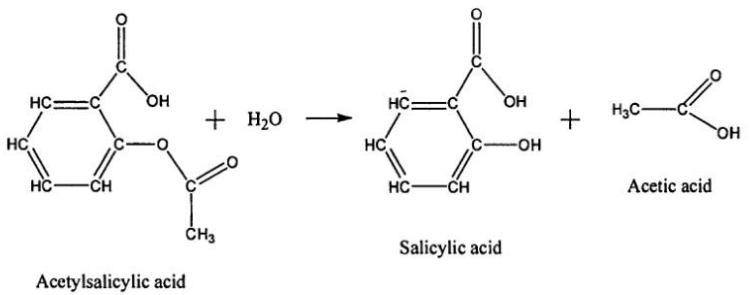
use this information to design *syntheses*, stepwise procedures by which a specific compound can be produced from a given starting material. Using their knowledge of reactivity of carbon, organic chemists have designed syntheses for nearly all the marvelous organic materials that we enjoy, from plastics to medicines. However, this pliability on the part of organic molecules also represents the challenge of organic chemistry. Synthetic schemes have to be carefully considered and may involve many steps, each of which may necessitate careful controls. The following demonstration provides a small taste of the steps that may be involved in such a synthesis.

In this demonstration, we first isolate the active ingredient of the modern form of aspirin, acetylsalicylic acid, using a time-honored organic chemistry procedure called *extraction*. The preparation of purple-cabbage indicator is a type of organic extraction: the organic purple dye is extracted from the cabbage with water. Here we use alcohol to extract acetylsalicylic acid from aspirin.

We will then convert our acetylsalicylic acid to acetic acid with a step-by-step organic synthesis. The equation for the reaction is given below, and figure 2.1.1 shows the structure of the molecules in the reaction. The lines between the symbols for the elements represent the bonds. Note that some of these are double bonds. Carbon is a very versatile element.

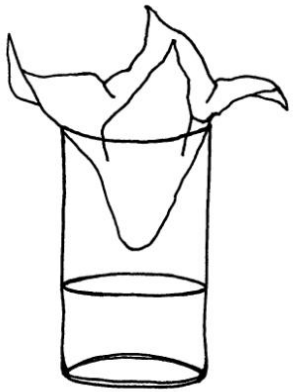


$$CH_3CO_2C_6H_4CO_2H + H_2O \rightarrow C_6H_4CO_2HOH + CH_3CO_2H$$

Figure 2.1.1. Acetylsalicylic acid, the active ingredient in aspirin, can be converted to salicylic acid and acetic acid, which is a principle component of vinegar.

Organic chemistry is a rigorous, demanding discipline, but with a little aspirin it can be less of a pain.

Extraction and Isolation of Acetylsalicylic Acid



Place ten to fifteen aspirin, plain or buffered, into a glass container. With your safety glasses on, pour in a half cup (120 milliliters) of rubbing alcohol; 70 percent isopropyl alcohol works just fine. This amount should be enough to cover the tablets with some to spare. It doesn't take much solvent to extract the acetylsalicylic acid from the tablets. Gently warm the container in a microwave on half (50%) power for thirty seconds, then remove it from the microwave oven. The solvent should be warm but not boiling. The warm solvent will extract the aspirin compound from the tablet and leave the starch binder and other components undissolved. Remember our discussion of "like dissolves like"? The nonpolar starch does not dissolve in the polar alcohol-water solvent. If you have an old spoon or fork, you may want to gently crush the residual material to maximize the amount of acetylsalicylic acid that is extracted. This process takes about fifteen to twenty minutes, but your patience should be rewarded.

Take a paper towel and spread it over the top of a large glass. Push it down slightly so that it resembles a funnel. Carefully pour the aspirin and alcohol solution through the paper towel filter. This will collect the tablet residue in the towel while allowing the clear liquid, called the *mother liquor*, to trickle to the bottom of the glass. Once all of the solution is filtered, put on your rubber gloves and dispose of the paper towel and tablet residue. Try not to touch the moist portion of the paper towel, as the solvent is laden with acetylsalicylic acid, which could remain on your skin after the solvent evaporates. You may want to wash your hands at this point, although aspirin is not a dangerous compound in the miniscule amounts that may be on your hands. The acetylsalicylic acid is now dissolved in the alcohol in the glass.

Run a small stream of cold tap water and fill the glass containing the mother liquor with the cold tap water until it is about three-quarters full. If your alcohol extraction was successful, there should be many very

small white flat crystals of acetylsalicylic acid filling the mixture. Acetylsalicylic acid is somewhat nonpolar and dissolves fairly easily in a somewhat nonpolar solvent like isopropyl alcohol. But as soon as the very polar water is added, the acetylsalicylic acid is forced out of solution by its decreased solubility and it forms crystals. These are not large single crystals but tend to look like white soap flakes and may appear gooey until they are dried.

It is always impressive to observe the volume of crystals formed, especially when compared to the original tablet volume. Set up another paper towel filter in a large glass and collect the acetylsalicylic acid crystals in the towel by pouring the alcohol-water-crystal mixture through the towel. Rinse the crystals out of the first glass using small amounts of cold tap water, and pour those small portions through the filter. This will also help rinse off the crystals in the paper towel. Keep the crystals in the paper towel and dispose of the used solvent that dripped through.

It is possible at this point to go on to the next procedure, but if you have the time, spread the paper towel with the crystals out on a countertop for air drying, which may take overnight. Make certain the crystals are protected from children and pets, and vice versa. Strong breezes would also be bad because the dry crystals are light and fluffy. Observe that there is no aroma associated with these crystals once they are dried, not even that of isopropyl alcohol. Once the crystals are dry, you can observe how light they are by picking up the paper towel. Most of the original weight of the wet crystals was solvent.

Acid-Catalyzed Hydrolysis to Salicylic Acid and Acetic Acid

If you let your crystals dry overnight, then find your safety glasses again and put them on. Take about a quarter of either the wet or dry acetylsalicylic acid crystals and place them into a glass container that can be used for warming. The dried crystals are very fluffy and should be handled carefully so they do not scatter. Take the bottle of aquarium pH-lowering solution recommended for purchase in the "Shopping List and Solutions," and add it dropwise until the entire sample of acetylsalicylic acid is com-

pletely covered. The pH-lowering solution is sulfuric acid that is not very concentrated and perfect for this reaction. It behaves as a catalyst in that it speeds up the reaction and is not consumed during the reaction. Be extra careful during this phase of the experiment: dilute sulfuric acid will remain at the end of the experiment, and even dilute acid should always be treated with cautious respect.

Gently warm this mixture for about fifteen seconds in a microwave oven on low power (50% power). Remove the container from the microwave and use your hands to waft any aroma from the top of the container toward your nose. At the end of the reaction, part of the acetylsalicylic acid will separate from that molecule because of the acidic environment. The part that leaves becomes acetic acid, the active principle of vinegar, and the aroma will eventually be detected by your nose. Once the acetic acid has evaporated, the crystal residue will be the simpler analgesic, salicylic acid. All solids can be disposed of in the trash, and all liquids can be rinsed carefully down the toilet.

The reaction you have just executed is an organic reaction known as an *acid-catalyzed hydrolysis.* The suffix *-lysis* means "to cut," and *hydrolysis* means "to cut with water." In this reaction, acetylsalicylic acid is "cut" with water to form salicylic acid and acetic acid, as shown in figure 2.1.1.

CHAPTER 1

Simply Organic

On the other hand, I used to find Paul Tichlorne plunged as deeply into the study of light polarization, diffraction, and interference, single and double refraction, and all manner of strange organic compounds.

—Jack London, *Moon-Face and Other Stories*, ca. 1905

Even while we talk some chemist at Columbia
Is stealthily contriving wool from jute.

—Robert Frost, *Build Soil*, ca. 1950

It is instructive to look around at the number of things composed primarily of organic materials—that is, composed of the covalently bonded carbon-hydrogen compounds called hydrocarbons—either processed or unprocessed. From asphalt to aspirin, our world is awash in hydrocarbons.

These hydrocarbons include plastics, which nowadays make up part of everything from automobiles to office supplies, to farm implements, to clothes. Any food, from steak to French fries and sugar to sardines, is

organic, which brings us to the biggest category: all living things. Plants, animals, fungi, and bacteria. Our fuels—gasoline, natural gas, propane, and butane—are organic because they derive from once-living things, such as trees, dinosaurs, and fish. Petroleum products range from asphalt to acetone. Coal is a lump of organic material. Our soaps are organic, as are our shampoos, whether they are specially touted as such or not. Makeup? Organic. Toothpaste? Deodorant? Mostly an organic base with a few active ingredients thrown in. Our medicines? Organic, or if the active ingredient isn't organic, the starch carrier or gelatin capsule is. Any flavored drink may be mostly water, but the colorings and flavorings, either natural or from coal tar, are organic. Clothing, natural or synthetic, is made up of organic fibers. Many times the word *organic* is taken to mean "produced naturally rather than manufactured," but in truth, all hydrocarbons are organic, regardless of how they came into being. But there can be no doubt that the first organic compounds were natural. The body wearing the clothes is organic, too.

Why are so many materials made of hydrocarbons? Actually, the mystery does not go that deep. Deep into Earth, that is. When we compare the mass of Earth, including its inorganic core, with the total mass of hydrocarbons, hydrocarbons are not that common after all. Carbon does not rank in the top eight elements that compose our planet (which are, in order of abundance, iron, oxygen, silicon, magnesium, nickel, sulfur, calcium, and aluminum) or even among the top eight elements making up the Earth's crust (which are, in order of abundance, oxygen, silicon, aluminum, iron, magnesium, calcium, potassium, and sodium). But the carbon we have is concentrated at the very upper edge of Earth's crust because of carbon's small atomic mass. During the upheavals over the eons of Earth's existence, the lighter elements have shifted to the top, like peppercorns in a sea of peas. Once in the crust, carbon was able to form the largest variety of compounds primarily because of its unique ability to form long, stable chains of bonds, a talent called *concatenation.* The strength of the stable bonds of hydrocarbons is evident when those bonds are broken and that energy is released: hydrocarbons make excellent fuels.

Hydrocarbons can grow into beautifully complex and intricate chains because carbon can form four separate bonds with other elements, and it can form stable bonds with itself. There are, of course, other elements that

can self-bond, such as N_2 and O_2, and there are still other elements that can form chains, such as a cyclic form of sulfur, S_8. But this ability to form so many varieties and lengths of chains, and remain pliable or fluid while doing so, is a gift that is uniquely carbon's. Carbon compounds can also have a three-dimensional character that is necessary to build our three-dimensional world. Methane, the most basic organic molecule, is formed from one carbon and four hydrogen atoms. Carbon sits at the center of this molecule, and the four hydrogen nuclei extend outwards to the four corners of a regular tetrahedron, as shown in figure 2.1.2. This type of drawing is called a *projection* drawing because the solid and dashed wedges indicate which bonds would project into and out of the plane of the page in the true three-dimensional structure.

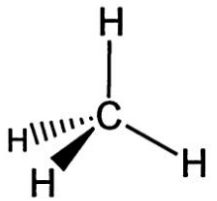


Figure 2.1.2. The structure of methane, CH_4. The straight-line bonds indicate hydrogens in the plane of the paper. The solid-wedge bond indicates a hydrogen coming out of the plane of the paper and the dashed-wedge bond indicates a hydrogen on the back side of the plane of the paper.

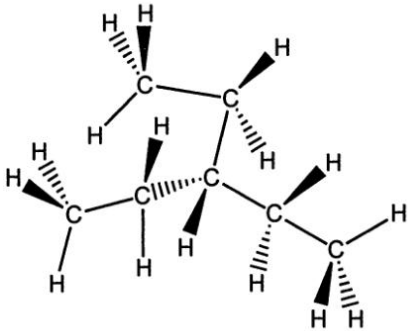


Figure 2.1.3. A seven-carbon chain twisting about its bonds.

From the angles of this one molecule, it may be imagined how intricate scaffolding may be built, twisting and turning into varied filigreed shapes. A relatively minor example, one involving only seven carbons, heptane, is shown in figure 2.1.3.

And carbon is even cleverer than this. Carbon can form double and triple bonds with itself, as shown in figure 2.1.4. Multiple bonds result in triangular and linear geometries, which extend the architectural choices. When a compound has all single bonds, it is said to be saturated. In other words, methane shown in figure 2.1.2, and heptane in figure 2.1.3, would be said to be saturated, while the structures in figure 2.1.4 would be said to be unsaturated. To gain an appreciation of the dif-

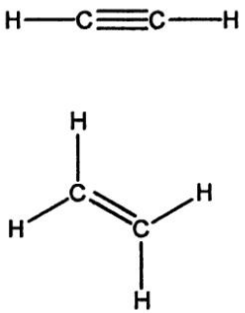


Figure 2.1.4. Double and triple bonds in carbon molecules. The double-bonded compound is commonly called ethylene, and the triple-bonded compound is commonly called acetylene.

ference that this simple change makes, think about all the fuss made over saturated fats versus unsaturated fats. What a difference a double bond makes! We'll revisit saturated fats when we discuss the role of fats in biochemistry.

As a result of this bonding virtuosity, carbon can also form circular, daisy chain–like *cyclic* compounds and even join several cycles together, as shown in figure 2.1.5. Beefed up by honeycombed rings, these types of compounds are robust enough to withstand the pressures of life and are found in many biologically essential materials. Once formed into a circle, carbon nuclei sometimes share electrons in a large molecular orbital that extends over the entire ring. The bond that results is given the descriptor *aromatic* because it is found in many odoriferous organic molecules, such as benzene, the compound that lends a pungent aroma to gasoline. Aromatic molecules are especially stable, owing to their shared molecular orbital, and are likewise found in many biologically important materials.

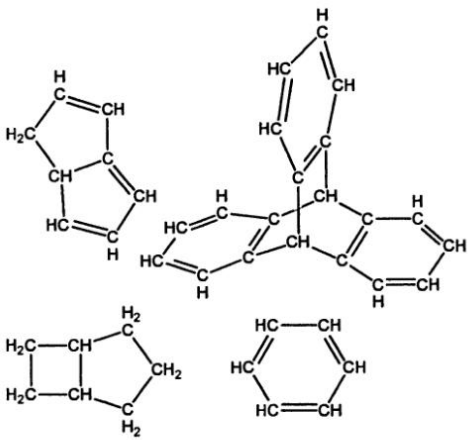


Figure 2.1.5. Some hydrocarbon structures that involve rings.

Obviously, with so much variety possible with organic molecules, chemists have spent a good deal of effort in classifying the various materials into families of compounds. The method that has evolved is to group compounds into families defined by the presence of certain identifying structures called *functional groups.* As examples, we will look at four families of hydrocar-

bons that contain oxygen in their functional group: alcohols, ethers, organic acids, and esters.

For alcohols, the functional group, or defining structure, is OH. Alcohols all incorporate an OH group, but the nature of the rest of the molecule determines the unique properties of that alcohol. Ethanol is the alcohol present in alcoholic beverages, isopropyl alcohol is the alcohol of rubbing alcohol, and methanol is sometimes used for fuel—and they are not interchangeable. While it may be acceptable for adults to imbibe small amounts of ethanol on special occasions, it is never advisable to drink isopropyl alcohol or methanol, as these alcohols can cause bodily damage or death. Methanol, which can contaminate bathtub gin, is notorious for causing blindness or brain damage. Figure 2.1.6 shows these three structures. Notice how a small structural change can have a big impact on chemical behavior.

The defining arrangement for the *ether* functional group is oxygen between two carbons. (See figure 2.1.7.) One particular ether, diethyl ether, is known for its soporific effects on the mammalian brain, an effect that was widely appreciated by surgical patients when it was perfected as an anesthetic.

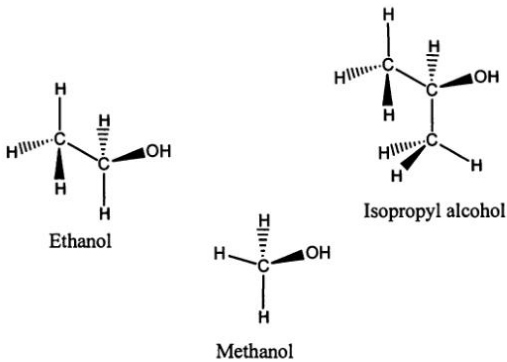
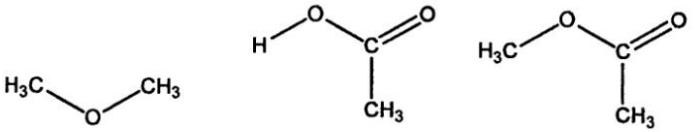


Figure 2.1.6. Three different alcohols with distinctly different properties.

Organic acids, shown in figure 2.1.7, also contain oxygen in their defining functional group, which is CO_2H. Acetic acid, which we have used extensively in our demonstrations in the form of vinegar, is an organic acid and has the formula CH_3CO_2H.

Examples of the third type of functional group shown in figure 2.1.7, esters, are derived from organic acids. In an ester, the hydrogen in CO_2H is replaced with an organic group. Some esters are noted for their pleasant fruity aromas and have been used to simulate the odor, and hence the flavor, of bananas, pears, and pineapple. Modern aspirin, acetylsalicylic acid, is an ester. In figure 2.1.7, we show an example of each: an ether, an acid, and an ester.



An ether **An acid** **An ester**

Figure 2.1.7. An ether, an acid, and an ester.

Carbon compounds may also incorporate atoms of other elements, called *heteroatoms*, such as nitrogen, sulfur, chlorine, bromine, or others. But whatever the identity of the bonded species, carbons will always sport four bonds, be they single, double, or triple bonds. When a carbon has four single bonds, an interesting property can be created: handedness.

Handedness in a molecule is similar to handedness in a human. Humans are configured with right hands and left hands, and these hands are distinctly different. One cannot be mistaken for the other. They match point by point when they are pressed palm to palm or held up to a mirror, but when you try to stack one hand on the top of the other—the palm of one hand on the back of the other—you find your thumbs going in two different directions. Molecules can also have a handedness. A carbon with four different attachments can match its mirror image face to face, but lain on top of its mirror image, it may no longer match. An example is shown in figure 2.1.8.

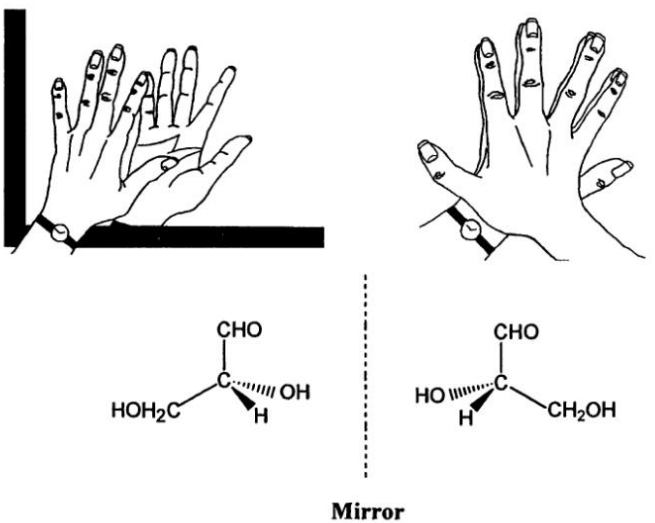


Figure 2.1.8. Chiral hands, chiral molecules.

As may be recalled from our discussion of the law of definite proportion, *isomers* are molecules that have been built from the same number and type of atoms but arranged in a different order. We cited, as examples, fulminic acid, cyanic acid, and isocyanic acid: HONC, HOCN, and HCNO, respectively. We saw that this simple rearrangement of elements made the first explosive, the second a poison, and the third a pacific participant in several, more constructive, organic syntheses. Isomers that differ only by being mirror images of each other are termed *chiral isomers* (pronounced *kiral*, with a hard *c* sound, the way *chemist* is pronounced *kemist*).

Chiral twins have different properties from one another. For example, one form of carvone, a chiral organic molecule, smells of spearmint, while its mirror image smells of caraway. One form of limonene, a chiral organic molecule, smells of lemon, while its mirror image smells of oranges. To understand why this subtle difference in shape should make such a large difference in properties, try shaking hands with yourself or putting your right shoe on your left foot. It just doesn't work. The shoe doesn't fit. In many biological systems, if the molecule doesn't fit, it doesn't work.

These mirror-image molecules can also be distinguished from each other by the way they interact with polarized light. Polarized light is light of a limited range of orientations. In the sunglasses business, light of all orientations is called "glare." To experience the difference between glare and polarized light, flip on and off a pair of polarized sunglasses while looking at sunshine reflected off a shiny surface. Polarized sunglasses only allow through light of a limited range of orientations, or polarization, and thereby cut down on the glare. When light encounters a chiral molecule, the light may experience a twist from the electric field of the unsymmetrical molecule, as a car will turn if the road banks one way or the other. If there is a large number of such molecules interacting with the light, the effect can be substantial enough to be measured.

Using L to stand for *levorotatory* and D to stand for *dextrorotatory* (which is the chiral molecule equivalent of left-handed or right-handed), chiral molecules can be sorted into L and D categories depending on how they interact with polarized light. Many bodily molecules are chiral, including the sugars that are building blocks in DNA and the amino acids that make up proteins. As it turns out, the body has a peculiar preference

for the L form. The mystery writer Dorothy Sayers used this idea in a 1930 story, *The Documents in the Case*, in which the victim is first assumed to have died of mushroom poisoning.[1] Closer examination of the toxins, however, reveal that they are of the wrong chiral form and therefore must be of synthetic, not natural, origin.

The origin of this left-handed preference of nature is not known but probably has the same explanation as the British tradition of driving on the left-hand side of the road: it's just the way things started out and it has always stayed the same. But not only can different mirror-image isomers cause different sensations of smell and taste, exposure to the wrong isomer of a biological compound can be dangerous. A notorious case of trouble caused by exposure to the wrong isomer is the case of Thalidomide, a sedative drug that was manufactured as a mixture of its two mirror-image forms. Unfortunately, the form that did not act as a sedative instead acted as a *teratogen*, a compound that causes birth defects. Because of such differences in activity, and also to lower the necessary dosage, it is desirable to produce medicines in a single isomeric form when possible. A good deal of research effort is currently being expended toward this goal.

Because the mirror-image isomers of chiral compounds are essentially separate materials, the number of chemically different hydrocarbons becomes all the more impressive. The agency that has assumed the responsibility for tracking such things in the United States, the American Chemical Society, now numbers the known organic chemicals at about twenty million, and more are discovered nearly every day. Obviously, finding names for all these progeny is a monumental task. Fortunately, the task, undertaken by the International Union of Pure and Applied Chemistry, has been made systematic.

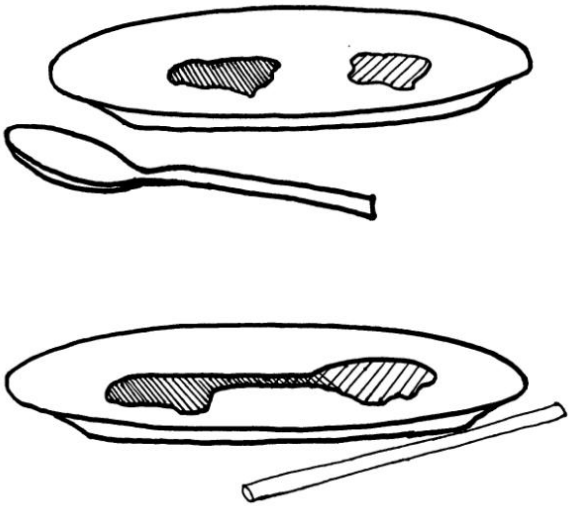
Organic compounds are named for their characteristic features, just as a skinny redhead might be nicknamed Slim or Red. The alcohols described previously are named alcohols because they have the characteristic OH group. The other part of the name—methyl, ethyl, isopropyl—refers to the type of chain to which the OH group is attached.

But this is where Slim and organic chemistry part company. An organic molecule cannot be named for just one characteristic; the molecular name must describe all the features of the molecule so that its name will be unique. To decide what a particular molecule should be called, the

name of the basic structure is determined first, usually a carbon-chain backbone such as methyl or ethyl. Then the names of all the functional groups, all the characteristic, identifying groups, are tacked on. As such, the names for organic molecules can become quite ponderous.

Tetramethyldiaminobenzhydrylphosphinous is said to be one of the longest dictionary entries, but the length is not all that unusual for organic chemicals. Some chemists have been known to wax creative when presented with the opportunity to name a new base structure. One new material was dubbed buckminsterfullerene because it resembles a geodesic dome, a design originated by the architect R. Buckminster Fuller. Barbituric acid, the starting material for the family of compounds known as barbiturates, is said to have been named after Barbara, the love interest of the scientist who first isolated the compound.

Aside from finding architects and lovers to name compounds after, organic chemists also spend their time investigating the amazing number of reactions that each one of these compounds can undergo. As we saw in our demonstration, moving or removing just one part can radically change the qualities of the material. So the shelves of chemistry libraries bulge with journals devoted to the intricacies of organic chemistry. And a great deal of work remains to be done. As our feedstock shifts from petroleum to the biomass or the reuse of recycled materials—as it inevitably must—organic chemists are revisiting classic chemistry and inventing chemistry that is new. But remember, all that organic goo must connect with a rocky, sandy soil; an ocean of water; and an atmosphere of air. The inorganic world is where we venture next.



Inorganic Chemistry Demonstration: Entropy, Ammonia, and Amoeba

Another year's installment of flowers, leaves, nightingales, thrushes, finches, and such ephemeral creatures, took up their positions where only a year ago others had stood in their place when these were nothing more than germs and inorganic particles.

—Thomas Hardy, *Tess of the d'Urbervilles*, ca. 1890

Take a glass of water and some of the food-coloring drops that were suggested for purchase in the "Shopping List and Solutions." Very gently add a drop of food coloring to the glass of water, holding the food-coloring bottle as close to the surface as possible to minimize agitation. Then relax and watch the beautiful ballet as the food coloring diffuses through the water. It will mix spontaneously due to entropy, the natural tendency of systems to go toward a state of maximum disorder.

Now, making certain your safety glasses are in place, take the iron acetate solution mentioned in the "Shopping List and Solutions" and put a puddle of it, about a half inch (about 1 centimeter) in diameter, on a dry ceramic or glass plate. Take care that the puddle does not smear. If the puddle clearly has a raised top, rounded by surface tension, then you are

ready for the next step. If not, there is probably some sort of residue on the plate. Get a clean, dry plate and try again.

Take some drops of household ammonia and make another puddle with the same rounded top, positioned about a quarter inch (about a half a centimeter) from the iron acetate puddle. Now carefully draw a line of liquid connecting the two puddles by dragging the end of a straw from one puddle to the other. The puddles should merge just at the point of contact.

Observe the two solutions diffusing into one another. The patterns formed can be quite lovely and delicate, like a liquid garden. The process can be set into slow motion by putting a drop of glycerin or mineral oil between the two reagents and connecting both puddles to the one in the middle. A similar reaction-diffusion pattern can be seen by joining a puddle of copper sulfate solution and ammonia or copper sulfate and baking soda solution.

The mixing is, once again, spontaneous, but there is an added element of entertainment in that a chemical reaction is taking place, too. Watching the amoebaelike progress of the two inorganic solutions toward each other and the waves of reaction spreading fingerlike across the plate, one can imagine the first formation of structures in the primordial soup and the slow, steady progress out of the mire.

CHAPTER 2
Chemistry Rocks

Once you are there you'll be like a drop of water in a piece of rock crystal—your medium will dignify your commonness.
—Thomas Hardy, *A Pair of Blue Eyes*, ca. 1900

We hope that we've convinced the reader of the significance of organic chemistry, but not to the detriment of inorganic chemistry. From gemstones to limestone and nitrates to phosphates, inorganic chemistry is of enormous importance, too. If organic chemistry can be described as the chemistry of hydrocarbons, then inorganic chemistry can be described as the chemistry of everything else—and everything else covers quite a lot. In fact, many of the materials we have already discussed are inorganic: metals, semiconductors, salts, and many acids and bases. Yet our cultural emphasis on organic compounds, stemming from the abundance and availability of organic starting materials in the form of petroleum and coal, has led us into an organic mind set. And this single-mindedness may have resulted in an unfortunate dependence on a limited resource. However, a look back at the elemental abundance found on

Earth's crust tells us that oxygen and hydrogen are much more abundant than carbon (oxygen would be the Godzilla on the graph and carbon would be the mouse), so there may be alternatives. Fuel cells that use hydrogen and oxygen are currently powering the space shuttle and have the potential to power cars as well as DVD players. It is nice to know that even though it will be difficult to perfect, the future holds alternatives to fossil oil. Here we will take a look at some of the topics that are currently the special purview of inorganic chemistry: coordination complex compounds of transition metals, representative-group chemistry, and radiochemistry.

The transition metals are located in a big block of elements that form the "transition" from the nonmetals to the metals, as shown in figure 2.2.1.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg						Transition Metals					Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac†	Rf	Db	Sg	Bh	Hs	Mt	•	•	•						

*Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 2.2.1. The transition metals are found in the block in the middle of the periodic table.

These elements have a peculiarly colorful chemistry that stems primarily from their facility at assuming different oxidation states. As you may recall from our discussion of redox chemistry, most elements are fairly happy to share electrons with other elements so that they all wind up with the optimum number of electrons. The nice thing about transition metals is that they can be satisfied with two or more different electron configura-

tions. Recall from the redox demonstration that light orange iron acetate turned green with the addition of ammonia and then red with the addition of hydrogen peroxide. The hydrogen peroxide caused iron to shift from an ion with two electrons missing (Fe^{2+}) to an ion with three electrons missing (Fe^{3+}). The first color change (orange to green) was the result of ammonia crowding around the iron. The second color change (green to red) was a result of the ammonia molecules interacting differently with the new ion. How closely surrounding ions or molecules are held to a charged ion and the way they arrange themselves around the charged ion is called their *coordination* with the ion. The resulting structure, ion and coordinating groups, is called the *coordination complex*. The study of the coordination complexes formed between transition metal ions and the molecules that surround them is called *coordination chemistry*.

The study of coordination chemistry stems from the observation that nothing is ever completely alone in solution. Even the most aloof ions, in solution, are surrounded by some entourage of counter-ions (ions with the opposite charge) and/or solvent. Because transition metals nearly always form positive ions (the rare exceptions occur with exotic metals or under exotic conditions), they are surrounded by water molecules, at the very least, with the more negative oxygen end of water closer to the positive ion. If there are other ions or molecules available in solution, such as the acetate ion or ammonia as in our demonstration, these too can coordinate with the central metallic ion, as shown in figure 2.2.2. There is generally room for four or six of these companion species, called *ligands*.

A ligand is any small molecule or ion that is attracted to and surrounds a metal ion. Common ligands are H_2O, NO_2, Cl^-, and NH_3 (water, nitrogen dioxide, chloride, and ammonia). Depending on the nature of the ligand and the charge on the ion, some are held relatively tightly and others are held loosely.

As we noted in our discussion of photochemistry—and as we encounter every day in our use of items from whitening toothpaste to rose-colored glasses—light interacts with chemicals. Whether they are brighteners or dimmers, these interactions occur on the molecular level. For inorganic coordination complexes, the color of light that interacts with the molecule will depend on the nature of ligands and how tightly or loosely they are held to the metal ion. Due to a complex combination of influences, including electrical attraction, intermolecular forces, and

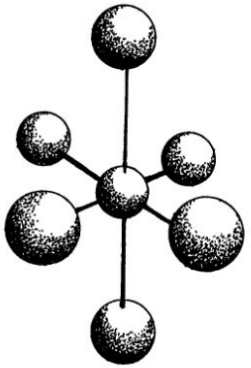


Figure 2.2.2. A central metal ion surrounded by six companion molecules or ions.

entropy, ammonia is strongly attracted to the iron ion. When ammonia was added to the iron solution, the ammonia molecules crowded toward the metal ion, displacing some of the water molecules and acetate ions, and in the process changed the color of the compound. When we added the peroxide, we changed the oxidation state of iron and how tightly the ligands were held. This rearrangement changed how light interacted with the complex—in other words, it changed the color.

Larger organic molecules can form complexes with metal ions, too. Radiator cleaner consists of a water-soluble complexing agent, such as the organic compound oxalic acid, which forms a water-soluble cage around metal ions and lifts them from the walls of the radiator. The metals that are found deposited on radiator walls, such as calcium, were once dissolved in the radiator water. We don't normally think of calcium as being a metal, but it is. Calcium is located on the left side of the periodic table, which makes it a metal, and it can form coordination complexes as transition metal ions do. When calcium forms a complex with oxalic acid, the calcium becomes water soluble.

Organic complexing molecules that move metal ions into solution are known at *chelating agents.* Perhaps the most important organic chelation is that which occurs in our own bodies. Most of the trace metal ions needed for life are bound to protein molecules in some fashion or another, and the protein can be thought of as chelating agents. Hemoglobin is, in one respect, a chelated form of iron. Without the hemoglobin-iron coordination complex, oxygen could not be transported through our blood. As the protein in hemoglobin clusters itself around the iron ion, it creates a neat pocket for the oxygen gas. Blood-borne hemoglobin then carries this oxygen to where it is needed by the cells.

The block of two columns on the extreme left of the periodic table (including calcium) and the six columns on the extreme right of the periodic table, as shown in figure 2.2.3, are the *representative* elements.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac†	Rf	Db	Sg	Bh	Hs	Mt	•	•	•						

*Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 2.2.3. The representative elements.

These elements are a diverse bunch, containing as they do metals and nonmetals and, at room temperature and normal pressure, some gases, some liquids, and some solids. Within the representative group are several important families of elements with chemistries all their own.

The first column on the far left contains the family of alkali metals, several of which are familiar: lithium (Li), sodium (Na), potassium (K). Most of these elements, as well as the rest of the representative metals, are never found in a natural metallic state. They are present in coordination complexes or in salts. In tales of the Death Valley desert, a generic character named Alkali Sam or Alkali Pete or just old Alkali often crops up, a name derived from the desert salts surrounding this salty character.

Sodium and potassium salts are found everywhere in minerals and soils, and, consequently, natural bodies of water. Their presence in ocean waters had led to their inclusion in the organisms that evolved there. Nowadays a health concern is associated with large concentrations of sodium ions in the body, but the emphasis here should be put on *concentration*. It is not so much the presence of sodium that causes a problem as it is the absence of water. As a culture we have turned to added sodium and away from water, which can be a debilitating combination. It is a sad denial of our saltwater beginnings to tip the balance this way.

The second column from the left contains the alkaline earth metals, beryllium, magnesium, calcium, strontium, barium, and radium (Be, Mg, Ca, Sr, Ba, and Ra, respectively). Magnesium and calcium are present everywhere and are needed by our salty bodies and the salty bodies of our fellow creatures. Calcium is vital to bones, teeth, seashells, and exoskeletons. Calcium plays a critical role in the operation of our muscles as well as communication between cells. Because strontium is in this family, radioactive strontium, a fission product of certain atomic reactions, can be absorbed by the body and used as it would use calcium. Radium, another radioactive element, is also found in this family.

The third and fourth columns of the representative group are over on the right-hand side of the periodic table, a grouping that could be described as the "semiconductor" metals. They make good semiconductors because of their unique location on the periodic table. They are close enough to the transition metals to be somewhat conductive like the transition metals, but they can form covalent bonds like the other materials on the right-hand side of the periodic table. Combinations of tin, lead, gallium, indium, and aluminum (Sn, Pb, Ga, In, and Al, respectively) have been used to make semiconducting materials that have a wide range of properties. Gallium is unique in that it is a solid metal that will melt at body temperature, so it will turn into a puddle when held in the hand. Aluminum, as we have seen, is one of the most common elements in Earth's crust; however, it was not widely used as a metallic material until the early 1900s because aluminum is very reactive. Before aluminum could be fully exploited, a method had to be found for making the metal from the salt. The importance of recycling aluminum metal does not arise from its rarity but rather from the amount of energy and materials that must be expended to claim it from the rocks and purify it.

In the representative elements we find the block that contains carbon, nitrogen, oxygen, phosphorus, and sulfur—the elements, along with hydrogen, that form the basis for life. But just one chapter back we called the chemistry of carbon-hydrogen compounds, hydrocarbons "organic chemistry" and stated we would treat organic chemistry and inorganic chemistry as separate topics. Are we now allowed to blur the lines and include the elements of organic chemistry with inorganic chemistry? Not only are we allowed to, but we must. It was not the chemists who blurred the lines but nature itself. In our interdependent, symbiotic world, there

can be no complete distinction between the workings of animal and earth, though for the convenience of the chemist we may seek to impose one. Nowhere does this interdependence show up more impressively than in the inorganic/organic cycles with which elements such as carbon and nitrogen are alternatively used by life, returned to the earth, then the atmosphere, and then reclaimed to further the cause of life.

In the nitrogen cycle, atmospheric, inorganic nitrogen, N_2, reacts with atmospheric, inorganic oxygen, O_2, in a reaction sparked by lightning. The nitrogen oxides thus formed, NO, NO_2, N_2O_4, can dissolve in rainwater, which brings them within reach of certain soil bacteria. These bacteria can use them to manufacture the nitrogen-carbon-oxygen-hydrogen organic molecules known as amino acids. Plants and then animals take in the nitrogen-containing organic compounds created by the bacteria, metabolize them, excrete them, and return them to the cycle as organic and inorganic compounds and salts. In Edgar Allan Poe's short story "Cask of Amontillado," he used the presence of nitrate salts to indicate death and decay.[1]

> "The nitre!" I said; "see, it increases. It hangs like moss upon the vaults. We are below the river's bed. The drops of moisture trickle among the bones."

To complete the cycle, another bacterial bug that flourishes under anaerobic (i.e., oxygenless) conditions feeds on nitrogen-containing compounds of decay and returns nitrogen gas, N_2, to the air.

Similarly, carbon cycles through an inorganic and organic existence. Carbon (C) begins as inorganic carbon dioxide in the air and is fixed through photosynthesis into organic sugars in plants. These sugars—metabolized and excreted or exhaled by animals, plants, and bacteria—return as carbon dioxide to make another round.

A companion element to carbon, directly below it in the periodic table, is silicon. Silicon (Si) can also form long chains of linked silicon nuclei, and it also assumes a tetrahedral shape like carbon. But silicon does not readily form the double and triple bonds of carbon, so it does not appear to possess the versatility necessary for a complex life form, though some science fiction writers would have it otherwise. Still, silicon forms the basis for quartz, gemstones, and glass, which contribute to the beauty of life.

The rest of the representative-group elements, to the right on the periodic table, are again better addressed as families, this time single-column families. The elements in the column that includes fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) are called the *halogen* family, as in a halogen lamp. In a halogen lamp, there is a gas-phase halogen gas in a small bulb within a bulb. (You can see it if you look closely.) When the tungsten filament of the lamp heats up, a small amount of its surface vaporizes. The purpose of the halogen gas is to keep the filament from vaporizing completely. When the tungsten atoms fly from the surface, they encounter the gas and are brought back toward the surface. This redeposition considerably increases the filament lifetime. Halogens are also found extensively in nature, especially in the ocean and in minerals and, once again, in living things. Iodine is an essential element in the human body. It is necessary for the functioning of the thyroid gland, which is why salt manufacturers add iodine to salt.

To the extreme right on the periodic table are the noble gases—helium, neon, argon, krypton, xenon, and radon. These, as pointed out previously, are very unreactive, which is why we give children helium balloons without worrying about explosions. (We don't give them to babies, but this is because of the balloon material, not the helium.) Radon is notorious as a source of radiation exposure precisely because it is a noble gas—unreactive and a gas—and can percolate through soil and permeate homes that have poor ventilation. Though chemically unreactive, radon can undergo radioactive decay. If inhaled, the emitted particles can damage lung tissue.

Radon is located toward the bottom of the periodic table, as are almost all of the radioactive elements. Unfortunately, the word *radioactivity* conjures up images of bombs, disease, disaster, and destruction. On an intellectual level, it can be acknowledged that radioactivity has provided us with x-rays, imaging techniques, and effective, noninvasive treatments of disease. But on a gut level, we have been conditioned to react negatively to all things associated with radioactivity. However, danger from chemicals is always relative—too much aspirin can be as deadly as too much water if you can't swim—and such is the case with radioactive chemicals. While radioactivity and the elements that produce it should be treated with respect, if handled properly they do not present an uncontrollable danger.

Radiochemistry, the chemistry of radioactive elements, is essentially dominated by the same type of coordination chemistry as the transition metals. One of the worries we have concerning nuclear proliferation is that the chemistry of the uranium and plutonium is really rather straightforward inorganic chemistry. Most of the radioactive elements are found in the group called the *rare earth elements* (those last two detached rows at the bottom of the periodic table), though there are elements with radioactive isotopes scattered throughout the periodic table. As noted earlier, isotopes are atoms of an element that differ only in the number of neutrons: the same number of protons, but a different number of neutrons. Some isotopes possess an unstable number of protons and neutrons. These radioactive isotopes fly apart in an effort to achieve stability, releasing particles and a great deal of energy as they do.

Carbon has a common radioactive isotope, as does potassium, so anything that is living or was ever living or contains something that was once living has some amount of radioactivity. The presence of radioactive carbon is used for *carbon dating*. The radioactive isotope that makes carbon dating possible is called carbon-14 because the number of protons and neutrons in the nucleus totals fourteen (six protons because it is carbon and eight neutrons for this isotope of carbon). Carbon-14 is continuously being produced by cosmic rays bombarding the upper atmosphere. Taken in as carbon dioxide by plants and consumed as sugar and starch by animals that eat plants, carbon-14 becomes uniformly distributed throughout living things and remains at a remarkably constant level. That is, as long as the living things are still living. As soon as a living thing ceases to live, it no longer takes in carbon-14 and the carbon-14 in the dead thing begins to revert to carbon-12. By comparing the amount of carbon-14 in a dead material with the amount that would be expected in living material, scientists can judge approximately how long something has been dead. This technique is limited to dating plant- or animal-derived artifacts less than fifty thousand years old, but that's still pretty good. The technique of carbon dating was used to determine that the Dead Sea Scrolls are about two thousand years old.[2]

We also encounter radioactive elements every day in devices that normally perch quietly and inconspicuously on the ceiling of kitchens and halls: smoke detectors. Smoke detectors? Radioactive? Yes. The working element of a smoke detector is a radioactive source, a sample of americium

(Am), which sends a stream of radiation to a detector. The smoke alarm goes off when this stream is interrupted by smoke—or steam, which is why smoke detectors in the kitchen can have an annoying habit of going off even when there isn't a fire. But smoke detectors have saved an impressive number of lives, so resist the temptation to disable the annoying smoke detector and provide the kitchen with better ventilation instead.

Radiation, from radioactive elements, has found another application that is perhaps a bit more controversial than smoke detectors—the use of radiation to kill bacteria on food. The method does work well; it extends the shelf life for many foods. But some people object to using food that has been irradiated, perhaps for fear of contamination.

Contamination should not be a concern. Food that is irradiated does not come in contact with the radioactive source. There are, however, other thought-provoking objections. Some are concerned that the radiation may initiate reactions in the food itself and could form compounds not normally present. Others say we should worry about anything that will kill virtually all of the bacteria present on an item of food. Why? Because bacteria are not necessarily a bad thing. Bacteria are part of the grand scheme. Nature is very good at preserving life, including the life of bacteria, and has no particular bias for human life. So if we manage to kill off some bacteria, that would create a void, and a new kind of bacteria might evolve to fill that void. We wouldn't be able to predict if they'll be human friendly or not. This adjustment on the part of nature is possible because natural systems are fluid—that is, they change. We tend to think of our world in terms of permanence because, for the most part, the adjustments are very slow. But biological systems respond to stress, as do the chemical reactions from which they are formed. Further discussion of biochemical molecules is the topic we take up next.

Biochemistry Demonstration: Fat, Flatulence, and Bean Soup

How on earth are you ever going to explain in terms of chemistry and physics so important a biological phenomenon as first love?

—Albert Einstein, ca. 1940

It is a fact of life: we need to eat healthy foods, and healthy foods give us gas. The problem is that the starches in grassy foods are not completely digested in the human small intestine before they enter the large intestine. This inefficiency is no problem for nature, however. In one of those wonderful symbiotic schemes of which nature is so fond, colonies of bacteria, acknowledged delicately as "intestinal fauna," live in our intestine. As we mentioned in our discussion of the properties of the gas phase, these bacteria have the necessary enzymes to digest grassy foods and feed on the leftovers quite happily. In the process, however, they produce gas. The digestive process also produces sulfides, sulfur-containing organic chemicals that we associate with flatulence: that rotten-egg odor produced by bacteria performing the same function in rotting eggs. The odor of flatulence comes from these sulfides, carried with the gas, which is why intestinal gas is sometimes more odiferous than other times.

The problem of odor is an artificial problem, imposed only by societal norms, but the bloating caused by an overabundance of intestinal gas can be distracting at best and debilitating at worst, so there are reasons to avoid an excessive amount. One way, of course, is not to eat the foods that cause gas, such as raw vegetables and beans. But many of these foods are convenient and concentrated sources of essential proteins, vitamins, and roughage, and should not be avoided entirely. If desired, an enzyme, alpha-galactosidase, can be taken before eating and aid in the digestion of starch before the bacteria have a chance to feed. In this demonstration, we will show these enzymes at work.

Donning your safety glasses, make up two solutions of just less than a quarter of a teaspoon of cornstarch (1 milliliter) in one cup (240 milliliters) of water. Crush a tablet of a digestive aid that is meant to be taken before meals to reduce intestinal gas. These pills should contain the enzyme alpha-galactosidase, which will digest starch. Check the label to make sure. Add the crushed tablet to one of the cups of cornstarch solution. Let the glasses sit for about an hour and then add a drop of iodine tincture iodine to each. Iodine is a well-known indicator for starch because iodine forms a lovely blue-colored complex with starch. The solution without the enzyme will turn a violet-blue color, indicating the presence of starch. The solution to which the enzyme was added should remain the brown color of the iodine tincture. If there is a blue color, it will be much weaker. This demonstrates that the starch has been broken down.

Enzymes and starches are under the purview of biochemistry, the kingdom we enter next.

CHAPTER 3

The Body of Chemistry Meets the Chemistry of the Body

For nitrates are not the land, nor phosphates; and the length of fiber in the cotton is not the land. Carbon is not a man, nor salt nor water nor calcium. He is all these, but he is much more, much more.

—John Steinbeck, *Grapes of Wrath*, ca. 1940

"Ben, I have just one word for you, one word . . ."
"What's that?"
"Plastics."

—Calder Willingham and Buck Henry, *The Graduate*, screenplay based on the novel by Charles Webb, ca. 1960

What do plastics have to do with people? As it turns out, quite a lot. Plastics are made by *polymerization*, the process by which simple molecules are linked together into extensive chains thousands of molecules long. There is not a more proficient polymerizer than a living cell.

From skin to hair and tonsils to toenails, the material that makes us is continuous, pliable, and polymeric. As we pointed out in our discussion

of organic chemistry, the success of organic life forms is based on carbon's ability to form long chains, and when units of these chains are repeated, there you have it: polymers. Our bodies, as well as the bodies of everybody and everything else, from amoebas on up, are composed of long chains of repeating fundamental units—*carbohydrates*, *lipids*, *amino acids*, and *nucleotides*—the polymers that are us.

Let's begin with the carbohydrates and the polymers they form. What are carbohydrates? We know that they are something to be avoided by adherents of certain dietary disciplines, but what are they? Originally carbohydrates were thought to be carbon surrounded by water (hence carbo*hydrate*), somewhat as our inorganic coordination complexes consisted of a metal surrounded by ligands. But we now know that the basic unit of a carbohydrate is a saccharide, which is a ring-shaped carbon molecule, such as shown in figure 2.3.1.

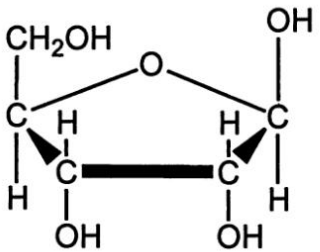


Figure 2.3.1. A saccharide, the basic unit of carbohydrates.

Carbohydrates are sugars—glucose, fructose, galactose. The familiar *sucrose* is a *disaccharide*: two saccharides linked together. When more than two saccharides are linked together, the result is a polysaccharide. Long-chain polysaccharides form the essential materials of starch, cellulose, and glycogen.

As is well known by those who are diet and health conscious, the body metabolizes sugars for energy and, when excess sugar is available, stores the sugar for later use. Animals store sugars as polymers of glucose called *glycogen*. Plants make a slightly different polymer of sugar for storage purposes, and this is what we call starch. Plants also use long chains of carbohydrates to make cellulose, a material for structural purposes, not food-storage purposes. The human body is not capable of recovering saccharides from cellulose, and sometimes indigestible carbohydrates are incorporated in foods to lower the calorie count per item.

Some types of lipids, or fats, are also stored by the body for eventual metabolism, and fats are another food that has been singled out for avoidance because of the negative effects of overconsumption. But there can be

no doubt that the body requires fats, especially the growing bodies of children. For instance, vitamins A, K, and D need fat to be absorbed. So the limitation on fats really needs to be tempered by knowledge of which fats to limit and which fats are essential. There are several different types of fats, and these have varied functions.

Two main varieties of lipids are fatty acids and steroids. The basic structures of these compounds appear quite different, as seen in figure 2.3.2, so it may seem curious that chemists lump them together.

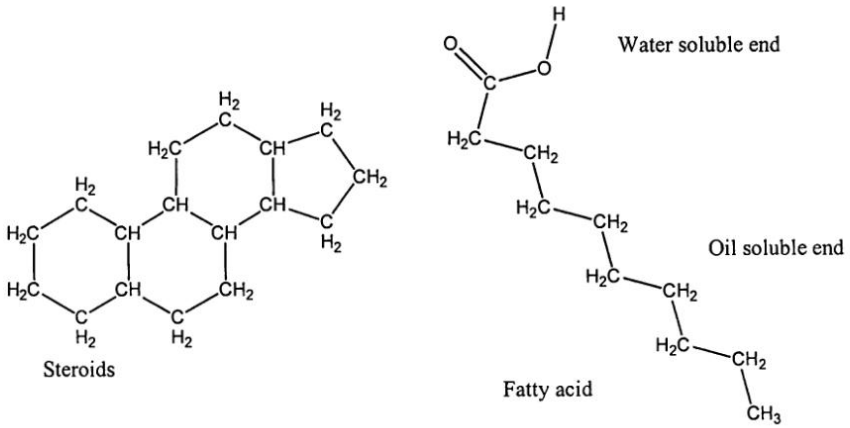


Figure 2.3.2. The two main categories of lipids: steroids and fatty acids.

These compounds are grouped together because they have the common property of being soluble in oily liquids. In the case of fatty acids, one end is soluble in oil and the other end is soluble in water, an ambiguity that turns out to be tremendously useful, as we shall see.

The fatty acids are long chains of carbons terminated by an organic acid group, COOH. In their various configurations, these fats store energy (and are the basic component of all those troublesome fat cells) and also serve to protect and insulate internal organs. They form the insulation on nerve fibers and are the basic component of the cell wall. One of these long-chain fatty acids, arachidonic acid, can be released when a cell is injured by cutting or smashing. This acid is converted into a compound that stimulates nerve cells (pain), rushes blood to the site (inflammation), and raises the temperature to speed up bodily repair processes (fever). That all this happens is remarkable enough. But the next time you cut

yourself, note how quickly it happens. Quickly, but not instantaneously. It takes time for the chemical reactions to take place, but an amazingly short time at that.

Steroids are lipids that have the same basic cyclic structure shown in figure 2.3.2. The steroids have a notoriety of their own, but again, they serve their purpose and cannot be dispensed with entirely. Steroids are components of cell membranes, nerve cell insulation, and the basis for steroid hormones.

Cholesterol is a steroid. And, as everyone knows, eating too much cholesterol can be bad, but there is no way that cholesterol can be entirely eliminated from the diet. The body manufactures cholesterol because the body needs cholesterol for many essential functions. So what is the problem with cholesterol? The problem is that when there is too much in the body, it can accumulate on the blood vessel walls and cause constrictions where the blood should freely flow. Recall that in our discussion of organic chemicals, we said that saturated compounds are ones that have all single bonds, C–C, which means no double, C=C, or triple, C≡C carbon/carbon bonds. It turns out that saturated fats are also the solid fats like lard or solid vegetable shortening. Saturated fats last longer without spoiling, so manufacturers of margarine used to purposefully *hydrogenate* their products—that is, break up double and triple bonds by adding hydrogen—to prevent spoilage. However, it is now recognized that saturated fats can stimulate the body to synthesize cholesterol and inhibit its elimination. Unsaturated fats, on the other hand, seem to promote the elimination of cholesterol.[1] The quantity of cholesterol, however, is not the whole problem.

Unwanted deposits of cholesterol occur because cholesterol, being a lipid with no water-soluble end, needs help to be transported around in the bloodstream. The transporters are called low-density lipids. They form little bubbles around the cholesterol, not unlike soap solvates dirt, using their oily hydrocarbon ends to connect with the cholesterol and their organic-acid ends to connect with the watery fluid of blood. The structure of the low-density lipids (abbreviated LDL) helps them deposit their cholesterol load when they reach the cells where it is needed, but, unfortunately, their structure also facilitates the dumping of excess cholesterol on blood vessel walls when the cells have all they need. When we speak of

"bad cholesterol," what we really mean is the LDL-cholesterol complex. People who are prone to high blood cholesterol levels should avoid eating cholesterol, but they also must avoid saturated fats because these fats contribute to LDL production.

There is, however, another lipid structure, called high-density lipid (HDL), that will wash the excess cholesterol from the walls and down to the liver to be broken down. When we speak of "good cholesterol," what we mean is the HDL-cholesterol complex. So it might first seem that cholesterol deposits could be avoided by maintaining a proper balance of LDLs versus HDLs, but it is more complicated than that. Overall levels of fat must be lowered, too. Excess fats will stimulate the production of cholesterol by the liver, and a person on a high-fat diet can actually reabsorb some of the cholesterol that has been moved to the liver. So there is no free lunch on a high-fat diet.[2] The key to a healthy diet is what we've known all along: balance. Some fruits, some vegetables, some carbs, some fat, some protein.

What are proteins? Polymers, of course—polymers of basic units called amino acids. Amino acids are small organic molecules that contain a nitrogen group and an organic acid. A generic amino acid is shown in figure 2.3.3. The organic acid group is the carbon with the oxygen double bonded and an OH group attached by a single bond. The nitrogen group, NH_2, is called the amino group (hence *amino acid*). The "R" to the side is a symbol meant to stand in for various other groups that can be added at this position and in this way make up a variety of amino acids.

Note that there is a carbon with four attachments. Amino acids can have a "handedness," and naturally occurring amino acids have a preferred handedness. If a molecule of the wrong configuration is introduced—if just two bonds are interchanged—the molecule no longer fits and the results can be deadly.

There are twenty different amino acids that are found naturally in the human body. Polymers of these amino acids form protein structures such as fingernails and cartilage as well as enzymes and hormones. Some of the amino acids can be manufactured in the body, but about an equal number

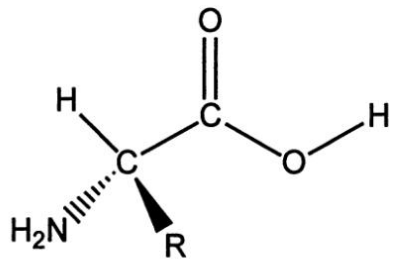


Figure 2.3.3. A generic amino acid.

must come from the diet. All of the necessary amino acids are found in animal protein such as meat and eggs, but they can be acquired from nonmeat sources, too. There is no vegetable that contains all the needed proteins, but as long as many different varieties—squash, corn, rice, beans, soy, and nuts—are consumed, the body's protein requirements can be met.

Of the many materials we have discussed so far, it may be the proteins that perform the most functions. Their long chains include both acid (COOH) and base (NH_2), and the intermolecular forces among the various R attachments allow the protein chains to fold in on themselves in many complex but reproducible configurations. The forces that hold the proteins in their folded form are the same intermolecular forces that we encountered before and as such can be easily disrupted. The vast majority of biologically active proteins perform well only in their natural environs and when disturbed, or *denatured*, by even small changes, can no longer function. The protein of a raw egg can be transformed from its functioning configuration by the addition of even small amounts of heat, which is what cooking is all about. Hemoglobin is a protein that incorporates iron ions. The brown color of cooked or spoiled meat results from a change in oxidation state of the iron in hemoglobin, just as we saw when we changed brown iron acetate to a red complex by adding hydrogen peroxide.

It would not be possible to catalog in this small amount of space the number of materials that proteins form in the body and their many roles, but perhaps another look at one class in particular—enzymes—will serve to communicate the impressive dexterity of proteins.

Enzymes are the catalysts of the body. They facilitate the rapid reactions that are necessary for life. (Recall the message that must be communicated to your brain when you cut your finger, if the communication were not rapid enough, irreparable damage could be done.) Enzymes perform their catalytic function through their three-dimensional structure. Each enzyme has a unique shape that allows it to bond to target molecules. We illustrated one way this binding might speed chemical reactions in our discussion of reaction rates. When two reactants bind to the enzyme, the enzyme can hold them together in optimum alignment until they react.

The manner in which the body uses enzymes is quite elegant. Enzymes need not always be turned on, continuously catalyzing reactions. If the product of the reaction is not required, the enzyme needs to be shut down. Many times, in a gracefully choreographed equilibrium ballet, the same product that the enzyme produces can work to switch it off. The overabundance of the product shifts the reaction away from producing products to breaking down the product instead. The body must maintain a delicate balance of materials, neither a dearth nor a deluge will do, so the shutdown mechanisms must work as well as the stimulating mechanisms, and amazingly enough, they do.

The number of proteins themselves must also be regulated. The system responsible for protein production also operates on the principles of equilibrium. For instance, the enzyme needed to break down lactose would only serve to thicken the blood and gum up the works if it were always present in the bloodstream, just waiting for a dairy product to be consumed. So the body breaks down and recycles the proteins of this enzyme, storing them in the protein soup that exists in the interior of every cell. When lactose is again in the bloodstream, the cell is stimulated to produce more of the enzyme to deal with it. How does the cell produce more enzymes? With another polymer, of course.

The polymer we are talking about this time, however, is unique in that it is built from three different types of fundamental units: a nitrogen-containing base, a sugar, and a phosphate group, as shown in figure 2.3.4. The linkage is between the phosphate group and the sugar, and, linked together, as shown in figure 2.3.5, they form an intricate scaffolding that twists and turns into the compact material called deoxyribonucleic acid: DNA. The stuff of genes and chromosomes.

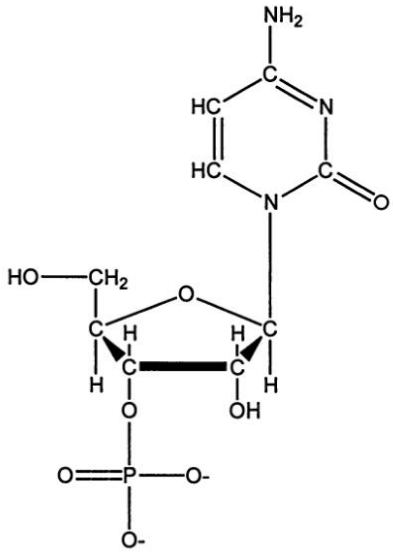


Figure 2.3.4. A phosphate group, a sugar, and a nitrogen-containing base.

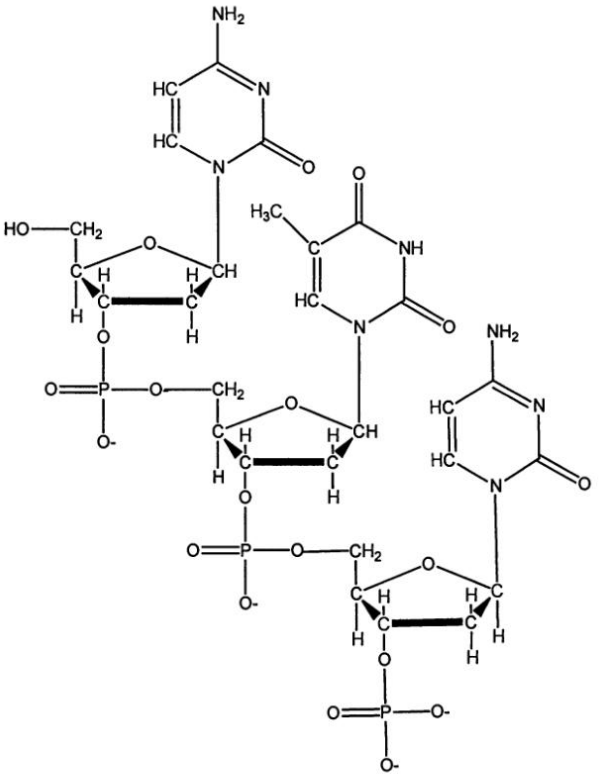


Figure 2.3.5. A segment of DNA showing the linking that occurs between nucleotides.

A chromosome, one long strand of DNA, is a molecule that contains information on how to make all the proteins of the body. A gene is one segment of the chromosome that tells how to make one specific protein. The sequence of nucleotides in a gene serves as a template that is ultimately translated into a sequence of amino acids in a protein.

DNA can be thought of as a diminutive recipe file. When the body needs a hormone, it goes to the DNA to get the instructions on how to make one. When it needs a skin cell or a fingernail, it goes to the DNA to get the recipe for the proteins. When a particular protein is needed—when there is a deficit or an increased demand by the body—stress is put on an equilibrium that causes a section of DNA to be unraveled and a protein to be assembled from its pattern. In this way, when the body needs more

hair, the cells are stimulated to produce hair protein. When the body needs more digestive enzymes, the message is received and more are produced. When the body needs adrenalin, the hormone is ready—at a rate that allows us to leap clear of cars or outrun a roach. But, as pointed out in the demonstration with which we began this chapter, for all the amazing ability of the cell to respond to the demands of the body for enzymes, there remains one enzyme that the human body cannot produce: the enzyme to completely break down beans.

Enzymes, such as the one we used in our demonstration, are governed by the principles of chemical kinetics—one of the many links between the basic principles of chemistry and the intricate chemistry of life. Our rapid and cursory survey of biochemistry here, combined with our previous discussions of biochemical systems, shows that in life all our chemical principles come into play: acid-base reactions, redox reactions, chemical bonding, intermolecular forces, concentration, solids and solubility, kinetics, and even phase transitions and the gaseous phase.

Equilibrium plays an essential part, as does the thermodynamics that governs it, energy and entropy alike. Where there is a need of a compound, the body produces it. When there is an excess, the body stops production—and consumes or excretes the excess. When we need energy, we eat. The living body functions by the supply and demand of chemical equilibrium.

It may seem odd to think of entropy in the context of biochemistry because biological systems seem so organized and ordered, but entropy is as big of a force in biological systems as everywhere else in the universe. Diagrams of cells in encyclopedias can leave the false impression that cells are like row houses in a city or apartments in a complex: all stacked and neat and shaped the same. But a look through a microscope will serve to correct this impression. Cells are really very irregular and messy. Each one seems to have its own shape and habit. The cell membrane is not rigid; it is fluid and constantly shape-shifting about. DNA is not a rigid printout of information but contains "jumping genes" and "junk genes," genes that can move around and genes that seem to serve no other purpose than to add to the confusion.

But there are reasons to appreciate all the messiness. The irregularity means no two natural biological systems will ever be completely alike. We have learned to understand this uniqueness and—with the techniques

of analytical chemistry that we will discuss next—exploit it. The tools of analytical chemistry now enable us to analyze and extract information from a flake of skin or a fleck of spit. Sherlock Holmes would be proud.

Analytical Chemistry Demonstration: The Proof Is in the Prints

Supposing the entity of the poet to be expressed by the number ten, it is certain that a chemist in analyzing . . . would find it to be composed of one part self-interest to nine parts of self-esteem. . . . Gringoire's nine parts of self-esteem, swollen and inflated by the breath of popular admiration, were in a state of prodigious enlargement, obliterating that almost imperceptible molecule of self-interest.

—Victor Marie Hugo, *Notre Dame de Paris*, ca. 1920

DNA evidence has proven to be very valuable, accurate, and reliable, but it is not always available. Fingerprints, however, are easy to see and are sought at every crime scene. To show how latent fingerprints might be made visual, put on your safety glasses and try the following demonstration.

Take some aluminum foil and shape a small square into a bowl or pan. Take a plastic food container with about a one-quart capacity. (A large butter tub will do nicely.) Wash it and its lid, then rinse and dry these

items. Find a small jar, an empty medicine bottle, a smooth drinking glass, or another transparent item that will fit into the butter tub and wash it first completely, inside and out, handling it with gloves or a towel to avoid unplanned fingerprints. Find a clean pair of tweezers or a pair of pliers, and you have all of the items assembled for your fingerprint-developing chamber.

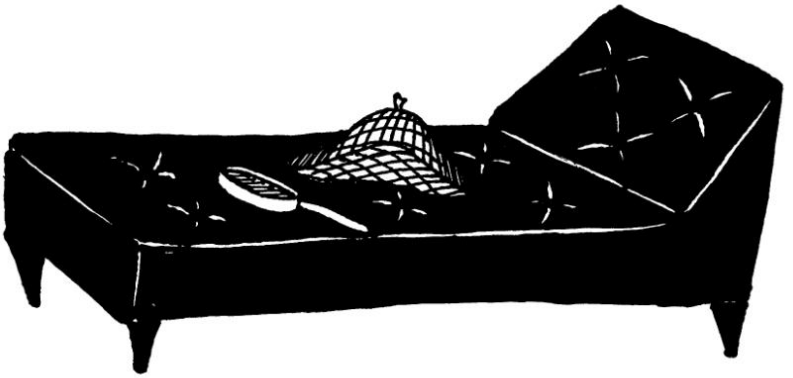
Get the superglue listed in the "Shopping List and Solutions" and make sure it is the kind that contains cyanoacrylate. The fingerprints will be developed on the small jar or similar item that you chose, so firmly grasp the item with your bare fingers, being careful not to smudge the prints, and set it down inside the butter tub. Jot down on a notepad where you touched the jar for future reference. Now take the small foil pan and place about thirty drops of superglue into it. The quantity of glue used at this point depends on the size of the chamber. A larger chamber will require more glue than a smaller chamber. Put the foil pan of glue into the bottom of the chamber next to the jar. You may need to handle the foil pan with tweezers or pliers here to avoid getting glue on your fingers as you lower the foil pan into the chamber. Carefully snap on the lid to the chamber, making certain that the glue doesn't spill from the foil pan, and set the chamber aside overnight. The glue will evaporate over time, and the glue vapor will react with the oils and compounds left behind on the jar by your fingers.

In the morning, carefully open the chamber and remove the jar by inserting a pencil, pen, or other long probe into the jar opening. Try not to smudge the fingerprint residue, which can now be observed on the jar. Are there prints on other parts of the jar that were not noted the previous day? There were on ours, and we tried to be careful. If you have a steady hand, some black paper, and some clear packing tape, you can lift the print off the jar and onto the tape. Carefully place a small piece of tape over your prints, taking care not to smear them, and then remove the tape with the prints. Because the developed prints are light gray, attaching the tape to the black card makes them more visible. Prints can be lifted off many surfaces, some of them pretty unlikely. For instance, with care, prints can be lifted from the *inside* of surgical gloves.

Put on a surgical glove and grasp a doorknob or other item firmly. Peel off the glove so it is inside out and place it into the developing

chamber. Spread it out a little so the vapor can reach all areas. Develop the prints as before. We managed to develop one print on the inside of our glove that we could lift off onto tape.

Blood-splatter evidence is also important in reconstructing crime scenes, and this additional demonstration shows how the presence of blood might be detected. Hemoglobin in the blood of mammals acts as a catalyst for the decomposition of hydrogen peroxide. A piece of raw meat will have enough blood for this demonstration, or the next time you purchase a piece of beef you could save the absorbent tissue under it and use that as your source of blood. You will need two small clear plastic cups and some red food coloring as a control. Put a small amount of red food coloring into one cup along with some water and then mix. Take the raw meat or the tissue from under the beef and squeeze a little of the blood into the other cup. Now pour about a teaspoon (5 milliliters) of hydrogen peroxide into each cup. The food coloring will slowly oxidize from the peroxide and the color will gradually fade. But the blood will cause rapid and vigorous hydrogen peroxide decomposition. The difference in the reactions clearly distinguishes the blood from food coloring.



CHAPTER 4

Chemist as Analyst

I found Sherlock Holmes alone, however, half asleep, with his long, thin form curled up in the recesses of his armchair. A formidable array of bottles and test-tubes, with the pungent . . . smell of hydrochloric acid, told me that he had spent his day in the chemical work which was so dear to him.

"Well, have you solved it?" I asked as I entered.

"Yes. It was the bisulphate of baryta."

"No, no, the mystery!" I cried.

—Arthur Conan Doyle, *Case of Identity*, ca. 1890

It is easy for sugar to be sweet and for nitre to be salt.

—Ralph Waldo Emerson, *Representative Men*, ca. 1850

Chemist as analyst? Certainly. But we don't use the couch to analyze a chemist; we use chemistry to analyze the couch. We have saved our discussion of analytical chemistry for near the end because in many ways it brings out the best in chemists. In analytical chemistry, all

the tools of chemistry and all the talents of chemists are brought to bear on two questions: what is it, and how much of it do we have? At some point, all chemists are analytical chemists and all chemistry requires analysis. There are several specialized areas of concern for analytical chemists such as the quality-control experts that ensure the quality of our food, the reliability of our medicines, and that every new car that rolls off the assembly line will have the same luster. But analytical chemistry is so pervasive that many of us routinely act as analytical chemists when we use tap-water-testing kits, pool-testing kits, radon-testing kits, fish-tank-testing kits, soil-test kits, lead-paint-testing kits, and even pregnancy-testing kits, sugar-testing kits, and the infamous Breathalyzer. The job of the analytical chemist is to find—or invent—the tool or tools necessary to determine the quantity of a given material or the nature of unknown materials.

Analytical chemistry is investigative work. Like a detective solving a mystery, an analytical chemist must proceed very carefully and painstakingly to find the correct answers. Just as the first officer at a crime must secure the scene and prevent evidence from being corrupted, analytical chemists must ensure that all the equipment and glassware to be used is scrupulously clean and free of contamination. Like a police investigator carefully collecting the minutest of evidence, analytical chemists sometimes deal with microgram (a millionth), nanogram (a billionth), and picogram (trillionth) quantities to get their answers. To get an accurate weight, the analytical chemist may even need to take into account the buoyancy of air.

Just as police officers need to maintain their weapons and routinely put in time on a shooting range, analytical chemists must always ensure that their instruments are calibrated and functioning properly. In police work, even if the butler confesses, without the proper police procedure, the most damning evidence can be thrown out. In the same manner, analytical chemists must be able to defend their results by reporting parameters such as *confidence limits*, *instrument noise levels*, and *significant figures*.

Analytical chemists must always be thorough. One thread from a carpet will not serve to locate a suspect at a crime scene, but a thread from a carpet, plus a hair from the dog, plus a smear of fresh paint may convince a jury. Many times an analytical chemist, too, must supply a body of evidence: corroborating results using alternate methods and many rep-

etitions of the same measurements to show, statistically, that the result is reasonable.

Like a scientific sleuth, an analytical chemist must sometimes reconstruct an event. When there is an explosion, there may be many causes, not all of which are malicious. But if traces of chemicals are found that have no other use but to make explosives, then that is good evidence the explosion was planned. When drug use is suspected, blood is examined, but evidence of heroin in the blood is not based on finding traces of heroin. It is based on finding heroin's metabolism product, morphine. Even the presence of morphine does not always indicate heroin consumption. Poppy seeds used for baking have been found to contain traces of opium and can produce traces of morphine in the urine. Prescription drugs can be metabolized by the body into what are, in essence, controlled substances, so other evidence must confirm or refute the presence of illicit drugs. In fact, the parallels between a professional analytical chemist and a criminal investigator are so numerous that we are going to use a hypothetical investigation by a forensic analytical chemist to illustrate how this important specialist proceeds.

It is the task of the forensic chemist to apply analytical chemistry to questions of interest to the legal system. The forensic chemist usually works at a government laboratory and may have the responsibility of going to the scene in question, collecting evidence, testing the evidence, and testifying in court. To show how all of this might work, let's begin with a hypothetical crime scene scenario and follow the progress of the forensic chemist as she proceeds.

Let's say that the police are called one night to an apartment building because of loud shouts coming from an apartment followed by the slamming of doors. When the police arrive they find the body of a woman lying in a pool of vomit. The medical examiner states from his preliminary exam that it looks as though the woman died an accidental death from anaphylactic shock, though he must, of course, perform an autopsy to be sure.

The cause of many deaths every year, anaphylactic shock is an allergic reaction so severe that it can cause the throat to constrict to the point of asphyxiation. The substance causing the allergic reaction, the *allergen*, could be nuts, eggs, bee venom, or any of a number of common substances. People prone to anaphylactic shock have usually suffered an

initial, milder reaction to the same allergen, and then their sensitivity increases dramatically with each exposure. People aware that they are prone to such extreme reactions carry an *epipen*, a small penlike device for injecting a dose of adrenalin, which will counteract the swelling and could save a life. According to the medical examiner in our story, the woman found in the apartment has every sign of having suffered this unfortunate but natural death. However, there are the reports of the loud shouts and the slamming door, so a forensic team is called in.

A forensic chemist routinely surveys and records all possible evidence at the scene. In this case, the chemist examines the contents of the cupboard and medicine cabinet and takes swabs of surfaces to see if she can determine the source of the allergen. She swabs the victim's hands and face to collect any chemical residue. She takes a sample of the victim's blood and stomach contents, which are available in the pool of vomit. She notes that the food in the cupboards has been carefully chosen to be free of peanut oil or peanut products, so she suspects that the woman had an allergy to peanuts, a common culprit in anaphylactic shock. She carefully samples all the food in the refrigerator and all containers on the shelves. She examines the pockets and purse of the victim but does not find anything worthy of note. She opens drawers in the kitchen and bedroom with the same result. She looks in the medicine cabinet and sees only common over-the-counter pharmaceuticals such as aspirin, antacid, and bandages. As she packs up and gets ready to leave, she stops for a minute and tells the officer in charge that additional investigative work needs to be done. Based on just what she has seen so far, she believes it was murder. Do you?

While the police officers act on her suggestion, our forensic chemist goes back to her lab to confirm some of her suspicions. To begin with, if the cause of death was a severe reaction to peanuts, then there should have been peanut oil or peanut residue somewhere on the victim's person. The chemist takes her swabs and her samples and begins her analysis.

The first problem confronting our forensic chemist may be separation. Police will separate witnesses, taking them into individual rooms to hear their accounts to avoid interference from other principals. Likewise, an analytical chemist will strive to separate the components of an unknown mixture so that the separate materials can be analyzed without

interference from other species. If the components are in separate phases, then a straightforward technique such as filtration can be used. For instance, our forensic chemist filters her sample of stomach contents then cools the filtrate to see if more materials will separate out.

If the component of interest is organic, it can be separated from its inorganic companions by a simple extraction such as was used to extract acetylsalicylic acid from aspirin in the organic chemistry demonstration. But the result of an extraction of stomach contents and blood will be a mixture of organic materials. If the attempt is to separate two organic materials, then a method such as *chromatography* might do the trick. Chromatography is a separation technique in which a solvent washes over a mixture and carries the various solutes different distances. An analogy might be found in panning for gold: the water continually running over the sand washes away the less dense particles and leaves behind the gold.

The technique of chromatography can be demonstrated in an uncomplicated fashion using the acetone found in fingernail-polish remover and some tree leaves. Crush and tear apart two or three green, fresh tree leaves and put them in the bottom of a glass drinking glass. After putting on your safety goggles, add about three inches of acetone (fingernail-polish remover), which should just cover the pile of leaves. Let this leaf mixture rest for several minutes so that the acetone can extract compounds from the leaf.

Cut two strips of paper towel long enough to reach from the top to the bottom of the glass. Wrap one end of the paper-towel strips around a pencil and secure them with a piece of adhesive tape. The paper-towel strips should now be just a bit shorter than the height of the glass, just long enough to touch the liquid.

Lay the pencil across the top of the glass and dangle the paper towel strips into the acetone-leaf mixture. Over a period of several hours, you should see at least two distinct bands of color on the paper towel as the acetone moves up the towel by capillary action. The acetone is carrying the leaf color pigment with it, but how easily the pigment travels with the solvent depends on the type of pigment, so when there is more than one pigment present, they separate into bands. Take a moment and look at the colors of the bands. One band should be green, but the other band or bands may be yellow, orange, or red. In the fall, we say that leaves "turn color," but, in fact,

the color is always there. It is actually the chlorophyll that is missing in the fall, and with the chlorophyll gone the other colors come through.

The acetone/towel/leaf system is an example of *solution chromatography*, but there are other chromatographies that work on the same principle: different materials can separate when they travel with their solvent along an absorbent surface. In gas chromatography, the solvent is a gas, and the gas blows over a column of solid particles. The solutes picked up by the gas will separate into bands as the material dissolves, is reabsorbed, and dissolves again in the gas. Ion chromatography, which uses water as a solvent, can be used to sort inorganic salts. High-performance liquid chromatography (HPLC) uses high pressure to force liquid samples through a densely packed column and achieve an even greater degree of separation.

Once our forensic chemist has separated all the organic material from her swabs, her next step might be concentration. The problem of concentration has to be addressed if the *analyte*, the substance being tested for, is present in only small amounts. Although analytical methods are improving all the time and the sensitivities of instruments are constantly increasing, there is still always some lower limit below which the analyte cannot be detected by a particular instrument. For instance, it may be difficult to test for small quantities of a toxin in the blood. Our bodies naturally concentrate toxins in the liver, and the analyst may take advantage of this fact if the liver is available, but if it is not, concentration may be achieved by evaporation, precipitation, or centrifuging—a process wherein a test tube sample is spun at a high rate of speed until the heaviest components settle to the bottom.

A different approach is taken with small samples of DNA. With a technique termed the *polymerase chain reaction*, or PCR, the DNA is not concentrated; instead, DNA is multiplied. The polymerase chain reaction uses the body's own chemical machinery, harvested from cells and brought to a test tube, to make copies of DNA until the concentrations are high enough to analyze.

Because the analyte she is after, peanut residue, is organic, the analytical method of choice for our forensic chemist will probably be GCMS, which stands for gas chromatography with mass spectroscopy. In this technique, the material is separated into its components using chromatog-

raphy, as outlined above. As the carrier gas, analogous to the acetone in the leaf pigment demonstration, flows over the sample, the components of the mixture are separated into bands that progress down a tube with absorbent packing called a *column*. The challenge is to analyze them on the other end of the column as quickly as they exit the column. The analysis can be accomplished by a number of methods, but one of the most popular is mass spectroscopy.

Spectroscopy is the general name for any technique that has a *spectrum* as its final result. A spectrum is a graph of two variables: the quality being tracked and its quantity. For instance, people in the United States display a wide spectrum of height, ranging from very short to very tall. If we were to make a plot of the number of people versus relative height, we might have a spectrum such as shown in figure 2.4.1.

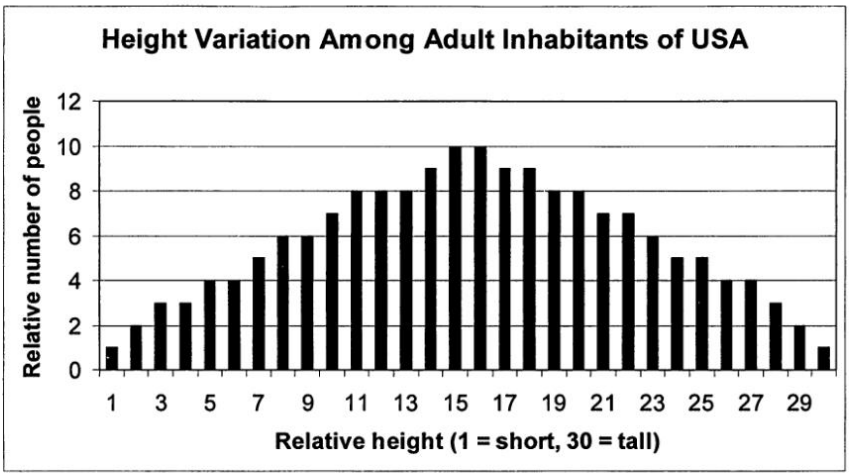


Figure 2.4.1. A hypothetical spectrum of height for people in the United States.

In mass spectroscopy, the fragments of molecules are sorted by mass, as shown in figure 2.4.2.

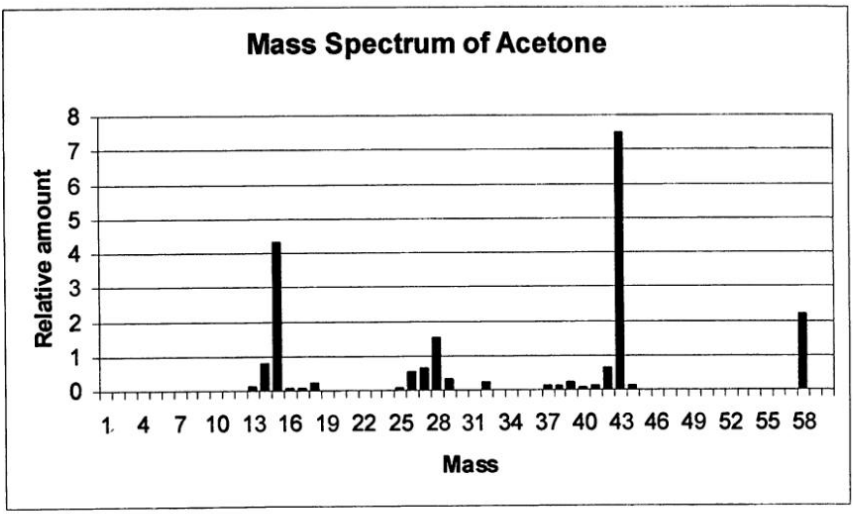


Figure 2.4.2. A mass spectrum of acetone. Molecules of acetone are broken up by a stream of electrons. The amount and relative mass of each fragment is measured. From this information and by comparing the fragment pattern with known patterns, the identity of the molecule can be established.

Mass is a pretty good identifying property. If you had one round object that weighed ten pounds (5 kilograms) and another that weighed one ounce (28 grams), you would quickly be able to sort out the shot put from the tennis ball. But the situation for mass spectroscopy is not so straightforward. In order to separate the molecules according to mass, they have to be turned into ions first, and the method for turning molecules into ions can be shattering. The molecules are hit by a stream of electrons as soon as they emerge from the chromatography column. Here again we see the power of electrons. We stated earlier that electrons are to molecules as fleas are to an elephant, but imagine splitting up our elephant with a powerful stream of fleas! Electrons may be small, but they have the power to cause chemistry.

The molecular fragments are generally missing electrons, so they have a net charge. Just as we saw with the electromagnet that we assembled from wire, a nail, and a battery, the electric field of the moving charge interacts with a magnetic field. The fragments are made to travel in a curved path by a magnetic field, with the radius of the curve being

determined by the mass and the charge on the fragment. Thus the fragments are sorted by mass.

To interpret this spectrum, as with all of analytical chemistry, a little clever detective work has to be involved. The analytical chemist will look for the most massive fragment, or the *parent peak*, because this is the one that is the closest to the original mass, perhaps missing only one or two hydrogen atoms. The parent peak is not necessarily the most abundant but will have the most mass. The *cracking pattern*, or the manner in which the molecule breaks up under a stream of electrons, will depend on the relative frailty of the individual bonds. Because of this, the chemist considers the fragmenting pattern because the same type of molecule will tend to shatter in the same manner under similar conditions. Libraries of shattering patterns are maintained on computer and can be compared with the unknown. In this case, the parent peak, the one with the highest value for mass, is the peak around mass fifty-eight. Acetone has the formula C_2H_6CO. By consulting the appendix, we can see that an acetone molecule should have a mass of about fifty-eight: two carbon atoms at 12.01 amu plus six hydrogen atoms at 1.00 amu plus another carbon atom at 12.01 amu plus an atom of oxygen at 16.00 amu. So we have pretty good evidence that our compound is acetone. But we need corroborating evidence to be sure. A compound with the formula C_3H_8N would have a mass of fifty-eight, too.

At the end of this test, the chemist hopes that the run was a good one and that the interpretation was accurate—or that there is enough sample for another try—because this technique is a *destructive technique*: the sample is now gone and cannot be reconstructed. Fortunately, there are other spectroscopic methods that are not as destructive. One of these is light spectroscopy.

As we saw when we exposed bleach to a black light, different types of light interact with matter differently, and the type of light a material interacts with can be characteristic of the material. This light-matter interaction is exploited in light spectroscopy. A sample of the material is exposed to a light beam that has been separated into components the way a prism will separate light into colors. A certain band of light is allowed to impinge on the sample and then the amount of light that makes it through the sample is detected on the other side and recorded. A new frequency of light is allowed to shine on the sample, and then the amount of

this light that makes it through is again recorded, and so on. Of course, if the process were as stepwise and tedious as we have outlined, then light spectroscopy would be a very laborious technique, which, in fact, it was at one time. But many improvements later, spectroscopy is now a very fast and accurate technique.

The types of light spectroscopy commonly employed include ultraviolet spectroscopy, infrared spectroscopy, and microwave spectroscopy, though the last is less common in the forensic lab. Ultraviolet spectroscopy is often used to analyze inorganic compounds, while infrared spectroscopy is often used to analyze organic compounds. In fact, some of the terminology used for infrared spectroscopy again reminds us of our forensic chemist: the region where the absorption spectrum shows the features that are uniquely characteristic of the compound being analyzed is called the "fingerprint" region, a concept our forensic chemist should be comfortable with!

However, light spectroscopy, like mass spectroscopy, does not print out the name of the compound on a slip of paper and hand it to you. The way a molecule interacts with light is going to depend on the nature and arrangement of all of its pieces, so the response to light is varied and complicated. The analytical chemist can again resort to a library, but if the separation was not exactly clean and there are contaminants with their own, interfering, peaks, then more detective work remains to be done.

Inorganic compounds are generally less delicate than organic compounds (salts, for instance, do not burn as ethanol will) and are generally easier to analyze by nondestructive techniques. For instance, a classic analysis for an inorganic ion is to see what will make it precipitate. Carbonate ions from baking soda form a precipitate with copper ions, while the sulfate and nitrate ions in solution do not. Atomic Absorption spectroscopy (referred to around the lab as AA) is perhaps a more sensitive inorganic-analysis technique in skilled hands, but it is a destructive technique. In AA, a solution containing the analyte is *atomized*; that is, it is made into a fine mist, just as in an atomizer on a perfume bottle or a bottle of window cleaner. Once atomized, the solution to be analyzed is sprayed into an acetylene flame that has been carefully adjusted so that it has the proper temperature.

The sample needs to be introduced into the right place in the flame.

Flames themselves have a fascinating chemistry in that some regions of a flame are hotter than others and some regions promote oxidation reactions while others promote reduction. And there is, of course, the most interesting aspect of flame chemistry: flames produce heat and light. The color of the light will depend on the material that is in the flame, just as the color of fireworks depends on the material in the ordnance. In one configuration, the AA instrument takes advantage of this fact to analyze the material that has been atomized into the flame; a light detector near the flame records the different colors of the flame and their intensity, which is proportional to the amount of each material in the flame.

In another configuration, an AA instrument uses other commonly exploited physical phenomena: the fact that materials tend to absorb the same frequency of light as they emit. Rose-colored glasses make the world rosier because the materials from which the lens are made absorb all the colors except rose, and materials can be identified by the colors they absorb. In AA, light from a lamp designed to emit a very narrow range of color is directed onto the sample in the flame. The lamp is designed so that the material for analysis is also the material producing the light in the lamp. In other words, if the analyst wants to analyze for sodium, then a sodium-containing lamp is used. The lamp then emits a light that is characteristic of sodium, and if there is any sodium in the sample, it will absorb this light and the detector will see that some of the light is missing.

The methods employed by our intrepid forensic chemist are infrared and mass spectroscopy. At the end of her efforts, she has found that indeed there are traces of peanut oil on the victim's mouth, so the questions become this: Where did it come from? Where did it go? Our heroine analyzes the samples of foods and medicines she took from the apartment but finds nothing. She notes that the victim must have read labels very carefully so as to avoid even seemingly innocent products such as some ice creams, baked goods, salad dressings, and soups that could contain peanut oil. The stomach and blood showed no other toxins, though there is evidence of a severe allergic reaction. She is pondering this thought and carefully cataloging her results when the phone rings. The officers are calling to tell her she was right. They found what she told them to look for: an unused epipen—a syringe full of lifesaving medicine—discarded in a dumpster behind the apartment building along with a pair of surgical gloves.

How did our chemist know to tell the officers to seach for an epipen outside the apartment? When she looked in the cupboard, the medicine cabinet, and on the victim she didn't find an epipen. She knew that the victim had been very careful about picking her foods to be allergen free, so the victim was aware of her allergy. Anyone who was aware she had such a dangerous allergy would most certainly have an epipen where she could get to it—unless she were prevented from getting to it. Our forensic chemist now knows that on the surface of the gloves she will find peanut oil . . . and a nice set of fingerprints inside!

So the job of the analytical chemist may be complex, difficult, demanding, and exacting—but it still pays better than crime. And though certain people may have sensitivities to some plants, and though some plants may be poisonous to all people, the interactions between plants and animals are not always so adversarial. Plants can sometimes be very beneficial. In fact, when it comes to plants and animals, they have a future together—the future of chemistry.

Demonstration for the Future: Medicine Cabinet Chemistry

For our last demonstration, go to your medicine cabinet and take a synthetic mimic of the extract of Salix willow bark, modified to buffer the acidic effect. In other words, take an aspirin.

What does aspirin have to do with the future of chemistry? Read on.

CHAPTER 5

Harry, Hogwarts, and Folk Pharmacopoeias—Mysteries in the Past and Magic in the Future

"You are here to learn the subtle science and exact art of potion-making. . . . As there is little foolish wand-waving here, many of you will hardly believe this is magic. . . . (T)he beauty of the softly simmering cauldron with its shimmering fumes, the delicate power of liquids that creep through human veins, bewitching the minds, ensnaring the senses . . . I can teach you how to bottle fame, brew glory, even stopper death— . . ."

"Potter!" said Snape suddenly. "What would I get if I added powdered root of asphodel to an infusion of wormwood?"

—J. K. Rowling, *Harry Potter and the Sorcerer's Stone*, ca. 1997

Do you believe then that the sciences would ever have arisen and become great if there had not beforehand been magicians, alchemists, astrologers, and wizards who thirsted and hungered after . . . forbidden powers?

—Friedrich Wilhelm Nietzsche, ca. 1890

There are tens of millions of known chemical compounds and more being assembled every day. The number of future combinations of elements is virtually infinite, and the periodic table continues to expand. We've become almost too good at our craft. Like kids in a candy store, the question is not whether there is more chemistry to be discovered but where we should focus first. With all the problems facing human survival, we can't afford to sit like a million monkeys working in a million labs and hope that solutions will arise. Take, for example, the problem of drug discovery. How do we decide, out of the tens of millions of compounds out there, which medicines to test as cures for diseases? In the past, there have been some fortunate accidents, but we can't rely on luck.

In the process of rational drug design, there are a couple of choices. First, we can try variations on compounds that have worked well in the past. This approach is reasonable, respectable, and often successful. When a particular type of bacterium evolves a strain that is immune to our medicines, we can take a medicine that worked previously and tack on a new group of atoms or change a bond to see if we can make it effective again. This approach, called the *combinatorial approach*, has yielded many useful compounds. But the approach has also been likened to a tree with many roots: it can sample a lot of soil, but only soil in the vicinity of the tree. If there is a new drug with a completely new structure, then the combinatorial approach may not find it.

Another approach that has been successful in the past, whether or not by design, is to let the millions of years of human-plant interaction do the work of the millions of tests. Aspirin was "discovered" when someone decided to see if there was anything to the old folk remedy of chewing on willow bark to relieve pain and of drinking willow bark tea to reduce fever.[1] Quinine was "discovered" when a desperate monk gave a dying noble woman an extract of bark recommended to him by the indigenous

people of Peru.[2] There is currently serious and intense research being directed toward the study of folk medicines, especially medicines derived from plants.

J. K. Rowling's popular Harry Potter series no doubt owes its success to her enchanting characters, intriguing stories, clever dialogue, and engaging setting.[3] But there may be another factor, too. The references to magic and magical herbs, stones, and fungi resonate with a cultural memory: we find it easy to believe in magic because our forbearers experienced what appeared to be magic. Many of the "magical" herbs mentioned in the Harry Potter series, such as wormwood, named for its power for expunging intestinal worms, have real efficacy.[4] Imagine suffering with intestinal worms and finding a preparation of wormwood could rid you of the parasites. Imagine being plagued with goiter and then finding relief in iodine-containing charred seaweed. Imagine suffering from scurvy and finding respite in the juice of limes. These were all real cures that were used in the past and, to the sufferer, had to seem magical.

Take another look in your medicine cabinet to see other products that had their origin in plant remedies: beta blockers, birth control, sedatives, laxatives, antiseptics, soap. . . . So the next time you take a much-needed medicine, go out and hug a tree.

The study of the chemistry of plants is termed *phytochemistry*, and the fact that a number of effective drugs have been found in natural plant products (some say as many as a third of the current manufactured drugs) begs the question: Why? Why should it be that plants produce materials that interact with humans? Why should certain plant products make us healthy, some make us happy, some make us sleepy, and some make us dead?

Certainly it could be coincidence. We evolved on the same planet—humans and plants—so our chemistries should be similar. Medicines of plant origin are more likely to be compatible with our systems because we share the same chemical space. But there is also a well-known plant-animal mutualism: what's good for the gooseberry is good for the goose. Plants consume carbon dioxide and produce oxygen; animals consume oxygen and produce carbon dioxide. Bees pollinate flowers; flowers feed bees. The most ferocious, carnivorous cat will occasionally munch grass for the fiber it needs. Ovaries of some plants grow into fruit so animals

will eat the seed and carry it away—thus avoiding competition with the parent plant for resources.

Some chemicals that plants produce are useful to us because plants protect themselves from the same things we do—bacteria, viruses, and fungi. But herbs can do more than act as antiseptics. As Snape scolds Potter, Harry needs to know his herbs: asphodel, an herb, is used to "make a sleeping potion so powerful it is known as the Draught of Living Death."[5] And it is true.[6] Harry is cautioned that monkshood and wolfsbane are effective poisons.[7] And they are.[8] Snape instructs Harry to copy down the name "aconite"—and history tells us that aconite and belladonna were once used together to produce the hallucination of flying.[9]

Why would plants produce chemicals with these peculiar properties? Do plants have headaches? Do they have trouble sleeping? Why have they evolved chemicals with analgesic, sedative, or psychoactive properties?

Again, it could be just an accident. Plants evolved chemicals to kill predators, but a toxin that would kill an insect might just tantalize or sedate a human. The difference between a sedative and a poison is often a matter of dosage. The ingestion of toxins below lethal levels for the sake of euphoric effects has become known as *intoxication*, as a nod to its toxic origins.

On the other hand, plants may have developed some sedatives and analgesics because there are advantages to the plant. If a plant is being eaten for food, there may be no incentive for the predator to restrain itself from consuming the entire growth, but if the plant were being eaten for the sensory benefit, the animal might eat only enough to bring on the effect and then stop, stupefied. What would be the benefit to the plant? Maybe fertilization. An animal that is sedated by a plant may be more likely to defecate in the plant's vicinity instead of wandering away with the plant's sacrificed nutrients. Or the advantage for the plant might be pruning. Herbaceous plants can propagate by leaf cuttings and seed. Pinching off the tops of these types of plants allows the plant to concentrate it efforts on the remaining growth. If there were a sedative in the plant, then the pruning would be self-limiting. The same chemical that acts as a sedative for animals might be a poison for bugs, which would limit the insect pruning, too.

From whatever evolutionary pressures, however, plants have

evolved compounds that have an effect on us. Coffee, tea, tobacco, licorice, codeine, cocaine, and opium—all of these were originally herbal cures. Plants are sources of effective antiseptics, analgesics, antibiotics, vermifuges, sedatives, stimulants, abortifacients, poisons, laxatives, diuretics, antidiarrheals, and, yes, recreational drugs. As Harry Potter's potions master says, bottled fame, brewed glory, and even stoppered death.

Pharmacognosy is the study of natural product drug discovery and development, and pharmacognosy includes in its scope the investigation of ethno-botanical claims—in other words, folk medicine. These researchers look at practices of modern cultures, such as the inhabitants of the rainforest, and they also look at historical practioners, such as the monks and mendicants of the European Middle Ages—and the old wives, the wizards, and the witches.

There is a new realization that many of the people who were persecuted as witches and sorcerers in the European Middle Ages were, in fact, innocent midwives and healers, and some of their so-called magical remedies had certifiable efficacy. They recommended analgesic clove oil for toothache, vitamin-containing herbal teas for pregnant women and listless children, and calcined egg shell for upset stomach, a source of calcium carbonate, a main ingredient in antacids prescribed today.

But not all of the medical practices of the ancients were useful. They did not follow standard, sound scientific procedures such as keeping records of successful trials and failure, and they did not carefully sort out cause and effect. Their medical philosophies were known to include treating the weapon that caused the wound instead of the wound and using medicines with effects that resembled the disease that they were meant to cure—which could be the origin of taking a "hair of the dog that bit you" as a cure. The Arabs brought a lot of practical medical knowledge, as well as the knowledge of the ancient Greeks and Romans, to the Western Europeans in the early Middle Ages. Consequently, European healers started imitating Arabic speech in hopes of improving their own efforts, hence "magic" words like alakazam and abracadabra. J. K. Rowling captures the notion well when she has her apprentice sorcerers chant their spells in erudite Latin-sounding magical phases.[10]

But sometimes the ancient healers *did* know what they were doing—but didn't want anyone else to know. The European Middle Ages predated

patent medicine by many years, so successful healers had to guard their secrets if they wanted to keep their jobs. Many of the medicines that they used were fairly recognizable, such as aromatic herbs, so they would disguise the actual active ingredient by serving it in a foul-tasting and foul-smelling concoction. They constructed smoke screens of elaborate rituals so that the administration of the medicine was only one of many more impressive steps. It is no accident the novice Harry Potter "had been really looking forward to" his first magic wand.[11] Other practitioners of magic were known to wave a stick around so that the patient would be watching the stick and not see what they were slipping into the stew. The hocus-pocus might also have acted as a sort of primitive malpractice insurance. If the cure was ineffective, the witch or wizard could always claim that their instructions hadn't been followed. Or that a certain herb should have been picked at midnight during a full moon.

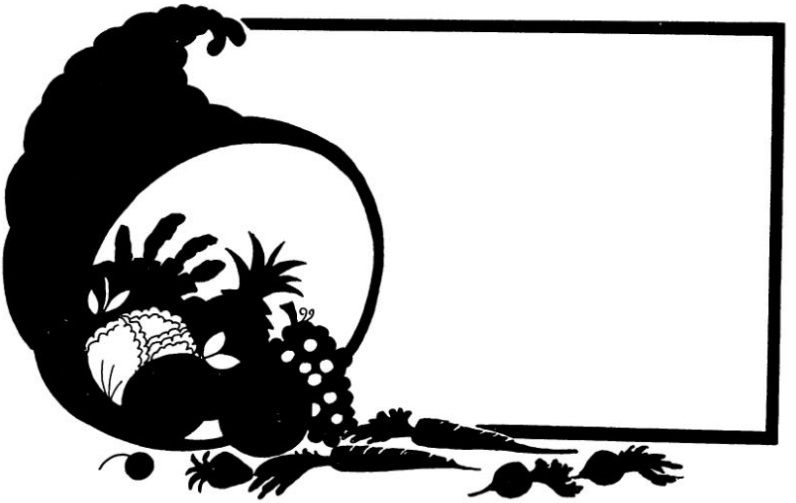
If there is so much nonsense, how do we separate the useful herbs from the hooey? Or can we? Is there any real point in examining ethnic medical traditions? Yes. Studying how the herbs are used now—and how they were used in the past—tells us more than just grinding up plants and running them through a mass spectrometer. It is important to know how the herb is prepared when evaluating its efficacy. The proper preparation may be essential to release the active ingredient. It is also necessary to know how the herb was presented. Many times drugs are synergistic, only working in combination with other drugs, an effect that could not be discerned by testing them separately. The possibility of interactions is also the reason it is imperative to check with a doctor when combining any drugs, even herbal preparations. Sometimes very adverse interactions can occur. The wonderful relief from intestinal parasites provided by wormwood could easily turn into disaster or even death: wormwood, along with other herbs, is used to prepare absinthe, a notoriously addictive liqueur known to cause blindness, nerve damage, and mental instability in habitual users.[12] Investigations into the traditional manner in which an herb was used can provide information that might otherwise be overlooked.

As well as investigating folk pharmacopeias, pharmacognosy looks for new drugs from natural sources, too, and there is the promise of many interesting chemicals to be found. There are trees that live thousands of

years. What do they know that we don't? And when it comes to growing limbs, trees have it all over us. Under attack by insect pests, plants have been found to send out chemical signals to attract other insects that feed on the harmful bugs. Recently, it was shown that some plants under attack can even send out warning signals to other plants to arm themselves against impending danger.[13] There may be a wealth of other such chemical compounds in plants that are only present part of the time, such as when the plant is under duress or in certain atmospheric conditions. Such as midnight under a full moon?

There are no doubt other useful materials elsewhere in nature, too: in the oceans, polar icecaps, volcanoes, and maybe even other planets and moons. Before we can take advantage of these resources, there are a host of problems to be solved—but the possibility of a chemical cornucopia if we solve them. Where do we focus our efforts? The answer may be found in the words of the venerable scientist and science writer, Isaac Asimov. He said, "The most exciting phrase to hear in science . . . is not 'Eureka!' but 'That's funny . . .'"

We will find our direction when a discovery is made. When someone picks up a pebble and notes a new pattern. Or finds a new insect or an odd new ore. It will take someone with curiosity and a desire to know. Someone who enjoys history, music, and art—and perhaps peculiar chemistry books.



EPILOGUE

I celebrate myself, and sing myself,
And what I assume you shall assume,
For every atom belonging to me as good belongs to you.

—Walt Whitman, *Leaves of Grass*, 1855

If all our readers, provoked by this too-brief outline of the science of chemistry, should arise as one and storm out in quest of further edification—nothing could please us more. There is so much more to be told.

But we've been on an excellent journey. We have examined the structure and behavior of minute particles of matter, and we have seen how their microscopic properties multiply to form the world around us. We surveyed classical chemistry and demonstrated these lively reactions with ordinary materials. We have seen how chemistry relates to everyday experience, and we've developed an intuitive understanding of the essentials of chemistry by example and analogy. We've seen how principles and theory derived in the past have showered us with a wealth of technology and materials—and we have seen the challenges that lie ahead. In this new millennium, there will be new medicines and innovative

approaches to healing. There will be bridges that will bend, not break, when the earth quakes. There will be new sources of fuels as abundant as the sunlight and enough food to feed a hungry world. There will be a new understanding of all the sciences, and we will learn how to protect this planet and life in all its forms.

But where do we start? Who determines where to apply our resources? If we find a new life form in the ocean that produces a potent new drug, to whom does it belong? Who would be allowed to harvest it? Develop it? Ensure its preservation? People. All people. The chemistry of the future is going to depend on more than chemists. It's going to require international cooperative efforts that draw on the talents of philosophers and prospectors; ecologists and ethicists; economists and statisticians; lawyers and law enforcement; botanists and bacteriologists; herbalists and historians; authors and their audiences; laboratory, electrical, and computer technologists; and people ready to make educated, informed decisions.

There is so much work to be done, and so many reasons to do it.

The work is far from finished. And the joy never ends.

APPENDIX

Elements Listed by Name, Symbol, and Atomic Number

Elements Sorted by Name

Symbol	Name	Atomic number	Mass*
Ac	Actinium	89	(227)
Al	Aluminum	13	26.98
Am	Americium	95	(243)
Sb	Antimony	51	121.76
Ar	Argon	18	39.95
As	Arsenic	33	74.92
At	Astatine	85	(210)
Ba	Barium	56	137.33
Bk	Berkelium	97	(247)
Be	Beryllium	4	9.01
Bi	Bismuth	83	208.98
Bh	Bohrium	107	(264)
B	Boron	5	10.81
Br	Bromine	35	79.90
Cd	Cadmium	48	112.41
Ca	Calcium	20	40.08
Cf	Californium	98	(251)
C	Carbon	6	12.01

Ce	Cerium	58	140.12
Cs	Cesium	55	132.91
Cl	Chlorine	17	35.45
Cr	Chromium	24	52.00
Co	Cobalt	27	58.93
Cu	Copper	29	63.55
Cm	Curium	96	(247)
Db	Dubnium	105	(262)
Dy	Dysprosium	66	162.50
Es	Einsteinium	99	(252)
Er	Erbium	68	167.26
Eu	Europium	63	151.96
Fm	Fermium	100	(257)
F	Fluorine	9	19.00
Fr	Francium	87	(223)
Gd	Gadolinium	64	157.25
Ga	Gallium	31	69.72
Ge	Germanium	32	72.64
Au	Gold	79	196.97
Hf	Hafnium	72	178.49
Hs	Hassnium	108	(269)
He	Helium	2	4.00
Ho	Holmium	67	164.93
H	Hydrogen	1	1.01
In	Indium	49	114.82
I	Iodine	53	126.90
Ir	Iridium	77	192.22
Fe	Iron	26	55.85
Kr	Krypton	36	83.80
La	Lanthanum	57	138.91
Lr	Lawrencium	103	(262)
Pb	Lead	82	207.20
Li	Lithium	3	6.94
Lu	Lutetium	71	174.97
Mg	Magnesium	12	24.31
Mn	Manganese	25	54.94
Mt	Meitnerium	109	(268)
Md	Mendelevium	101	(258)
Hg	Mercury	80	200.59

Mo	Molybdenum	42	95.94
Nd	Neodymium	60	144.24
Ne	Neon	10	20.12
Np	Neptunium	93	237.05
Ni	Nickel	28	58.69
Nb	Niobium	41	92.91
N	Nitrogen	7	14.01
No	Nobelium	102	(259)
Os	Osmium	76	190.23
O	Oxygen	8	16.00
Pd	Palladium	46	106.42
P	Phosphorus	15	30.97
Pt	Platinum	78	195.08
Pu	Plutonium	94	(244)
Po	Polonium	84	(209)
K	Potassium	19	39.10
Pr	Praseodymium	59	140.91
Pm	Promethium	61	(145)
Pa	Protactinium	91	231.04
Ra	Radium	88	(226)
Rn	Radon	86	(222)
Re	Rhenium	75	186.21
Rh	Rhodium	45	102.91
Rb	Rubidium	37	85.47
Ru	Ruthenium	44	101.07
Rf	Rutherfordium	104	(261)
Sm	Samarium	62	150.36
Sc	Scandium	21	44.96
Sg	Seaborgium	106	(266)
Se	Selenium	34	78.96
Si	Silicon	14	28.09
Ag	Silver	47	107.87
Na	Sodium	11	22.99
Sr	Strontium	38	87.62
S	Sulfur	16	32.07
Ta	Tantalum	73	180.95
Tc	Technetium	43	(98)
Te	Tellurium	52	127.60
Tb	Terbium	65	158.93

Tl	Thallium	81	204.38
Th	Thorium	90	232.04
Tm	Thulium	69	168.93
Sn	Tin	50	118.71
Ti	Titanium	22	47.87
W	Tungsten	74	183.84
U	Uranium	92	238.03
V	Vanadium	23	50.94
Xe	Xenon	54	131.29
Yb	Ytterbium	70	173.04
Y	Yttrium	39	88.91
Zn	Zinc	30	65.39
Zr	Zirconium	40	91.22

*The masses can be interpreted as amu per atom (see chap. 2) or grams per mole (see chap. 9). The numbers in parentheses are approximate because these elements are artificially made. They do not have a natural abundance on which to base an average mass.

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Cd	Cadmium	48	112.41
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Cf	Californium	98	(251)
Cl	Chlorine	17	35.45
Cm	Curium	96	(247)
Co	Cobalt	27	58.93
Cr	Chromium	24	52.00
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Cu	Copper	29	63.55
Db	Dubnium	105	(262)
Dy	Dysprosium	66	162.50
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Hf	Hafnium	72	178.49
Hg	Mercury	80	200.59
Ho	Holmium	67	164.93
Hs	Hassnium	108	(269)
I	Iodine	53	126.90
In	Indium	49	114.82
Ir	Iridium	77	192.22
K	Potassium	19	39.10
Kr	Krypton	36	83.80
La	Lanthanum	57	138.91
Li	Lithium	3	6.94
Lr	Lawrencium	103	(262)
Lu	Lutetium	71	174.97
Md	Mendelevium	101	(258)
Mg	Magnesium	12	24.31
Mn	Manganese	25	54.94
Mo	Molybdenum	42	95.94
Mt	Meitnerium	109	(268)
N	Nitrogen	7	14.01
Na	Sodium	11	22.99
Nb	Niobium	41	92.91
Nd	Neodymium	60	144.24
Ne	Neon	10	20.12
Ni	Nickel	28	58.69
No	Nobelium	102	(259)
Np	Neptunium	93	237.05
O	Oxygen	8	16.00
Os	Osmium	76	190.23
P	Phosphorus	15	30.97
Pa	Protactinium	91	231.04
Pb	Lead	82	207.20
Pd	Palladium	46	106.42
Pm	Promethium	61	(145)
Po	Polonium	84	(209)
Pr	Praseodymium	59	140.91

Pt	Platinum	78	195.08
Pu	Plutonium	94	(244)
Ra	Radium	88	(226)
Rb	Rubidium	37	85.47
Re	Rhenium	75	186.21
Rf	Rutherfordium	104	(261)
Rh	Rhodium	45	102.91
Rn	Radon	86	(222)
Ru	Ruthenium	44	101.07
S	Sulfur	16	32.07
Sb	Antimony	51	121.76
Sc	Scandium	21	44.96
Se	Selenium	34	78.96
Sg	Seaborgium	106	(266)
Si	Silicon	14	28.09
Sm	Samarium	62	150.36
Sn	Tin	50	118.71
Sr	Strontium	38	87.62
Ta	Tantalum	73	180.95
Tb	Terbium	65	158.93
Tc	Technetium	43	(98)
Te	Tellurium	52	127.60
Th	Thorium	90	232.04
Ti	Titanium	22	47.87
Tl	Thallium	81	204.38
Tm	Thulium	69	168.93
U	Uranium	92	238.03
V	Vanadium	23	50.94
W	Tungsten	74	183.84
Xe	Xenon	54	131.29
Y	Yttrium	39	88.91
Yb	Ytterbium	70	173.04
Zn	Zinc	30	65.39
Zr	Zirconium	40	91.22

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Elements Sorted by Atomic Number

(the periodic table is also a list of elements by atomic number)

Symbol	Name	Atomic number	Mass*
H	Hydrogen	1	1.01
He	Helium	2	4.00
Li	Lithium	3	6.94
Be	Beryllium	4	9.01
B	Boron	5	10.81
C	Carbon	6	12.01
N	Nitrogen	7	14.01
O	Oxygen	8	16.00
F	Fluorine	9	19.00
Ne	Neon	10	20.12
Na	Sodium	11	22.99
Mg	Magnesium	12	24.31
Al	Aluminum	13	26.98
Si	Silicon	14	28.09
P	Phosphorus	15	30.97
S	Sulfur	16	32.07
Cl	Chlorine	17	35.45
Ar	Argon	18	39.95
K	Potassium	19	39.10
Ca	Calcium	20	40.08
Sc	Scandium	21	44.96
Ti	Titanium	22	47.87
V	Vanadium	23	50.94
Cr	Chromium	24	52.00
Mn	Manganese	25	54.94
Fe	Iron	26	55.85
Co	Cobalt	27	58.93
Ni	Nickel	28	58.69
Cu	Copper	29	63.55
Zn	Zinc	30	65.39
Ga	Gallium	31	69.72
Ge	Germanium	32	72.64
As	Arsenic	33	74.92
Se	Selenium	34	78.96
Br	Bromine	35	79.90

Kr	Krypton	36	83.80
Rb	Rubidium	37	85.47
Sr	Strontium	38	87.62
Y	Yttrium	39	88.91
Zr	Zirconium	40	91.22
Nb	Niobium	41	92.91
Mo	Molybdenum	42	95.94
Tc	Technetium	43	(98)
Ru	Ruthenium	44	101.07
Rh	Rhodium	45	102.91
Pd	Palladium	46	106.42
Ag	Silver	47	107.87
Cd	Cadmium	48	112.41
In	Indium	49	114.82
Sn	Tin	50	118.71
Sb	Antimony	51	121.76
Te	Tellurium	52	127.60
I	Iodine	53	126.90
Xe	Xenon	54	131.29
Cs	Cesium	55	132.91
Ba	Barium	56	137.33
La	Lanthanum	57	138.91
Ce	Cerium	58	140.12
Pr	Praseodymium	59	140.91
Nd	Neodymium	60	144.24
Pm	Promethium	61	(145)
Sm	Samarium	62	150.36
Eu	Europium	63	151.96
Gd	Gadolinium	64	157.25
Tb	Terbium	65	158.93
Dy	Dysprosium	66	162.50
Ho	Holmium	67	164.93
Er	Erbium	68	167.26
Tm	Thulium	69	168.93
Yb	Ytterbium	70	173.04
Lu	Lutetium	71	174.97
Hf	Hafnium	72	178.49
Ta	Tantalum	73	180.95
W	Tungsten	74	183.84

Re	Rhenium	75	186.21
Os	Osmium	76	190.23
Ir	Iridium	77	192.22
Pt	Platinum	78	195.08
Au	Gold	79	196.97
Hg	Mercury	80	200.59
Tl	Thallium	81	204.38
Pb	Lead	82	207.20
Bi	Bismuth	83	208.98
Po	Polonium	84	(209)
At	Astatine	85	(210)
Rn	Radon	86	(222)
Fr	Francium	87	(223)
Ra	Radium	88	(226)
Ac	Actinium	89	(227)
Th	Thorium	90	232.04
Pa	Protactinium	91	231.04
U	Uranium	92	238.03
Np	Neptunium	93	237.05
Pu	Plutonium	94	(244)
Am	Americium	95	(243)
Cm	Curium	96	(247)
Bk	Berkelium	97	(247)
Cf	Californium	98	(251)
Es	Einsteinium	99	(252)
Fm	Fermium	100	(257)
Md	Mendelevium	101	(258)
No	Nobelium	102	(259)
Lr	Lawrencium	103	(262)
Rf	Rutherfordium	104	(261)
Db	Dubnium	105	(262)
Sg	Seaborgium	106	(266)
Bh	Bohrium	107	(264)
Hs	Hassnium	108	(269)
Mt	Meitnerium	109	(268)

*The masses can be interpreted as amu per atom (see chap. 2) or grams per mole (see chap. 9). The numbers in parentheses are approximate because these elements are artificially made. They do not have a natural abundance on which to base an average mass.

ENDNOTES AND CREDITS

CREDITS

Original artwork by Linda Muse appears on pages 15, 17, 27, 29, 33, 69, 73, 83, 95, 114, 115, 117, 119, 123, 131, 141, 182, 187, 198, 212, 233, 241, 247, 271, 273, 282, 287, 311, and 315.

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