently it burns in the cylinder is just as important. The octane rating scale was developed to rate the burning characteristics of a gasoline.

How good is your gas: Octane ratings

In the early stages of the development of the internal combustion engine, scientists and engineers found that certain hydrocarbons burned well in an internal combustion engine. They also found that certain hydrocarbons did not burn well in these engines. A hydrocarbon that did not burn well was n-heptane (straight-chained heptane). However, 2,2,4-trimethylpentane (commonly called *isooctane*) had excellent burning characteristics. These two compounds were chosen to define the *octane rating scale*. The hydrocarbon n-heptane was assigned an octane rating of zero, while isooctane

was given a value of 100. Blends of gasoline are then burned in a standard engine and are rated according to this scale. For example, if a particular gasoline blend burns 90 percent as well as isooctane, then it's assigned an octane value of 90. Figure 15-3 shows the octane scale and the octane values of certain pure compounds.

Look carefully at Figure 15-3. A couple of things are useful to note in terms of octane rating and chemical structure. The n-pentene has an octane value of 62. Its octane value can be increased to 91 by introducing a double bond (making it 1-pentene) and making it an unsaturated compound. The octane value increases by almost 30 points with the introduction of the double bond.

The process of catalytic reforming introduces chains, and catalytic cracking introduces double bonds. Not only do these two processes increase the amount of gasoline that's produced, but they also improve the quality of the gasoline's burning characteristics. Also notice that benzene, an aromatic compound, has an octane value of 106. Its burning characteristics are better than isooctane. Other substituted aromatic compounds have octane ratings of almost 120. However, benzene and some related compounds are health hazards, so they're not used.

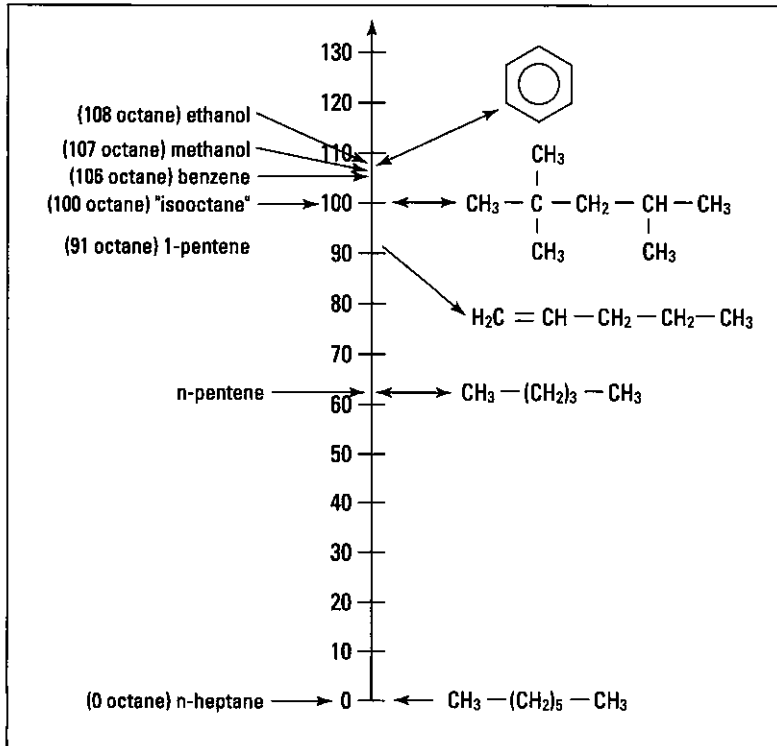


Figure 15-3:
The octane
rating scale.

The octane rating that is posted on gas pumps is really an average of two kinds of ratings. The *Research octane rating* (R) relates to the burning characteristics of the fuel in a cold engine. The *Motoring octane value* (M) refers to how the fuel behaves while you're cruising down the interstate. If you average R and M — $(R+M)/2$ — you get the posted octane rating.

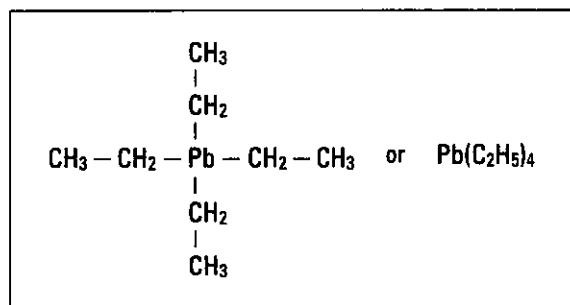
Additives: Put the lead in, get the lead out

The first gasoline engines had a compression ratio that was much lower than today's automobile engines, and they required lower octane gas. However, as engines became more powerful, gasoline with a higher octane rating was required. Catalytic cracking and reforming added significant cost to the gasoline. The search was on for something cheap that could be added to gasoline to effectively increase the octane rating. The substance tetraethyllead, or TEL, was found.

In the early 1920s, scientists discovered that adding a little bit of TEL to gasoline (1 milliliter per liter of gasoline) increased the octane rating by 10 to 15 points.

Tetraethyllead is basically a lead atom with four ethyl groups attached to it. Figure 15-4 shows the structure of TEL.

Figure 15-4:
The composition of tetraethyllead.



TEL was quite effective as an additive to increase the octane rating and prevent engine knocking. It was used for many years. However, the Clean Air Act of 1970 indirectly did it in.

Oops! We're polluting the air

Hydrocarbon fuel burns in the cylinders of internal combustion engines. During this process, not all of the hydrocarbon molecules are converted to water and CO/CO_2 . Before the Clean Air Act of 1970 came into play, unburned hydrocarbons and oxides of both sulfur and nitrogen were being released into the environment from automobiles (along with lead from the TEL, which

was later discovered to be very toxic). These gaseous pollutants dramatically increased the amount and severity of air pollution and gave rise to health hazards such as photochemical smog. (For a more complete discussion of air pollution, see Chapter 18.)

Bring on the catalytic converter

In the United States, The Clean Air Act of 1970 mandated the reduction of automotive pollutant emissions. The most effective way to accomplish the reduction of emissions was through the use of a *catalytic converter*. It's shaped like a muffler and connected to the exhaust system of an automobile. It has a solid catalyst, either palladium or platinum, inside. When the exhaust gases pass over the catalyst, the catalytic converter helps to complete the oxidation of the hydrocarbons and carbon monoxide to carbon dioxide and water. In other words, it helps to change the harmful gases from gasoline to mostly harmless products.

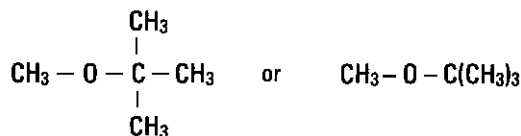
Lose the lead

The catalytic converter worked well at reducing the automotive emissions as long as there was no lead in the fuel. But if leaded gasoline was used, the lead vapor in the exhaust gases would coat the catalyst, rendering it useless. So there was a big push by the government and environmental groups to "get the lead out." Now it's very difficult to find leaded gasoline in the United States, although it's still available in some foreign countries.

With TEL no longer available as an octane booster, chemists tried to find other compounds to replace it. Aromatic compounds were effective in enhancing the octane value, but they were discovered to be serious health hazards. Recently, methyl alcohol, tert-butyl alcohol, and methyl tert-butyl ether (MTBE) have been used as octane boosters.

MTBE (see Figure 15-5) showed great promise because it not only boosted the octane rating but also acted as an *oxygenate*, a compound containing oxygen that increases the efficiency of the complete hydrocarbon combustion. But it has already been removed from gasoline due to increasing evidence that it's related to respiratory illnesses and possible cancers in humans. As for the other compounds, although none of them are as effective as TEL, the partial redesign of the internal combustion engine has allowed the use of slightly lower octane fuels.

Figure 15-5:
Methyl tert-butyl ether (MTBE).



Chapter 16

Polymers: Making Big Ones from Little Ones

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In This Chapter

- ▶ Understanding polymerization
 - ▶ Differentiating the different types of plastics
 - ▶ Finding out about recycling plastics
-

I once heard someone say that man never really invents anything new; he just copies nature. I'm not sure I believe that, with all the new inventions that have been developed recently. But I certainly think it's true in the case of polymers. Nature has been building polymers forever. Proteins, cotton, wool, and cellulose are all polymers. They all fall into a class of compounds called *macromolecules* — very large molecules. Man has learned to produce macromolecules in the lab, changing the face of our society forever.

When I was a child, my father, very much a traditionalist, said that he wanted things made of metal, not that cheap imported plastic stuff. Wow, would he be shocked today. I'm surrounded by synthetic textiles (clothing and carpet, for example), I ride around in autos that are fast becoming cocoons of plastic, my home is filled with plastic bottles of all shapes, sizes, and hardness, and I have friends with knees or other parts that have been either replaced or enhanced with polymers. I cook with a skillet that has a nonstick surface, I use a nylon spatula, I watch a TV with a plastic case, and I go to sleep on a foam pillow. Our world is truly part of the Age of Plastics.

In this chapter, I show you how the process of polymerization takes place and how chemists go about designing polymers with certain desired characteristics. I also show you some different kinds of polymers and how they're created. And I discuss some ways for getting rid of plastics before we bury ourselves in a mountain of milk jugs and disposable diapers. Welcome to the wonderful world of polymers!

Natural Monomers and Polymers

Nature has been building polymers for a long time. Cellulose (wood) and starch are prime examples of naturally occurring polymers. Take a look at Figure 16-1, which shows, the structures of cellulose and starch.

Notice anything similar about the two structures in the figure? They're both made up of repeating units. In fact, the repeating unit in both cases is a glucose unit. Both starch and cellulose are natural *macromolecules* (large molecules), but they're also examples of naturally occurring *polymers*, macromolecules in which there's a repeating unit called a *monomer*. (Polymer should stand for "many mer." The *mer* in this case is the monomer.) In the case of starch and cellulose, the monomer is a glucose unit. The structure of polymers is similar to taking a bunch of paper clips (monomers) and hooking them together to make a big long chain (polymer).

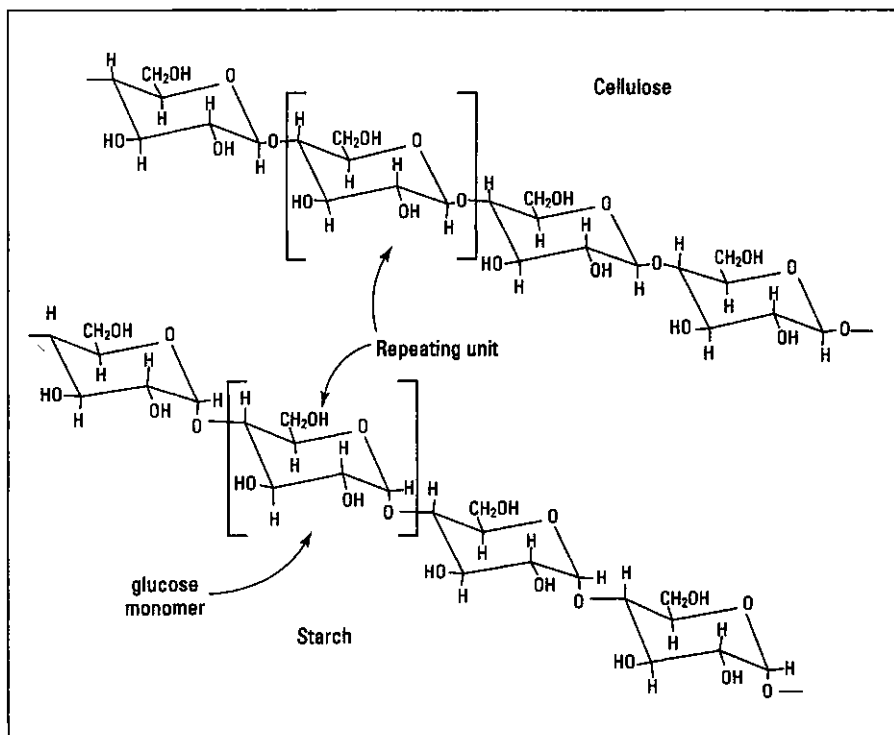


Figure 16-1:
Cellulose
and starch.

Notice another thing about cellulose and starch. The only way they differ is in how the glucose units are attached to each other. This minor change makes the difference between a potato and a tree. (Okay, it's not *quite* that simple.) Human beings can digest (metabolize) starches but not cellulose. A termite can digest cellulose just fine. In natural polymers, just like in synthetic ones, a minor change sometimes makes a big difference in the properties of the polymer.

Classifying Unnatural (Synthetic) Monomers and Polymers

Chemists took this idea of hooking together small units into very large ones from nature and developed a number of different ways of doing it in the lab. Now there are many different types of synthetic polymers. In this section, I introduce you to some of them and talk about their structures, properties, and uses.

Because chemists are big on grouping things together, they've put polymers into different classes. That works out just fine. Grouping gives chemists something to do and makes it easier for normal folks to get familiar with the various kinds of polymers out there.

We all need a little structure

One way of classifying polymers is by the structure of their polymer chain. Some polymers are *linear*. They're composed of many long strands thrown together like pieces of rope. *Branched* polymers have short branches coming off the main polymer strand. Imagine taking those long pieces of rope and tying short pieces of rope to them along the entire length. *Crosslinked* polymers have the individual polymer chains linked together by side chains. Imagine taking those pieces of rope and making them into a hammock.

Feel the heat

Another way of classifying polymers is by their behavior under heat. *Thermoplastic* polymers become soft when they're heated. Polymers of this type are composed of long linear or branched strands of monomer units hooked together. Have you ever left a pair of plastic sunglasses or a child's

plastic toy on the dashboard of your car in the middle of the summer? These plastics become really soft. Because they soften and melt, they can be remolded time and time again. This makes thermoplastics much easier to recycle. A vast majority of the plastics produced in the United States are of the thermoplastic type.

Thermosetting polymers don't soften when heated, and they can't be remolded. During production of this type of polymer, crosslinking (bridges between the polymer strands) is created in the plastic by heating it. Bakelite is a good example of a thermosetting plastic. It's a hard, strong nonconductor. These properties make it ideal as an insulator and as a handle for frying pans and toasters.

Used and abused

A third way of classifying polymers is by their use by the consumer.

A *plastic* refers to the polymer's ability to be molded. Whether they're of the thermoplastic or thermosetting type, these polymers are molded during the manufacture of the end product. And they're used to make our dishes, toys, and so on.

Fibers are linear strands held together by intermolecular forces such as hydrogen bonding between the polymer strands. These polymers are generally called textiles. They're used to make our clothes and our carpets.

Elastomers, sometimes called rubber, are thermoplastic materials that become slightly crosslinked during their formation. Because of this, they stretch and bounce. Natural rubber (latex) is classified as an elastomer along with its synthetic counterparts. These types of polymers are used for things like latex gloves and rubber bands and balls.

Chemical process

One of the best ways of classifying synthetic polymers is by the chemical processes used to create them. These processes normally fall into one of two categories:

- ✓ Addition polymerization
- ✓ Condensation polymerization

Let's hook up: Addition polymerization

Many of the common polymers you come into contact with every day are called *addition polymers* — polymers that are formed in a reaction called

addition polymerization. In this type of reaction, all the atoms that start out in the monomer are incorporated into the polymer chain. The monomers involved in this type of polymerization normally have a carbon-to-carbon double bond that's partially broken during polymerization. This broken bond forms a *radical reactive site*, or *radical*, which is a highly reactive atom that has an unpaired electron. The radical then gains an electron by joining up with another radical, and a chain is started, which eventually becomes the polymer. Scratching your head a bit? Looking at examples often helps folks understand chemical processes, so following are some examples of addition polymerization.

Polyethylene: Sandwich wrap and milk jugs

Polyethylene is the simplest of the addition polymers. It's also one of the most economically important. Ethane is heated at a high temperature in the presence of a metal catalyst, like palladium. Ethane loses two atoms of hydrogen (which make hydrogen gas) and forms a double bond:



The ethylene (ethene) that's produced here is the monomer used in the production of polyethylene. The ethylene is then subjected to high heat with a catalyst in the absence of air. The high heat and catalytic action causes one of the carbon-to-carbon double bonds (C=C) to break, with one electron going to each carbon. Both carbons now have an unpaired electron, so they become radicals. Radicals are extremely reactive and attempt to gain an electron. In terms of this polymerization reaction, the radicals can gain an electron by joining up with another radical to form a covalent bond. This happens at both ends of the molecule, and the chain begins to grow. Polyethylene molecules up to a molecular weight of 1 million grams/mol may be produced in this way (see Figure 16-2).

Different catalysts and pressures are used to control the structure of the final product. The polymerization of ethylene can yield three different types of polyethylene:

- ✓ Low-density polyethylene (LDPE)
- ✓ High-density polyethylene (HDPE)
- ✓ Crosslinked polyethylene (CLPE)

Low-density polyethylene (LDPE) has some branches on the carbon chain, so it doesn't pack together as closely and tightly as the linear polymer. It forms a tangled network of branched polymer strands. This type of polyethylene is soft and flexible. It can be used for food wrap, sandwich bags, grocery bags, and trash bags. And it, like all the forms of polyethylene, is resistant to chemicals.

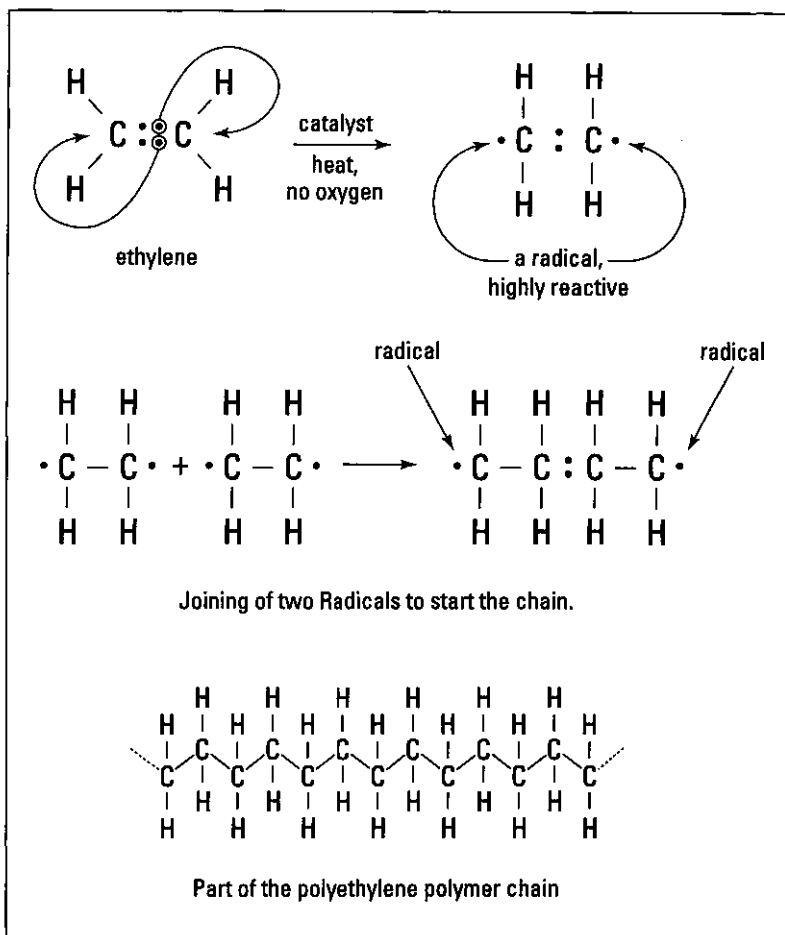


Figure 16-2:
The addition
polymer-
ization of
ethylene.

High-density polyethylene (HDPE) is composed of linear chains that are closely packed. This type of polymer is rigid, hard, and tough. Milk jugs, toys, and TV cabinets are made from HDPE. The Hula-Hoop was one of the first products ever made from this form of polyethylene.

Crosslinked polyethylene (CLPE) has crosslinking between the linear strands of monomers that are bonded together, producing a polymer that's extremely tough. The lid on that HDPE milk jug is probably CLPE. Soft drink bottle caps are also CLPE. The soft drink bottles are made of another type of polymer that I discuss a little later in the chapter.

Polypropylene: Plastic ropes

If you substitute another atom for a hydrogen atom on ethylene, you can produce a different polymer with different properties. If you substitute a methyl group for a hydrogen atom, you get propylene. Propylene, just like ethylene, has a double bond, so it can undergo addition polymerization in the same way as ethylene. The result is polypropylene (see Figure 16-3).

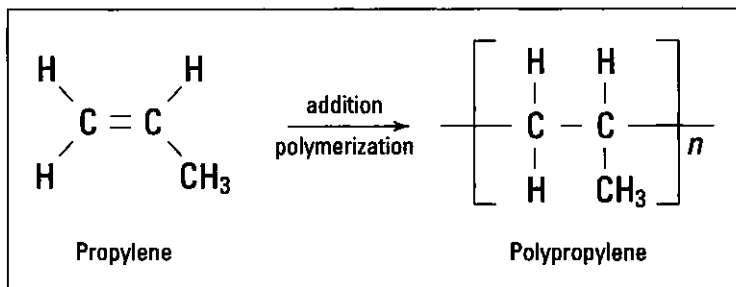


Figure 16-3:
Propylene
and poly-
propylene.

The small n in Figure 16-3 indicates that there are a number of the repeating units. Notice that this polymer has a methyl group side chain. Any time that the structure of a molecule is changed, the properties of the molecule change. By carefully adjusting the reaction conditions, chemists can construct polymers that have the side chains on the same side of the molecule, on alternating sides of the molecule, or distributed randomly. The position of these side chains changes the properties of the polymer somewhat so that polypropylene can be used for a wide variety of purposes, such as indoor-outdoor carpeting, battery cases, ropes, bottles, and automotive trim.

Polystyrene: Styrofoam cups

If you substitute a benzene ring for one of the hydrogen atoms on ethylene, you make styrene. Addition polymerization gives you polystyrene, as shown in Figure 16-4.

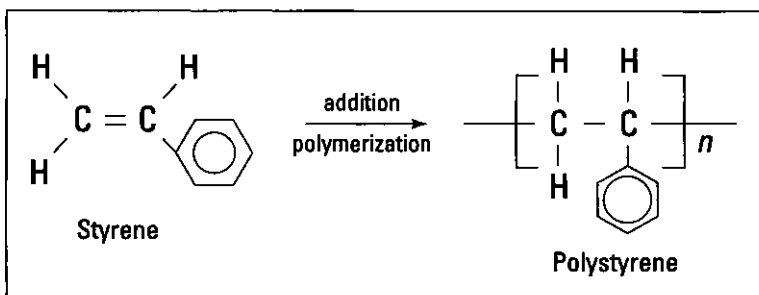
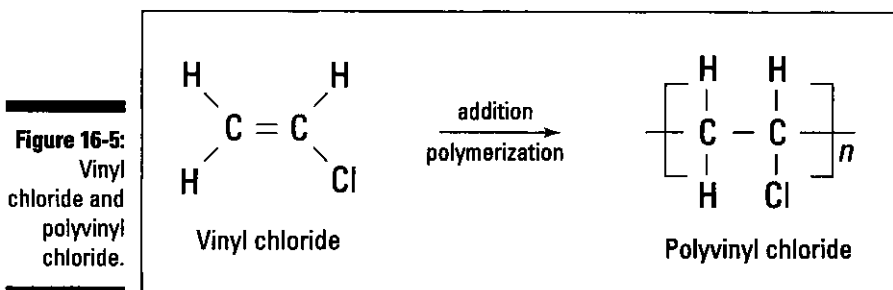


Figure 16-4:
Styrene and
polystyrene.

Polystyrene (Styrofoam) is a rigid polymer used for making foam drink cups, egg cartons, clear rigid drinking glasses, insulating materials, and packing materials. Environmentalists have criticized its use because it's more difficult to recycle than some other plastics and is so widely used.

Polyvinyl chloride: Pipes and simulated leather

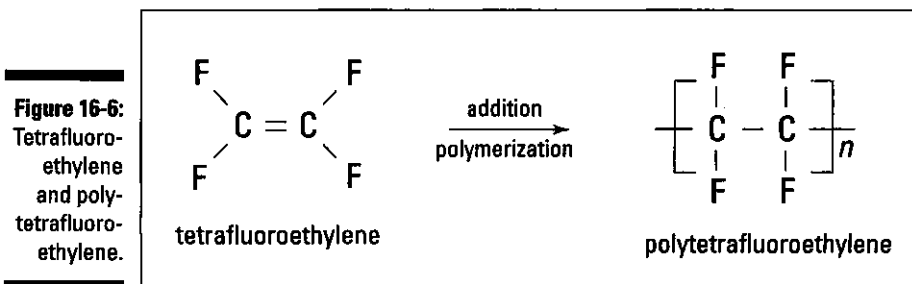
Substituting a chloride for one of the hydrogen atoms on ethylene gives you the vinyl chloride monomer that can polymerize to polyvinyl chloride (PVC), as shown in Figure 16-5.



PVC is a tough polymer. It's used extensively in rigid pipes of all types, flooring, garden hoses, and toys. Thin sheets of PVC used as simulated leather crack easily, so a *plasticizer* is added (a liquid that's mixed with plastics to soften them and allow them to more closely resemble leather). However, after many years, plasticizers can evaporate from plastic, making it brittle and allowing it to crack.

Polytetrafluoroethylene: Slick stuff

Replace all the hydrogen atoms on ethylene with fluorine atoms, and you have tetrafluoroethylene. The tetrafluoroethylene can be polymerized to polytetrafluoroethylene, as shown in Figure 16-6.



Polytetrafluoroethylene is a material that's hard, heat resistant, and extremely slick. This material is used as bearings, valve seats, and (most importantly to me) nonstick coating for pots and pans.

You can find some other addition polymers in Table 16-1.

Table 16-1		Other Addition Polymers
Monomer	Polymer	Uses
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{CN} \end{array}$ <p>Acrylonitrile</p>	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{CN} \end{array} \right]_n$ <p>Polyacrylonitrile</p>	Wigs, rugs, yarn
$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{O}-\text{C}-\text{CH}_3 \\ & & \\ & & \text{O} \end{array}$ <p>Vinyl acetate</p>	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{O}-\text{C}-\text{CH}_3 \\ & \\ & \text{O} \end{array} \right]_n$ <p>Polyvinyl acetate</p>	Adhesives, latex, paint, chewing gum resin, textile coatings
$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{C}-\text{O}-\text{CH}_3 \\ & & \\ & & \text{O} \end{array}$ <p>Methyl methacrylate</p>	$\left[\begin{array}{cc} \text{H} & \text{CH}_3 \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{C}-\text{O}-\text{CH}_3 \\ & \\ & \text{O} \end{array} \right]_n$ <p>Polymethyl methacrylate</p>	Contact lenses, glass substitute, bowling balls
$\text{H}_2\text{C}=\text{CCl}_2$ <p>Vinylidene chloride</p>	$\left[\begin{array}{cc} \text{H} & \text{Cl} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{Cl} \end{array} \right]_n$ <p>Polyvinylidene chloride</p>	food wrap

Let's get rid of something: Condensation polymerization

A reaction in which two chemical species combine with each other by eliminating a small molecule is called *condensation polymerization*. Polymers formed in this fashion are known as *condensation polymers*. Unlike in addition polymerization, no double bond is needed in this type of reaction.

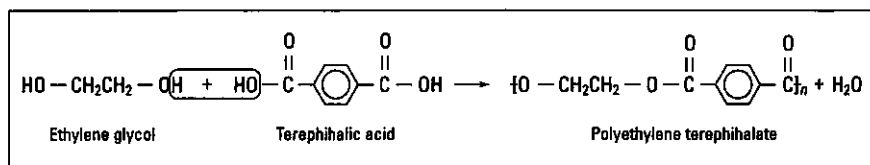
A small molecule — normally water — is eliminated. Commonly, one molecule is an organic acid, and the other is an alcohol. These two molecules react, splitting off water and forming an organic compound called an ester. If a polymer chain grows, it forms a polyester.

Following are some examples of condensation polymers. These examples involve techno-speak specific to functional groups in organic chemistry, and they involve a lot of complexly named organic compounds. If you aren't familiar with functional groups or how organic compounds are named, just flip to Chapter 14 for the details.

Polyester: Leisure suits and soft drink bottles

If you take ethylene glycol, with its alcohol functional groups on both carbons, and react it with terephthalic acid, with its two organic acid functional groups, you can eliminate water and form the condensation polymer polyethylene terephthalate (PET), a polyester. Figure 16-7 shows the synthesis of PET.

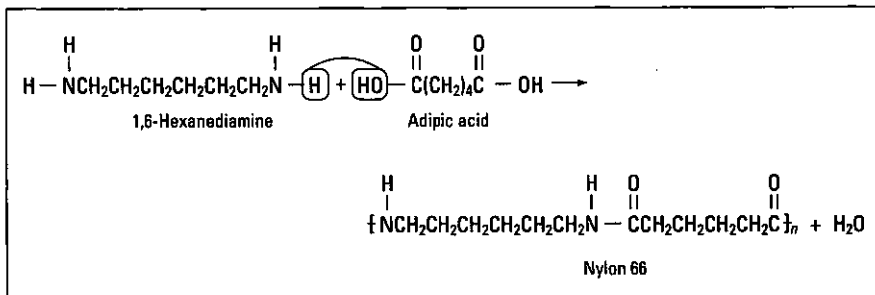
Figure 16-7:
Synthesis
of PET.



This is the polyester you find in clothing (boy, did I ever love that baby-blue leisure suit I had in the 70s!), artificial automotive tire cord, substitute blood vessels, film, and soft drink bottles.

Polyamides: Sheer enough for a woman, strong enough for a (police)man

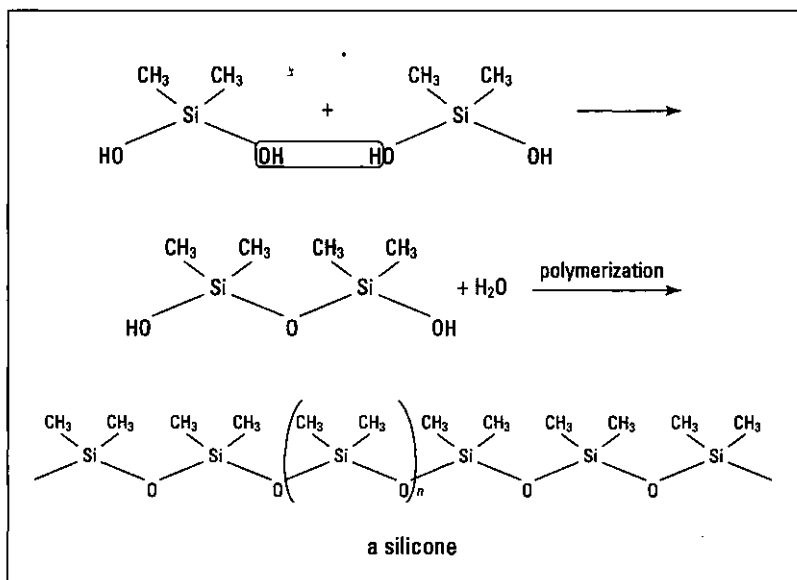
If you react an organic acid with an amine, you split off water and form an amide. If you use an organic acid that contains two acid ends and an amine that has two amine ends (a diamine), then you can polymerize a polyamide. The polyamide is commonly referred to as *nylon*. Figure 16-8 shows the reaction between 1,6-hexanediamine and adipic acid to form Nylon 66. (The 66 indicates that there are 6 carbon atoms in both the amine and the organic acid.)



The synthesis of nylon in 1935 had a major impact on the textile industry. Nylon stockings first went on sale in 1939, and nylon was used in parachutes extensively during World War II. Make a slight substitution in one of the carbon backbones, and you have a material strong enough for a bullet-proof vest.

Silicones: Bigger and better

Because silicon is in the same family as carbon, chemists can produce a class of polymers that contains silicon in its structure. These polymers are known as silicones. Figure 16-9 shows the synthesis of a typical silicone.



The silicone polymers are held together by the strong silicon-oxygen bond, and they can have molecular weights in the millions. They're used as gaskets and seals, and they're found in waxes, polishes, and surgical implants. The press has given the most attention to their use as surgical implants.

Silicone-based implants and prostheses have been used for years. They've been used as shunts, ear prostheses, finger joints, and, of course, breast implants. The implants themselves are filled with silicone oil. Occasionally, an implant leaks, and the silicone oil escapes into the body. In 1992, some evidence was found that silicone oil may trigger an autoimmune response. Although studies have not established a cause-and-effect relationship, many implants have been removed, and silicone oil is no longer used in the United States.

Polymers have reshaped our society as well as our figures. They're useful in a very wide variety of ways, relatively inexpensive, and durable. Because they're so durable, figuring out how to dispose of them is a major problem.

Reduce, Reuse, Recycle — Plastics

Plastics have basically an infinite lifetime. Nothing in nature does a good job at degrading them. If you bury that plastic plate, Styrofoam cup, or disposable diaper in a landfill and then dig it up ten years later, there will be no change. You could even dig it up a hundred years later and get the same results. Waste containing plastics will be with us for a long time.

Some plastics can be burned as fuels. They have a high heat content, but they often produce gases that are toxic or corrosive. Society can reduce its reliance on plastics to a certain degree. Using cardboard hamburger boxes and cellulose shipping packing instead of Styrofoam helps, but our best answer so far has been in the area of recycling.

Thermoplastic polymers can be melted down and reformed. But in order to do this, the plastics must be separated into their various components. Most plastic containers contain a symbol on the bottom that indicates what type of plastic the containers are made of. Recyclers can use these symbols to separate the plastics into various categories to make recycling easier. Figure 16-10 shows the recycling symbols for plastics and indicates what type of plastic each symbol represents.








	PET Polyethylene terephthalate
	HDPE High density polyethylene
	PVC Polyvinyl chloride
	LDPE Low density polyethylene
	PP Polypropylene
	PS Polystyrene
	Other

Figure 16-10:
Plastic
recycling
codes.

PET bottles and HDPE milk jugs are probably the plastics recycled the most. But the major problem isn't the chemistry involved in the recycling process: The major problems are encouraging individuals, families, and businesses to recycle and developing an easy means to collect and sort the plastics for recycling. These polymers are too valuable a resource to simply be buried in some landfill.

Chapter 17

Chemistry in the Home

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In This Chapter

- ▶ Discovering the chemistry behind cleaners and detergents
 - ▶ Finding out about the chemistry of cosmetics
 - ▶ Looking at the chemistry of drugs and medicines
-

You'll probably come into direct contact with more chemicals and chemistry in your own home than anyplace else. The kitchen is filled with cleaners, soaps, and detergents, most of which are contained in plastic bottles. The bathroom is filled with medicines, soaps, toothpaste, and cosmetics. My wife is glad to have her own private chemist handy, especially when it's time to clean the silver or find a solvent to remove an adhesive. And all that doesn't even cover the myriad chemical reactions that take place while cooking. No wonder consumer chemistry is sometimes called "kitchen chemistry."

In this chapter, I cover a few topics from the chemistry of consumer products. I show you the chemistry behind soaps, detergents, and cleaners. I talk a little bit about medicines and drugs, and I show you some things about personal care products, permanents, tanning products, and perfumes. I hope that you'll gain an appreciation for chemistry and what it has done to make your life better and easier. (Note that lots of common chemicals in the home are acids and bases. Chapter 12's main thing is acids and bases, which makes it nice complementary reading to this chapter.)

Chemistry in the Laundry Room

Have you ever become distracted and forgotten to put the laundry detergent in the washer? Or have you ever been suckered into trying one of those miracle solid ceramic laundry detergent discs? I doubt that the clothes came out very clean. You may have gotten some surface dirt off, but the grease and oil stayed right where it was. The grease and oil stayed on the clothes because "like dissolves like." Grease and oils are nonpolar materials, and water is a polar substance, so water isn't going to dissolve the grease and oil. (Chapter 7 gets into detail about this whole polar/nonpolar business, if you're interested.) I guess you could dump some gasoline (a nonpolar material) into the washer,

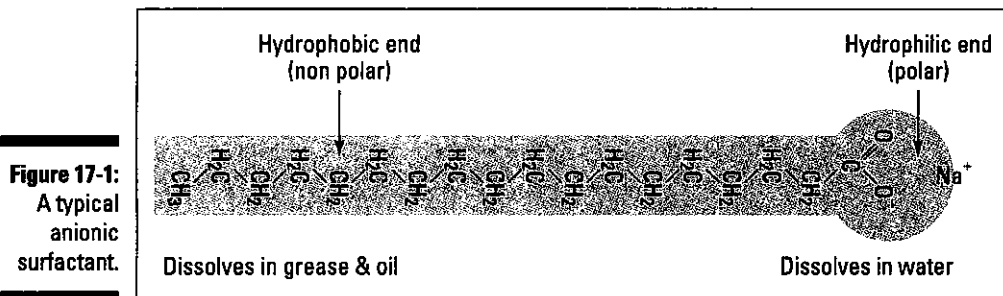
but I don't think that's a good solution to the problem. Wouldn't it be wonderful if something existed that could bridge the gap between the nonpolar grease and oil and the polar water? Something does. It's called a *surfactant*.

Surfactants, which are also called surface active agents, reduce the surface tension of water, allowing it to "wet" nonpolar substances such as grease and oil. Surfactants are able to do this because they have both a nonpolar end and a polar end.

The nonpolar end is called the *hydrophobic* (water-fearing) end. This end is normally composed of a long hydrocarbon chain. (If you're feeling ambitious, Chapter 14 covers more than you'll probably ever want to know about hydrocarbons.) The nonpolar end dissolves in the nonpolar grease and oil.

The other part of the surfactant molecule, the polar end, is called the *hydrophilic* (water-loving) end. This end is normally an ionic end with a negative charge (*anionic*), a positive charge (*cationic*), or both (*amphoteric*). There are even some surfactants that have no charge (*nonionic*). (Ions, anions, cations — Chapter 6 explains 'em all.)

A vast majority of the surfactants on the market are anionic surfactants, because they're cheaper to produce. Figure 17-1 shows a typical anionic surfactant.



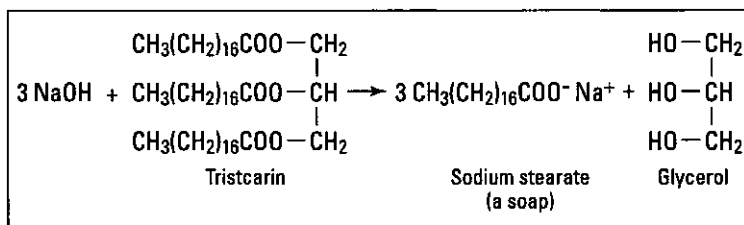
When a surfactant is added to water, the hydrophobic end dissolves in the oil and grease, while the hydrophilic end becomes attracted to the polar water molecules. The grease and oil are broken into very tiny droplets called *micelles*, with the hydrophobic (hydrocarbon) end of the surfactant sticking into the droplet and the hydrophilic end sticking out into the water. This gives the droplet a charge (a negative charge in the case of an anionic surfactant). These charged droplets repel each other and keep the oil and grease droplets from joining together. These micelles remain dispersed and eventually go down the drain with the used wash water.

The two general types of surfactants that are used in the cleaning of clothes are soaps and detergents.

Keep it clean: Soap

Soaps are certainly the oldest and most well-known surfactant for cleaning. The use of soap dates back almost 5,000 years. The specific type of organic reaction involved in the production of soap is a hydrolysis reaction of fats or oils in a basic solution. This reaction is commonly called *saponification*. The products of this reaction are glycerol and the salt of the fatty acid. Figure 17-2 shows the hydrolysis of tristearin to sodium stearate, a soap. (This is the same soap, or surfactant, shown in Figure 17-1.)

Figure 17-2:
Production
of a soap by
saponifica-
tion.



Grandma made her soap by taking animal fat, adding it to water and lye (sodium hydroxide, NaOH), and boiling it in a huge iron kettle. The lye came from wood ashes. After cooking for hours, the soap rose to the top. It was then skimmed off and pressed into bars. However, Grandma didn't know much about reaction stoichiometry. She usually had an excess of lye, so her soap was very alkaline.

Today, soap is made a little differently. The hydrolysis is generally accomplished without the use of lye. Coconut oil, palm oil, and cottonseed oil are used in addition to animal tallow. For bar soaps, an abrasive, such as pumice, is occasionally added to aid in the removal of tough grease and oil from your skin. In addition, perfumes may be added, and air may be mixed with the soap to get it to float.

Soap, however, has a couple of big disadvantages. If soap is used with acidic water, the soap is converted to fatty acids and loses its cleaning ability. And if soap is used with hard water (water containing calcium, magnesium, or iron ions), a greasy insoluble precipitate (solid) forms. This greasy deposit is commonly called bathtub ring. And it's a bummer. Not only does the deposit form in your bathtub, but it also appears on your clothes, dishes, and so on. A couple of ways are available to avoid this deposit. You can use a whole-house water softener (see "Make it soft: Water softeners," later in this chapter), or you can buy a synthetic soap that doesn't precipitate with hard-water ions. These synthetic soaps are called *detergents*.

Get rid of that bathtub ring: Detergents

Detergents have the same basic structure as the soap in Figure 17-1. Their hydrophobic end — composed of a long nonpolar hydrocarbon chain that dissolves in the grease and oil — is the same, but their hydrophilic (ionic) end is different. Instead of having a carboxylate ($-\text{COO}^-$), the hydrophilic end may have a sulfate ($-\text{O}-\text{SO}_3^-$), a hydroxyl (OH^-), or some other polar group that doesn't precipitate with hard water.

Laundry detergents contain a number of other compounds in addition to the detergent surfactant. The compounds in laundry detergents are

- ✓ **Builders:** These compounds increase the surfactant's efficiency by softening the water (removing the hard water ions) and making it alkaline. The builder that was used in early laundry detergents was sodium tripolyphosphate. It was cheap and safe. However, it was also an excellent nutrient for water plants and caused an increase in the growth of algae in lakes and streams, choking out fish and other aquatic life. States began banning the use of phosphates in detergents in order to control this problem. Sodium carbonate and zeolites (complex aluminosilicates — compounds of aluminum, oxygen, and silicon) have been used as replacements for the polyphosphates, but both are less than ideal. There really hasn't been an effective, cheap, and nontoxic replacement for the polyphosphate builders. This is an area of research that's still quite active.
- ✓ **Fillers:** Compounds such as sodium sulfate (Na_2SO_4) are added to give the detergent bulk and to keep it free-flowing.
- ✓ **Enzymes:** These biological catalysts are sometimes added to help remove protein-based stains such as blood and grass.
- ✓ **Sodium perborate:** NaBO_3 is sometimes added as a solid bleach to help remove stains. It works by generating hydrogen peroxide in water. It's much more gentle on textiles than chlorine bleach. However, it's most effective in hot water, which can present a problem for those of us who like to wash in cold water.
- ✓ **Suspension agents:** These compounds are added to help keep the dirt in solution in the wash water so that it doesn't redeposit itself on another portion of the clothes.
- ✓ **Corrosion inhibitors:** These compounds coat washer parts to help prevent rust.
- ✓ **Optical brighteners:** These compounds are used to make white clothes appear extra clean and bright. These very complex organic compounds deposit themselves as a thin coating on the clothes. They absorb ultraviolet light and re-emit it as a blue light in the visible part of the spectrum. This process is shown in Figure 17-3.

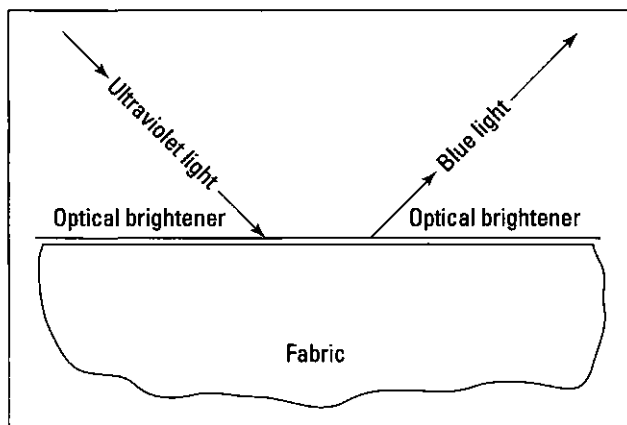


Figure 17-3:
Optical
brighteners.

Coloring agents and perfumes are added to laundry detergent, as well. I bet you didn't know that washing clothes was so complex.

Make it soft: Water softeners

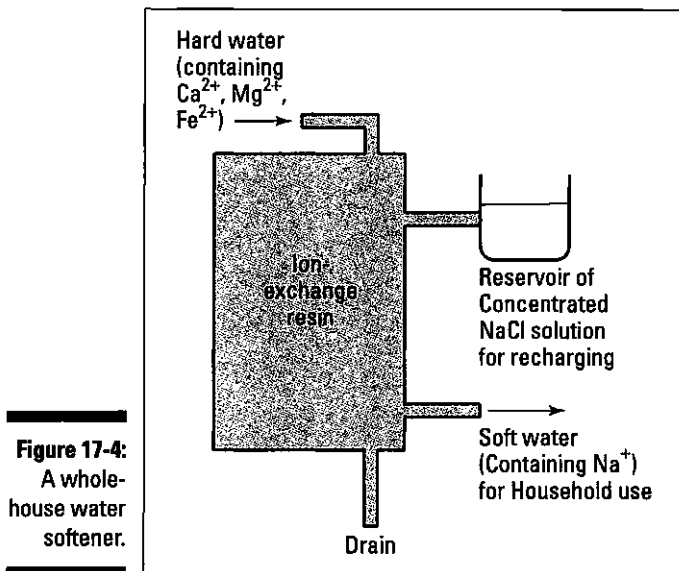
Using synthetic detergents is one way to combat the problem of hard water and bathtub ring. Another way is to simply remove the cations responsible for the hard water before they reach the house. You can accomplish this feat through a home water softener (see Figure 17-4).

A water softener consists of a large tank containing an ion-exchange resin. The resin is charged when a concentrated sodium chloride solution runs through it. The sodium ions are held to the polymer material of the resin. The hard water passes through the polymer, and the calcium, magnesium, and iron ions are exchanged for the sodium ions on the resin (that's where the term *ion-exchange* resin comes from). The softened water contains sodium ions, but the hard-water ions remain in the resin. After a while, the resin must be recharged with more sodium chloride from the reservoir. The wastewater that contains the Ca^{2+} , Mg^{2+} , and Fe^{2+} is drained from the resin tank.

What's that froth in the lake?

The original synthetic detergents weren't capable of being broken down by bacteria and other natural forces. In other words, they weren't *biodegradable*. These detergents accumulated

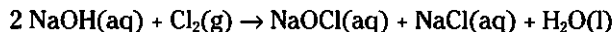
in lakes and streams and caused a thick coating of suds. They were quickly reformulated to solve the problem.



If you limit your sodium intake because of high blood pressure, you should avoid drinking softened water because it has a high sodium ion concentration.

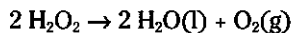
Make it whiter: Bleach

Bleaches use redox reactions to remove color from material (see Chapter 9 for a discussion of redox reactions). Most bleaches are oxidizing agents. The most common bleach used in the home is a 5 percent solution of sodium hypochlorite. This type of bleach is produced by bubbling chlorine gas through a sodium hydroxide solution:



The chlorine released by hypochlorite bleaches can damage fabrics. Also, these types of bleaches don't work very well on polyester fabrics.

Bleaches containing sodium perborate have been introduced to the market, and they're gentler on fabrics. This type of bleach generates hydrogen peroxide, which in turn decomposes with oxygen gas as one of the products:



Chemistry in the Kitchen

You can take a peek under the kitchen sink and see countless products that are made with chemicals (and stored in plastic bottles that are made through chemistry).

Clean it all: Multipurpose cleaners

Most multipurpose cleaners are composed of some surfactant and disinfectant. Ammonia is commonly used because of its ability to react with grease and because it leaves no residue. Pine oil, a solution of compounds called terpenes, is used for its pleasant odor, its ability to dissolve grease, and its antibacterial nature.



Be careful when mixing household cleaning products — especially bleach with ammonia or muratic acid (HCl). This solution generates toxic gases that can be quite dangerous.

Wash those pots: Dishwashing products

Dishwashing detergent is much simpler than laundry detergent. It has some surfactant (normally a nonionic one), a little colorant, and something to make your hands feel soft.

Dishwashing detergent is not nearly as alkaline as laundry detergent. However, automatic dishwasher detergents are highly alkaline and contain only a little surfactant. They use the high pH to saponify the fats (like the process used to make soap) and a high water temperature as well as agitation to clean the dishes. They're composed mostly of sodium metasilicate (Na_2SiO_3), for its alkalinity; sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$), which acts as a detergent; and a little chlorine bleach.

Chemistry in the Bathroom

A lot of chemistry goes on in the bathroom. There are all those skin and hair care products, as well as products to make you look good and smell good and even taste good.

Detergent for the mouth: Toothpaste

Walk down any toothpaste aisle, and you'll see a wide variety of toothpastes with different colors, flavors, and so on. Although they may look different, they all contain the same basic ingredients. The two primary ingredients are surfactant (detergent) and abrasive. The abrasive is for scraping the film off the teeth without damaging the teeth themselves. Common abrasives are chalk (CaCO_3), titanium dioxide (TiO_2), and calcium hydrogen phosphate (CaHPO_4). Other ingredients are added to give the toothpaste color, flavoring, and so on. Table 17-1 gives the general formula for toothpaste. The percentages and specific chemical compounds may vary from toothpaste to toothpaste.

<i>Function</i>	<i>Possible Ingredient</i>	<i>Percentage</i>
Solvent and filler	Water	30–40%
Detergent	Sodium lauryl sulfate, soap	4%
Abrasive	Calcium carbonate, calcium hydrogen phosphate, titanium dioxide, sodium metaphosphate, silica, alumina	30–50%
Sweetener	Glycerine, saccharin, sorbitol	15–20%
Thickener	Gum cellulose, carrageenan	1%
Fluoride	Stannous or sodium fluoride	1%
Flavoring	Oil of wintergreen, peppermint, strawberry, lime, and so on	1%

The addition of stannous or sodium fluoride is effective in the prevention of dental cavities, because the fluoride ion actually becomes part of the tooth enamel, making the enamel stronger and more resistant to the attack of acids.

Phew! Deodorants and antiperspirants

Sweating helps your body regulate its internal temperature. Sweat contains amines, low molecular weight fatty acids, and proteins, in addition to sodium chloride and other inorganic compounds. Some of these organic compounds have a disagreeable odor. Bacterial action can certainly make the odor worse. Deodorants and antiperspirants can be used to control the socially unacceptable odor. (Quite a professional way to discuss stinky B.O., eh?)

Deodorants contain fragrances to cover up the odor and an antibacterial agent to destroy the odor-causing bacteria. They may also contain substances such as zinc peroxide that oxidize the amines and fatty acids to less odorous compounds.

Antiperspirants inhibit or stop perspiration. They act as an *astringent*, constricting the sweat gland ducts. The most commonly used antiperspirants are compounds of aluminum — aluminum chlorohydrates ($\text{Al}_2(\text{OH})_5\text{Cl}$, $\text{Al}_2(\text{OH})_4\text{Cl}_2$, and so on), hydrated aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), and others.

Skin care chemistry: Keeping it soft and pretty

Beeswax. Whale wax. Borax. You may be surprised at what's in some of that stuff you put on your skin.

Creams and lotions

The skin is a complex organ composed primarily of protein and naturally occurring macromolecules (polymers — see Chapter 16). Healthy skin contains about 10 percent moisture. Creams and lotions work to soften and moisturize the skin.

Emollients are skin softeners. Petroleum jelly (mixture of alkanes, with 20-plus carbons, isolated from crude oil), lanolin (mixture of esters isolated from sheep wool fat), and coco butter (mixture of esters isolated from the cacao bean) are excellent skin softeners.

Skin creams are normally made of oil-in-water or water-in-oil emulsions. An *emulsion* is a colloidal dispersion of one liquid in another (see Chapter 11 for a discussion of colloids). It tries to soften and moisturize the skin at the same time. Cold creams are used in the removal of makeup and as moisturizers, while vanishing creams make the skin appear younger by filling in wrinkles. Typical formulations for cold cream and vanishing cream are

Cold Cream Formulation

20–50% water
30–60% mineral oil
12–15% beeswax

Vanishing Cream Formulation

70% water
10% glycerin
20% stearic acid/sodium stearate
5–15% lanolin or whale wax
1% borax
trace of perfume

Body and face powders

Body and face powders are used to dry and smooth the skin. The main ingredient in both types of powder is talc ($\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2$), a mineral that absorbs both oil and water. Astringents are added to reduce sweating, and binders are added to help the powders stick to the skin better. Face powders often contain dyes to give color to the skin. Table 17-2 shows a typical formulation for body powder, and Table 17-3 shows a typical formulation for face powder.

<i>Ingredient</i>	<i>Function</i>	<i>Percentage</i>
Talc	Absorbent, bulk	50–60%
Chalk (CaCO_3)	Absorbent	10–15%
Zinc oxide (ZnO)	Astringent	15–25%
Zinc stearate	Binder	5–10%
Perfume, dye	Odor, color	trace

<i>Ingredient</i>	<i>Function</i>	<i>Percentage</i>
Talc	Absorbent, bulk	60–70%
Zinc oxide	Astringent	10–15%
Kaolin (Al_2SiO_5)	Absorbent	10–15%
Magnesium and zinc stearates	Texture	5–15%
Cetyl alcohol	Binder	1%
Mineral oil	Emollient	2%
Lanolin, perfume, dyes	Softening, odor, color	2%

Making up those eyes

Eye shadow and mascara are composed primarily of emollients, lanolin, beeswax, and colorants. Mascara darkens the eyelashes, making them appear longer. Typical formulations for eye shadow and mascara are

Eye Shadow

55–60% petroleum jelly

5–15% fats and waxes

5–10% lanolin

15–25% zinc oxide

1–5% dyes

Mascara

45–50% soap

35–40% wax and paraffin

5–10% lanolin

1–5% dyes

Kissable lips: Lipstick

Lipstick keeps the lips soft and protects them from drying out, while adding a desirable color. It's composed mostly of wax and oil. These ingredients must be balanced carefully so that the lipstick goes on easily without running and comes off easily, but not too easily, when the wearer is ready to remove it. The color normally comes from a precipitate (solid) of some metal ion with an organic dye. This is commonly called a *lake*. The metal ion tends to intensify the color of the dye. A typical lipstick formulation is shown in Table 17-4.

Table 17-4 **A Typical Lipstick Formulation**

<i>Ingredient</i>	<i>Function</i>	<i>Percentage</i>
Castor oil, mineral oil, fats	Dye solvent	40–50%
Lanolin	Emollient	20–30%
Carnauba wax or beeswax	Stiffener	15–25%
Dye	Color	5–10%
Perfume and flavoring	Odor and taste	trace

Beautiful nails: Nail polish

Nail polish is a synthetic lacquer that owes its flexibility to a polymer and a plasticizer (a liquid mixed with plastics to soften them). The polymer is normally nitrocellulose. The solvents used in the polish are acetone and ethyl acetate, the same substances used for nail polish removers.

Smelling GOOD! Perfumes, colognes, and aftershaves

The major difference between perfume, cologne, and aftershave is the amount of fragrance used. Perfumes are commonly composed of 10 to 25 percent fragrance, while colognes use 1 to 3 percent, and aftershaves use less than 1 percent. These fragrances are usually organic esters, alcohols, ketones, and aldehydes. Perfumes also contain *fixatives*, compounds that help keep the fragrances from evaporating too rapidly.

Interestingly, several fixatives have disagreeable odors or histories themselves: Civetone comes from the glands of the skunk-like civet cat, ambergris is sperm-whale vomit, and indole is isolated from feces. I don't think I'll comment on this.

Perfumes are usually mixtures of *notes*, fragrances with similar aromas but different volatilities (the ease with which a substance is converted into a gas). The most volatile is called the *top note*. It's what you initially smell. The *middle note* is the most noticeable smell, while the *end note* fragrances are responsible for the lingering odor of the perfume. Figure 17-5 shows the chemical structure of several of the fragrances commonly used in perfumes.

Don't you think it's neat being able to see an odor?

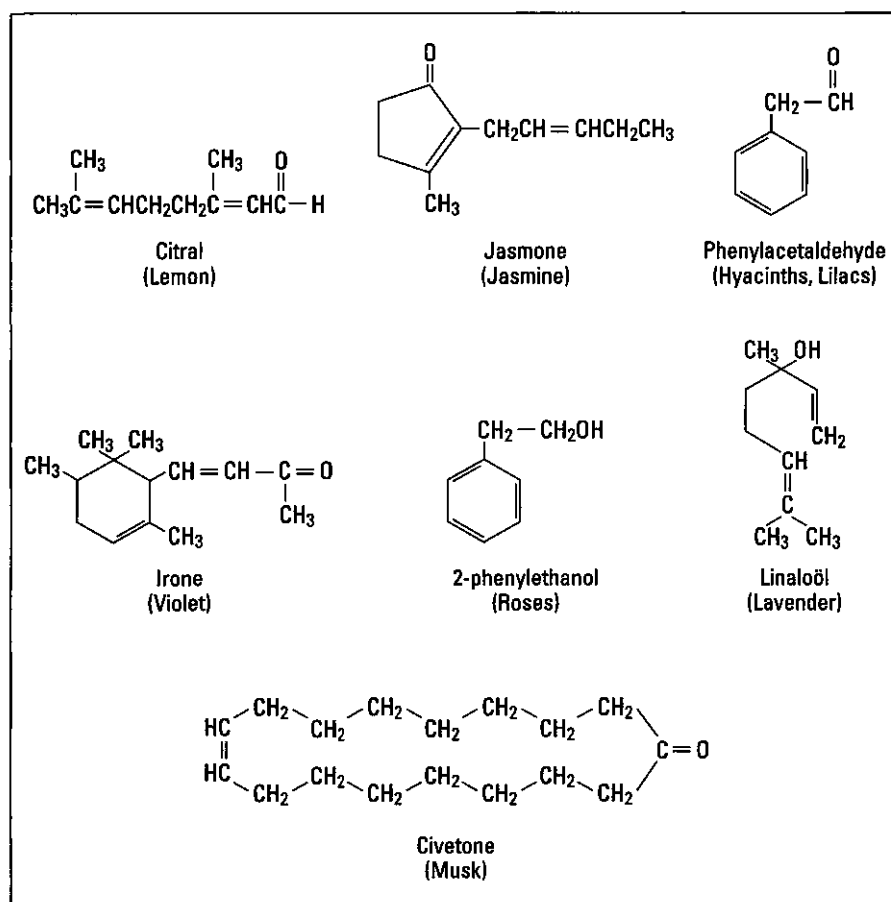


Figure 17-5:
Perfume
fragrances.

Suntan lotion and sunscreen: Brown is beautiful

A suntan is nature's way of protecting our bodies against the harmful UV rays of the sun. The UV spectrum is composed of two regions: the UV-A region and the UV-B region. The UV-A region has slightly longer wavelengths and tends to produce a tan rather than a burn. UV-B radiation is what's responsible for those quick sunburns most of us are familiar with. Repeated exposure to both of these harmful UV rays, especially UV-B rays, is related to an increase in the occurrences of skin cancers, such as melanoma.

Suntan lotions and sunscreens protect the skin by partially or totally blocking the sun's radiation in the UV range, allowing you to be exposed to the sun for longer periods of time without burning. Some suntan lotions and sunscreens block both the UV-A and UV-B regions. Other types selectively block the UV-B regions, allowing the UV-A rays through, which gives the body a chance to produce *melanin*, a dark pigment that acts as a natural shield against the sun's UV rays, *and* that desirable brown skin tone.

These products are given a Sun Protection Factor (SPF) rating. The *SPF value* is a ratio of the amount of time required to tan (or burn) with versus without the product. An SPF value of 10, for example, indicates that when using the product, you can be exposed to the sun 10 times as long without burning.

There's some debate about whether SPF values above 15 are any more effective than the value 15, because few tanning products effectively block the UV-A radiation. The FDA is currently examining tanning products carefully.

A number of chemical substances are effective at blocking UV radiation. An opaque cream of zinc oxide and titanium dioxide is the most effective type of sunscreen. In addition, para-aminobenzoic acid (PABA), benzophenone, and cinnamates are commonly used to block UV radiation. Recently, there has been a move away from the use of PABA, though. It's somewhat toxic, and a significant number of individuals are allergic to it.

Figure 17-6 shows the structures of several compounds used in suntan and sunscreen products. The dihydroxyacetone shown in the figure produces a tan without exposure to the sun. It reacts with the skin to produce a brown pigment.

Clean it, color it, curl it: Hair care chemistry

Hair is composed of a protein called keratin. The protein chains in the hair strand are connected to each other by what's called a *disulfide bond*, a sulfur-to-sulfur bond from the cystine (an amino acid component of hair) on one protein chain to another cystine on another protein chain.

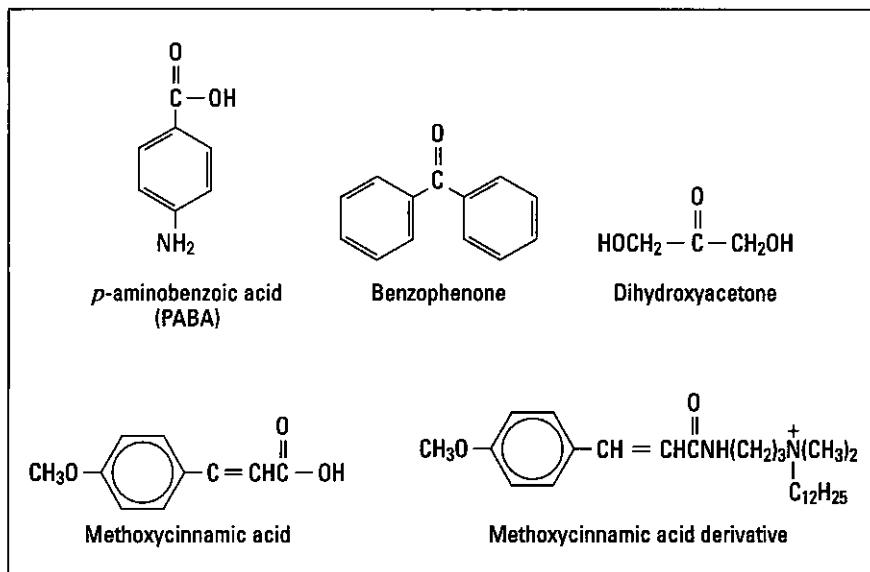


Figure 17-6:
Tanning and
sunscreen
products.

Figure 17-7 shows a portion of hair and disulfide crosslinks joining two protein chains. These crosslinks give hair its strength. (I say more about this disulfide bond in “Permanents — that aren’t,” a little later in this section.)

Shampoos: Detergents for the hair

Modern shampoos are simple surfactants, such as sodium lauryl sulfate and sodium dodecyl sulfate. Shampoo contains other ingredients, however, that react with the metal ions in hard water to help prevent the soap from precipitating with these metal ions (in other words, to help prevent insoluble precipitates — solids, deposits, bathtub ring — from forming in your hair).

Other ingredients give a pleasant odor, replace some of the natural lubricants in the hair (conditioners), and adjust the hair’s pH. (Hair and skin are slightly acidic. A very alkaline, or basic, shampoo will damage hair, so the pH is commonly adjusted to the 5 to 8 pH range. A higher pH may also make the scales on the hair cuticles fan out and reflect the light poorly, making the hair look flat and dull.) A protein is sometimes added to the shampoo to help glue damaged split-ends together. Colorants and preservatives are also commonly added, too.

Color that hair!

Hair contains two pigments — melanin and phaeomelanin. Melanin has a dark-brown color, and phaeomelanin has a reddish-brown color. The natural color of the hair is determined by the relative amounts of these pigments. Red heads have much less melanin; brunettes have much more. Blondes have very little of either.

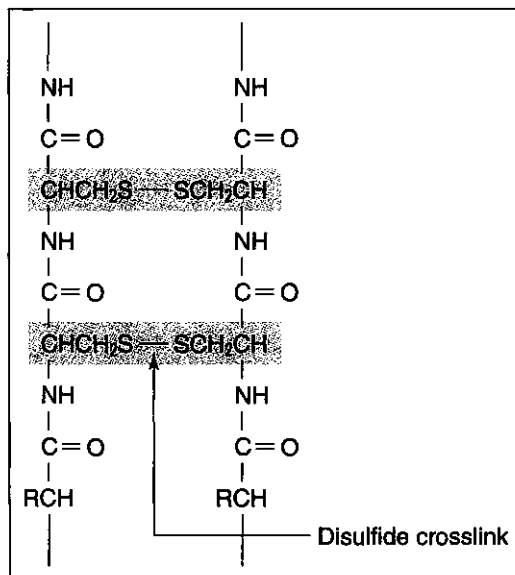


Figure 17-7:
Disulfide
bond in hair.

You can *bleach* hair by using hydrogen peroxide to oxidize these colored pigments to their colorless forms. However, bleached hair becomes weaker and more brittle, because the hair protein is broken down into lower molecular weight compounds. Perborate compounds, which tend to be more expensive than bleach, and chlorine-based bleaches are also sometimes used to bleach hair.

You can change the color of your hair temporarily by using dyes that simply coat the hair strands. These compounds are composed of complex organic molecules. They're too large to penetrate the hair strand, so they simply accumulate on the surface. You can add semi-permanent color by using dyes with smaller molecules that can penetrate into the hair. These dyes frequently contain complexes of chromium or cobalt. The dyes withstand repeated washing, but because the molecules contained in the dye were small enough to penetrate the hair initially, they eventually migrate out.

Permanent dyes are actually formed inside the hair. Small molecules are forced into the hair and then oxidized, normally by hydrogen peroxide, into colored complexes that are too large to migrate out of the hair. The color then becomes permanent on the portion of the hair that was treated. To maintain the color, you have to repeat the process as new hair grows out. This maintenance program keeps hairdressers in business.

Another type of hair coloring is made to change color gradually, over a period of weeks, so that the change goes unnoticed (fat chance!). A solution of lead acetate is applied to the hair. The lead ions react with the sulfur atoms in the hair protein, forming lead (II) sulfide (PbS), which is black and very insoluble. Instead of losing its color in the sunlight like other dyes, PbS-treated hair actually darkens.

Take it off, take it all off! Depilatories

Depilatories remove hair by chemical reaction. They contain a substance, usually sodium sulfide, calcium sulfide, or calcium thioglycolate, that disrupts the disulfide linkages in the hair and dissolves it. The formulations commonly contain a base such as calcium hydroxide to raise the pH and enhance the action of the depilatory. A detergent and a skin conditioner such as mineral oil are also generally added to depilatories.

Permanents — that aren't

Disulfide bonds are responsible for the shape of your hair, whether it's straight or curly. In order to affect the shape of hair, those disulfide bonds must be broken and reformed into a new orientation. Suppose, for example, that you want to make your straight hair curly, so you go to the beauty parlor for a permanent. The hairdresser initially treats your hair with some reducing agent that breaks the disulfide bonds; thioglycolic acid ($\text{HS-CH}_2\text{-COOH}$) is commonly used. Then the hairdresser changes the orientation of the protein chains of the hair by using curlers. Finally, the hairdresser treats your hair with an oxidizing agent such as hydrogen peroxide to reform the disulfide bonds in their new locations. Water-soluble polymers are used to thicken the solutions, ammonia is used to adjust the pH to a basic level, and a conditioner is used to complete the formulation. Figure 17-8 shows this process.

Hair is straightened in exactly the same fashion, except it's stretched straight instead of curled. Obviously, as new hair grows in, you need to repeat the process.

I guess *permanent* refers to the fact that trips to the beauty parlor become a permanent part of your life.

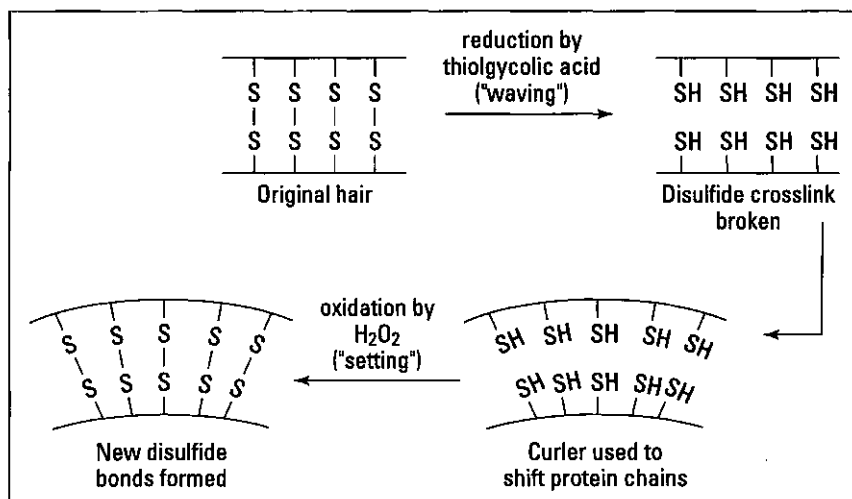


Figure 17-8:
The process
of getting a
perm.

Chemistry in the Medicine Cabinet

Okay, take a quick peek in the medicine cabinet. There are a lot of drugs and medicines inside there. I could spend pages and pages talking about the chemistry of their reactions and interactions, but I'm just going to say a few brief words about a couple of them.

The aspirin story

As early as the fifth century B.C., it was known that chewing willow bark could relieve pain. But it wasn't until 1860 that the chemical compound responsible for the analgesic effect, salicylic acid, was isolated. It had a very sour taste and caused irritation of the stomach. In 1875, chemists created sodium salicylate. It caused stomach irritation, but it was less bitter than the salicylic acid. Finally, in 1899, the German Bayer Company began marketing acetylsalicylic acid, made by reacting salicylic acid with acetic anhydride, under the trade name of *aspirin*. Figure 17-9 traces the history of aspirin.

Aspirin is the most widely used drug in the world. More than 55 billion aspirin tablets are sold annually in the United States.

Minoxidil and Viagra

Science proceeds by hard work, training, intuition, hunches, and luck. That luck is sometimes called *serendipity*, which is another name for an accidental discovery. Or, as I like to say, "finding something you didn't know you were looking for." Chapter 20 tells the stories of ten serendipitous discoveries. But because I'm in the medicine cabinet anyway, I may as well mention a couple of serendipitous discoveries right now.

Male pattern baldness affects many millions of men and women in the world. Minoxidil, the current over-the-counter treatment for baldness, was discovered quite by accident. It was being used as an oral treatment for high blood pressure, when patients reported hair growth. Now it's usually applied topically instead of orally.

The much-publicized properties of Viagra were discovered in much the same fashion. It was also being used as a treatment for high blood pressure, as well as angina (heart pain), when its side effect was reported. In fact, it has been said that male patients refused to return the unused portion of their medications during clinical trials.

Both serendipitous discoveries have spawned multimillion-dollar industries and made countless men and women very happy. They're *growing* industries, for sure.

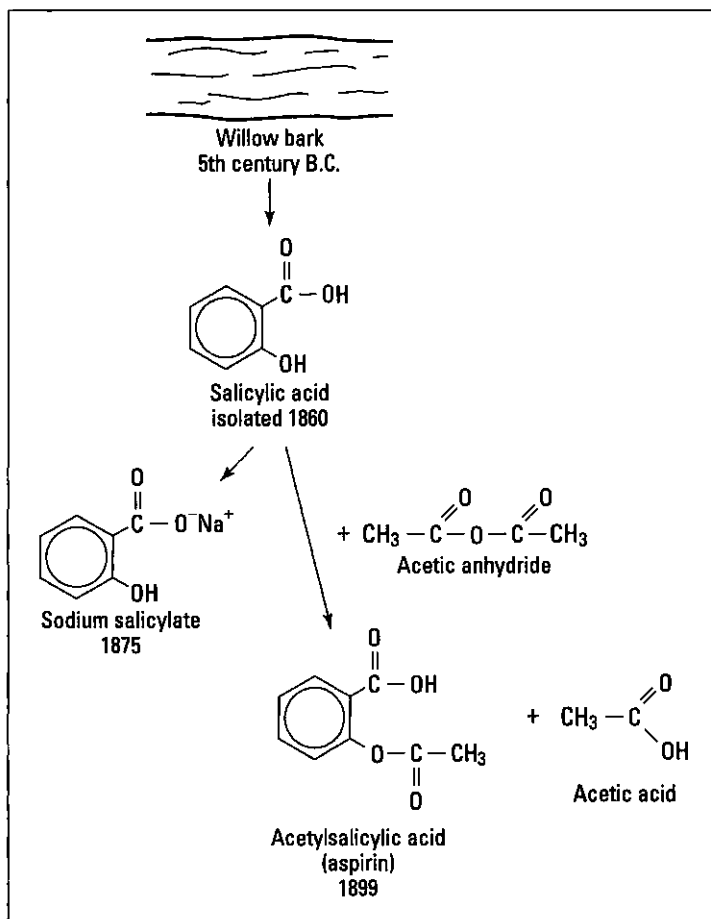


Figure 17-9:
The aspirin
story.

Chapter 18

Cough! Cough! Hack! Hack! Air Pollution

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In This Chapter

- ▶ Finding out about the parts of the atmosphere involved in air pollution
 - ▶ Looking at ozone depletion and the Greenhouse Effect
 - ▶ Examining the causes of photochemical smog and acid rain
-

This chapter looks at the global problem of air pollution. (I consider the perfume department of a large department store at Christmas time the ultimate in air pollution, but I won't discuss that here.) I show you the chemical problems involved with air pollution, and I explain how air pollution is linked to modern society and its demand for energy and personal transportation.

Civilization's Effect on the Atmosphere (Or Where This Mess Began)

The air that surrounds the earth — our *atmosphere* — is absolutely necessary for life. The atmosphere provides oxygen (O₂) for respiration and carbon dioxide (CO₂) for *photosynthesis*, the process by which organisms (mainly plants) convert light energy into chemical energy; it moderates the temperature of the earth and plays an active part in many of the cycles that sustain life. The atmosphere is affected by many chemical reactions that take place or exist on earth.

When few humans were on earth, mankind's effect on the atmosphere was negligible. But as the world's population grew, the effect of civilization on the atmosphere became increasingly significant. The Industrial Revolution, which gave rise to the construction of large, concentrated industrial sites, added to man's effect on the atmosphere. As humans burned more *fossil fuels* — organic substances, such as coal, that are found in underground deposits and used for energy — the amount of carbon dioxide (CO₂) and *particulates* (small, solid

particles suspended in the air) in the atmosphere increased significantly. During the Industrial Revolution, humans also began to use more items that released chemical pollutants into the atmosphere, including hairsprays and air conditioners.

The increase in CO₂ and particulates, combined with the increase in pollutants, has disrupted delicate balances in the atmosphere. High concentrations of these atmospheric pollutants have led to a multitude of problems such as *acid deposition*, acidic rain that damages living things, buildings, and statues, and *photochemical smog*, the brown, irritating haze that often sits over Los Angeles and other cities.

To Breathe or Not to Breathe: Our Atmosphere

The earth's atmosphere is divided into several layers: the troposphere, the stratosphere, the mesosphere, and the thermosphere. I want to focus on the two layers closest to the earth — the troposphere and stratosphere — because they're the layers affected the most by humans. They're also the layers that have the greatest direct effect on human life.

- ✓ The *troposphere* lies next to the earth and contains the gases we breathe and depend on for survival.
- ✓ The *stratosphere* contains the ozone layer, which protects us from ultraviolet radiation.

The troposphere: What humans affect most

The troposphere is composed of about 78.1 percent nitrogen (N₂), 20.9 percent oxygen (O₂), 0.9 percent argon (Ar), 0.03 percent carbon dioxide (CO₂), and smaller amounts of various other gases. The troposphere also contains varying amounts of water vapor. These gases are held tight to the earth by the force of gravity. If a balloonist were to rise high into the troposphere, he or she would find the atmospheric gases much thinner due to the decreased pull of gravity on the gases. This effect tells us that the dense layer of gases held tight to the earth is more at risk from the effects of pollution.

The troposphere is the layer where our weather occurs. It's also the layer that takes the brunt of both natural and man-made pollution because of its proximity to the earth.

Nature pollutes the atmosphere to a certain extent — with noxious hydrogen sulfide (H₂S) and particulate matter from volcanoes, and the release of

organic compounds from plants such as pine trees. But these pollutants have a minor effect on the troposphere. Humankind, on the other hand, pollutes the troposphere with a large amount of chemicals from automobiles, power plants, and industries. Acid rain and photochemical smog are some of the results of man-made pollutants.

The stratosphere: Protecting humans with the ozone layer

Above the troposphere is the stratosphere, which is where jets and high-altitude balloons fly. The atmosphere is much thinner in this layer because of the decreasing pull of gravity. Few of the heavier pollutants are able to make it to the stratosphere, because gravity holds them tight and close to the surface of the earth. The protective *ozone layer* resides in the stratosphere; this protective barrier absorbs a large amount of harmful ultraviolet (UV) radiation from the sun and keeps it from reaching the earth.

Even though heavier pollutants don't make their way to the stratosphere, this layer isn't immune to the effects of mankind. Some lighter manmade gases do make it into the stratosphere, where they attack the protective ozone layer and destroy it. This destruction can have far-reaching effects on humans because UV radiation is a major cause of skin cancer.



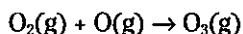
A chemical substance can be both a good guy and a bad guy. The only difference is where, and in what concentration, it's found. For example, a person can overdose on water if he or she drinks enough of it. The same goes with the ozone in the stratosphere. On one hand, it shields us from harmful UV radiation. But on the other, it can be an irritant and destroy rubber products (see "Brown Air? (Photochemical Smog)" for details).

Leave My Ozone Alone: Hair Spray, CFCs, and Ozone Depletion

The ozone layer absorbs almost 99 percent of the ultraviolet radiation that reaches the earth from the sun. It protects us from the effects of too much ultraviolet radiation, including sunburns, skin cancers, cataracts, and premature aging of the skin. Because of the ozone layer, most of us can enjoy the outdoors without head-to-toe protection.

How is ozone (O₃) formed? Well, oxygen in the *mesosphere* — the part of the earth's atmosphere between the stratosphere and the *thermosphere* (the layer that extends to outer space) — is broken apart by ultraviolet radiation

into highly reactive oxygen atoms. These oxygen atoms combine with oxygen molecules in the stratosphere to form ozone.



As a society, humans release many gaseous chemicals into the atmosphere. Many of the gaseous chemicals rapidly decompose through reaction with each other, or they react with the water vapor in the atmosphere to form compounds such as acids that fall to earth in the rain (see “I’m Meltingggggg!” — Acid Rain,” later in this chapter). Besides forming acid rain, some of these chemicals also form photochemical smog (see “Brown Air? (Photochemical Smog),” later in this chapter).

But these reactions occur rather quickly, and we can deal with them in a variety of ways, many of which are related to breaking the series of reactions that produce the pollutant by stopping the release of a critical chemical into the air.

Some classes of gaseous chemical compounds are rather *inert* (inactive and unreactive), so they remain with us for quite a while. Because these inert compounds stick around, they have a negative effect on the atmosphere. One such troublesome class of compounds are the *chlorofluorocarbons*, gaseous compounds composed of chlorine, fluorine, and carbon. These compounds are commonly called *CFCs*.

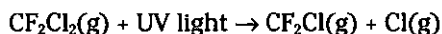
Because CFCs are relatively unreactive, they were extensively used in the past as refrigerants for such items as refrigerators and automobile air conditioners (Freon-12), foaming agents for plastics such as Styrofoam, and propellants for the aerosol cans of such consumer goods as hair spray and deodorants. As a result, they were released into the atmosphere in great quantities. Over the years, the CFCs have diffused into the stratosphere, and they’re now doing damage to it.

How do CFCs hurt the ozone layer?

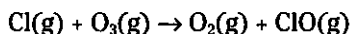
Although CFCs don’t react much when they’re close to earth — they’re pretty inert — most scientists believe that they react with the ozone in the atmosphere and then harm the ozone layer in the stratosphere.

The reaction occurs in the following way:

1. A typical chlorofluorocarbon, CF_2Cl_2 reacts with ultraviolet radiation, and a highly reactive chlorine atom is formed.

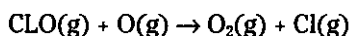


2. The reactive chlorine atom reacts with ozone in the stratosphere to produce oxygen gas molecules and chlorine oxide (ClO).



This is the reaction that destroys the ozone layer. If things stopped here, the problems would actually be minimal.

3. The chlorine oxide (ClO) can then react with another oxygen atom in the stratosphere to produce an oxygen molecule and a chlorine atom; the newly created oxygen molecule and chlorine atom are now available to start the whole ozone-destroying process all over again.



So one CFC molecule can initiate a process that can destroy many molecules of ozone.

Because they're harmful, are CFCs still produced?

The problem of ozone depletion was identified in the 1970s. As a result, the governments of many industrialized nations began to require the reduction of the amount of CFCs and halons released into the atmosphere. (*Halons*, which contain bromine in addition to fluorine and chlorine, were commonly used as fire-extinguishing agents, especially in fire extinguishers used around computers.)

CFCs were banned for use as propellants in aerosol cans in many countries, and the CFCs used in the production of plastics and foams were recovered instead of released into the air. Laws were enacted to ensure that the CFCs and halons used as refrigerants were recovered during the recharging and repair of units. In 1991, Du Pont started producing refrigerants that weren't harmful to the ozone layer. And in 1996, the United States, along with 140 other countries, stopped producing chlorofluorocarbons altogether.

Unfortunately, though, these compounds are extremely stable. They'll remain in our atmosphere for many years. If the damage man has done to the ozone layer isn't too great, it may replenish itself (like new skin grows to replace sunburned skin). But it may well be several years before the ozone layer returns to its former composition.

Is It Hot in Here to You? (The Greenhouse Effect)

When most people think about air pollutants, they think of such chemicals as carbon monoxide, chlorofluorocarbons, or hydrocarbons. Yet carbon dioxide,

the product of animal respiration and the compound used by plants in the process of photosynthesis, can also be considered a pollutant if present in abnormally high amounts.

In the late 1970s and early 1980s, scientists realized that the average temperature of the earth was increasing. They determined that an increase in carbon dioxide (CO_2) and a few other gases, such as chlorofluorocarbons (CFCs), methane (CH_4 , a hydrocarbon), and water vapor (H_2O), were responsible for the slight increase in temperature through a process called the *greenhouse effect* (named so because the gases serve pretty much the same purpose as the glass walls and roof of a greenhouse — the gases themselves are called *greenhouse gases*).

Here's how the greenhouse effect works: As radiation from the sun travels through the earth's atmosphere, it strikes the earth, heating the land and water. Some of this solar energy is sent back (reflected) into the atmosphere as heat (infrared radiation), which is then absorbed by certain gases (CO_2 , CH_4 , H_2O , and CFCs) in the atmosphere. These gases, in turn, warm the atmosphere. This process helps to keep the temperature of the earth and atmosphere moderate and relatively constant, and as a result, we don't experience dramatic day-to-day temperature fluctuations. So, in general, the greenhouse effect is a good thing, not a bad thing.

But if there's an excess of carbon dioxide and other greenhouse gases, too much heat gets trapped in the atmosphere. The atmosphere heats up, leading to the disruption of many of the delicate cycles of the earth. This process is commonly called *global warming*, and it's currently happening with the earth's atmosphere.

We depend on burning fossil fuels (coal, natural gas, or petroleum) for energy. We burn coal and natural gas to produce electricity, we burn gasoline in the internal combustion engine, and we burn natural gas, oil, wood, and coal to heat homes. In addition, industrial processes burn fuel to produce heat. As a result of all this burning of fossil fuels, the carbon dioxide level in the atmosphere has risen from 318 parts-per-million (ppm) in 1960 to 362 parts-per-million (ppm) in 1998. (For a discussion of the concentration unit *ppm*, see Chapter 11.) The excess carbon dioxide has led to an increase of about a half-degree in the average temperature of the atmosphere.

A half-degree increase in the average temperature of the atmosphere may not sound like much, but this global warming trend may have serious effects on several of the ecological systems of the world:

✓ The rising atmospheric temperature may melt ice masses and cause sea levels around the world to rise. Rising sea levels may result in the loss of coastal land (Houston might become a coastal town) and make many more people vulnerable to *storm surges* (those extremely damaging rushes of seawater that occur during very bad storms).

- ✓ The increased temperature may affect the growth patterns of plants.
- ✓ The tropical regions of the world may increase and lead to the spread of tropical diseases.

Brown Air? (Photochemical Smog)

Smog is a generic word people use to describe the combination of smoke and fog that's often irritating to breathe. There are two major types of smog:

- ✓ London smog
- ✓ Photochemical smog

London smog

London smog is a gaseous atmospheric mixture of fog, soot, ash, sulfuric acid (H_2SO_4 — battery acid), and sulfur dioxide (SO_2). The name comes from the air pollution that plagued London in the early part of the twentieth century. The burning of coal for heat in the highly populated city caused this smog. The dangerous mixture of gases and soot from the coal stoves and furnaces killed more than 8,000 people in London in 1952.

Electrostatic precipitators and scrubbers (see “Charge them up and drop them out: Electrostatic precipitators” and “Washing water: Scrubbers,” later in this chapter), combined with filters, have been effective in reducing the release of soot, ash, and sulfur dioxide into the atmosphere and have reduced the occurrence of London smog.

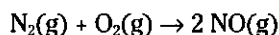
Photochemical smog

Photochemical smog is produced after sunlight initiates certain chemical reactions involving unburned hydrocarbons and oxides of nitrogen (commonly shown as NO_x — which stands for a mixture of NO and NO_2). The common automobile engine produces both of these compounds when it's running.

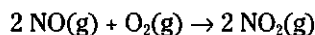
Photochemical smog is the brown haze that sometimes makes it difficult to see in such cities as Los Angeles, Salt Lake City, Denver, and Phoenix. (This smog is sometimes called *Los Angeles smog* — sometimes sunny California isn't so sunny.) These cities are especially vulnerable to photochemical smog; they have a large number of automobiles, which emit the chemicals that react to produce the smog, and they're surrounded by mountain ranges. The mountain ranges and the westward winds create an ideal condition for thermal inversions, which trap the pollutants close to the cities. (In a *thermal*

inversion, a layer of warmer air moves in over a layer of cooler air. The warm air traps the cooler air and its pollutants close to the ground. The process can be compared to sheets trapping certain noxious gases in a bed. The gaseous pollutants are trapped and can't move higher in the atmosphere. They stay close to us humans, causing all kinds of problems.)

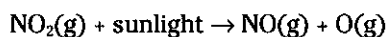
The chemistry of photochemical smog is still not crystal clear (pun intended), but scientists do know the basics that go into creating the smog. Nitrogen from the atmosphere is oxidized to nitric oxide in internal combustion engines and then released into the atmosphere through the engines' exhaust systems:



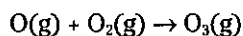
The nitric oxide is oxidized to nitrogen dioxide by atmospheric oxygen:



Nitrogen dioxide is a brownish gas. It's irritating to the eyes and lungs. It absorbs sunlight and then produces nitric oxide and highly reactive oxygen atoms:

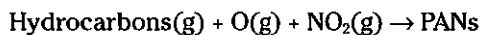


These reactive oxygen atoms quickly react with diatomic (two-atom) oxygen gas molecules in the air to produce ozone (O_3):



This is the same ozone that acts as a shield against ultraviolet radiation in the stratosphere. But when it's down closer to the earth, it acts as a powerful irritant to the eyes and lungs. It attacks rubber, causing it to harden, and thus shortens the life of automobile tires and weather stripping. It also affects crops such as tomatoes and tobacco.

The unburned hydrocarbons from auto exhaust also react with the oxygen atoms and ozone to produce a variety of organic aldehydes that are also irritants. These hydrocarbons can react with diatomic oxygen and nitrogen dioxide to produce peroxyacetylnitrates (PANs):



These PANs are also eye and lung irritants; they tend to be very reactive, causing damage to living organisms.

The combination of the brown nitrogen dioxide, the ozone, and the PANs is photochemical smog. It reduces visibility and is a major cause of respiratory problems. And, unfortunately, controlling it has been difficult.

Auto emissions have been closely monitored, and strict controls have been put into place to minimize the amount of unburned hydrocarbons released into the atmosphere. The Clean Air Act of 1990 was passed to help reduce hydrocarbon emissions from automobiles. The catalytic converter was developed to help react the unburned hydrocarbon and produce a less dangerous emission of carbon dioxide and water. (As a side benefit, lead had to be eliminated from gasoline because it “poisoned” the catalyst and made the catalytic converter useless. The big campaign to “get the lead out” removed a major source of the deadly heavy metal from the environment.)

Although such measures as catalytic converters and activated carbon canisters, which are used to help reduce gasoline fumes, have been somewhat effective, photochemical smog still presents a problem. Until mankind develops an acceptable substitute for the internal combustion engine or requires mass transit, photochemical smog will remain with us for years to come.

“I’m Meltingggggg!” — Acid Rain

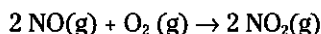
The wicked witch in *The Wizard of Oz* dissolved in water. Sometimes buildings do the same because of the action of acid rain on the limestone and marble.

Rainwater is naturally acidic (with a pH less than 7) as a result of the dissolving of carbon dioxide in the moisture of the atmosphere and the forming of carbonic acid. (See Chapter 12 for more about carbonic acid as well as the pH scale.) This interaction results in rainwater having a pH of around 5.6. The term *acid rain*, or *acid deposition*, is used to describe a situation in which rainfall has a much lower (more acidic) pH than can be explained by the simple dissolving of carbon dioxide. Specifically, acid rain is formed when certain pollutants in the atmosphere, primarily oxides of nitrogen and sulfur, dissolve in the moisture of the atmosphere and fall to earth as rain with a low pH value.

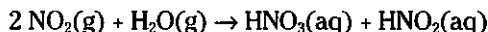
Oxides of nitrogen (NO, NO₂, and so on) are produced naturally during lightning discharges in the atmosphere. This is one way that nature “fixes” nitrogen, or puts it in a form that can be used by plants. However, man adds tremendously to the local amount of atmospheric nitrogen oxides through the use of automobiles. The internal combustion engine reacts the gasoline hydrocarbons with the oxygen in the air, producing carbon dioxide (and carbon monoxide) and water. But the nitrogen that’s present in the air (about 78 percent of the air is nitrogen) may also react with the oxygen at the high temperatures present in the engine. This can produce nitric oxide (NO), which is then released into the atmosphere:



As the NO enters the atmosphere, it reacts with additional oxygen gas to produce nitrogen dioxide (NO₂):

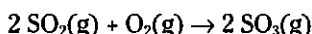
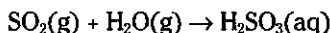


This nitrogen dioxide can then react with the water vapor in the atmosphere to form nitric and nitrous acids:

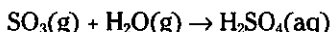


These dilute acid solutions fall to earth as rain with a low pH value — generally in the 4.0 to 4.5 range (although rains with a pH as low as 1.5 have been reported).

A significant amount of acid rain in the eastern part of the United States is caused by oxides of nitrogen, but the acid rain of the Midwest and West is caused by mostly oxides of sulfur, which are primarily generated by power plants and the burning of coal and oil. Sulfur-containing compounds are found as impurities in coal and oil, sometimes as high as 4 percent by weight. These compounds, when burned, produce a sulfur dioxide gas (SO₂). Many millions of tons of SO₂ are released into the atmosphere each year from power-generating plants. The SO₂ reacts with the water vapor in the atmosphere to produce sulfurous acid (H₂SO₃), and with the oxygen in the atmosphere to produce sulfur trioxide (SO₃):



This sulfur trioxide then reacts with the moisture in the atmosphere to produce sulfuric acid (H₂SO₄), which is the same acid found in your automobile battery:



So the sulfurous and sulfuric acids that are dissolved in the rainwater form the acid rain that falls to the earth. Anyone for a bath in battery acid?

The acids formed in the atmosphere can travel many hundreds of miles before falling to earth as acid rain and leaving their mark on both nonliving and living things. The acids of the rain react with the iron in buildings and automobiles, causing them to corrode. The acids also destroy the details of fine works of art when they react with marble statues and limestone buildings to form soluble compounds that wash away. (Want to see this in action? Put a drop of vinegar, an acid, on a piece of marble and then watch the bubbles form as the acid dissolves the marble. Careful, though. Don't try this on anything too valuable — maybe that ugly marble cheese slicer that Aunt Gertrude gave you last Christmas.)

It's not surprising that acid rain has a bad effect on vegetation. Acid rain has been identified as the major cause of death of many trees and even whole forests. Even if trees aren't killed immediately by acid rain, forests sometimes grow slower because of its effects. The growth may be hindered by the release of aluminum from the soil, which interferes with the absorption of nutrients, or it may be slowed by the bacteria found in the soil.

In addition, acid rain has altered the ecosystems of many lakes in Canada and the United States. Fish kills have been reported, and entire species of fish have vanished from certain lakes. In fact, the ecosystems of entire lakes have been destroyed by acid rain, rendering the lakes lifeless.

Steps have been taken to reduce acid rain and its effects. Increasing fuel efficiency and the use of pollution control devices on automobiles have helped reduce the amount of nitrogen oxide released into the atmosphere. But fossil fuel power plants produce the most tonnage of acid-causing pollutants. A number of controls have been adopted to decrease the amount of sulfur-containing gases released into the atmosphere, including electrostatic precipitators and scrubbers, which are discussed in the following two sections. But although they've been effective in reducing the amount of acid-causing material released into the atmosphere, much more still needs to be done before the problem of acid rain is reduced to a manageable level.

Charge them up and drop them out: Electrostatic precipitators

When you were a child, did you ever run a comb through your hair on a cold winter morning and then use it to pick up little scraps of paper? An electrostatic precipitator does much the same thing.

Electrostatic precipitators give a negative electrical charge to pollutant particles. The sides of the precipitator have a positive charge, so the negative particles are then pulled to the positively charged walls. They stick to the walls and accumulate there. Then they can be removed (it's like sweeping out those dust bunnies from under the bed).

In one type of electrostatic precipitation system, the SO_2 produced by the burning of fossil fuels is reacted with lime (CaO) to produce solid calcium sulfite (CaSO_3):

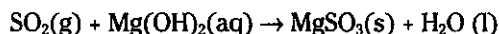


The finely divided calcium sulfite is electrostatically precipitated and collected. It can then be disposed of properly in a chemical landfill.

Washing water: Scrubbers

Scrubbers are thingsies that remove impurities from pollutant gases by using a fine spray of water to trap the gases as an aqueous solution or force them through a reacting mixture. The process is similar to using a water spray to settle dust in arid regions.

You can use a scrubber as an especially efficient system for removing sulfur dioxide by forcing the SO_2 through a slurry of magnesium hydroxide and converting it to magnesium sulfite, which can then easily be collected:



Is the quality of air getting better?

The quality of air in cities such as Los Angeles has improved over the last 15 years. Pollution controls have reduced the oxides of nitrogen and unburned hydrocarbons released by automobiles, and the levels of photochemical smog have been significantly reduced.

Pollution controls have also reduced the levels of sulfur dioxides released from power plants, which has helped lower the occurrence of acid rain. In addition, the ban on CFCs released into the atmosphere should eventually have an effect on ozone depletion. So in many respects, yes, the quality of our air is improving.

But humans are still releasing tremendous amounts of carbon dioxide into the atmosphere

and using up large amounts of the earth's valuable plant and animal material (biomass). It is this biomass that really would tend to use up this excess carbon dioxide.

The effect on the environment is debated on a daily basis. All agree that the effect is negative. The question is simply a matter of degree. If mankind can reduce its dependence on fossil fuels for electricity and heat by using solar, nuclear, or perhaps even fusion power, then maybe we'll be able to make advances in reducing the amount of carbon dioxide released into the atmosphere. This strategy, combined with limits on the destruction of forests, may bring the problem of global warming under control.

Chapter 19

Brown, Chunky Water? Water Pollution

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In This Chapter

- ▶ Understanding where our water supply comes from
 - ▶ Clarifying how the structure of water makes it vulnerable to pollution
 - ▶ Taking a look at several types of water pollutants
 - ▶ Finding out about water treatment
-

Water is absolutely necessary to our survival. After all, the human body is about 70 percent water. Most of the water on earth, however, is found as seawater. Only about 2 percent of the water on the earth is fresh water, and a little over three-quarters of that is in the form of ice and glaciers. But it's that very small amount of fresh water suitable for drinking (*potable water*) that most people are concerned about.

I'm sure you're quite aware of the water you drink and the water you use for bathing, cooking, and watering your lawn. But unless you live in a rural agricultural area, I doubt that you think much about the water used to grow the plants and animals we depend on for food.

In addition, water is used to carry waste products from our homes and to generate electricity. It's also used in chemical reactions and cooling towers. And then there's recreation — boating, swimming, and fishing. All these things depend on an adequate supply of good, pure water.

But where does water come from? How does it get contaminated, and how does it get cleaned? These are some of the questions I discuss in this chapter. So sit back, grab your glass of water, and dive in.

Where Does Our Water Come From, and Where Is It Going?

The actual amount of water on earth is relatively constant, but its location and purity may vary. Water moves throughout the environment by what is called the *water cycle*, or the *hydrologic cycle*. Figure 19-1 diagrams this cycle.

Evaporate, condense, repeat

Water *evaporates* (goes from a liquid to a gas when heated) from lakes, streams, oceans, trees, and even humans. As water evaporates, it leaves behind any contaminants that it may have accumulated. (That's where the salt comes from on your sweatband and cap.) This process of evaporation is one of nature's ways of purifying water.

The water vapor may then travel many miles, or it may stay relatively local, depending on the prevailing winds. Sooner or later, the vapor *condenses* (goes from a gas to a liquid when cooled) and falls back to the earth as rain, snow, or sleet.

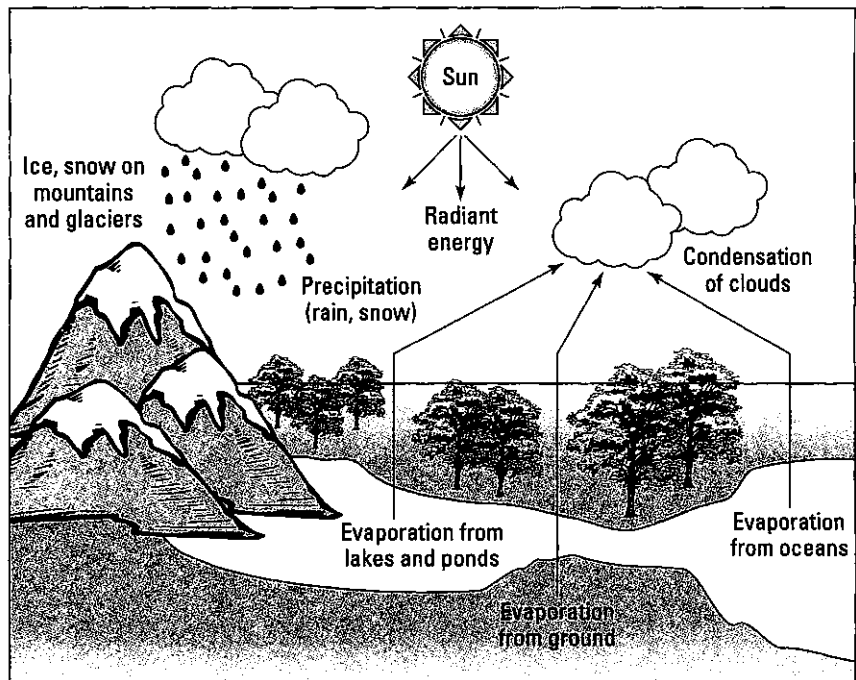


Figure 19-1:
The water
(hydrologic)
cycle.

Where the water goes

Water may fall to earth and collect in a lake or stream. If it does, it eventually finds its way back to the sea. If it falls onto the land, it can form *runoff* and eventually enter a lake or stream, or it can soak into the ground and become *groundwater*. The porous layer of soil and rock that holds the groundwater forms a zone called an *aquifer*. This zone provides us with a good source of groundwater. We tap into these aquifers by using wells.

Human activities can affect this water cycle. Cutting vegetation can increase the rate of runoff, causing less water to become absorbed into the soil. Man-made dams and reservoirs increase the surface area available for water evaporation. Using more groundwater than can be replenished may deplete the aquifers and lead to water shortages. And society can contaminate the water in a wide variety of ways that I discuss in this chapter.

Water: A Most Unusual Substance

Water is a polar molecule. Chapter 7 covers polar molecules in detail, but here's a quickie version relating to water: The oxygen in water (H_2O) has a higher *electronegativity* (attraction for a bonding pair of electrons) than the hydrogen atoms, so the bonding electrons are pulled in closer to the oxygen. The oxygen end of the water molecule then acquires a partial negative charge, and the hydrogen atoms take on a partial positive charge. When the partially positively charged hydrogen (where's my editor on *that* clunker of a phrase?) of one water molecule is attracted to the partially negatively charged oxygen of another water molecule, there can be a rather strong interaction between the water molecules. This interaction is called a hydrogen bond (H-bond). This is not to be confused with a hydrogen *bomb*. Two very different things. Figure 19-2 shows the hydrogen bonds that occur in water.

Hydrogen bonds, caused by the polar covalent bonds of water molecules, give water some very unusual properties:

- ✔ **Water has a very high surface tension.** The water molecules at the surface of the water are only attracted downward into the body of the liquid. The molecules in the body of the liquid, on the other hand, are attracted into all different directions. Bugs and small lizards can walk across water because they don't exert enough force to break the surface tension. The high surface tension of water also means that evaporation rates are really less than you'd expect.
- ✔ **Water becomes a liquid at temperatures commonly found on earth.** The boiling point of a liquid is normally related to its molecular weight. Substances that have molecular weights close to the molecular weight of water (18 g/mol) boil at far lower temperatures; these substances become gases at normal room temperature.

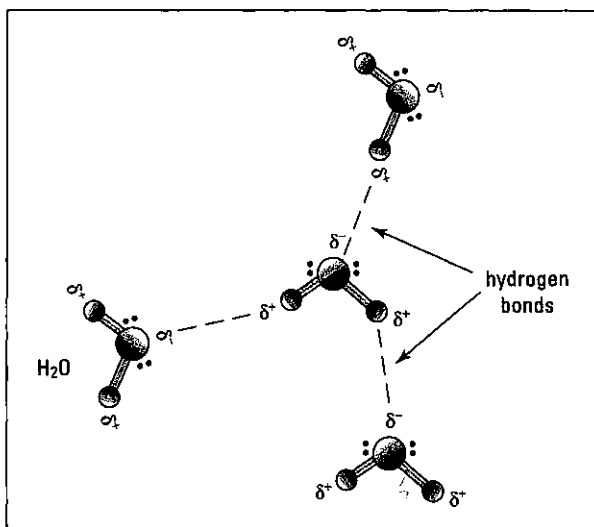


Figure 19-2:
Hydrogen
bonding
in water.

✔ **Ice, the solid state of water, floats when placed in water.** Normally, you may think of a solid as having a higher density than its corresponding liquid, because the particles are closer together in the solid. When water freezes, however, it's locked into a crystal lattice that has large holes incorporated into it by its hydrogen bonds. So the density of ice is less than that of water (see Figure 19-3).

The floating property of ice is one of the reasons that life, in all its diversity and magnitude, is able to exist on earth. If ice were denser than water in the winter, the water at the top of lakes would freeze and sink. Then more water would freeze and sink, and so on. Pretty soon, the lake would be frozen solid, destroying most of the life — such as plants and fish — in the lake. Instead, ice floats and forms an insulating layer over the water, which allows life to exist, even in the winter.

✔ **Water has a relatively high heat capacity.** The *heat capacity* of a substance is the amount of heat a substance can absorb or release in order to change its temperature 1 degree Celsius. Water's heat capacity is almost 10 times greater than iron and 5 times greater than aluminum. This means that lakes and oceans can absorb and release large amounts of heat without a dramatic change in temperature, which moderates the temperature on earth. Lakes absorb heat during the day and release it at night. Without water's high heat capacity, the earth would undergo dramatic swings in temperature during its day/night cycle.

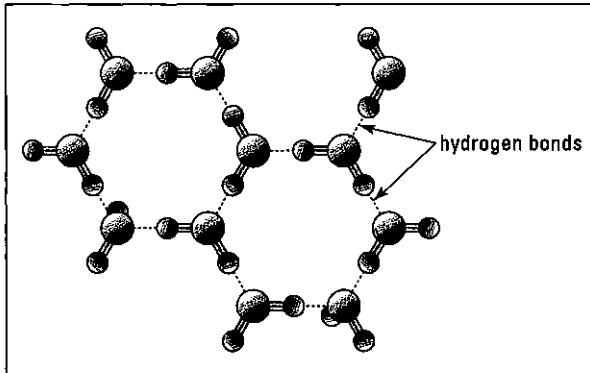
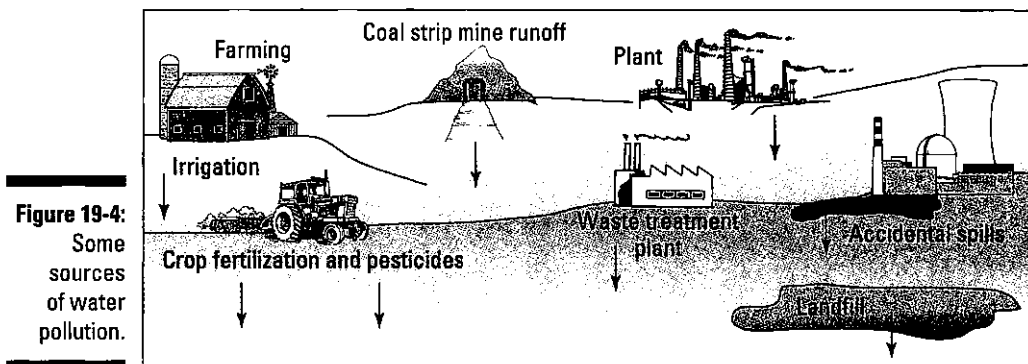


Figure 19-3:
The
structure
of ice.

- ✔ **Water has a high heat of vaporization.** The *heat of vaporization* of a liquid is the amount of energy needed to convert a gram of the liquid to a gas. Water has a heat of vaporization of 54 calories per gram (see Chapter 2 for more about the calorie, a metric unit of heat). This high heat of vaporization allows us to rid our bodies of a great deal of heat when sweat is evaporated from the skin. This property also helps to keep the climate on earth relatively moderate without extreme short-term swings.
- ✔ **Water is an excellent solvent for a large number of substances.** In fact, water is sometimes called the universal solvent, because it dissolves so many things. Water is a polar molecule, so it acts as a solvent for polar solutes. It dissolves ionic substances easily; the negative ends of the water molecules surround the cations (positively charged ions), while the positive ends of the water molecules surround the anions (negatively charged ions). (Turn to Chapter 6 for specifics on ions, cations, and anions.) With the same process, water can dissolve many polar covalent compounds, such as alcohols and sugars (see Chapter 7 for more on these types of compounds). This is a desirable property, but it also means that water dissolves many substances that are not desirable to us or that make water unusable. We lump all those substances together under the terms *pollutants* or *contaminants*.

Yuck! Some Common Water Pollutants

Because water is such an excellent solvent, it easily picks up unwanted substances from a variety of sources. Figure 19-4 shows some sources of water contamination.



I call Figure 19-4 Pollution Place, because it shows so many pollution sources in the same place. Naturally, you won't find this many pollution sites this close together in too many places in the United States.

Pollution sources are normally classified as point sources or non-point sources:

- ✓ *Point sources* are pollution sites that have a definite identifiable source. Discharges from a chemical industry or raw sewage from wastewater treatment plants are common examples of point-source pollution. Point sources are easy to identify, control, and regulate. The Environmental Protection Agency (EPA) is the governmental agency that regulates point sources.
- ✓ *Non-point sources* are pollution sources that are rather diffuse in nature. Good examples of this type of pollution are water contamination caused by agricultural runoff or acid rain. Controlling and regulating this type of pollution is much more difficult because you can't identify a particular company or individual as the polluter. In recent years, federal and state agencies have attempted to address non-point source pollution. The Clean Water Action Plan of 1998 was one such attempt that focused on watersheds and runoffs.

We really didn't get the lead out: Heavy metal contamination

Water supplies are closely monitored for heavy metals, because they tend to be very toxic. Major sources of heavy metal contamination include landfills, industries, agriculture, mining, and old water distribution systems.

Lead is one type of heavy metal pollutant that has received a lot of press in recent years. Large amounts of lead entered the environment from the use of

leaded gasoline: The tetraethyl lead that was used to boost the gasoline's octane was oxidized in the combustion process, and a large amount of lead was emitted through exhaust systems. Rain runoff carried the lead into streams where it was deposited. Another source of lead was old pipes in municipal buildings and homes. These pipes were commonly joined with a lead solder that then leached lead into the drinking water.

Mercury is released into the aquatic environment from mercury compounds used to treat seeds from fungus and rot. Runoff from fields washes the mercury compounds into the surface water and sometimes into the groundwater supply.

The automobile is also an indirect source of another heavy metal contaminant, chromium. Chromium compounds (such as CrO_4^{2-}) are used in chrome plating for bumpers and grills. This plating also requires the use of the cyanide ion (CN^-), another major pollutant. These contaminants used to be discharged directly into streams, but now they're either pretreated to reduce to a less-toxic form or precipitated (formed into a solid) and disposed of in landfills.

Mining also adds to the heavy metal pollution problem. As the earth is mined, deposits of minerals, which contain metals, are exposed. If the chemicals used in extracting ore or coal deposits are acidic, then the metals in the minerals are dissolved, and they may make their way into the surface water and sometimes the groundwater. This problem is sometimes controlled with a process that isolates mine drainage and then treats it to remove the metal ions.

Biological concentration is a problem that occurs when industries release heavy metal ions into the waterways. As metal ions move through the ecosystem, they become more and more concentrated. (The same thing happens with radioisotopes — see Chapter 5 for details.) The ions may be released at a very low concentration level, but by the time they move up the food chain to us, the concentration may be at the toxic level. This situation happened in Minamata Bay, Japan. An industry was dumping mercury metal into the bay. As the metal moved through the ecosystem, it was eventually converted to the extremely toxic methylmercury compound. People died as a result of the toxins, and others became permanently affected.

Acid rain

Oxides of nitrogen and sulfur can combine with the moisture in the atmosphere to form rain that can be highly acidic — acid rain. This rain can affect the pH of lakes and streams and has been known to seriously affect aquatic life. In fact, it's made some lakes devoid of life altogether.

Acid rain is a good example of a non-point source of pollution. It's difficult to pinpoint a single entity as the cause. Air pollution controls have decreased

the amount of acid rain produced, but it's still a major problem. (If you'd like more info on acid rain, flip to Chapter 18.)

Infectious agents

This category of contamination includes fecal coliform bacteria from human wastes and the wastes of birds and other animals. Fecal coliform bacteria was once a major problem in the United States and most parts of the world. Epidemics of typhoid, cholera, and dysentery were common. Treatment of wastewater has minimized this problem in industrialized nations, but it's still a definite problem in underdeveloped nations.

Many experts think that more than three-quarters of the sicknesses in the world are related to biological water contaminants. And even now in the United States, beaches and lakes are still closed at times because of biological contamination.

Stricter controls on municipal water treatment, septic tanks, and runoff from feedlots will help decrease the biological contamination of our water.

Landfills and LUST

Landfills — both the public and hazardous chemical kind — are a major source of groundwater contamination. The landfills that are constructed today require special liners to prevent hazardous materials from leaching into the groundwater. Monitoring equipment is also required to confirm that the hazardous materials don't leak from the landfills. However, very few landfills in the United States have liners and monitoring systems.

Many landfills contain *VOCs* (volatile organic chemicals). This group of chemicals includes benzene and toluene (both carcinogens), chlorinated hydrocarbons, such as carbon tetrachloride, and trichloroethylene, which previously was used as a dry-cleaning solvent. Even though these compounds are not very soluble in water, they do accumulate at the parts-per-million level. Their long-term effect on human health is unknown at this time.

Most people think of toxic wastes in terms of an industrial dump, but the municipal landfill is becoming a more popular site for the disposal of hazardous household wastes. Every year, tons of the following toxic materials are placed in commercial landfills:

- ✓ Batteries containing heavy metals like mercury
- ✓ Oil-based paints containing organic solvents
- ✓ Motor oil containing metals and organic compounds

- ✓ Gasoline containing organic solvents
- ✓ Automobile batteries containing sulfuric acid and lead
- ✓ Antifreeze containing organic solvents
- ✓ Household insecticides containing organic solvents and pesticides
- ✓ Fire and smoke detectors containing radioactive isotopes
- ✓ Nail polish remover containing organic solvents

Some cities and states are trying to reduce the amount of toxic substances released into the environment by providing special collection sites for materials such as used motor oil. But much more needs to be done.

LUST (leaking underground storage tanks) is another source of VOCs. The major culprit? Old, rusted gasoline storage tanks — especially from filling stations that have long been out of business. It takes less than a gallon of leaked gasoline to contaminate the water supply of a mid-sized town. Recent federal regulations have required the identification and replacement of leaking tanks, but abandoned service stations have become a major problem. It's estimated that as many as 200,000 tanks still need to be replaced.

The problem of hazardous materials in landfills and the contamination of our water supply prompted Congress to pass the Superfund program. This program was designed to identify and clean up potentially harmful landfills and dumps. Some progress has been made, but there may be thousands of dump sites that need to be cleaned at a monumental cost to the taxpayer.

The alternatives to landfills are recycling and incineration. Some of the material that commonly goes into a public landfill can be recycled — paper, glass, aluminum, and some plastics, for example — but more needs to be done. Incineration of some materials can be accomplished with the generation of electricity. Modern incineration produces very little air pollution.

Agricultural water pollution

Many types of water pollution are associated with the agricultural industry. For example, the excessive use of fertilizers, which contain nitrate and phosphate compounds, have caused a dramatic increase in the growth of algae and plants in lakes and streams. This increased growth may interfere with the normal cycles that occur in these aquatic systems, causing them to age prematurely — a process known as *eutrophication*.

In addition, pesticides used in treating crops may be released into the waterways. These pesticides, especially the organo-phosphorus ones, may undergo biological concentration (see "We really didn't get the lead out: Heavy metal contamination," earlier in this chapter). Many of us remember

the reported impact of DDT on fish and birds. Because of the effects of DDT, the United States has banned its use, but it's still manufactured and sold overseas.

The release of soil and silt into the waterways is another form of pollution associated with the agricultural industry. The soil builds up in the water and interferes with the normal cycles of lakes and streams. It also carries agricultural chemicals into the waterways.

Polluting with heat: Thermal pollution

People usually think of things like lead, mercury, toxic organic compounds, and bacteria as being major pollutants. However, heat can also be a major pollutant. The solubility of a gas in a liquid *decreases* as the temperature increases (see Chapter 13 for more about the solubility of gases). This means that warm water doesn't contain as much dissolved oxygen as cool water. And how is this related to pollution? The amount of oxygen in water has a direct impact on aquatic life. The reduction of the dissolved oxygen content of water caused by heat is called *thermal pollution*.

Industries, especially those that generate electric power, use a tremendous amount of water to cool steam and condense it back to water. This water is normally taken from a lake or stream, used in the cooling process, and then returned to the same body of water. If the heated water is returned directly to the lake or stream, the increase in temperature may cause the oxygen levels to decrease below those required for the survival of certain types of fish. The increased temperature may also trigger or repress natural cycles of aquatic life, such as spawning.

Federal regulations prohibit the release of heated water back into lakes or streams. Industries cool the water by allowing it to remain in pools or running it over the outside of cooling towers. The cooling towers help the water release its heat to the atmosphere. Both of these methods, however, lose a lot of water to evaporation. (And believe me, there are some places in the United States that certainly don't need the increased humidity.)

Using up oxygen — BOD

If organic material (such as raw sewage, organic chemicals, or a dead cow) finds its way into the water, it decays. The decaying process is basically the oxidation of the organic compounds by *aerobic bacteria*, or oxygen-consuming bacteria, into simpler molecules such as carbon dioxide and water.

The process requires dissolved oxygen (DO) from the water. The amount of oxygen needed to oxidize the organic material is called the *biological oxygen demand (BOD)*, and it's normally measured in parts per million (ppm) of oxygen needed. If the BOD is too high, too much dissolved oxygen is used, and there's not enough oxygen remaining for the fish. Fish kills occur, leading to an even higher BOD.

In extreme cases, there's not enough oxygen for the aerobic bacteria to survive, so another group of bacteria, *anaerobic bacteria*, assumes the job of decomposing the organic material. Anaerobic bacteria doesn't use oxygen in the water; instead, it uses oxygen that's in the organic compounds. Anaerobic bacteria reduces the waste instead of oxidizing it. (See Chapter 9 for a discussion of oxidation and reduction.) The bad news is that anaerobic bacteria decomposes organic matter into foul-smelling compounds such as hydrogen sulfide (H₂S), ammonia, and amines.

In order to stop overloading the BOD of the waterways, most chemical industries pretreat (normally with oxidization) their waste chemicals before releasing them into the water. Cities and towns do the same with their wastewater treatment plants.

Wastewater Treatment

The days when towns and cities in the United States could dump raw, untreated sewage into the waterways are largely over. Every once in a while, a treatment plant malfunctions or becomes overloaded due to some natural disaster and has to dump raw sewage, but those situations are few and far between.

It's not like that in the rest of the world. In South Asia and most of Africa, for example, very little of the sewage gets treated. But in the United States, sewage gets at least primary treatment; it often gets secondary and tertiary treatment, too. Figure 19-5 diagrams both the primary and secondary treatment of sewage.

Primary sewage treatment

In *primary sewage treatment*, raw sewage basically undergoes settling and filtration. The sewage first goes through a grate and screen system to remove large items. (I don't even want to talk about what those items are.) It then moves through a grit chamber where more material is filtered. Finally, it goes

to a primary sedimentation tank, where the material is treated with solutions of aluminum sulfate and calcium hydroxide. The two solutions form aluminum hydroxide, a gelatinous precipitate (solid) that accumulates dirt and bacteria as it settles. This primary treatment removes about 50 to 75 percent of the solids, but it only reduces the biological oxygen demand (BOD) by about 30 percent.

If primary treatment is all that the wastewater undergoes, then sometimes chlorine is added to kill a majority of the bacteria before the wastewater is returned to the waterways. It still contains a high BOD, though. So if the waterway is a lake or slow-moving stream, then the high BOD causes problems — especially if a number of towns use the same type of sewage treatment. The problems can be prevented with secondary sewage treatment.

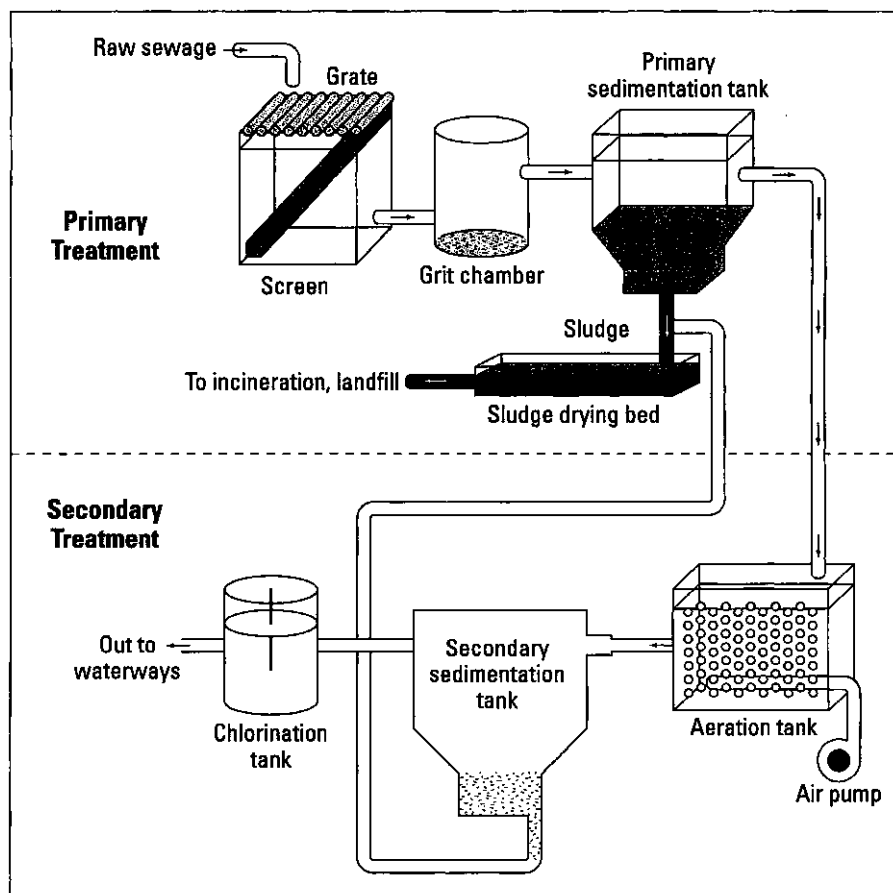


Figure 19-5:
Primary and
secondary
sewage
treatment.

Secondary sewage treatment

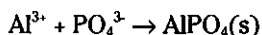
In *secondary sewage treatment*, bacteria and other microorganisms are given the opportunity to decompose the organic compounds in the wastewater. Because aerobic bacteria (oxygen-consuming bacteria) produces products that are less noxious than those produced by anaerobic bacteria (bacteria that uses oxygen in the organic compounds instead of oxygen in the water), the sewage is commonly aerated in order to provide the needed oxygen.

Both the primary and secondary processes produce a material called *sludge*, which is a mixture of particulate matter and living and dead microorganisms. The sludge is dried and disposed of by incineration or in a landfill. It can even be spread on certain types of cropland, where it acts as a fertilizer.

But even secondary treatment can't remove some substances that are potentially harmful to the environment. These substances include certain organic compounds, certain metals such as aluminum, and fertilizers such as phosphates and nitrates. Tertiary sewage treatment can be used to remove these substances.

Tertiary sewage treatment

Tertiary sewage treatment is essentially a chemical treatment that removes the fine particles, nitrates, and phosphates in wastewater. The basic procedure is adjusted for the specific substance to be removed. Activated charcoal filtration, for example, is used to remove most of the dissolved organic compounds. And alum ($\text{Al}_2(\text{SO}_4)_3$) is used to precipitate phosphate ions: by dissolving and freeing the aluminum cation.



Ion exchange (Chapter 9), reverse osmosis (Chapter 11), and distillation (Chapter 15) are also occasionally used with this type of treatment. All these procedures are relatively expensive, though, so tertiary treatment isn't done unless really necessary.

Even after tertiary treatment is completed, the wastewater must still be disinfected before it's released back into the waterways. It's commonly disinfected by bubbling chlorine gas (Cl_2) into the water. Chlorine gas is an extremely powerful oxidizing agent, and it's very effective at killing the organisms responsible for cholera, dysentery, and typhoid. But the use of chlorine has come under question lately. If residual organic compounds are in the wastewater, they can be converted into chlorinated hydrocarbons. Several of these compounds have been shown to be carcinogenic. The levels of these compounds are being closely monitored during testing of wastewater.

Ozone (O_3) can also be used to disinfect wastewater. It's effective at killing viruses that chlorine can't kill. It's more expensive, however, and doesn't provide the residual protection against bacteria.

Drinking Water Treatment

One of the things we tend to take for granted is the availability of good drinking water. Most people of the world aren't as fortunate as we are.

The water is brought in from a lake, stream, or reservoir and initially filtered to remove sticks, leaves, dead fish, and such. The turbidity (haziness) that's commonly present in river or lake water is removed through treatment with a mixture of alum (aluminum sulfate) and lime (calcium hydroxide), which forms gelatinous aluminum hydroxide and traps the suspended solids. This is basically the same treatment used in wastewater treatment plants (see "Primary sewage treatment").

Then the water is filtered again to remove the solid mass of fine particles (called a *flocculate* or *floc*) leftover from the initial filtering treatment. Chlorine is added to kill any bacteria in the water. Then it's run through an activated charcoal filter that absorbs (collects on its surface) and removes substances responsible for taste, odor, and color. Fluoride may be added at this time to help prevent tooth decay. Finally, the purified water is collected in a holding tank, ready for your use.