These acid- or alkaline-balanced products may be advertised as "pH balanced." But what does pH mean? We can get a clue from revisiting the pool test kit. The phenol red indicator is also labeled "pH indicator": pH is a measure of how acidic or basic a solution is. It is a measure of the acid quality of a solution.

Because there are many pairs of substances in which one substance ameliorates, or neutralizes, the effect of another, there are many substances that can be classified as acids and bases. However, we will focus on the most common group here: substances that produce the polyatomic ions of *hydronium* and *hydroxide*, the two principles of acid and base in water. *Poly* in *polyatomic* simply means more than one, as in *polytheist* or *polygamy*. Polyatomic ions are ions made up of more than one atom. The hydronium ion is created when a hydrogen ion from an acid combines with water. The resulting polyatomic ion has a positive charge: H_3O^+. The hydroxide ion forms when a base removes a hydrogen ion from water. The resulting polyatomic ion has a negative charge: OH^-. The pH of a solution is a measure of how many hydronium ions there are in a sample of the solution, acidic solutions having more hydronium ions and alkaline solutions having fewer. Note that if a hydroxide and a hydronium ion were to come together, the extra hydrogen on the hydronium ion could combine with the hydroxide ion; thus, the positive charge would cancel the negative charge, and the result would be two molecules of water. Acid and base neutralize each other.

$$H_3O^+ + OH^- \rightarrow H_2O + H_2O$$

Or, in a more compact notation,

$$H_3O^+ + OH^- \rightarrow 2\ H_2O$$

The pH scale ranges from 0 to 14, a pH of 7 being neutral. But pH is not a linear measure like a ruler or a thermometer; a pH scale is another logarithmic scale like the decibel scale. It's Godzilla versus Mighty Mouse situation such as we encountered when displaying the relative abundances of the elements. To picture both acidic and basic solutions on the same chart, we have to choose a nonlinear scale. On the pH scale, a solution registering 3 is ten times as alkaline as a solution registering 2; a

solution registering 4 is one hundred times as alkaline as a solution registering 2. More simply put: the greater the pH, the more basic and less acidic the solution.

But why is a pH indicator found in a swimming pool test kit? Why is it important to know how acidic or alkaline a swimming pool is? Let's plunge into that topic.

For Example: Swimming Pool pH

Swimming pool chemistry is fairly convoluted and we will be probing more as we go along. But before going off the deep end, we will consider pH here and how it affects swimming pool chemistry.

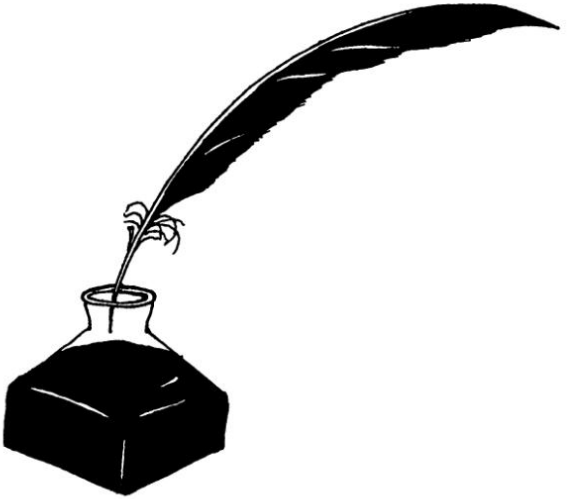
One reason pH control is important, of course, is that people don't want to swim in solutions as acidic as vinegar or as alkaline as ammonia. For another reason, pools would be big stagnant ponds without all the pumps and filters, excellent breeders of algae, bacteria, and mosquitoes. To counteract all the natural growth, chlorine is often added to the water in the form of sodium hypochlorite, the same substance that is the active ingredient of household bleach. Sodium hypochlorite is a weak base, as bicarbonate is a weak base. However, the solution to the natural-growth problem is not as straightforward as dumping in a little bleach. The chlorine levels must stay high enough to inhibit bacterial growth without irritating the eyes and noses of the swimmers. Chlorine levels must also remain fairly constant while being exposed to sunlight, variations in temperature, and metal, plastic, and ceramic surfaces.

The best antibacterial action is derived from the bleach when the pool water is acidic, but acidic water is not pleasant to swim in and can be corrosive to the metal fittings of plumbing, filters, and pumps. Similarly, a swimming pool solution that is too alkaline can also be corrosive. So a balance must be struck. Anyone who has ever owned a pool or has had experience with pool maintenance is aware that this can be a daily chore during times of peak pool usage. It would be an hourly chore were steps not taken to buffer the pool. In swimming pools, the buffering action is achieved by having sufficient quantities of both bleach and acid. In pool maintenance manuals, "sufficient quantities" is termed "total alkalinity" and is a quantity that must be measured and regulated along with the pH and chlorine content of the pool. The acid content of the pool is adjusted by adding swimming pool acid and the alkalinity is adjusted by adding the prescribed base. However, if too much base is added, another problem results: *scale*.

Scale is a rock-hard crust that can form in pipes and pots that are used with hard water. Before the general availability of household water softeners, scale was a much more common experience. Insoluble scale forms from calcium ions when carbonate ion is present. This fact highlights, once more, the versatility of carbonates. We have seen carbon dioxide form carbonates and hence carbonic acid in water; we have used sodium bicarbonate (baking soda) as a base; and finally we have pointed out that carbonates can make fairly insoluble solids. These many talents of the carbonate ion make baking soda good for more than cooking. Baking soda makes an excellent deodorizer because it can react with both acidic and basic smelly compounds and can form nonvolatile, and hence nonsmelly, compounds with many more. A lot of chemistry in a little box!

Some calcium and other minerals are found naturally in any water that has percolated through the ground. So if the swimming pool is allowed to become too alkaline, it will grow cloudy, at best, with suspended particles of insoluble salts or encrusted with growths of scale at worst. This appearance of a solid in a liquid solution is called *precipitation*, just as rain is called *precipitation*, because of the propensity of the solids to come out of the solution just as rain comes out of the sky.

In the next chapter, we look at some other solid-forming solutions, as well as some whys, wherefores, and useful applications of these crusty precipitation reactions.



Demonstration 5: Blue Blob, Black Ink

Dr. Archie watched her contemplatively, as if she were a beaker full of chemicals working.
—Willa Cather, *The Song of the Lark*, ca. 1915

Blue Blob

Adjust your safety glasses comfortably over your eyes, and then add a tablespoon (15 milliliters) of baking soda to a half cup of water (120 milliliters) and stir. Allow the undissolved material to settle to the bottom (this should take about a minute), and then carefully pour off the clear liquid into another glass, leaving the solids. Pour a tablespoon (15 milliliters) of the copper sulfate solution described in the "Shopping List and Solutions" into the decanted baking soda solution. Beautiful blue flakes should immediately form and settle out of solution. You should also see some bubbles, and the *supernatant*, the liquid over the blue blob precipitate, should be a pastel blue. The bubbles are from excess acid in the copper solution reacting with the bicarbonate ion.

The blue blob reaction occurs because the water decanted from the

baking soda contains dissolved sodium and bicarbonate. A small amount of the bicarbonate loses a hydrogen to water and becomes the carbonate ion. The copper solution has copper ions and sulfate ions. When the copper ion finds the carbonate ion, it is love at first sight. These two ions combine and hold on tight. In fact, they hold on so tightly they form a solid and fall out of solution. They precipitate.

Black Ink

With safety glasses securely in place, add a teaspoon (5 milliliters) of hydrogen peroxide to a quarter cup (60 milliliters) of iron acetate solution (see the "Shopping List and Solutions"). The solution should turn a nice reddish brown as the ferrous ion becomes the ferric ion. Slowly add a half cup (120 milliliters) of cold, brewed brown tea. You should get a black, mushy precipitate that will eventually settle to the bottom. Historically, this material was used as black ink, and this precipitation reaction was used to produce it.

CHAPTER 5
Chemical Partners: Who Does What to Whom

(T)his last misdeed had a decisive effect upon him; it rushed across the chaos of his intellect and dissipated it, set the light on one side and the dark clouds on the other, and acted upon his soul . . . as certain chemical reagents act upon a turbid mixture, by precipitating one element and producing a clear solution of the other.

—Victor Hugo, *Les Misérables*, ca. 1860

To a chemist, saying a solution is "clear" is not saying the solution is without color. Saying a solution is clear means it has no suspended solids. A precipitation reaction is one in which two clear solutions mix to form a solid in solution. Why should two clear solutions decide to form a solid? Consider the following analogous social situation. Two celebrants may come to a party together because it is convenient to share a ride. In the course of an evening, however, they separate and come in contact

with other people. If, across the crowded room, they find someone with whom they form a special bond, they may leave the party with this person and, with luck, stay bonded. If, across the crowded beaker, an ion should find another ion with which it forms a strong bond, a precipitate will result. When two ions join to form a solid, the solid is called a *salt*.

The social analogy can be extended—unfortunately. Even strongly bonded chemical species can be enticed to change partners temporarily. Put your safety glasses back on again for a minute. Dissolve a teaspoon (5 milliliters) of alum in a half cup (120 milliliters) of water. Add less than a quarter teaspoon (1 milliliter) of ammonia and stir. You should see a thick white precipitate. Add four drops of aquarium pH-lowering solution and stir. Keep adding drops until the white precipitate dissolves and you have a clear solution again. Ammonia is a base, and the aquarium pH-lowering solution is an acid. (Recall that a lower pH means a more acidic solution.) Whether or not a precipitate will form will depend on the salt's environment.

The social analogy can be extended again. Dissolution is the opposite of precipitation, and in the complete absence of water, all unions of salts are solid. Water, however, can be a home wrecker. When a salt is wet, the molecules of water can insinuate themselves between ions. Table salt, sodium chloride, is solid enough in the shaker, but when it is wet, the molecules of water work their way between the chloride ion and sodium ion and keep them apart. Why doesn't water come between the carbonate ion and the copper ion in the insoluble copper carbonate of the earlier demonstration? It boils down to a trade-off: if the divorce is more costly than any possible benefit, the union stays solid. If not, let the proceedings begin.

To understand the factors involved in the cost/benefit analysis for salt dissolution, we first need to revisit an idea introduced earlier. We said that atoms like to gain or lose electrons if doing so brings them closer to their ideal of a filled shell, but we also said that when nonmetals combine, they tend to share, rather than appropriate, electrons to fill their needs. As it turns out, some elements have a stronger attraction for electrons than others. The ability to attract electrons has been termed *electronegativity*, and the degree of electronegativity depends on the positions of the elements on the periodic table.

Of all the elements on the periodic table, fluorine is the most elec-

tronegative, as shown in figure 1.5.1. This means that fluorine is the most likely to command the lion's share of the electrons. In a fluorine compound, the electrons will cluster around fluorine more than any other element. On the periodic table, the closer an element is to fluorine, the more electronegative it is. Because electronegativity is a measure of the element's attraction for electrons when it is in combination with another element, electronegativity isn't a concept for the noble gases, helium (He) through radon (Rn). This family doesn't form compounds under normal conditions.

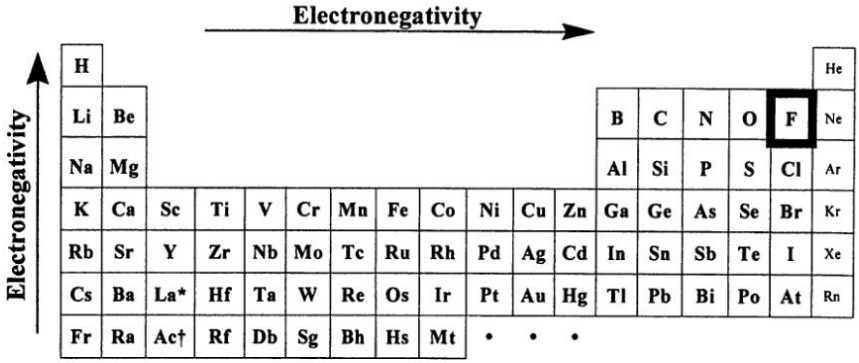


Figure 1.5.1. A periodic table showing the trends in electronegativity. Elements tend to become more electronegative toward the right and to the top of the periodic table. Fluorine is the most electronegative element. The noble gases are not assigned an electronegativity because they do not normally enter into chemical reactions.

Isn't that convenient? Not only does the periodic table tell us the number of protons in the nucleus, the number of electrons in a neutral atom of the element, and something of an element's reactivity from the family it belongs to, but the periodic table can also be a device for predicting relative electronegativity. The explanation for this correspondence comes from understanding atomic structure: the elements toward the top of the periodic table don't have very many filled shells, so a new electron can feel more of the attraction of the positive nucleus without other electrons blocking the way. Fluorine enjoys its status as the most electronegative element on the periodic table for at least two reasons. First, fluorine has only one filled shell, and second, of all the second-row elements without a filled shell, it has the greatest nuclear charge: nine protons. The only second-row element

with a greater nuclear charge is neon, and it has all the electrons it wants. Then what about hydrogen? It has *no* filled shells, and an electron added to hydrogen would be fully exposed to the positively charged nucleus. Why doesn't hydrogen have a large electronegativity? Because even on the atomic level, it turns out, size matters.

Generally speaking, atoms tend to get bigger as you move down the periodic table because the elements have more electrons and these electrons are filling up shells. Hydrogen isn't as electronegative as fluorine because it hasn't acquired any filled shells and it is too small to comfortably support a large negative charge. The difference between a fluoride ion carrying a negative charge and a hydrogen ion carrying a negative charge is like the difference between someone carrying a twenty-pound sack of dog food or a twenty-pound cannonball. The dog food is easier to carry because the weight is spread out over a larger area. The cannonball is harder to carry because the weight is concentrated at one point. When the hydrogen atom carries a negative charge, all that charge is concentrated into a very small volume. When all the various factors weigh in, hydrogen has an electronegativity comparable to that of phosphorus, as shown in figure 1.5.2.

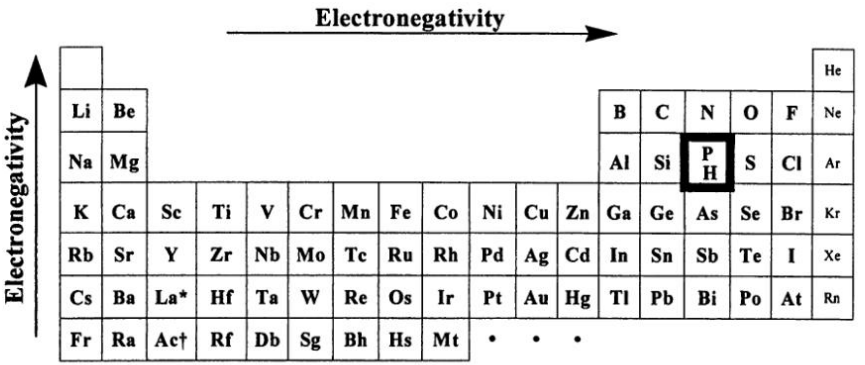


Figure 1.5.2. Hydrogen has an electronegativity comparable to that of phosphorous.

So what is the result of all these attractions and electron swappings among the elements in a compound? Something called *molecular polarity*.

Polarity is a familiar concept. Batteries have positive poles and negative poles. Magnets have north poles and south poles. When the electrons preferentially sit on one end of a molecule because that is where the electronegative elements are, the molecule has a positive pole and a negative pole; thus, it has polarity. A molecule with a more positive end and a more negative end is said to have a *dipole* as it has "two poles."

Polar molecules behave somewhat as bar magnets do: the positive end of one polar molecule lines up with the negative end of another, as the north pole of one bar magnet will line up with the south pole of another. Water (H_2O), shaped in a **V** with the oxygen in the middle and the hydrogens at the tips of the **V**, is a polar molecule. Oxygen is more electronegative than hydrogen, so the electrons gravitate toward the oxygen end and away from the hydrogen end. The negatively charged oxygen ends of several water molecules can be attracted to a positively charged ion, building a cage around it and keeping it separated from its negatively charged partner. Similarly, the positively charged hydrogen ends of several water molecules can align themselves with negatively charged ions, building a similar cage around them. This situation is shown schematically in figure 1.5.3.

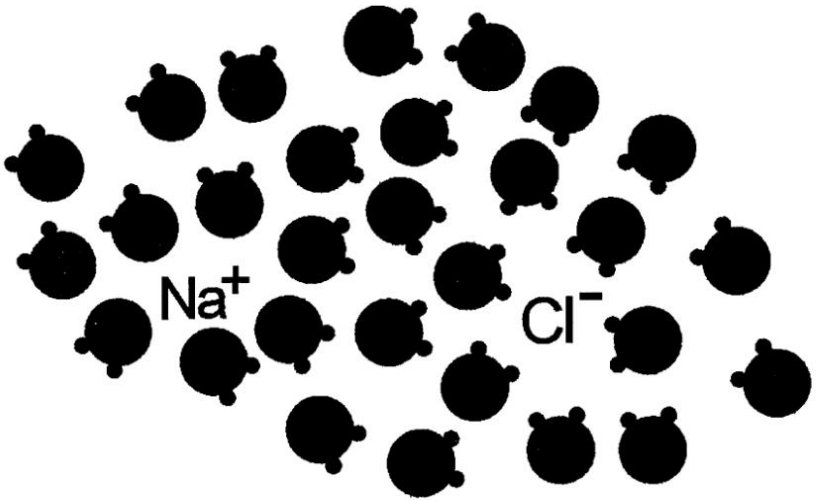


Figure 1.5.3. Water molecules separating a sodium ion and a chloride ion by forming solvent cages around the ions.

Water molecules like to build cages around ions because this is a more relaxing situation for them. Just as it requires energy to keep magnets

apart that are attracted to each other, it takes energy to hold apart molecules that are attracted to each other or to an ion. Allowing water molecules to form cages around ions allows them to relax and release energy.

However, energy is also needed to break the salt apart, so there is the trade-off. If it costs more to break the salt apart than the profits gained by allowing the water molecules to relax into cages, then the salt will precipitate out of solution or not dissolve in the first place. If it costs less to break the salt apart than the profits gained by allowing the water molecules to build cages, then the salt will stay in solution or dissolve.

By revisiting the periodic table, we can conclude that the metals in the first column (lithium [Li], sodium [Na], potassium [K], and so on) like to form positive ions with a positive-one charge because losing one electron will give them a nicely filled outermost shell. Salts derived from these positive ions are almost always soluble because the attraction of one positive charge is relatively weak. Compare the bar magnets suggested in the "Shopping List and Solutions" with a refrigerator magnet. The positive ions formed from the elements in column one would have a relatively weak attraction for negative ions, more like the refrigerator magnet than the bar magnet.

On the other hand, the elements of the second column like to lose two electrons when they form ions and therefore have a positive-two charge. These ions have a stronger attraction for negatively charged ions and will tend to form more insoluble compounds than their counterparts in the first column. But beyond these basic observations, the factors that determine which salts form more permanent unions are again about as convoluted as the human counterpart. Size, shape, and flexibility play roles, too. And even when these considerations label a salt soluble or insoluble, the actual amount that does or does not dissolve depends on the nature of the solvent, how much salt is in the solution, the temperature of the solution, and the pH of the solution.

A convincing demonstration of the importance of the nature of the solution is to try to dissolve a teaspoon (5 milliliters) of table salt in a cup (240 milliliters) of water versus the same quantity in salad oil or mineral oil. Table salt in water will dissolve readily. Table salt in oil settles to the bottom, undissolved. Try stirring both before making a final determination. Stirring helps salts dissolve because the dissolution process starts at

the solid's surface and stirring can help expose more surfaces to the solution. However, no amount of stirring will force all the table salt into an oily solution.

The quantity dependence of solubility can be demonstrated with baking soda and water. If a pinch of baking soda is added to a clear glass (not plastic) holding about two cups of water, the pinch should dissolve. In fact, up to ten or fifteen healthy pinches of baking soda should dissolve. At some point, however, the added pinches start turning the solution cloudy, and eventually the added pinches settle to the bottom, even with stirring. To demonstrate the effect of temperature on solubility, the solution can be placed in the microwave for thirty seconds, just enough time to warm it to the temperature of hot but drinkable soup. The resulting warm solution should be clear again, and all the baking soda on the bottom of the glass should dissolve with stirring.

The influence of other materials in solution can be shown with chalk. Compare chalk, which is calcium carbonate, with baking soda, which is the compound formed from sodium, hydrogen, and carbonate. When a teaspoon (5 milliliters) of baking soda is added to a cup (240 milliliters) of warm water, it dissolves. The same amount of powdered chalk would sink to the bottom like a rock. However, chalk will dissolve when placed in vinegar. Because vinegar is an acid and chalk is reacting with the acid, the chalk, by definition, is a base, but a base that will not dissolve in neutral solutions such as plain water. In vinegar, an acid, the carbonate base is neutralized and calcium goes into solution.

So with all of these variables—the nature of the salt, nature of the solution, amount of salt, and temperature of the solution—it seems that precipitation and solubility are fairly complicated. Things don't just immediately fall into place. We will nonetheless be revisiting these concepts in many different guises as we proceed because precipitation and solubility factor into a lot of chemical situations. For instance, seashells form when calcium excreted from a sea creature mixes with the carbonate in the water to form calcium carbonate. Eons of seashells collecting on the bottom of the ocean account for the composition of the chalk and limestone that finds its way to our blackboards and sidewalks.

Precipitation is useful in hazardous waste treatment. If harmful metals can be precipitated out of solution, they can be segregated as solids that take up less space than liquid waste and are easier to transport

and store. Other, troublesome, precipitation reactions occur in an unexpected place: the human body. Gout is a condition caused by uric acid precipitates accumulating in the joints. Gallstones and kidney stones are precipitates. These pathological precipitates, however, are not the norm. The body is a pretty soupy mixture because the essence of life is the ability to change in response to the environment, so most bodily substances must be able and ready to move. This mobility can be accomplished with water because water is so very good at keeping substances in solution. The body can last much longer without food than without water, and without water, the body and mind become lethargic. Many conditions, as well as moods, can be positively influenced, if not completely corrected, by increasing the daily intake of water. Many times, when it comes to health, water is the solution.

Another common precipitation product is soap scum. Soap scum generally floats on water rather than raining out, so it is normally not thought of as a precipitate—but that is a matter of semantics. Scum can form in bathtubs when soap mixes with hard water; that is, water that contains calcium and magnesium ions. Water that contains calcium and magnesium ions is called "hard" because these ions tend to form insoluble precipitates (that is, little rocks) in the water.

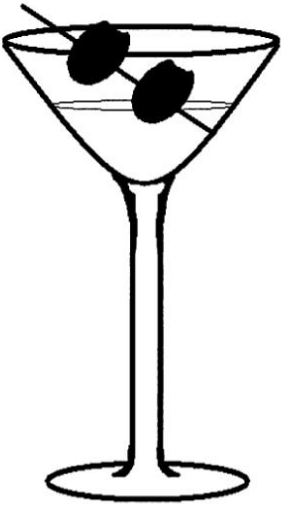
For Example: Hard Water, Soft Water

The good thing about water is that so many things dissolve in it. The bad thing about water is that so many things dissolve in it. Pure water is a poor conductor of electricity, but don't go standing in a full bathtub to change a lightbulb because it is very difficult to obtain pure water. Water with salts dissolved in it is a good conductor of electricity. The ability of water to dissolve things accounts for the fact that all groundwater contains dissolved ions, including calcium and magnesium salts.

As dropping a piece of chalk in water confirms, calcium salts can be pretty insoluble, and while the buildup of calcium salts on tea kettles can be annoying and scum can be frustrating, the buildup of crusty deposits of scale in pipes and swimming pools can precipitate serious problems. At one time, negatively charged phosphate ions were added to detergents so the calcium would preferentially form salts with the phosphates, instead of forming scum, which would free the detergent to perform its function. But phosphates are quite efficient fertilizers. So waste streams from laundry caused waste water conduits to become clogged with unusually dense growth, which is why phosphate use had to be restricted. Nowadays scum formation is not so much of a problem because of the widespread use of water softeners. Water softeners remove calcium and other precipitate-forming ions from the water before they go through the household pipes.

The principles at play in water softeners are the same as those in precipitation reactions. Water is run over a dense material saturated with sodium ions like a gigantic network of salts. The sodium salts are soluble, whereas the calcium analogs of the same salts are not. So the calcium replaces the sodium and becomes trapped on or in the solid. The water, now enriched in sodium instead of calcium, can be used without worry that it will precipitate soap or form the crusty deposits of scale. In the regeneration cycle of the water softener, the solid support is backwashed with water saturated with so much sodium salt that the sodium eventually replaces the calcium on the solid, and the water softener is ready to start softening again.

But a material doesn't have to be a salt to dissolve in water. Sugar, decidedly not a salt, dissolves in water, too. Which brings up the question: What makes sugar so different from salt? They are both white crystalline compounds that dissolve in water and are difficult to tell apart without tasting. But you could survive for a least a while on a diet of sugar water; on saltwater, you would not survive. What is the difference? It's all in the bond. The chemical bond.



Demonstration 6: Bond. Chemical Bond.

Only the chemist can tell, and not always the chemist,
What will result from compounding
Fluids or solids.
And who can tell
How men and women will interact
On each other, or what children will result?
There were Benjamin Pantier and his wife,
Good in themselves, but evil toward each other:
He oxygen, she hydrogen,
Their son, a devastating fire.
—Emily Dickinson, *Complete Poems*, ca. 1924

I fear . . . the chemical action which would be set up in my soul by a false homage to a symbol.
—James Joyce, *Portrait of the Artist as a Young Man*, ca. 1915

Take one of the clear plastic bottles suggested in the "Shopping List and Solutions," put on your safety glasses, and pour in about two inches (5

centimeters) of mineral oil. Add about two inches (5 centimeters) of copper sulfate solution. Put the cap on the bottle and shake it. The mixture should separate into two layers with the copper solution layer remaining bright blue and the mineral oil layer remaining clear. Add a quarter teaspoon (1 milliliter) of tincture of iodine. Put the cap on and shake.

When you stop shaking, the two layers should separate again, but this time the mineral oil layer should appear violet. Tincture of iodine contains both I^- and I_2 but mostly a complex of the two, which is brown. The copper ions in the copper sulfate oxidize I^- to the molecular form I_2, which ruins the complex. The molecule I_2 is violet and soluble in oils such as mineral oil.[1]

Now add a teaspoon (5 milliliters) of household ammonia. Put the cap on and shake. This time when the layers separate, the copper layer should be a dark royal blue because the copper is now forming strong partnerships with ammonia and it is no longer available to the iodine. Some iodine reverts to I^-, the complex re-forms, and the mineral oil clears up. You may need to add several portions of ammonia, but eventually the mineral oil clears.

The molecule I_2 dissolves in the mineral oil, but the ion I^- does not. The ion I^- dissolves in water but not in mineral oil. Water, a polar molecule, is attracted to the ion I^-, builds a cage around it, and pulls I^- into the water solution (otherwise known as *aqueous* solution). The molecule I_2 has no polar end to attract water molecules, so the water molecules are more attracted to each other and squeeze I_2 out of solution. The mineral oil accepts I_2 because mineral oil is a nonpolar molecule and has no cage-building propensities. Earlier we said that salts were formed when positive ions are attracted to negative ions and that these materials form a bond. Now we need to add that this type of bond is, specifically, an *ionic bond.* This special designation is necessary because not all materials are salts and not all chemical bonds are ionic. The bonding that occurs in nonsalty materials, such as I_2, is called *covalent*. The differences between the types of bonding and the materials they produce deserve a chapter of their own, such as the one that follows.

CHAPTER 6

The Tie That Binds the Chemicals That Bond

Close relation in a place like London is a personal mystery as profound as chemical affinity. Thousands pass, and one separates himself from the mass to attach himself to another, and so make, little by little, a group.

—Henry Adams, *The Education of Henry Adams*, ca. 1918

Polarity, or action and reaction, we meet in every part of nature; in darkness and light; in heat and cold; in the ebb and flow of waters; in male and female; in the inspiration and expiration of plants and animals; in the systole and diastole of the heart; in the undulations of fluids, and of sound; in the centrifugal and centripetal gravity; in electricity, galvanism and chemical affinity.

—Ralph Waldo Emerson, *Essays*, ca. 1840

The illustration for the demonstration with which we began this discussion was a martini glass with two olives. But unlike the toothpick

holding the olives together, a bond is not a material entity. A bond is a force, in the same sense that magnetism and gravity are forces. The origin of the force in a chemical bond is electrical, but electrical interactions that are complicated by attractions and repulsions, the presence of many electrons and protons, and charges that are moving in complicated patterns. Trying to categorize substances by type of bond is somewhat like a cosmetician trying to categorize humans by skin tone. Certainly there are dark-skin people and light-skin people, but there are also many variations within the range of human skin. In the same way, we can say there are three basic categories of chemical bonds—ionic, covalent, and metallic—but these are really just variations on a theme: nuclei are bonded together when there is a mutual attraction, and the basis for this mutual attraction is electrical. All bonds have a bit of each quality—covalent, ionic, and metallic—to a greater or lesser degree. Such fuzziness is not immediately useful, however, so for now we will proceed as though it were possible unequivocally to place each molecule in one category or another and use the categorization to assign properties to the different materials.

To begin with, we have an excellent tool for predicting just exactly what kind of ion an element is most likely to form—and that is the chemist's closest friend, the periodic table—which is shown here again for easy reference.

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 1.6.1. The periodic table of the elements.

As we've pointed out, the periodic table can be broken down into three major parts: the metals, the nonmetals, and the metalloids. The metals are to the left of the zigzag staircase that starts between B (boron) and Al (aluminum) and ends between Po (polonium) and At (astatine). The nonmetals are to the right of the staircase. The metalloids are the elements immediately above and below the staircase. But once again, there is a range of properties and no exact demarcation. Nature doesn't care what we choose to call metal and what we choose to call nonmetal. However, some elements (such as copper, Cu, three elements to the left of the staircase) are clearly in the metal block. They have behaviors that are clearly metal-like (copper solid is shiny and bendable and is a great conductor of electricity). The behaviors of other elements in the nonmetal block are clearly nonmetal-like: nitrogen gas and oxygen gas are such poor conductors of electricity that current flow can be stopped by simply separating wires in air. So the division of the periodic table into metals and nonmetals can be a useful organizing principle.

The nonmetals to the right of the staircase usually like to form negative ions when they form ions. Metals to the left of the staircase usually like to form positive ions when forming ions. Opposite charges attract. When ions of opposite charges are in the same vicinity, they are attracted to each other. If they form a bond based on this attraction between ions, the bond is called an ionic bond. For instance, the bond between sodium and chlorine in table salt, sodium chloride, is a very good example of what is considered an ionic bond. The ionic bond originates from the attractions between positive and negative ions, as the name implies, and ionic bonds are so wonderfully predictable and explainable that one almost wishes that all bonds could be simple ionic bonds. But then we wouldn't have the virtually infinite variety of materials that are necessary to the world we know. Variety is always an interesting, but complicating, factor.

As we noted previously, ions form because atoms tend to gain or lose electrons until they have a filled valence shell. For historical reasons, a filled shell is called an *octet*, despite the fact that not all filled shells consist of eight electrons. We speak of ions being formed when atoms gain or lose electrons to fill their octets, but there are ways atoms can fill their octet that do not involve abandoning or stealing electrons. Octets can be completed by sharing electrons, too.

Electron sharing results in the type of bonding that usually occurs between two nonmetals (that is, two elements that are both on the far right of the periodic table). This type of bonding is termed *covalent* bonding. As we've seen, the valence electrons are those electrons in the outermost shell of an atom. For instance, carbon, in the fourth position on the second row, has six total electrons (being the sixth element listed on the periodic table), but only four of these are valence electrons, that is, electrons in the outer shell. *Covalent* means that electrons are being shared cooperatively and act as valence electrons for both the elements in the bond.

The theoretical rationale for electron sharing is that both elements in a covalent bond have about the same attraction for electrons. Being on the same side of the periodic table and having similar electronegativity, there would be no way of deciding who gets the electrons and who gives them up. Oxygen is on the right on the periodic table, and, as we said before, hydrogen has an electronegativity similar to elements on the right of the periodic table. So the bond between oxygen and hydrogen in water is covalent. When the valence electrons from oxygen and hydrogen finish arranging themselves around the nuclei, each element has a filled octet. (Recall that hydrogen's "octet" is full with two electrons.) Two electrons fill the octet for each hydrogen, and eight electrons fill the octet for oxygen, four of which are electrons shared with the hydrogen nuclei.

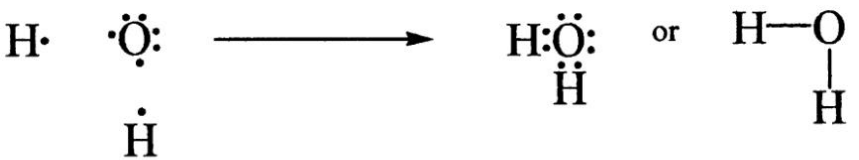


Figure 1.6.2. Covalent bonds form between hydrogen and oxygen when they fill their respective shells by sharing electrons.

There is, however, a fundamental contradiction. We have stated that opposite charges attract and like charges repel, and that electrons all have a negative charge. If this is true, then why don't collections of valence electrons explode into flying showers of electrons instead of settling into strong chemical bonds?

That is a very good question and we are glad you asked. It turns out

that this question long bedeviled chemical theorists, too. They called the observed attraction between elements *chemical affinity* just to give it a name, but they did not understand the nature of the attraction. With an understanding of atomic structure, however, came a rationalization for such attractions: they can be seen as negative electrons running interference between positively charged nuclei.

Though the complete picture is a good deal more complex, a reasonable analogy can be found in magnets. If two bar magnets are brought together so that like poles align, they repulse one another. This situation is similar to bringing two bare, positively charged nuclei together. They do not bond because of the repulsion between them. If, however, a third bar magnet is placed between the original two, with the south pole aligned with the two north poles, then the magnet in the middle will attract the other two and the three will stay together. In a bond, the negative electrons between the two positively charged nuclei attract both positive nuclei and act like a glue to hold the nuclei together.

Analogies, however, are never perfect. The electrons do not occupy some specific space between the nuclei like a third bar magnet but spread themselves out into fuzzy clouds, called *molecular orbitals*, that can assume shapes nearly as diverse at the fluffy celestial formations we have compared them to. When one of these orbitals has a significant electron density between the two nuclei, the formation acts as a bonding orbital. If one of these electron clouds results in a significant electron density outside the nuclei, the electrons can lessen the bonding rather than enhance it. In this case the electron cloud, the electron orbital, is called an antibonding orbital. These two situations are depicted in figure 1.6.3. On the left-hand side, figure 1.6.3a, two atoms have come together so that there is some electron density between the nuclei. The electrons are attracted to the adjoining nuclei and a bond is formed. On the right-hand side, figure 1.6.3b, two atoms come together so that there is a lack of electron density between them. The exposed, positively charged nuclei repel each other, and no bond is formed.

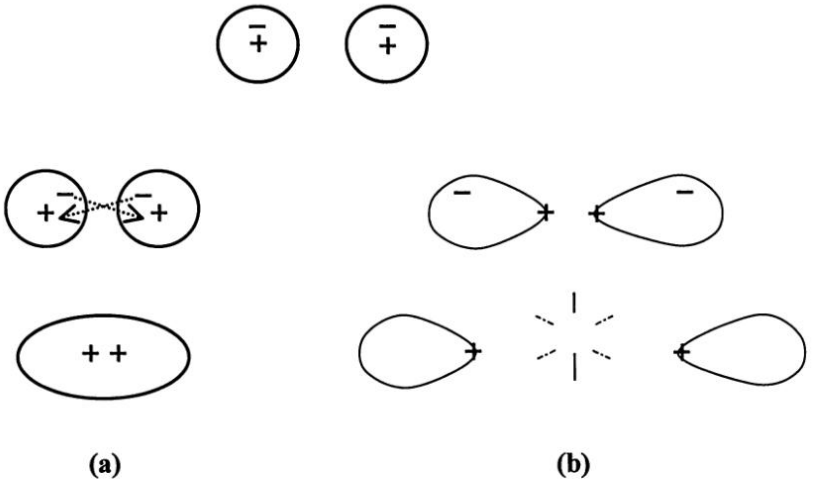


Figure 1.6.3. When two atoms come together, they may find themselves (a) with an electron cloud, between the two nuclei, or (b) outside the center of the two nuclei. In the first case, (a), there will be an attraction between the electron cloud of one atom and the nucleus of the other and a bond may form. In the second case, (b), the two positively charged nuclei are exposed to, and repelled from, each other. A bond will not form.

The antibonding orbitals are generally at a higher energy than the bonding orbitals, but if the right amount of energy impinges on the bonding orbital, perhaps in the form of light energy, electrons can be excited from one orbital to another. If electrons are excited to an antibonding orbital from a bonding orbital, the bond may break. Many substances, such as some beers, are stored in brown glass to prevent light from degrading the material inside by just such a mechanism.

As we said above, bonds aren't always purely ionic or purely covalent. The best models for ionic bonds include some electron sharing. And covalent bonds don't always share electrons completely evenly. Any difference in electronegativity between bonding nuclei means that the electrons will be attracted more to one nucleus than the other. However, a bond could be considered purely covalent if it is between two identical nuclei, as in hydrogen gas, H_2, or oxygen gas, O_2. An extreme example of equality in electron sharing is the metallic bond. In a metal, all the atoms are identical and share electrons so readily that the metal can be thought of as one big molecule.

In solids, there can be electrons in a bonding system between pairs of nuclei called the *valence band.* There can also be a gigantic orbital that extends over all of the nuclei called the *conduction band.* The conduction band can be thought of as a huge orbital. The bonding electrons in the valence band stay associated with their pair of nuclei. Electrons in the conduction band are free to move from nucleus to nucleus and travel from one end of the metal to the other. An analogy might be made to a banking network. At the local level, there are town banks with local tellers that live and work in the same place. These tellers are the valence-band electrons, keeping the foundations of the bank together. The upper-level managers can be thought of as the conduction-band electrons: their work keeps them moving from bank to bank over the entire network.

Materials that have plenty of electrons in the conduction band are, logically enough, called *conductors*, and energy supplied by a battery can cause these electrons to move in what is generally called an *electric current.* Other solids do not have electrons in a conduction band and do not conduct electricity. They are called *insulators.* Materials that are intermediate between conductors and insulators are called *semiconductors*, a fairly innocuous-sounding name for a revolutionary material.

For Example: Semiconductors

The invention of transistors, based on semiconductors, has changed the world. What are semiconductors? As the name implies, they are materials with electrical properties between those of conductors and insulators. Semiconductors are materials that conduct some of the time.

In a semiconductor, there are normally too few electrons in the conduction band to conduct current. However, the energy gap between the conduction band and the valence band is small enough that the electrons, with a little provocation, can jump

the gap and make the material conductive. This provocation can come in the form of applied voltage, heat, or light. Some solids are natural semiconductors, or what are termed *intrinsic* semiconductors. Others, however, can be made more able to jump the gap by a process called *doping*, though this has nothing to do with athletes or drugs.

Silicon is normally the first material that comes to mind when speaking of semiconductors, but silicon is, in fact, not an intrinsic semiconductor. Solid silicon must be doped to become a semiconductor. Doping is the process of adding a miniscule amount of impurity to a solid such as silicon. Two of the favorite dopants for silicon are phosphorus and aluminum because they are on either side of silicon on the periodic table. They have about the same size and electronegativity, so they can easily fit next to silicon in a solid. They change the conductive properties of silicon because they have, respectively, one more and one fewer electron than silicon.

As can be seen from the periodic table, silicon has four valence electrons available for bonding. Accordingly, it bonds with four other silicon atoms when it solidifies, giving each a shared tally of eight electrons, a nicely filled shell. If, however, an atom of phosphorus were to slip into the mix, then there would be one extra electron that didn't quite fit. This extra electron is more easily promoted to the conduction band and therefore allows the material to conduct more readily when hooked up to a battery. If an atom of aluminum, with three valence electrons, insinuates itself into the silicon solid, then there is a hole where a valence electron would normally be found. This extra hole also allows current to flow more readily because electrons motivated to move now have a place to go. Silicon doped with something that donates extra electrons is called an *n*-type semiconductor because an electron contributes a negative charge. Silicon doped with something that has fewer electrons is called a *p*-type semiconductor because it contributes a *positive* charge.

When a piece of *p*-type material is joined to a piece of *n*-type material, an arrangement called a *diode* is formed. A diode is a device that will allow current to flow in only one direction. A bit of *p*-type semiconductor attached to a bit of *n*-type semiconductor will allow current to flow only when electrons are going into the negative side, over to the positive side, and out. A battery hooked with its negative side attached to the *n*-type side of a diode acts like a river supplying water to flow over a dam. The positive end of the battery is the reservoir into which the water flows.

Conversely, if the negative side of a battery is hooked up to the *p*-type material and the positive side of a battery is hooked up to the *n*-type material, then there is a tug-of-war for the electrons that ends in a stalemate and no current flows.

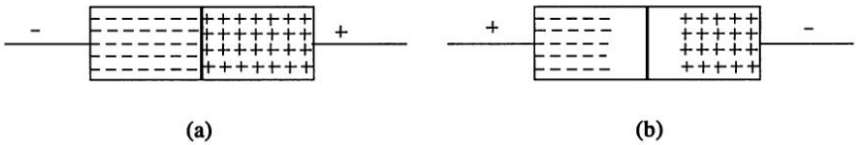


Figure 1.6.4. A diode can be constructed by joining an *n*-type semiconductor to a *p*-type semiconductor. When an electron supply is hooked up as shown in (a), current will flow through the diode. When an electron supply is hooked up as shown in (b), there is a tug-of-war for the electrons and no current flows.

This behavior becomes useful when a third bit of semiconductor material is added, making a *pnp* or *npn* sandwich. Current cannot flow in *either* direction in a *pnp* or *npn* sandwich—unless some other source injects or pulls out electrons from the middle layer of the sandwich, making *ppp*- or *nnn*-type materials, which can conduct.

The situation begs for an analogy. A *pnp* or *npn* material is like a dammed-up river. Changing the *n* in *pnp* to *p* by pulling out electrons is like opening up the dam and allowing the water to flow. The same is true for *npn* if electrons are injected into the *p* material. What injects or pulls out electrons? A battery. A battery hooked to the middle material can raise or lower the electron dam.

So what purpose does this serve? Now a small current can control a large current, switching it on and off with a little electron flow. To appreciate some of the significance of the situation, let's think historically for a moment. Europeans in the very early Middle Ages were technology poor and relied on manual labor. If they needed to grind flour, then several serfs were tethered to a grist mill and told to start pushing. The Black Death, however, decimated the ranks of the workers, so the remaining people found themselves becoming more creative with levers and gears and other simple machines. They soon found that one worker with a lever and system of gears could raise the dam, which allowed the water to flow over a water wheel, which turned the grist mill and did the work of many serfs.

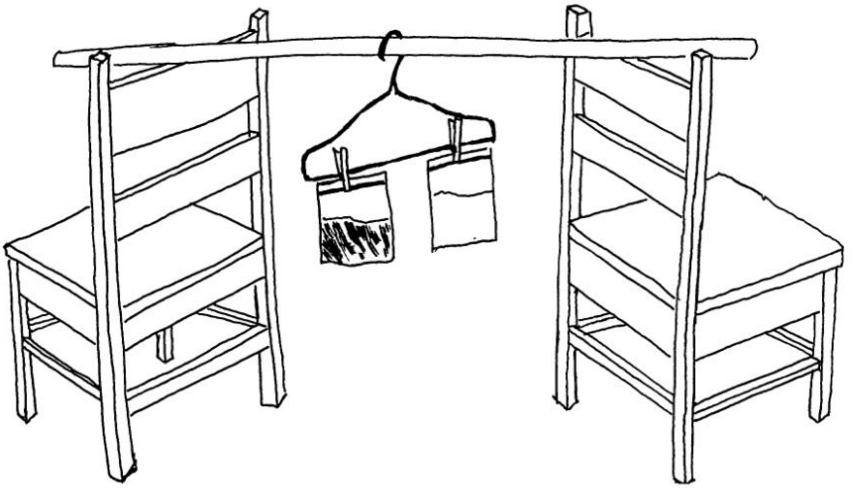
The change in medieval Europe was more gradual than the change we

have experienced due to semiconductors, but the societal impact is comparable. Instead of a worker with a lever acting as a dam switch, we now have a battery in a circuit board switching currents off and on. Semiconductor switches, called transistors, are used for the on/off, zero/one logic that forms the basis of computers.

How can switches be used to generate all the many complicated functions of computers? First, by counting. Computers can count using just zeros and ones, which corresponds to "switch on" versus "switch off." Though we are used to counting in groups of ten, probably because we evolved with ten fingers, other systems are possible. Clocks count in groups of sixty (sixty seconds make a minute, sixty minutes make an hour) and eggs are packaged in groups of twelve—a dozen. Computers count in groups of two and use zero and one (switch off and switch on) for the digits. Computers also use AND, NOT, and OR, the same words that are used to link keywords in an Internet search (a system called *Boolean logic*) and if/then logic. For example, if the switch is on for the letter A, AND the switch is on for the printer, then the printer will print the letter A.

But if switches are all that is needed for computers, then why can't computers be built without transistors? The answer is that they could be, and they were. Switches are nothing new and even electronic switches are nothing new. In the past, vacuum tubes were used for the on/off switches (the zeros and ones) instead of transistors. Though they have other advantages and are used in other applications, the problem with using vacuum tubes in computers is that they are large and they create a lot of heat. The early computers required a lot of space and a lot of cooling. For any task of reasonable complexity, a great number of switches were required. With transistors, a very large number of switches can be put in a very small area without generating very much heat.

Once the basic principles of semiconductors were worked out, scientists directed their efforts toward devising different kinds of semiconductors. Nowadays there are semiconductors that sense heat or various colors of light. There are devices based on semiconductor logic that do everything from timing lightbulbs to piloting space craft. The construction of these various materials requires a confident command of the principles of chemical bonding and of the basic principles of chemical reactions, two of which—the conservation of mass and the law of definite proportions—are demonstrated next.



Demonstration 7: Gemstone Chemistry

"However," said she, "chemical laws exist." For, being a woman, she had need of belief.
—Anatole France, *Penguin Island*, ca. 1900

Get two sandwich-sized self-sealing plastic bags and two gallon-sized self-sealing plastic bags and put on your safety glasses. Get a coat hanger and find a place to hook the hanger so it is suspended and can behave as a balance. A broom handle supported by two chairs might be the best arrangement for suspending the hanger. Into each large bag, place one level plastic teaspoonful (5 milliliters) of cream of tartar and one-half cup of hydrogen peroxide (60 milliliters). Mix these ingredients well by kneading the outsides of each bag with your fingers. Do not seal the bags yet.

Into each small sandwich-sized bag, pour a teaspoon (5 milliliters) of copper sulfate solution (prepared as described in the "Shopping List and Solutions"). Seal these bags completely, and place one into each of the two large bags. Now seal the two large bags and suspend them with clothes pins from the coat hanger, one on each side. Adjust their positions on the coat hanger by moving the clothes pins back and forth until the

bags balance each other and the coat hanger is level. The homemade balance will work best if the entire coat-hanger assembly is hooked over something round so that the hook of the hanger can rock back and forth in an unrestricted manner. Once you have the bags balanced, secure the position of the clothes pin with adhesive tape. Check to see that the bags are still balanced.

Now comes the tricky part. In one of the big bags, open the little bag from the outside, without opening the big bag. Pour the copper solution from the little bag into the cream of tartar–hydrogen peroxide mixture in the big bag. The reaction begins slowly, but within ten seconds it should be fizzing away. The dramatic sky-blue copper tartarate eventually gives way to a lime-green mixture of the tartarate compound with orange copper oxide. The reaction generates enough heat that you can observe condensation on the inside of the big bag and feel warmth on the outside. The impressive colors produced by the reaction are reminiscent of gemstones for a very good reason: the colors of gemstones such as azurite and turquoise derive from copper salts. Various copper salts appear as dashes and streaks of color in polished stone.

Heat, bubbles, and color change—these are all indications that a reaction has occurred. The material now in the reaction bag is no longer the original material. However, if you were careful while opening the inside bag, the hanger assembly should have remained in balance. This balancing act is an example of *conservation of mass*: the idea that mass is neither created nor destroyed by chemical means. The mass of the reagents, the materials in the unreacted bag, remains the same as the mass of the products, the blue and green materials in the bag that were allowed to react. No matter how things change, some things just stay the same.

The second part of this demonstration has already been performed. Recall that the phenol red swimming pool pH indicator turned yellow in water and red-violet in baking soda solution. Recall that the vinegar-iron solution turned red when hydrogen peroxide was added. These observations indicate that there is a difference between water, hydrogen peroxide, ammonia solution, and vinegar solution. What is the difference? Water has the formula H_2O, two hydrogen and one oxygen. Hydrogen peroxide has the formula H_2O_2, two hydrogen and two oxygen. The active principle in bases such as bicarbonate solution is the hydroxide ion, OH^-, one

hydrogen, one oxygen. The active principle in acids such as vinegar is the hydronium ion, H_3O^+, one oxygen and three hydrogen.

There you have it: H_2O, H_2O_2, OH^-, H_3O^+. Not much difference typographically. But chemically, they're worlds apart, which exemplifies a principle called the *law of definite proportions.* It is not just the elements that determine the nature of a compound but the proportions, too. The ramifications of the conservation of mass and the law of definite proportions are the subjects we tackle next.

CHAPTER 7

Sticking to Principles

The meeting of two personalities is like the contact of two chemical substances: if there is any reaction, both are transformed.

—Carl Gustav Jung, ca. 1920

Some people are just naturally good cooks, adding a dash of this and a pinch of that. For the rest of us, there are recipes. We like explicit directions that spell out the required ingredients, the required amounts, the steps in producing the desired product, and number of servings that will be produced. While there may be some popular notion that chemists fit in the group that adds a pinch of this and a dash of that—and a good deal of creativity and art can enter into chemical research—the second group is where they spend most of their time. Balanced chemical equations, such as $2\ H_2 + O_2 \xrightarrow{spark} 2\ H_2O$, are chemical recipes.

We will begin our discussion of these recipes by examining two of the main principles on which they are based: the conservation of mass and the law of definite proportions. The law of definite proportions defines our ingredient list and the conservation of mass tells us how big a cake we'll bake.

The law of definite proportions tells us that our ingredients have a specific chemical formula; for example, H_2O is the chemical formula for water. In essence, the chemical formula consists of a list of the elements that built the substance and the numbers of atoms of each that were required. There are subtleties, however, in the arrangement of elements, just as there are subtleties in the arrangement of elements in the periodic table. More information can be gleaned from the chemical formula than just the number and type of components.

For instance, the formula that we use for table salt, NaCl, always appears in the same order, sodium first and then chlorine. This order is based on a general agreement among chemists that the positive ion of an ionic compound should be named first. Because of the tendency of metal ions to form positive ions, metals are generally named first, followed by the nonmetal. It has also become standard practice to place the center element of a covalently bonded group at the head of the group. Thus ammonia—which has three hydrogens bonded via covalent bonds to a central nitrogen—has the formula NH_3. Carbon dioxide, whose formula is CO_2, has a central carbon with oxygens on either side. Looking at the formula, we know there are two oxygen nuclei involved because of the subscript two on the oxygen.

Moreover, the order of the elements in a chemical compound is important; thus, CH_3CH_2OH is distinguished from CH_3OCH_3. Both substances have two carbon nuclei, six hydrogen nuclei, and one oxygen, but the first material is ethyl alcohol, sometimes called grain alcohol, and the other is dimethyl ether, which has decidedly different properties. Compounds that have the same number and type of elements but arranged in a different order are called *isomers*.

There are the three famous isomers: fulminic acid, cyanic acid, and isocyanic acid. Fulminic acid, HONC, is used to make the explosives that share their name with the verb *to fulminate*, meaning "to verbally rage." Cyanic acid has the formula HOCN and is used to make poisonous cyanates. Isocyanic acid, HCNO, is less familiar because it calmly goes about its business as a starting material for making organic compounds and doesn't explode or poison you outright.

The law of definite proportions states simply that the formula for any one material is set and invariable. Any change to the chemical formula

results in a new material with new properties (just as altering the ingredients in a batter can mean the difference between a layer cake and a pancake). When there is a formula-altering reaction, the recipe is given by a chemical equation. By convention, chemists place the beginning materials, the reactants, on the left, followed by an arrow, and the ending materials, the products, on the right. For instance,

$$C + O_2 \rightarrow CO_2$$

which means carbon plus oxygen will yield carbon dioxide.

There is a difference, however, between cookbook recipes and chemical reactions: not all chemical reactions go to completion. For many chemical reactions, a certain amount of the reactants remain in their unreacted state, like pudding that is imperfectly set. A pudding that is not properly set will have some portion that is pudding and some portion that is liquid. Most chemical reactions are like imperfect puddings: some portion of the reactants turn into products, but some other portion does not. The conservation of mass holds just as true for these not-perfect-pudding reactions, but for the sake of illustration, we will initially assume that all reactions go to completion; that is, we will assume all of the reactants turn into product, a pudding perfectly set. When a reaction goes to completion the amount of product is wholly predictable from the conservation of mass: if two pounds of reactants go into the recipe, two pounds of product come out.

The conservation of mass may seem like a statement of the obvious. If a chemical reaction occurs, such as the reaction in the above demonstration, we feel intuitively that the mass after the reaction should be the same as the mass before the reaction. The proof, however, is not always obvious. If a modern cook weighs all the ingredients for a pancake before cooking it and then weighs the pancake afterward, the cook is not surprised to find the mass is less. Bubbles can be seen during pancake cooking, an indication that a gas-phase product is escaping, and the pancake after cooking has a drier consistency, an indication water has been lost. But if this cook had been born at a time before the composition of air and water vapor were clearly understood, then the cook would know only that the pancake weighed less and would not necessarily conclude

that mass had been conserved. One cook who was not fooled, however, was the chemist Lavoisier.

We met Lavoisier earlier, in conjunction with our discussion of redox reactions. We now add that Lavoisier was also instrumental in establishing the validity of the principle of the conservation of mass. He used the reaction

$$C + O_2 \rightarrow CO_2$$

but in true bourgeois style, he employed a diamond for his source of carbon and used sunlight focused through a huge lens to provide heat for the reaction. He carried out the experiment in a sealed vessel and showed by the inrush of air after the reaction that part of the air had been consumed. Before breaking open the vessel, however, he weighed it and showed that it weighed the same after the diamond-burning reaction as it weighed before: mass had been conserved.

Before Lavoisier's work could be translated into modern chemical reactions, several other important advances had to be made. Prominent among these was John Dalton's description of atoms. Though the idea had been kicking around since at least the time of the ancient Greek philosophers, Dalton took the important step of proposing that the atoms of different elements were different, and one of the characteristics that made them different was mass. Each element had atoms of different characteristic mass. This notion cleared the way for assigning a mass—an atomic mass—to each of the elements. In the above reaction between diamond and oxygen, the chemical formulas imply that a molecule of carbon dioxide forms when two oxygen atoms combine with one carbon atom. Dalton's atoms also assure us of the conservation of mass: there is one carbon and two oxygens on the left, and there is one carbon and two oxygens on the right—the same number of atoms, with the same mass, just arranged differently. If the number and type of atoms is the same on the left as on the right—the reaction is said to be *balanced*.

The reaction might be compared to the work of a florist. If a florist were to put a vase on the scale and a bunch of flowers beside the vase, we would not expect the scale's reading to change after the florist had picked up all the flowers and arranged them in the vase. Chemical reactions are

like new floral arrangements—not new flowers, just new arrangements—so the mass is the same before and after the rearrangement of the chemical reaction.

Balanced chemical reactions convey essential information concerning how much reactant we will need to produce a given amount of product, or, conversely, how much product will be produced for a given amount of reactant. This type of information is important when one is dealing with reactions in beakers on benches. But when dealing with tank loads of chemicals in silo-sized reactors, this type of information is critical. Fortunately, chemical industries have chemists devoted to the study of the best ways of handling all sorts of tricky chemical situations from large quantities of heat, to large quantities of materials, to acid, to base, to gas-phase reactions: they are the intrepid chemical engineers.

For Example: Engineering—Chemical, That Is

When people think of the chemical industry, they may think of the manufacturer of pesticides, pharmaceuticals, solvents, lubricants, or other relatively complex processes. Many people are surprised to learn that the vast bulk of the chemical industry revolves around the manufacture of four relatively simple chemicals: sulfuric acid, phosphoric acid, sodium hydroxide, and our old friend, sodium chloride.

Of these, sulfuric acid and its precursors are the largest volume chemicals produced in the world. Sulfuric acid has a syrupy appearance in its concentrated form (known as *oleum*) and was once known as *oil of vitriol* because of this appearance. Sulfuric acid is a highly corrosive acid that will attack plastic, wood, skin, mucous membrane, and most metals in its concentrated form, but it can be stored in glass. Very dilute sulfuric acid (a small amount of acid mixed with a large amount of water) is the effective ingredient in the aquarium pH-lowering solution suggested for purchase in the "Shopping List and Solutions." Sulfuric acid in a more con-

centrated form is the acid solution used in automobile lead-acid batteries. Nowadays automobile batteries are sealed in such a way that the average automobile user has no reason to check or fill the battery with fluid. A typical driver can enjoy an extensive motoring career without ever encountering sulfuric acid from a battery. But for those who have had contact with battery acid, the contact is memorable. The sensation to the skin is immediate and the effect on clothing is profound and irreversible.

The use of sulfuric acid in automobile batteries, however, does not account for its production in such vast quantities. The largest single use for sulfuric acid is fertilizers, especially a sulfuric-acid/phosphate-containing-rock mixture called superphosphate. Because phosphorus is a major mineral nutrient needed by plants and because phosphorus is a major component of bones, bone meal was once a commonly used fertilizer. Today, however, phosphate rock, treated with sulfuric acid to become more soluble, can be used, too.

Sodium hydroxide or lye, NaOH, is used in the production of soap, textiles, petroleum products, dye, detergent, and paper. Sodium hydroxide is produced by running an electric current through a mixture of water and NaCl (table salt). The balanced equation is straightforward:

$$2\ H_2O + 2\ NaCl \rightarrow 2\ NaOH + Cl_2 + H_2$$

The number in front of the formula for water and also in front of the formula for table salt indicates the number of units of each that enter into the reaction. Two water molecules react with two units of sodium chloride to form one unit of sodium hydroxide, one molecule of chlorine gas, Cl_2, and one molecule of hydrogen gas, H_2. In other words, if we were to write each reactant individually, the reaction would be

$$H_2O + H_2O + NaCl + NaCl \rightarrow NaOH + NaOH + Cl_2 + H_2$$

The tally of hydrogen before the reaction is two from each water, or four hydrogens. The total of hydrogen after the reaction is two from H_2 plus one from each NaOH, or four hydrogens. Thus we have the same amount of hydrogen before and after reaction but found in different compounds. The hydrogen is balanced. The tally of oxygen before the reaction is one

from each water, or two oxygens; the total oxygens after the reaction is one from each NaOH, or two oxygens. The oxygen is balanced. The tally of sodium, Na, before the reaction is one from each NaCl; the total for sodium after the reaction is one from each NaOH. The sodium is balanced. The total of chlorine is one from each NaCl before the reaction and two from Cl_2 after the reaction.

For the chemical engineer, however, the problem with this particular method for producing NaOH is not balancing the reaction but dealing with the by-products. The by-products of this reaction, Cl_2 and H_2, are both gases under normal conditions, and gases occupy more space, pound per pound, than their solid counterpart. The production of gaseous by-products was the basis of the bottle rocket demonstration. The baking soda reacted with the vinegar, creating a carbon dioxide gas that expanded to occupy a greater volume than the reactants and forced the cork to pop. For every ton of sodium hydroxide produced, there are about one and three-quarters tons of gas produced. For every cubic foot of sodium hydroxide, NaOH, produced, about two thousand cubic feet of gases are generated. This volume difference would be like a seventeen-inch television set swelling up to fill two rooms of a house. That's a lot of gas and it could cause a very big pop. Thus containment, ventilation, and emissions pose major challenges for those in the chemical-producing industries.

But just as an underestimation of such problems could cause a chemical engineer's career to falter, so would an overestimation that caused unnecessary expenditure. Therefore, the chemical engineer must also be aware that an estimate, such as the one given above, is based on the assumption that each molecule of gas occupies a volume as though it were all alone in the world. In actuality, there are attractions and repulsions between the molecules. The attractions between molecules are why gases can be made to condense to liquids. The repulsions between molecules are what make materials more and more difficult to compact as the volume becomes smaller and smaller. These attractions and repulsions, collectively called the *intermolecular forces*, have to be taken into account by the chemical engineer. These intermolecular forces are also the basis for many other intriguing observed properties of materials, which is what we explore next.

Demonstration 8: Layer upon Layer

Now if she meet a man—suppose our hero,
With whom her chemistry shall war yet mix,
As if she were her Borgia to his Nero,
'Twill look like one of Satan's little tricks!
—Edgar Lee Masters, *Spoon River Anthology,*
ca. 1920

After putting on safety glasses, take a small clear glass and pour in glycerin (suggested for purchase in the "Shopping List and Solutions") until the glass is about an inch (2.5 centimeters) full. Take some water dyed with food coloring and gently pour about the same height onto the glycerin. You should observe two distinct layers in the glass.

Add a layer of canola oil to this and observe the three distinct layers. Stir the mixture. The colored water will mix with the glycerin, but the canola oil will still settle into a separate layer once agitation has ceased. It may take several minutes for the layers to separate.

Add a layer of liquid soap to the solution and watch it settle between the glycerin-water layer and the canola-oil layer. Now, when the combined layers are mixed (gently so as not to cause bubbles), the soap will cause the canola oil to blend with the glycerin. The result is a uniform

mixture. The mixture may eventually reseparate into different layers, but it takes longer than when the detergent wasn't present.

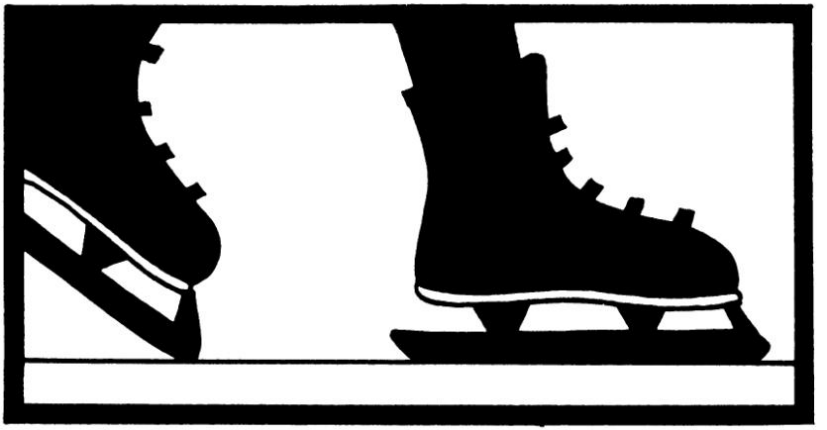
The solutions initially separated because of a difference in *intermolecular attraction*, a type of *intermolecular force*. These attractions occur *between* molecules, as distinguished from *intra*molecular forces—chemical bonds—which bind the nuclei *within* a molecule.

The difference is one of book bindings versus sticky notes. Book bindings are like chemical bonds. Book bindings are meant to be permanent. The glue that is used to hold the pages together is not easily separated. Once the book binding is separated, you have a stack of pages; you no longer have a book. Sticky notes are like intermolecular attractions. Sticky notes are meant to be temporarily stuck to a surface and easily freed and moved. If you stick a sticky note to a book and then remove it, you still have an intact book and sticky note. Sticky notes stick, by the way, because of intermolecular attractions.

We have already encountered the effects of intermolecular forces in our discussion of precipitates and solubility. Here the intermolecular attractions between water molecules are instrumental in the ion-cage formation that allows some salts to go into aqueous solution. The glycerin molecule shares some similarities with water, but the individual glycerin molecules are still strongly attracted to each other and admit water to their ranks only when there is sufficient provocation. In this demonstration, the provocation occurs in the form of stirring, but no amount of stirring will force the canola oil into the glycerin solution until soap is added.

Soap is the grand diplomat of intermolecular forces. Soap gets along with and experiences attractions to both water and oil, which is the basis for its efficacy as a cleaning agent. Soap combines with grease, oil, and dirt, and then with water, which allows the dirt to be washed away with the water.

But soaplike molecules, molecules that have an attraction to both waterlike substances and oil-like substances, have a much more important role than cleaning skin: they form the walls of the very cells of the skin. Intermolecular forces may at first seem relatively unimportant when compared to chemical bonds, but while chemical bonds determine the structure of a single molecule, it is intermolecular forces that will determine how this molecule will behave around other molecules. And the behavior of molecules, as observed in the properties of molecular substances and mixtures, is what life is all about.



CHAPTER 8

Slipping and Sliding, Intermolecularly

(H)e found himself at first gazing at the portrait with a feeling of almost scientific interest. That such a change should have taken place was incredible to him. And yet it was a fact. Was there some subtle affinity between the chemical atoms, that shaped themselves into form and colour on the canvas, and the soul that was within him?
—Oscar Wilde, *The Picture of Dorian Gray*, ca. 1890

Intermolecular forces play an important role in chemistry. Intermolecular forces are the attractions and repulsions felt *between* atoms and molecules and differ from chemical bonds. Breaking a chemical bond creates a new material that reacts differently with other chemicals. Breaking an intermolecular attraction does not change the chemical formula or chemical reactivity. But intermolecular forces can determine how quickly a reaction will occur—or if it can ever occur. And intermolecular forces determine whether a material will be a liquid, a solid, or a gas at a given temperature—an important consideration for those of us who like to drink, eat, and breathe.

In the late 1800s and early 1900s, scientists were still struggling to understand intermolecular forces, so it is doubtful that Oscar Wilde had a clear picture of intermolecular forces in mind when he wrote of the "subtle affinity" between chemical atoms in *The Picture of Dorian Gray.* Nonetheless, his description of "subtle affinity" is quite apt. Intermolecular forces are complex, consisting of attractions as well as repulsions. Intermolecular *attractions* are those between water molecules that allow water to condense once it has been sufficiently cooled—and intermolecular *repulsions* are what make water feel like a solid mass when it is forcefully encountered. (Have you ever been knocked over by a wave?) If it were not for intermolecular attractions, our bodies would vaporize into gases, and if it were not for intermolecular repulsions, we would collapse into unimpressive puddles.

We begin with intermolecular repulsions. In the "Water Witch" demonstration presented earlier, we saw a thin stream of water being attracted to a plastic spoon with an acquired static charge. Similarily, if a piece of adhesive tape is yanked rapidly from a roll, it too will attract a thin stream of water. However, if two pieces are yanked from the roll and dangled from the fingers, these pieces will attempt to escape from each other. They acquired the same charge when they were removed from the roll of tape and are repelled because like charges repel. When two atoms or molecules are attracted to each other, they will come only so close and no closer. Electrons have intimacy issues. When two distinct atoms or molecules come too close together, the repulsion between the electron clouds will keep them apart.

Intermolecular attractions are also electrical in nature, but the situation here can be more complicated because intermolecular attractions can depend more on the shape of the molecule, a shape that is constantly undergoing slight changes. Molecules are in constant motion—vibrating, rotating, and flying off in all directions. The problem is one of catching a boomerang as opposed to a baseball. Moreover, molecules do not move at the same speed but in a range of speeds. They are not all rotating or vibrating at the same frequency but with a range of frequencies.

These variables make a straightforward calculation of the magnitude of the intermolecular attractions in any one situation virtually impossible. But despite their individuality, molecules do stick together. And under-

standing this stickiness is critical to the understanding of the behavior of materials. As a start to unraveling this sticky business, we identify three ways molecules can be attracted to each other: positive-ion-to-negative-ion attraction, dipole-to-dipole attraction, and a newcomer on our horizon: dispersion forces.

Positive-ion-to-negative-ion attractions are straightforward and strong interactions: so strong, in fact, that they tend to dominate when they are present. As we pointed out in our discussion of precipitation, when opposite ions find each other, they can form an ionic bond and come out of solution. Ionic attractions do not, however, always prevail. Water molecules can keep ions apart by forming cages around the ions. These water cages are the result of dipole-to-dipole and dipole-to-ion attractions.

To better understand dipoles, recall that earlier we explained that electrons will tend to associate themselves with the more electronegative entity in a bonding situation and that this can cause an unequal distribution of electrons. One end of a bond is more negative or more positive than the other. When this is the situation, we say that the bond is *polar*. When polar bonds are directly opposite from each other, they can offset, or cancel, each other, and though the bonds may be polar, there is no polarity for the molecule as a whole. This is the case with carbon dioxide, CO_2. In carbon dioxide, the electron density is shifted toward the more electronegative oxygens, but carbon is seated in the center of two oxygens, as OCO, so the tug-of-war is a stalemate.

Water, however, is a different story. As noted earlier, the water molecule, H_2O, is shaped in a **V** with the oxygen in the middle and the hydrogens at the tips of the **V**. As a result, water is a polar molecule. Oxygen is more electronegative than hydrogen, so the electrons gravitate toward the oxygen end and away from the hydrogen end. Water is said to have a *net dipole moment*, meaning that when all the forces have balanced out, one end is more negative than the other.

As we've seen, polar molecules interact with each other somewhat as bar magnets do, and the interaction is termed a *dipole* interaction. In a dipole interaction, the positive end of one polar molecule lines up with the negative end of another, as the north pole of one bar magnet will line up with the south pole of another—but these magnets are rotating, vibrating, and flying in all directions.

Earlier we were interested in how this interaction helped to build

cages around ions to keep them in solution, but the interaction is important in the absence of ions, too. Dipole interactions serve to hold water together in the condensed state. Water is especially adept at dissolving and condensing because water molecules are small and able to experience yet another type of intermolecular attraction. A strong dipole/dipole attraction called a *hydrogen bond.*

A hydrogen bond is not a chemical bond in the sense that breaking a chemical bond causes a change in the molecular formula. So the term hydrogen *bond* is a bit of a misnomer, but a hydrogen bond is a particularly strong attraction. Hydrogen bonds occur when a hydrogen is *chemically* bonded to a very electronegative element, such as oxygen, fluorine, or nitrogen, and attracted—via intermolecular attraction—to an electronegative element on another molecule. The situation is shown in figure 1.8.1. Hydrogen bonding is also an especially important factor in the behavior of water because water has two opportunities for the formation of hydrogen bonds: it has two hydrogens chemically bonded to the oxygen in the molecule.

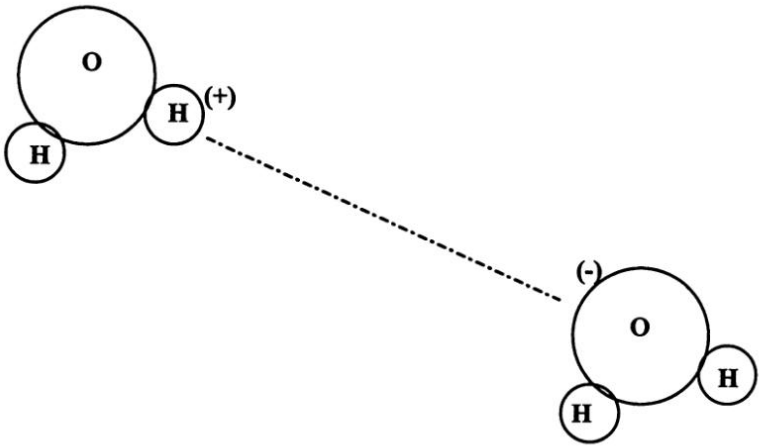


Figure 1.8.1. The attraction between the slightly positive hydrogen end of one water molecule and the slightly negative oxygen end of another is called hydrogen bonding. Hydrogen bonding is an intermolecular attraction, not a chemical bond. To experience hydrogen bonding, the hydrogen must be chemically bonded to a highly electronegative element such as oxygen, nitrogen, or fluorine.

Because it can form two hydrogen bonds, water is very talented at forming cages and dissolving ions. Because of this special ability of water to dissolve, water is the vehicle for many key chemical reactions, including those responsible for life. Many liquids we deal with on a daily basis are either water or water solutions.

Another common liquid is liquid oil, either in the form of cooking oil or gasoline or other petroleum product. Not only are these materials definitely not water, but they do not mix very well with water. Oils and petroleum products are termed *hydrocarbons* because they are composed mainly of hydrogen on chains of carbon, and their intermolecular attractions are different from those of water.

At first it might be thought that the bonds in hydrocarbons would be polar, too. Carbon and hydrogen aren't very close to each other on the periodic table and therefore should have a significant difference in electronegativity. But as you will recall, hydrogen does not follow the general trend—it is too small to carry much of a negative charge—so hydrogen is actually very close to carbon in electronegativity. In addition, the hydrogens can be distributed evenly around carbon in hydrocarbons, so the slight polarity of the carbon-hydrogen bond tends to be balanced out. But hydrocarbons obviously do form liquids, and even solids called waxes, so there must be some form of intermolecular attraction.

Condensation of hydrocarbons can be better understood when it is realized that it is usually the larger hydrocarbons that condense more readily. Methane, composed of one carbon and four hydrogens, is a gas (swamp gas to be exact) at normal temperatures and pressures. Octane, composed of eight carbons in a chain and sixteen hydrogens, is a liquid under normal conditions. The long-chain hydrocarbons are more apt to be liquids at room temperature and pressure because the long chains become intertwined. Tangled up, at close range, even the weak attractions between the slightly polar bonds can contribute to the stickiness, too.

On the other hand, nitrogen gas, N_2, can have no difference in electronegativity because two identical atoms are joined, so the bond cannot be inherently polar. And there is no opportunity for tangling because there are no chains of nitrogen, just two-atom pairs. Yet liquid nitrogen exists, and it is common enough to be used for wart removal. What holds nitrogen molecules together in liquid nitrogen? An attraction called a *dis-*

persion force or an *induced dipole attraction* or a *London force*, named after the scientist Fritz London, who described it.

Whichever name it is given, the origin of this attraction is the mushy electron cloud that surrounds the nitrogen molecule. Because the electrons can be considered mobile in the electron cloud, they can be pictured as congregating momentarily at one end of the molecule or the other. This momentary uneven distribution of electrons is termed a *temporary dipole*, but it acts in the same manner as a permanent dipole. It is attracted to other dipoles, temporary or otherwise. The redistribution of electrons may be spontaneous, or if there is an ion or a molecule with a permanent dipole in the vicinity, this species might induce a momentary dipole, too. This situation is shown in figure 1.8.2.

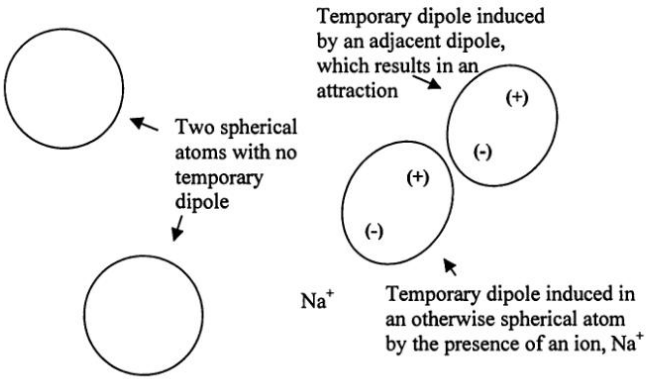


Figure 1.8.2. The sodium ion is inducing a temporary dipole in an atom with a normally spherical electron cloud. The induced dipole is causing another atom to have a momentary dipole. These temporary dipole attractions are sufficient to cause even noble gases to condense at low temperatures.

Just as the temporarily charged spoon in the "Water Witch" demonstration caused the water to bend toward it, an induced dipole in one species can induce a dipole in another. The dispersion forces aren't as effective over distance as dipole attractions, but they are sufficient to account for the existence of liquid helium as well as liquid nitrogen and liquid oxygen.

Helium, however, does not condense nearly as readily as water because helium has only one intermolecular attraction at work. Water has an accumulation of intermolecular attractions. In saltwater there can be all permutations of interactions: dipole/dipole, dispersion/dispersion,

ion/ion, dipole/dispersion, dipole/ion, and ion/dispersion. So the situation, as we noted, is quite complicated. Added to this confusion is the fact that the attractions fall off with distance, which is always changing because of the many modes of motion of the molecules, and the situation becomes quite desperate.

Fortunately, we do not have to dissect each interaction to understand the net effect—one that manifests itself in several well-known phenomena such as friction, cohesion, adhesion, capillary action, solubility, and the action of soap.

Frictional forces are perhaps the most complex and bedeviling forces we have to deal with on a day-to-day basis. Frictional forces arise from two sources—physical barriers to motion and intermolecular forces—and for this reason can never be completely defeated. The physical barriers to motion are the microscopic ridges and rough spots that are always found if you look closely enough. When an attempt is made to drag one material past another, the rough spots of one side can catch in the rough spots of the other side and cause friction, or resistance to motion. Removing the rough spots helps, but only to a point. When materials become very smooth, there is greater opportunity for intermolecular attractions.

Grease sometimes helps reduce friction because grease forms a film that keeps the moving materials apart. The friction within the grease, as it is pulled one way or the other, eventually causes the grease to decompose, which is why bearing grease in a machine must be periodically replaced, as well as oil and lubricants in automobiles.

Cohesion is the tendency of like molecules to stick to one another. For instance, oil likes to stay with oil and water with water, which is why they separate when allowed to stand. Surface tension, manifest in the curved rise of water over the top of a glass or spoon, is the result of cohesion. Water, because of its special propensity to form hydrogen bonds, displays a good deal of cohesion and therefore surface tension. The surface tension of ponds is strong enough to support a world of water-walking creatures.

Adhesion, as in adhesive tape, is the tendency of different materials to stick together. Adhesion is a major factor responsible for surface waves in bodies of water. Although the physics is a complex trade-off involving many forces, waves begin by water sticking to the wind blowing past. The idea of pouring oil on troubled waters, often used as a metaphor for a

calming effect, has a physical basis and was actually used with limited success by whaling vessels in the past. Oil will disrupt the adhesion between water and wind and can calm some waves caused by wind. Of course, large waves that have already formed and are being carried forward by their own momentum will not be affected. So don't take the time to look for the bottle of salad oil when the tsunami is coming—just run.

There is a good deal of adhesion between molecules with similar structure, such as water and rubbing alcohol, and water and grain alcohol, the structures of which are shown in figure 1.8.3.

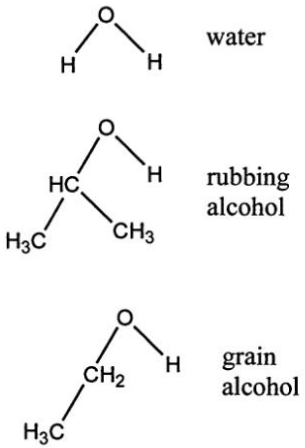


Figure 1.8.3. A comparison of the structure of rubbing alcohol, grain alcohol, and water.

The mutual solubility of water and alcohol is the reason a highball doesn't normally separate into layers. Some syrups, such as grenadine, may take longer to mix because of the intermolecular attractions within the syrup itself. But if one waits long enough, the syrups in fancy layered drinks eventually distribute throughout the drink. But the point is usually drinking, not waiting, so the effect may go unobserved.

Adhesion is the basis for *capillary action*, or the tendency of liquids to travel against the pull of gravity. The molecules of the material traveling upward have a greater attraction for the surface on which they move up than the bulk of the liquid being pulled down by gravity. Paper towels work on the principle of capillary action, which is why paper towels work better on some liquids than others. Try soaking up water versus glycerol or cooking oil by making a puddle of each and dipping in the corner of a paper towel. The water travels up the paper towel much more quickly than the oil does. Water is more attracted to the molecules of the paper towel. Oil molecules are more attracted to each other.

Adhesion is also the basis for the adage *like dissolves like*. "Like dissolves like" means oil-like liquids dissolve oil-like liquids and waterlike liquids dissolve waterlike liquids. "Like dissolving like" explains why

adding an antistatic dryer sheet to the water when soaking a pot with baked-on grease will help to remove the greasy material. These sheets add a very thin coating of oil to the clothing being dried, which prevents friction from stripping off electrons and causing a static charge. This same nonpolar oil can combine with the nonpolar baked-on material and help lift it free of the pot. In the same manner, cooking oil can help to remove bandages from skin without exfoliating the skin. The oil combines with the oil-like materials in the glue. "Like dissolving like" also explains the action of soap.

Soaps are made from long hydrocarbon chains with an oxygen-containing group attached at one end. The end with the oxygen-containing group is soluble in water because that end is polar and able to form hydrogen bonds. Other hydrocarbons, like grease, for instance, are soluble in the hydrocarbon end of the soap and are carried into water solution by the water-soluble end. This same type of molecule, one that is water soluble on one end and grease soluble on the other, is vital to the structure of cells and other life-giving chemistry. For instance, the body needs many nonpolar substances to be transported through water-based blood, and molecules that straddle both worlds—polar and nonpolar—aid in this transportation. Still unimpressed with the importance of intermolecular forces? Then consider this: without intermolecular forces, there could be no flush toilets.

For Example: The Physics of the Flush Toilet

Flush toilets are easily one of the most significant advances of civilization. Not only do they remove an unsightly and potentially dangerous breeding ground for bacteria, they do so in such a civilized manner: waste is removed quickly and efficiently, and the odors that would be associated with the stored waste are cleverly kept from us by a wall of water. The flush toilet pushes waste up and over an inverted-U-shaped

hill and blocks the entrance with water so that sewer gases will not find their way back into the room. None of this would be possible if it were not for intermolecular forces.

The flushing action of the toilet commences when the bowl is filled from a reservoir until the water level tops the inverted-U-shaped trap and starts to spill over the other side. Once water starts to flow over the side of the trap, it pulls the rest of the water with it, as a chain would pull the links that are attached to it down to a lower level. With water, intermolecular attractions form the chain that pulls the water molecules one after another. This siphoning action has to initiate quickly so that water will surge over the trap and make a moving seal.

The difference in pressure between the filled bowl and the empty pipe shoves the water over the top, but it is the attractions between the water molecules that keep the flow moving along and continues through siphoning action to drain the bowl. That intermolecular attractions are involved in the flush toilet can be confirmed with a thought experiment: can you imagine a toilet with sand as the working fluid? This medium might be a kitty's dream, but it won't work with a flush! Siphon action depends on one molecule dragging along another once it is over the hump.

Water also works well for waste disposal because so many materials dissolve in water. But as we all know, there is a big difference between toilet water—as in water in the toilet—and toilet water, as in eau de toilet. The properties of the solution depend on the solvent, the solute, and the amount of solute it contains. Discussion of these important parameters is where we are headed next.

Demonstration 9: Concentrating on Color, Salty Dog

Like a chemist, Napoleon considered all Europe to be material for his experiments. But, in due course, this material reacted against him.

—Frederic Bastiat, *The Law*, ca. 1870

Put on your safety glasses. Pour one-half cup of water (120 milliliters) into each of two clear plastic cups. Add a plastic teaspoon (5 milliliters) of copper sulfate solution (prepared as outlined in the "Shopping List and Solutions") to one cup and two plastic teaspoons (10 milliliters) of copper sulfate solution to the other cup. Stir the two glasses and compare the intensity of the color by looking down from the top of the two glasses while they are on a white piece of paper. The color of the glass with one teaspoon of copper sulfate solution (the less-concentrated solution) should appear several shades lighter in color than the glass with two added teaspoons of solution. Color is a property influenced by concentration.

Solubility is also influenced by concentration as we discussed in conjunction with precipitation. A few pinches of baking soda go into solution readily, but not much more than that. Now try the following. Make a sat-

urated baking soda solution by adding four tablespoons (60 milliliters) of baking soda to two cups (480 milliliters) of water. Stir the solution and allow it to settle for at least four minutes. Carefully decant the liquid over the undissolved baking soda into a clean glass, making certain no solid is transferred with the liquid. Take an identical clean glass and fill it with water to the same height as the baking soda–water glass. When you have two glasses with an equal amount of liquid, add a level quarter teaspoon (1 milliliter) of table salt to each glass and stir. While stirring, keep adding the same amount of table salt, in small increments (eighth teaspoon; half milliliter), to each of the glasses until one of the solutions turns cloudy. The cloudy solution will be the one with the baking soda. It turns cloudy because the baking soda is crowded out of solution by table salt. The other glass, the one with just water and added salt, should be completely clear. This technique, called *salting out*, is used industrially to move materials in and out of solution. Salting out was also used historically in the preparation of solid soap. The soap is forced out of solution by adding large amounts of salt. This effect can be demonstrated by pouring an eighth- to quarter-inch layer of liquid soap into a glass and sprinkling table salt on top. In a few minutes a nice, gooey, gelatinous solid will precipitate out.

CHAPTER 9

Concentration—On Being Alone Together

There was no trace then of the horror which I had myself felt . . . but his face showed rather the quiet and interested composure of the chemist who sees the crystals falling into position from his oversaturated solution.

—Arthur Conan Doyle, *Valley of Fear*, 1915

Chemistry is change—ore to metal, batter to bread, acid to salt—and a good deal of this change, this chemistry, occurs in solutions: ponds, cells, oceans, sauces, melts, and mixtures. Solutions are uniform mixtures, such as the uniform mixture of salt and water we call saltwater. Solutions are particularly conducive to chemical reactions because they provide the opportunity for molecules to come together and the mobility for the reaction to take place. The tablets that are dropped into water to make a fizzing tonic are able to make a fizz because they contain citric acid and baking soda. But even though the citric acid and the baking soda are present in the tablet before it is dropped into water, the dry tablet does not fizz. It will not fizz until the ingredients are in a solution. In solution, the acid and base have mobility and can react. Solutions provide what's needed for chemical reaction: mobility and opportunity.

Successful commercial and intellectual enterprises have long understood the need for mobility and opportunity for productive interaction among specialists. At conferences, people of like mind are brought together in high concentration. But as any successful conference organizer knows, the real chemistry doesn't happen when everyone is stationed in their seats listening to presentations—it happens at the wine-and-cheese tasting when people have the mobility to seek each other out. A solution is the chemical equivalent of a conference: a concentration of reactants with the mobility that they need to combine. A chemist, not unlike a conference organizer, understands the importance of controlled concentrations and orchestrates them when designing reactions.

Though water solutions, or *aqueous solutions* as they are known to the chemist, are probably the most familiar solutions, there are many other kinds of solutions. There are solid solutions such as metal alloys, although not all alloys form truly homogenous blends. Bronze is an alloy of copper and tin, brass is an alloy of copper and zinc, and steel is an alloy of iron and carbon.

There are also gas-phase solutions. The air we breathe is a solution of several gases. Nitrogen is present in the greatest proportion, about 70 percent, but oxygen is also mixed in, as well as argon, carbon dioxide, and usually water. The amount of water in air can vary from none to 100 percent humidity, while the amounts of nitrogen, oxygen, and argon stay fairly fixed. The presence of argon in the solution of gases we breathe may be a little surprising at first. But recall from our discussion of the periodic table that the lighter elements were those first produced in the cosmic porridge from which our planet emerged. Reactive elements were trapped in compounds; unreactive elements floated away. Most of the helium and neon were light enough to escape Earth's atmosphere, which left argon to represent the noble gases. Other gas solutions include carbonated soda, a solution of a gas (carbon dioxide) in water, and pond water, a solution of oxygen in water—which is how fish breathe.

To carry out metabolic functions, the body depends on the solubility of gases in blood, which, in turn, depends on the pressure *of that gas* and not any other. So the solubility of oxygen in blood depends on the pressure of oxygen in the inhaled air, and the solubility of oxygen in the cells depends on the pressure of oxygen in the cell. As metabolism takes place in the cell, oxygen is used up and carbon dioxide is produced. When

oxygen rich blood reaches the cell, oxygen passes from the blood—where the pressure is relatively high—to the cell, where it is relatively low. Carbon dioxide passes from the cell where its pressure is high to the blood where its pressure is low.

Because nitrogen is also always present in the air we breathe, there is always some amount of dissolved nitrogen in our blood, too. Divers who descend deep into the ocean need pressurized air tanks to deliver their breathing air because the pressure of the ocean is pushing in on their lungs. The pressure inside the tanks must be greater than the external pressure if it is to enter the lungs. If normal atmospheric air is used to fill the tanks, the blood being restocked at the lungs will be exposed to nitrogen at higher pressures, and there will be more nitrogen dissolving in the blood. The extra nitrogen in the blood is not necessarily a problem, unless the diver comes up too quickly. If the diver does ascend too rapidly, the extra nitrogen that was dissolved in the blood starts to come out of solution and can form bubbles before the body has a chance to exhale it. This condition can cause such severe pain that sufferers have been known to bend over in pain, hence the name: the bends.

A preventative measure often employed is to substitute helium for nitrogen in the breathing air mixture. Helium is not as soluble as nitrogen in blood and therefore does not cause the same problem. On a completely different note, the strange, Donald Duck sound helium imparts to the voice is the result of the less dense helium, as opposed to air, passing through the larynx. There is no intoxication caused by helium, as sometimes thought, but inhaling pure helium can be dangerous. Someone inhaling pure helium is not inhaling oxygen and can pass out from lack of oxygen.

Solutions consist of two parts: the solvent and the solute (or solutes). The solvent is the component present in the majority, and the solute is the component present in the minority. In saltwater, the quintessential solution, water is the solvent and salt is the solute. The importance of concentration as a property of solutions can be understood by considering saltwater. Concentrated saltwater can be used to rinse the mouth, but only dilute saltwater can be used to rinse the eyes. You would not want to confuse the two. Concentration matters.

There are some common measures of concentration that have found their way into everyday use. The measure of the concentration of ethanol in solution in alcoholic beverages is called *proof*. Proof is two times the per-

centage of ethanol in solution, volume for volume. For example, a 76-proof whiskey is 38 percent alcohol. Legend has it that the term came from the fact that a mixture of about 50 percent ethanol (100 proof) and water will burn, proving it is good alcohol. Alcohol-water solutions have the interesting property that their volumes are not additive in all ratios. For instance, equal quantities of rubbing alcohol and water mixed together does not form a solution that is double the original quantity—a result of those attractive intermolecular forces we discussed in the last chapter. Alcohol has an OH group as part of its molecule, and this OH group is attracted to H_2O. A mixed group of single men and single women might be expected to take up less space than the separated groups for the same reason: attractive interactions.

Another common measure of concentration is humidity. Humidity is a measure of the amount of water in air, and relative humidity is the amount of water currently in the air compared to the maximum amount of water that the air could hold at that same temperature and pressure. When it comes to solutions of solids in water, such as saltwater or sugar water, the concentrations can be given in grams per milliliter, as they are in many common medicines. When it comes to chemical reactions, though, it is more meaningful to talk about molecules per liter than grams per liter. To understand why, consider the following two statements. Which is more useful for calculating staff requirements if the teacher/student ratio needs to be maintained at twenty to one?

There are 11,756 kilograms of students in the new freshman class.

or

There are 190 students in the new freshman class.

Chemists usually characterize the concentration of a solution by a measure of the number of molecules per volume rather than the number of grams per volume because reactions happen when one molecule reacts with one molecule, not when one gram reacts with one gram. The difficulty is that molecules are very small, and a good many of them are required to make up a measurable amount. For instance, it requires about a trillion trillion water molecules in the liquid state to fill a 240-milliliter (one-cup) container. Therefore, it is infinitely easier to speak of collections of molecules rather than individual molecules. The name that chemists agreed on for a collection of molecules is a *mole*, and a mole is like a dozen—only different.

A dozen indicates a number of things, such as, perhaps, twelve eggs. A gross indicates a number of things, 144 things. A mole also indicates a number of things: a mole is 6.023 hundred billion trillion things, an almost unimaginably huge number.

For instance, if molecules were as big as marbles, then a mole would cover the land area of the United States to a depth of four meters (about the height of the first story of a house). Cells in the human body are too small to be seen without a microscope, and so small that about one hundred trillion cells are crammed into one human body. But to assemble a mole of cells, you would need six billion people, the population of the entire Earth in 1995. A pretty big number.

It is necessary to use this large a measure when it comes to molecules because molecules are so small. A mole of eggs would be 6.023 hundred billion trillion eggs. That would make an overwhelming omelet, but it's really an underwhelming quantity of molecules. A mole of sucrose molecules is about the same amount as you'd typically find in a serving of a carbonated soft drink. A mole of solid is about a handful, and a mole of gas is about six gallons (twenty-two liters) under normal conditions of temperature and pressure (a little more than a bucket and a little less than a bushel). In the appendix, the mass given for each element can be interpreted as atomic mass units per atom (amu per atom) or grams per mole. This is not just a fortunate coincidence. The magnitude of an amu was chosen so that amu per particle would correlate with grams per mole.

Earlier we mentioned that a common measure of acidity is pH, which is a measure of the concentration of hydronium ions (H_3O^+, the acidic agent) in solution. Now we can be more specific: a solution with a tenth of a mole of hydronium ions per liter has a pH of 1. A solution with a hundredth of a mole of hydronium ions per liter has a pH of 2. Every time the concentration of hydronium ions decreases by a multiple of ten, the pH goes up by one unit.

Another measure related to concentration is density. Density is a measure of the total mass of material per unit volume. For solutions in which chemical reactions are ongoing, measuring the density can be a way of measuring the progress of the reaction. Mass has to be conserved in the course of the reaction, but the volume that the mass occupies can change considerably due to rearranging molecules and rearranging intermolecular forces. Such variations in density are evident in bodies of water, the human body, and another interesting body: the body of wine.

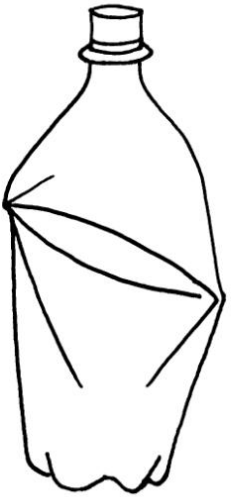
For Example: What Body, What Aroma, What Chemistry

The making of wine involves chemistry on many levels. For instance, winemakers and wine tasters rely on concentration properties to make and describe their . . . how shall we say . . . delicate, yet somewhat bold and enticing, product.

Professional wine tasters use a number of interesting terms such as *corky*, *buttery*, *chewy*, *fresh*, *fruity*, *honeyed*, *musty*, *round*, *complex*, *acid*, *thin*, *youthful*, *nutty*, *full*, or *zestful* to describe the attributes of wines, which include aroma, bouquet, nose, astringency, finish, texture, and body. It is this last attribute, body, that connects with the subject of this chapter: concentration. Body is the perceived density of the wine in the mouth and depends in good part on the amount of alcohol in the wine. Density, related to concentration, plays a vital part in wine making, too.

The *must* is the beginning mixture, the grape juice and crushed fruit ready to be fermented. Fermentation is the process wherein certain yeasts consume sugar and produce ethanol (alcohol) and carbon dioxide. Too little sugar leads to too little alcohol, and too much sugar changes the nature of the wine. The measured density of the *must* can be used to estimate the sugar content. From the measured sugar content, the alcohol content of the finished product can be predicted. On this basis, it can be decided if sugar needs to be added to the mixture. Because sugar is a reactant and used up, the density is also measured during the fermentation process to track how well fermentation is proceeding.

So, as we have seen, measurement and control of concentration is critical in chemistry as well as wine and good conferences. But the liquid state is not the only state in which chemistry is found. The gas phase supports interesting and important chemistry, too. There are bubbles in chemistry and there is chemistry in bubbles—in balloons and in the air we breathe.



Demonstration 10: The Soda Bottle Crunch

The great create an atmosphere which reacts badly upon the small. . . . It is like a chemical reagent. One day of it, like one drop of the other, will so affect and discolour the views . . . that it will thereafter remain forever dyed. A day of it to the untried mind is like opium to the untried body. A craving is set up which, if gratified, shall eternally result in dreams . . . until death and dissolution dissolve their power.

—Theodore Dreiser, *Sister Carrie*, ca. 1900

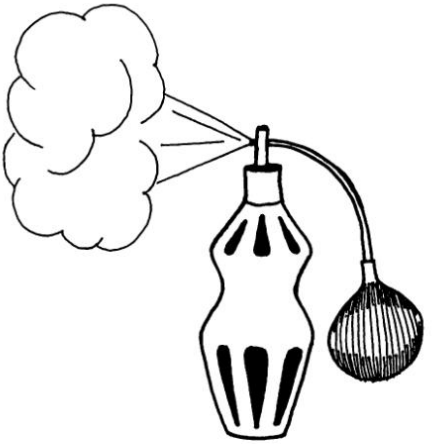
We are generally unaware of the atmosphere around us, just as fish are unaware of the sea. Nonetheless, we swim in an ocean of air and are occasionally reminded when a tree is knocked down by a storm or a tornado levels a town. This demonstration is also an effective reminder of the presence and power of the pressure of the atmosphere.

Have a sink or tub full of ice-cold water ready. Take a plastic soda bottle, fill it with hot tap water, and let the hot water sit in it for several seconds. Pour out the water and quickly screw on the cap. Put the capped

bottle in the cold water and wait a few seconds. The soda bottle should implode and crumble fairly impressively.

Heating a gas will cause it to expand, and cooling a gas will reduce the pressure it exerts. Hot tap water in the bottle heats the sides of the bottle, which, in turn, heats the air inside. When a cap is tightened on the bottle after heating it with hot water, the air trapped inside is warm air. When the bottle is plunged into the cold water, the gas inside is cooled, exerting less pressure on the inside wall than the atmosphere is exerting on the outside wall. The atmosphere can then push on the wall, and the result is a crushed soda bottle.

For more on properties of the gas phase—and what goes on in soda bottles—read on.



CHAPTER 10

It's a Gas

(C)hemistry, Madame Lefrançois . . . the composition of manures, the fermentation of liquids, the analysis of gases and the influence of miasmata—what, I put it to you, is all this, but chemistry pure and simple?
—Gustave Flaubert, *Madame Bovary*, 1857

Johannes van Helmont coined the word *gas* in the mid-1600s, probably derived from the word *chaos*.[1] If he did base his choice on *chaos*, it was an insightful selection, for more reasons than van Helmont knew. In van Helmont's day, most philosophers of nature thought of air as being one element, and many considered it to be a continuous fluid. Now we know that air is composed of at least three elements—nitrogen gas, oxygen gas, and argon gas—with various other compounds such as water and carbon dioxide mixed in. We also know that air is composed of molecules and atoms that are whizzing and whirling at tremendous speeds, crashing and careening. So Helmont was right about one thing. Molecules in the gas phase are caught in a continuous, crazy, chaotic dance. It is because of all this wonderful random cavorting of molecules that gases have the properties they have.

To describe the behavior of a sample of gas, we need four basic descriptors: the temperature of the gas, the pressure of the gas, the volume the gas occupies, and the amount of gas, usually given in the number of moles of whatever gases are present. For instance, if I told you I had a mole of a particular gas at 25°C (77°F) and this gas had a volume of 22.4 liters (about six gallons) at ambient pressure, you would have all the information you would need to predict the behavior of that gas should the pressure or temperature change. This information would be essential for our chemical engineer, our deep-sea diver, and even our winemaker. One of the products of fermentation is carbon dioxide, and if this gas is poorly contained or controlled, the corks that pop will be unintentional.

A gas can have considerable pressure. The pressure of the gases surrounding Earth, the atmosphere, crushed the soda bottle. The soda bottle could not be crushed when it was full, but was easily crushed when the air pressure was reduced on the inside. So why aren't we crushed when we exhale? Or for that matter why are we able to stand upright? The reason is that the pressure of the air is pushing in on us on all sides equally. If it were pushing only on the top of our heads, then yes, we would have a problem. The same principle applies to toothpaste tubes. You can squeeze out toothpaste only if you apply pressure to the middle or bottom. If you apply pressure equally to the bottom and the opening, the toothpaste stays in the tube.

The origin of the pressure exhibited by a gas, as well as the interplay among the parameters of pressure, temperature, volume, and the number of moles, is explained by a theory called the *kinetic molecular theory of gas*. The fundamental premise of this theory is that gases are made up of individual particles (hence *molecular*) and that these particles are in constant motion (hence *kinetic*, as in kinetic art). How this theory explains the properties of gases can be better understood if one compares the properties of gases to the properties of another collection of particles constantly in motion: a swarm of gnats.

Pressure is the cumulative force of molecules of a gas hitting an area, just as gnats randomly striking the walls of a container would exert a force on those walls. If the container were made smaller, then there would be an accompanying increase in the number of gnat-container collisions and an increase in gnat pressure. Likewise, all other things being equal (that is, the temperature and the amount of gas), the volume will directly

influence the pressure of a sample of gas. This effect can be demonstrated with the basting syringe mentioned in the "Shopping List and Solutions." Working with the syringe without the needle attached, you can draw a sample of air up into the syringe and then put a finger over the open end where the needle is normally attached. Applying pressure to the plunger will cause the volume to decrease. At first it is easy to compress the gas, but then it becomes more difficult. This difficulty is due to the fact that pressure and volume are inversely related: as the volume goes down, the pressure goes up, a relationship known as Boyle's law.[2]

Robert Boyle, an English natural philosopher in the 1600s, did not actually discover the relationship that has become known as Boyle's law—his investigations were to confirm observations reported by others—but he recognized the significance of the findings and enthusiastically brought them to the attention of his fellow scientists. And his enthusiasm was entirely justified. With this relationship, he removed chemistry from the realm of magic and established it as a quantitative science: a science of equations and measures and laws as firm as the laws of mathematics.

In fact, all the heroes of gas-phase chemistry seem to be a rather buoyant lot. The person most often cited, at least in the English-speaking world, as being associated with another important property of gases—that of the relationship between temperature and volume—was hot-air balloonist Jacques Charles.[3] This relationship is known as Charles's law. However, Charles, who did his studies on gases at the turn of the nineteenth century, was a better balloonist than an experimentalist. From his results, he could not draw any definite conclusions about the relationship between the volume and the temperature of a gas. The reason Charles's name became associated with the law is because the person who wrote the history books was English and thought Charles sounded like a good English name. The person who correctly described the relationship between temperature and volume was Joseph Louis Gay-Lussac, who was also born in the late 1700s.[4]

Gay-Lussac was a hot-air balloonist, too. In one instance, to gain altitude, he had to lighten the load of his hot-air balloon by tossing over a chair and some equipment. He later found out that bewildered peasants below had witnessed the fall of the chair from the sky and, lacking any other explanation, had been forced to credit the event to a divinity with a

sense of humor. Through more earthy experiments, Gay-Lussac established that the volume of a gas will expand as the temperature goes up and that it will expand in direct proportion; that is, if the temperature doubles, the volume will double, or if the temperature is halved, the volume is halved. It makes sense that a hot-air balloonist would be the one to describe this relationship because it is also the principle at work in hot-air balloons. Heated air expands, which means the same mass occupies a bigger volume, so the density goes down. Like a bubble in boiling water, the bubble of the hot-air balloon rises in the atmosphere.

It is difficult to demonstrate the expansion and contraction of gases with a convenient range of temperatures, that is, the freezing point of water to the boiling point of water. However, Gay-Lussac is sometimes credited with a companion relationship that is measurable: the fact that pressure increases with temperature. Measure the pressure in your tire in the morning before you drive to work and then after you arrive at work. The tire's increased temperature (due to friction with the road and from braking) will have caused an increase in pressure. Diesel engines work on this same principle but use volume to control temperature. Air is compressed, and the heat of the highly compressed air is used to ignite a spray of fuel.

The increased pressure of a gas when heated can also be explained in terms of the kinetic molecular theory. Energy added to a sample of gas causes the molecules to move around faster, and moving faster causes more frequent and higher energy collisions with the walls of their container, which makes the pressure go up. The gnat analogy is slightly less apt here, but then no analogy is perfect. It can be imagined that gnats would move around more in warmer weather, and, if contained, strike the sides of their container more often.

Because the behavior of gases depends on temperature, the scientists of the 1800s realized that they needed a temperature scale that did not have negative values. In calculations involving gases, such as the law of Gay-Lussac, a negative temperature could result in negative volumes, negative pressures, or other unrealistic outcomes. The question became, then, if you can't have a negative temperature, what point do you choose to be zero? Lord Kelvin, otherwise known as William Thomson, proposed a scale that had an *absolute zero*, or a temperature so low that nothing could ever be lower.[5] How would one derive such a scale? By watching

how pressure and volume change with temperature and using this information to predict the point at which pressure and volume would go to zero. Using this point as a zero, the *absolute temperature scale*, also called the Kelvin temperature scale, was constructed. It turns out that absolute zero is –459.67° F (–273.15° C). Pretty cool.

The gnat analogy works well for the next gas-phase relationship, too, commonly called Avogadro's law.[6] Avogadro's law is named for the Italian physicist Amedeo Avogadro, who proposed in the early 1800s that equal volumes of gas contain an equal number of moles, if the temperature and the pressure were not changed at the same time. In other words, two swarms of gnats take up twice the space as one swarm, and so do two swarms of gas particles.

However, we wish to note that the relationships described so far may seem a bit unrealistic in that only one parameter may be changed at a time: the pressure changes, or the temperature changes, or the number of moles changes, or the volume changes. In reality, of course, this would rarely be the case. Pressure, volume, and temperature would change simultaneously, or the number of moles would increase while the temperature and pressure were changing, too. Fortunately, the various influences can be combined in one rather straightforward equation that accounts for all parameters: temperature, pressure, volume, and the number of moles. The equation that manages this balance of influences is called the *ideal gas equation*, and with this equation one can normally make a very good estimate of a missing parameter, such as volume, if one knows the temperature, pressure, and amount of gas.

$$\frac{\text{Pressure} \times \text{Volume}}{\text{Temperature} \times \text{Number of moles}} = \text{a constant value}$$

This equation states that the ratio of the pressure-volume product to the temperature-amount product remains constant, so knowledge of three of the parameters will predict the fourth. For instance, if the temperature, volume, and pressure are known, the amount of gas can be calculated.

We say that the ideal gas equation provides an estimate because this equation is "ideal" in the sense that it is idealized, not in the sense that it is the best possible equation. The idealization is that the intermolecular

forces have been ignored. In truth, the intermolecular forces will come into play at some point, causing the gas to deviate from ideal behavior. Under pressure, a gas may condense. Pressure forces molecules into enough proximity that attractions exert their influence. On the other hand, if the pressure is too great, the gas may compress less than expected because repulsive forces serve to keep the molecules apart. But that's all right. Deviations from the ideal gas law serve to remind us that gases are not made up of featureless, geometric points but real materials with shape and volume and stickiness . . . and sometime even smell.

For Example: Gutsy Gas

Given the demand for over-the-counter flatulence-reducing digestive aids, it might be interesting to note some of the properties and behaviors of the digestive gas we try to inhibit.

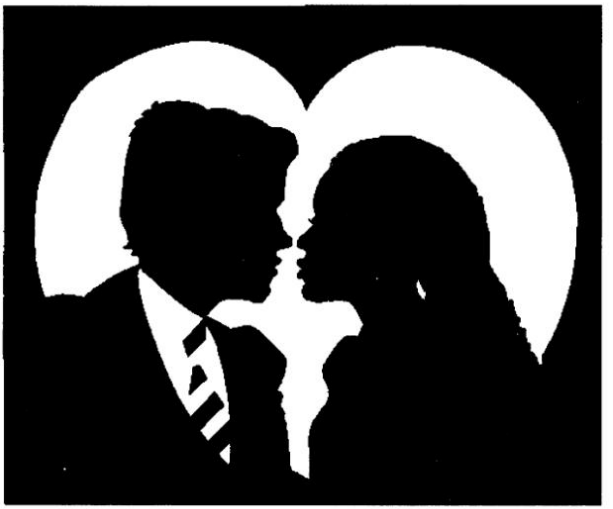
Flatulence is produced in the intestinal tract by the bacteria and yeast that live there. As we will explore in more detail during our discussion of biochemistry, these bacteria and yeast are essential because human bodies do not have the chemical equipment necessary to break down some of the complex sugars present in foods such as beans and peas. The bacteria and yeast, on the other hand, have the ability to break down these foods, but when they do, the side products are a mixture of gases, including carbon dioxide, hydrogen, and methane. These gases are themselves odorless, but in their travels through the intestinal tract they pick up minute impurities, including some odiferous sulfur-containing compounds. Methane is flammable, so it is true that some flatulence can be made to burn, but another myth—that burning flatulence can "flashback" into the intestines—is not. As we've noted, combustion requires oxygen, and the gases that are still in the intestine are relatively

oxygen deprived. But even if flashback is removed as a danger, it is still a bad idea to attempt to ignite flatulence. The drawbacks are obvious.

More germane to the present discussion, however, is why does intestinal gas exit at all? Common experience tells us that the gas-phase is less dense than liquid and that gas bubbles will rise out of liquidlike materials. Our discussion of the properties of the gas phase reinforces this notion. But intestinal gas seems to travel contrary to the expected direction.

The reason for this backward behavior is *peristalsis*, the squeezing action the intestines make as they push matter through the intestine toward the exit. Peristalsis is stimulated by eating or drinking, which is why flatulence may occur immediately after eating even though the current meal is still sitting in the stomach in its early stages of digestion. If some gas does manage to percolate upward against the action of peristalsis, the many twists and turns in the intestines serve to inhibit its progress. When one is lying down, however, the up-down issue is negated, which is why one may experience a bout of flatulence right after waking.

It is possible to find digestive aids that reduce the amount of flatulence produced. (And we will see how they work when we revisit this topic in our discussion of biochemistry.) It is also possible to avoid excess flatulence by staying away from the foods that produce it, such as rice, pasta, potatoes, breads, beans, and peas. All this avoidance, though, is not for health's sake but for the sake of societal taboos. The odor of flatulence, which will vary depending on the type of food ingested, is deemed offensive in many cultures. The sound, both as the gas moves through the intestine and in venting, is considered vulgar. But no link has been made between ill health and excessive flatulence; in fact, the contrary may be true, so it is probably not a good idea to routinely struggle to suppress intestinal gas. After all, gas production is a sign that your intestines are working well, which is always a good thing to know.



Demonstration 11: It's in the Air

What chemistry!
That the winds are really not infectious,
That this is no cheat, this transparent green-wash of the sea which is so amorous after me,
That it is safe to allow it to lick my naked body all over with its tongues . . .

The swell'd and convuls'd and congested awake to themselves in condition,
They pass the invigoration of the night and the chemistry of the night, and awake . . .

O love, solve all, fructify all with the last chemistry. . . .
—Walt Whitman, *Leaves of Grass*, ca. 1855

We noted during our discussion of concentration that many important reactions happen in solution because solutions provide mobility and means of contact. There are, however, many reactions that occur in the gas phase or between the gas phase and the solid or solution phase. Gas molecules, too, have mobility.

This mobility of molecules is called *diffusion*, and the diffusion of gases can be readily demonstrated. Choose an area free of stray breezes.

Put on safety glasses. Pour a little ammonia in a bowl, place it in one corner of the room, and then walk to the far corner of the room. If you wait a moment or two, the smell of ammonia should reach you because the gas-phase ammonia molecules are very lightweight and diffuse quickly. Insects rely heavily on diffusion. Pheromones, or chemical substances released as odors, are used as a primary method of communication among our more diminutive brethren. The male gypsy moth can detect a burst of a few hundred molecules of a sex attractant from a female gypsy moth located as far as three miles away.[1] Love is a wonderful thing.

Diffusion results from the fact that molecules that are in the gas phase are continuously in motion, though the average rate of movement will vary depending on the temperature and the mass of the molecule. The reasons are very intuitive. Higher temperatures indicate more energy is being provided to the system, so the particles travel faster, just as a baseball thrown with more energy will travel faster. Molecules of a higher mass travel more slowly than those of a lower mass, just as a bowling ball will travel more slowly than a basketball if both are kicked with the same energy. The mass dependence of diffusion can be demonstrated as follows.

Put on your safety glasses. Take two tall glasses of the same height and fill one with about two inches of vinegar and put an equal amount of household ammonia in the other. Be certain the heights of the liquids are equal.

Wet a paper towel and then add a few drops of phenol red indicator from the swimming pool test kit suggested for purchase in the "Shopping List and Solutions" onto the paper towel. Put the paper towel with the indicator spot over the mouth of the glass with vinegar. Slowly, in about three minutes, the paper towel should turn yellow. This color change is due to the acetic acid molecules escaping from the vinegar and diffusing, in the gas phase, to the indicator on the paper towel. When the towel is yellow, pick it up and place it over the glass with ammonia. The towel should now turn red, but much more quickly. It turns red because ammonia is a base, and it turns red more quickly because the molecules of ammonia are about 3.5 times as light as the molecules of acetic acid. They move more quickly through the air. Once the paper towel has turned red, it can be placed back over the acetic acid solution and it will turn yellow again, but the reaction will again be slower.

Now let's further explore diffusion and other nuances of gas-phase reactions.

CHAPTER 11

When Gases Put On Airs

Ashes denote that fire was;
Respect the grayest pile
For the departed creature's sake
That hovered there awhile.

Fire exists the first in light,
And then consolidates,
Only the chemist can disclose
Into what carbonates.

—Emily Dickinson, *Poems*, third series, ca. 1850

Chemical reactions that involve gas-phase reactants, their products, or both are enormously pervasive, essential—and peculiar. Here we will catalog some proclivities of reactions involving the gas phase and illustrate them through examples that may seem surprisingly familiar.

Most of the peculiarities of gas-phase reactions stem from the fact that gas-phase molecules are, on average, relatively far apart—relative, that is, to liquid- or solid-phase collections of molecules. They also fly

around at a greater speed than they would have in the liquid or solid state, and as a consequence, intermolecular forces are relatively unimportant. Because of solvent cages and viscosity resulting from intermolecular interactions, it may take solution-phase reactants longer to swim to one another, but it also takes them longer to swim apart, which can facilitate the reaction. In a liquid, reactants find themselves in the same vicinity for a longer period of time and might experience more collisions with one another. The more collisions, the greater the probability for a reaction. In the gas phase, the reactants have only one opportunity for reaction with each approach. If gas-phase molecules do happen to bump into each other, they are often as likely to fly apart as react.

So there are a number of factors working against the success of gas-phase reactions, yet several gas-phase reactions have a reputation for not only reacting but also reacting explosively—such as the reaction between gasoline fumes and oxygen. On closer examination, however, it can be seen that many of these reactions have to be initiated, or sparked, before they take off. Sparking might cause a reaction, where otherwise there would be none, because the spark results in the formation of what is known as a *radical*, that is, a chemical species with an unpaired electron.

The term *radical* may be familiar to watchers of the evening news. Political radicals may cause riots with their overreactions, and chemical radicals cause riots in the body: overabundances of radical species have been blamed for aging processes and cancer. Previously we discussed how atoms like to collect or shed electrons until they have nice filled shells. Now we can point out that these nice filled shells almost always end up with an even number of electrons. Atoms, and molecules as it turns out, like to have an even number of electrons because electrons come in pairs. Like shoes in a shoe box, they fit together as a pair, one beside the other. When something occurs to cause an unpaired electron, a radical, that species tends to be very reactive: it is looking for another electron. Free radicals in the gas phase increase the number of successful encounters significantly.

As we saw in our discussion of redox reactions, combustion reactions can travel through the gas phase quite rapidly. Solvent fumes, likewise, can be quite flammable, which is why they should be used away from any sparks or open flame and in a well-ventilated space. The liquid solvent

does not have to come in contact with the flame for there to be a problem. If solvent fumes mix with oxygen in the air, then a spark may be all that is required for a reaction.

The explosions that take place in the internal combustion engine are very similar. The gasoline is sprayed as a fine mist into the cylinder, where it is mixed with air and compressed before it is sparked. The final temperature is so high that nitrogen gas and oxygen gas from the air can react and form various nitrogen- and oxygen-containing compounds such as NO and NO_2. Collectively, these gases are sometimes referred to as NOx (pronounced *knocks*), and the red-brown color of the NOx compounds account for the red-brown color of smog. The fumes you may have noticed when preparing copper sulfate solution as described in the "Shopping List and Solutions" are NOx compounds.

Hydrogen mixed with oxygen triggers another notoriously explosive gas-phase reaction that most probably contributed to the explosion of the space shuttle Columbia as well as the Hindenburg disaster. Gas-phase explosions usually react via chain reactions: the electron in a radical finds a mate, but in the process steals an electron from another pair, which creates at least one other radical and possibly more, if a bond is disrupted.

Because of this chain of events, a gas-phase reaction can vary in its explosive character depending on the total pressure, that is, the number of potential target molecules present. At low pressures, the hydrogen-oxygen reaction fizzles because the reactants aren't at a high enough concentration. At moderate pressures, the reaction is explosive, but, interestingly, at very high pressures the mixture becomes less explosive again. The reason for the change is the *quenching* of radicals. At very high pressures, radicals can lose energy by collisions with the walls of their container and form passive pairs rather than explosive chain reactions. At still higher pressures, there are so many reacting molecules that the walls can't defuse the radicals quickly enough to stop an explosive situation, and an explosion may take care of the question of the wall—permanently. Oxygen figures prominently in many explosive reactions because oxygen gas exists naturally as a *diradical*: two of the electrons around the oxygen molecule are unpaired, and each unpaired electron is reactive.

So far we have been discussing reactions where both reactant and product are in the gas phase, but these are not the only reactions in which the gas phase is involved. Sometimes the reactant is solid, and the product

is in the gas phase. One might suppose that solid-to-gas reactions would behave rather lazily because molecules in a solid have limited mobility. However, gunpowder is an example of a solid-to-gas reaction that behaves quite vigorously when sparked. In gunpowder, solid nitrates, carbon, and sulfur turn into gaseous NOx, carbon dioxide, and sulfur oxides so rapidly that the expansion can typically project a bullet at speeds of around one thousand feet per second. Similarly, the decomposition of sodium azide, a sodium nitrogen compound, into nitrogen gas fills automobile airbags in a twentieth of a second. Sensors detect the impact and send an electric spark to an igniter reaction, which creates enough heat to start the decomposition of sodium azide into nitrogen gas.

Solution-phase reactions that produce gases include some reactions we want to avoid. It may be recalled that one of the admonitions in "A Few Necessary Words on Safety" was not to get creative with mixtures of chemicals, and one important reason, among others, is gas-phase products. Mixtures of household cleaners can produce noxious gases capable of causing difficulty in breathing or worse. Gas-phase products are particularly insidious in this regard because they spread throughout the room. Even seemingly innocent gases can cause suffocation if they are concentrated enough to displace the oxygen we need to breathe. At one point in European history, carbon dioxide was called *gas Sylvester*, Sylvester coming from the Latin for "forest." The gas could be found in caves that contained rotting wood because carbon compounds in wood decompose into carbon dioxide. Carbon dioxide gas is heavier than air, so in unventilated caves, it settled to the ground. Dogs coming into the caves would suffocate, while humans, breathing higher above ground, would survive. The whole process, of course, would be invisible and, at that point in European scientific understanding, very mysterious. For this and several other reasons, the early Europeans may be forgiven for their seemingly irrational belief in magic and superstitions. Seeing your dog drop dead from an invisible force that had no effect on you might convince anyone of the supernatural!

Reactions involving gas-phase reactants can also be difficult to coax along because the reactants have to be concentrated, or corralled, before a significant reaction can take place. Corralling gas-phase reactants generally means increasing the pressure of the particular gases. In one famous gas-phase reaction, one in which nitrogen and hydrogen react to

form ammonia, the pressure of the gases is high, the reaction mixture is heated, and a facilitator, a catalyst, is used.

The process, called the *Haber process*, produces ammonia, which can be converted into nitrates, an indispensable ingredient in gunpowder. Before this process was developed, nature supplied the nitrates. Some plants, such as pea and peanut plants, harbor bacteria in their roots that are able to *fix* nitrogen from the air, that is, convert gas-phase nitrogen into compounds that can be used by the plants. Animals eat the plants, and nitrates form in their nitrogen-rich manure. Large supplies of manure, such as those found in seasonal roosting areas for large flocks of birds, used to be harvested for nitrates. In Europe prior to World War I, such nitrates had to be imported, which meant the importing countries were vulnerable to blockade. So the hunt was on for a more domestic method of manufacturing ammonia from the nitrogen gas in the air.

The person who first devised a practical process, the German chemist Fritz Haber, received much adulation, many honors (including the Nobel Prize in 1918), and significant consideration when it came to the dispensing of funds and new facilities. When war ensued, he continued in the service of the German government and agreed to work on the development of mustard gas and other chemical weapons. At this point, his life then took a downturn. His wife committed suicide, Germany lost World War I, and Haber, a Jew, was forced to flee Germany when the Nazis came to power.[2]

Haber's breakthrough was to find the catalyst, a facilitator for the reaction, which in this specific case was an iron and iron oxide solid—rust. Solid catalysts can facilitate reactions because molecules are three-dimensional beasts, and when it comes to reactions, orientation matters. This restriction can be understood by considering interactions between other three-dimensional objects: a kiss is just a kiss, but three-dimensional humans have to be oriented correctly for the kiss to be on target and effective. One advantage of a solid catalyst may be that it can hold the reactants in a favorable orientation. Automobiles use catalytic converters to convert NOx back into nitrogen and oxygen and convert poisonous carbon monoxide to carbon dioxide.

Other reactions that involve gases and catalysts are ones in which the reactants are in the gas phase but the product is a solid or liquid. The Fisher-Tropsch process is an example of such a reaction.

In the Fisher-Tropsch process, carbon monoxide is generated by treating coal with steam, a process called coal gasification.

$$C + H_2O \rightarrow CO + H_2$$

The mixture of product gases, called synthesis gas, can be enriched in hydrogen via the *water-shift reaction*,

$$CO + H_2O \rightarrow H_2 + CO_2$$

If this is done enough times, fairly pure hydrogen can be generated for use in Haber ammonia synthesis. The carbon monoxide and hydrogen can also be converted to methanol, an alcohol that can be burned as a fuel, or, if repeated many times and with a catalyst, converted into the long-chain carbon compounds that make up waxes and oils.

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O \rightarrow\ \rightarrow \text{long chain of } CH_3CH_2CH_2CH_2 \ldots$$

So we see that interactions between solids, liquids, and gases are essential to many important industrial reactions. In addition, other reactions involving gas, solid, and liquid interactions are vital to us on a nonindustrial level. For instance, the interactions between us and the air we breathe.

For Example: Hardwired for Respiration

Perhaps the most striking example of a reaction involving the gas phase is respiration, the process by which organisms exchange gases with their environment. In the grand symbiosis of planet Earth, plants consume carbon dioxide and release oxygen, while their animal allies consume oxygen and release carbon dioxide. Plants, however, also need oxygen, and the explanation for this involves—perhaps surprisingly—batteries.

Batteries power electric devices by providing a stream of electrons. A stream of electrons has been compared to the flow of a river (in fact, both are called *currents*), and the analogy is a good one. Just as a stream of water can do work by turning a water wheel, a stream of electrons can do work, too. A battery produces a stream of electrons by having two reactions—one that produces electrons and one that consumes electrons—physically separated from each other but able to be connected by a wire.

A battery needs two reactions because the current of electrons can only flow if it has a source *and a place to go.* The second requirement—a place to go—is very important. If the stream is dammed up, the water does not flow. You don't have a stream, you have a pond. Similarly, for electrons to flow in an electric current, they must have a place to go. Storage batteries can store charge because their electrons can't leave if they have no place to go. To produce the stream of electrons, the ends of the storage battery have to be connected by a wire, creating the streambed, if you will.

Plant processes can also be powered by streams of electrons from coupled reactions—one that provides electrons and one that consumes electrons—and these reactions can also be separated. To allow the flow of electrons, plant reactions must also be connected, but instead of a wire, plants have something called an *electron transport chain*. Here's how it works.

Plants are autotrophs, which means they are capable of making their own food, but they don't make it out of thin air. They make it out of thick air: air thick with carbon dioxide, CO_2. Plants take in carbon dioxide and water and produce sugars and oxygen through a magnificently orchestrated chain of events called photosynthesis. Then, in a manner similar to that of their animal counterparts, plants metabolize sugars for energy and in the process consume oxygen. Each step in the process has to be powered, and the power can come from the flow of electrons, just as a flow of electrons might power an electronic device. The source for the electrons in devices is usually batteries, and the sources for electrons in leaves are batterylike, too. Just a lot smaller.

In the first phase of photosynthesis, called the light phase, the reaction

$$2\ H_2O \rightarrow 4\ H^+ + O_2 + 4 \text{ electrons}$$

provides electrons to chlorophyll, the green pigment molecule in plants. Sunlight prompts the electrons to flow from chlorophyll into the electron transport

chain, the wiring in the leaves. The use of light to excite electrons has become an everyday event with the proliferation of remote-control devices. Light from the remote control excites electrons in a semiconductor receiver located in, say, a TV. The resultant current, in turn, does work by switching on or off the electronic circuitry of the TV. In leaves, light excites electrons in chlorophyll, and the resultant current runs through the electron transport chain. The electron transport chain is a series of molecules that can pass along electrons. It is located in a plant structure called the thylakoid membrane.

As we pointed out, however, the electrons will not flow unless they have someplace to go. In the light phase of photosynthesis, the electrons moving down the electron transport chain are taken up by nicotinamide adenine dinucleotide phosphate, a molecule with nearly as many symbols in its formula as letters in its unwieldy name. Luckily, it suffices to refer to this entity by its initials, $NADP^+$, a practice common in the complicated world of biochemistry.

A salient feature of $NADP^+$ is its net positive charge, so it can act somewhat like an electron sponge.

$$NADP^+ + H^+ + 2 \text{ electrons} \rightarrow NADPH$$

In the process of flowing down the electron transport chain to $NADP^+$, the electrons do work. In this case, the work they produce is used to create a *proton gradient.*

At this point, we must interject an aside: hydrogen, as may be recalled, consists of one proton and one electron when it is a neutral atom. When its one electron has been stripped away, which is the case for H^+, the resulting hydrogen ion is often referred to as simply a proton because that is just what it is, a proton and nothing more. A *gradient* in science has the same connotation as a gradient on a hill or on a road, that is, a difference in size between two quantities, such as height, or in this case, the number of protons, separated by some distance. Therefore, the movement of hydrogen ions from one side of the thylakoid membrane to the other is referred to as setting up a proton gradient.

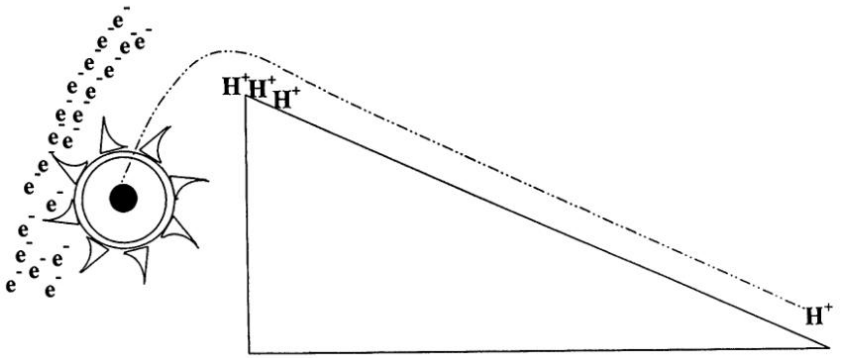


Figure 1.11.1. The work done by the flow of electrons down the electron transport chain is used to move protons to the top of a proton gradient.

Why would the leaf want to set up a proton gradient? So the protons, like the electrons, can flow from where they are in excess to where there is a deficit and in the process do work. The work that the protons do is to power the manufacture of a chemical found in all living cells: ATP.

Adenosine triphosphate, better known as ATP, is able to store energy for cellular processes. When ATP reacts, the energy stored in its bonds is used to drive various processes such as the transport of materials in the cell, the synthesis of compounds needed by the cell, and, in animals, muscular contraction. To generate enough ATP to do all this work, however, there have to be other ATP-generating mechanisms, which begin with the dark phase of photosynthesis.

The dark phase is "dark" because it does not require light. The dark phase is also called the *Calvin cycle* for the chemist who first described it, Melvin Calvin. In the dark phase, carbon, from carbon dioxide gas, is "fixed," that is, converted into a less volatile form, sugar, that can be used by plants and animals as a source of energy. Oxygen gas is produced in this step but given off to the atmosphere as a by-product:

$$6\ CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6\ \text{(glucose)} + 6\ O_2$$

One of the power sources for this reaction is the NADPH generated in photosynthesis. ATP is also involved in these reactions—in fact, used up in these reactions—but the next stage makes up for the lost ATP and

more. The next step is to break down the sugars for energy in a process called *cellular respiration.*

Both plants and animals carry out the cellular respiration stage of metabolism. Although photosynthesis can occur only during the day and some plants hibernate without photosynthesis in the winter, respiration must continue, day and night, winter and summer. The cellular respiration that takes place in the plant cell is remarkably similar to the cellular respiration that takes place in the animal cell. In cellular respiration, the sugars are broken down to produce ATP. Again, as in photosynthesis, the work is done by an electron current running through an electron transport chain. Electrons flowing down the electron transport chain create a proton gradient that can be used to drive ATP formation. One of the differences is that the source of electrons is the reduced form of the molecule nicotinamide adenine dinucleotide, or NADH, not water. And this time oxygen is used to pull the electrons out at the other end, rather than $NADP^+$, with the oxygen-consuming reaction

$$O_2 + 4 \text{ electrons} + 4\ H^+ \rightarrow 2\ H_2O$$

which explains why plants also need oxygen, as promised.

However, it is still possible for some cells to sometimes produce energy without oxygen. The oxygenless energy-producing process is called *fermentation*. Though fermentation is often taken as meaning the process that produces alcohol, it actually covers several processes that operate without oxygen. For instance, when our muscle cells are oxygen deficient, such as when we exercise vigorously and our breathing cannot keep up with our oxygen demand, our cells must rely on methods for producing energy that do not require oxygen. The end product of one of these alternate, oxygenless methods is a kind of acid known as lactic acid. As lactic acid builds in oxygen-deprived muscle cells, the cells are less able to function, and the result is weakness, pain, and fatigue. Yeast relies on another type of oxygenless energy generation that has ethanol as its end product. We take advantage of this fermentation when we make wine and other alcoholic spirits.

Although oxygenless metabolism may be a pain for us, there are microorganisms that thrive in oxygen-deficient atmospheres. The bac-

teria that spoil canned food that is not properly sterilized flourish in the absence of oxygen, and their gaseous waste can cause cans of spoiled food to bulge. But energy generation without oxygen is not as efficient, and the life forms that rely solely on oxygenless energy are not very big. There is speculation that dinosaurs grew as large as they did because there was more oxygen in the atmosphere at that time, and there seems to be some geological evidence that oxygen levels have slowly decreased.[3] Apparently, we are now about the right size to efficiently use the present oxygen supply, but should it go down again, things might be different.

Life would go on, but the creatures would resemble us even less than we do the dinosaurs, and less than the dinosaurs resemble the single cells from whence they came. But those single cells were responsible for producing the oxygen in the atmosphere that eventually accumulated to the point that allowed multicellular life, so it might be that this cycle would eventually repeat. We are used to thinking linearly, in terms of a beginning and an end, because that is how we reason. But nature is not so constrained. Nature tends to appreciate cycles, and life has its ups and downs.

Demonstration 12: How Does Your Garden Grow?

I feel like a white granular mass of amorphous crystals.
—Lafcadio Hearn, quoted in
The Life and Times of Lafcadio Hearn, ca. 1900

Gas and liquid phases are not the only forms of matter with reactions of interest to chemists. The solid phase, though seemingly fairly inanimate, can have a lively side, too.

Put on your safety glasses. Select a small glass or plastic bowl similar to a cereal bowl to serve as your garden, making sure it is a bowl you are willing to discard when the demonstration is over. Place this bowl inside a larger bowl, box, or container or on a large sheet of newspaper or aluminum foil, so that any crystals that fall from the garden will remain inside and make clean up easier. Find a location where your garden can sit undisturbed and unmolested and where the smell of ammonia will not bother anyone.

Take a small kitchen sponge, wet it, and wring it out so that it's just damp. Cut a strip of the damp sponge into little cubes and place the sponge cubes into the garden. Spread them evenly in the bottom, about one-half inch (1 centimeter) away from each other and the sides of the

bowl. The size and number of the cubes will depend on the size of the bowl. It will probably take three to five cubes. You are now ready to add the materials that will form your garden.

Take the laundry bluing, household ammonia, table salt, and distilled water that were suggested for purchase in the "Shopping List and Solutions" and get a plastic teaspoon. Add two teaspoons each of bluing, distilled water, and ammonia to the bowl. If you want, you can add color by dropping a few drops of food coloring directly on the cubes of sponge. Precise amounts are not crucial to the outcome. Swirl the bowl slightly. Sprinkle two teaspoons of table salt over the cubes. Don't worry if some salt gets into the solution on the bottom of the bowl. Let the bowl remain undisturbed overnight. The next day, sprinkle two more teaspoons of table salt over the cubes and let the bowl sit once more overnight. On day three you should repeat the addition of all materials from day one, taking care not to disturb any crystal growth that has occurred. The salts will blossom into profuse, delicate, fingerlike crystals. Looking at the crystals through a magnifying glass will further enhance the garden tour.

CHAPTER 12

Crystal-Clear Chemistry

The road is wide and straight and bright as crystal, and the sun is at the end of it.
—Feodor Dostoyevsky, *Brothers Karamazov*, ca. 1880

The word *chemical* can conjure up images of goo, globs, and glops, but usually not pictures of nice, neat, orderly structures. But solid-state chemicals can be wonderfully symmetric and elegantly structured. Beautiful, mathematical symmetry is evident in the crystal garden demonstration and is exhibited in even a grain of salt. Here we will examine the forces that bring about such structure and other phenomena associated with the solid state of matter.

Thus far, we have not dwelled on the three-dimensional nature of molecules because this added layer of complexity was not needed. Historically, this was the order of events, too—more or less. It wasn't until the mid-1800s, a half century after Dalton's theory of the atoms became generally accepted, that a substantial number of European scientists began to grapple with the possibility, and the consequences, of three-dimensional arrangements of atoms in molecules.

One of the first pieces of evidence that there might be something fundamentally important in the way the atoms arrange themselves in compounds came from the discovery of *isomers*, molecules with the same chemical formula but with different properties. As discussed earlier, both grain alcohol and methyl ether have the same molecular formula, C_2H_6O, but one is a liquid at room temperature, and the other is a gas. The odors are also distinctively different, though it is not recommended to inhale either one. In certain concentrations fumes of methyl ether or grain alcohol can kill. Glycogen and cellulose are both long chains of glucose molecules linked together, but while glycogen stores energy in the human body, the bonding in the cellulose isomer is such that the human digestive system cannot break it down into food. During the Irish potato famine of the mid-1800s, people were reduced to eating grass, but they starved anyway, because they could not metabolize the glucose chains found in the grass.

In the 1800s, even when it was recognized that two compounds might have the same formula but different arrangement of the atoms, it took a while before it was generally acknowledged that the three-dimensional angles and spacings between the atoms could influence their behavior. Louis Pasteur, savior of the French wine industry in the 1800s, found that a salt of tartaric acid, found in wine, existed in two distinct forms.[1] Crystals of the two forms could, with care, be separated by tweezers if viewed through a magnifying glass. Because the crystals were both tartaric acid, the elements in the molecules were bonded in the same order, so the difference had to be the way the bonds were arranged in space.

When this logical explanation was first put forward, however, it was not met with instant universal approbation. The proponents of the idea were labeled daft, or worse, and had to endure the criticism. But time proved them out. To explain the observed crystal structure in salt, sugar, and the crystal garden, we now embrace the three-dimensional nature of atoms, molecules, and ions in our three-dimensional world.

To understand the forces behind the three-dimensional structure of molecules, we need to refer back to an earlier analogy. We said that the nucleus of the atom, being made up of protons and neutrons, is thousands of times as massive than the electrons that surround it. The electrons, we continued, are like fleas on an elephant. But though the fleas are small, they certainly influence the behavior of the elephant, and three-dimen-

sional structure of molecules is one place where this influence is felt. The three-dimensional structure of crystals comes about because of one basic fact: electrons like to be paired, but the pairing is strictly monogamous. Once paired, electrons hold all other pairs at a polite distance. In the parlance of the chemist, this is called *electron pair repulsion.* To see how this plays out in molecules, consider water.

As you may recall from our discussion of intermolecular forces, the water molecule has a **V** shape in which the oxygen is at the point of the **V** and a hydrogen sits at each tip. At the time we did not say why water assumes this shape, but we can address that question now. As can be discerned from the periodic table, shown in figure 1.12.1, oxygen has eight electrons around it, but two of these are in the first closed shell. The outer six, the valence electrons, are the ones that really influence the chemical behavior of the atom. Oxygen will be happiest, it may be recalled, when it has acquired two more electrons to fill its outer shell. Hydrogen has one electron and is looking for one more to fill its first shell, as can be determined by again consulting the periodic table, shown in figure 1.12.1.

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 1.12.1. Hydrogen, situated at the beginning of the first row, needs one more electron to fill its shell. Oxygen, situated two from the end of the second row, needs two more electrons to complete its shell.

Chemists use a visual aid called *Lewis dot structures* (named after the United States chemist G. N. Lewis) to show how nuclei in molecules

arrange themselves so that as many nuclei as possible are surrounded by filled shells of electrons.[2] The device starts by putting a dot for each valence electron (hence Lewis *dot* structure) around the symbol for the elements. Hydrogen and oxygen might be represented as follows:

In this Lewis dot structure, hydrogen has one dot for its one electron; oxygen has six dots for its six valence electrons.

Displayed in this manner, it is easier to see how two hydrogens might combine with one oxygen to make water. They can share electrons so that each hydrogen has a filled shell of two electrons and oxygen has a filled shell of eight electrons.

However, this arrangement still does not look a lot like a **V**. To explain the V, it is necessary to evoke electron pair repulsion, as well as the occupancies of the valence shells, in a key theory called, appropriately enough, *valence shell electron pair repulsion* theory, or VSEPR. In this theory, electrons are identified as *bonded pairs*, which are electrons in bonds, or as *lone pairs* (or *unbonded pairs*), which are electron pairs not in bonds. For instance, the bonded pairs are the pairs of electrons being shared between oxygen and hydrogen in the Lewis dot structure for water given above. The lone pairs are the pairs on either side of oxygen that are not being shared.

The tenets of VSEPR are straightforward:

- lone pairs (unbonded pairs) repel each other
- lone pairs (unbonded pairs) repel bonded pairs, only less so; and
- bonded pairs repel bonded pairs, but even less so.

Understanding these principles allows us to analyze the shape of the water molecule as follows.

All the electron pairs, those in bonds and those in lone pairs, want to get as far away from each other as possible, but the two lone pairs on oxygen want this the most. So the lone pairs spread apart and, in this action, force the

bonded hydrogens closer together, as is shown in figure 1.12.2.

But figure 1.12.2 still looks only two dimensional because we are forced to draw it on two-dimensional paper. To visualize the situation in three dimensions, try using balloons. Choose balloons of the same shape and size but two different colors, such as red and green. Blow up two of the red balloons and two green balloons to the same volume and tie their ends all together. (This is easier to do if you don't overinflate the balloons.) You should end up with a three-dimensional cluster in which the balloons are forced out in four separate directions. The three-dimensional shape you have created is called a *tetrahedron.*

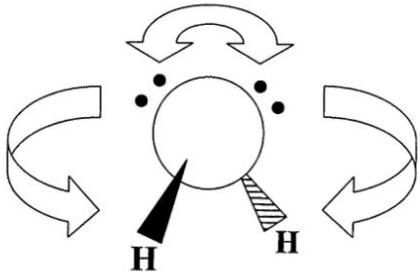


Figure 1.12.2. The electrons in lone pairs repulse each other more than the electrons in bonded pairs, so the lone pairs spread out and the hydrogens are squeezed together, which gives water its V shape.

Now blow up four more balloons, but make the red balloons bigger than the green ones (but keep each red balloon the same size as the other and each green balloon the same as the other). When you tie these together as before, you have a situation that is more representative of water: the larger balloons will force themselves farther away from each other and squeeze the smaller ones together. Taken together, the three-dimensional shape of the molecules determined by VSEPR and the trade-off between ionic attractions, covalent bonding, and intermolecular forces account for the three-dimensional structure of crystals.

Some crystals are *ionic*, that is, long networks of ions held together by ionic attractions. Sodium chloride, table salt, is an ionic solid. In crystals of sodium chloride, a sodium ion is surrounded by six chlorine ions—one on top, one on the bottom, and one at each compass point—and each chloride ion is surrounded by six sodium ions in the same manner. Crystals of sugar, on the other hand, are held together by intermolecular attractions. They fit together for optimum balance of attraction and repulsion so that a quite orderly crystalline structure results. Pure metals are stacks of identical atoms so the bonding between one pair cannot be any different than the bonding between the next pair. Consequently, it is impossible to