say that the outermost bonding electrons belong to any one atom, and this independence is reflected in the excellent electrical conductivity of metals: when hooked up to a power source, such as a battery, electrons will travel freely from one atom to another in a current.

Covalently bonded solids such as quartz, diamond, and graphite form another class of crystals. Quartz is a continuous network of silicon dioxide bonded in a uniform, crystalline arrangement. Sand is a mixture of quartz and other rocks. Glass is solid quartz that has melted and resolidified without the same crystalline uniformity, in the way that melted butter does not re-form the same type of solid when it cools. Glass has been known to form naturally in lightning strikes on sand.

Diamond is a network of carbon atoms, each carbon entity bonded to the next through a covalent bond in a tetrahedron arrangement, as shown in figure 1.12.3. Diamond's sibling, solid graphite, is also made of pure carbon, but in graphite the carbons are bonded in sheets that can slide over one another, as shown in figure 1.12.4. The difference in properties—and in price—is considerable. Graphite is actually the more stable form of solid carbon, as we will discuss shortly, but the length of time required for the transformation is about as long as the age of planet Earth.

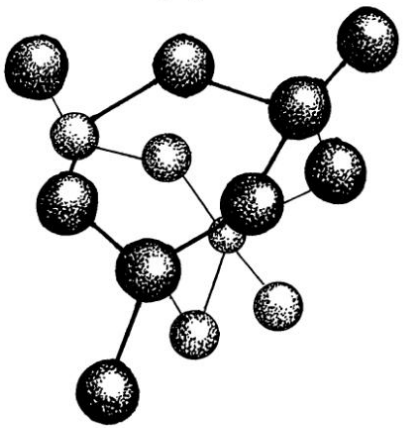


Figure 1.12.3. Diamond is a covalently bonded network of carbon atoms that assume a tetrahedron shape at each carbon.

An interesting sort of hybrid of ionic and covalent molecules can be found in salts of *polyatomic ions*. Polyatomic ions are charged groups that contain several different types of atomic nuclei—such as $CO_3^{2-}$, an ion that is familiar to us from our baking soda demonstrations. Baking soda is sodium bicarbonate, which is $NaHCO_3$. Another polyatomic ion that we have dealt with, although not explicitly until now, is the sulfate ion, $SO_4^{2-}$. As may be recalled, the superscript 2–, read "two minus," indicates that the ion has a minus two charge. Copper sulfate, the compound that forms the lovely blue-colored solutions we have used in several demon-

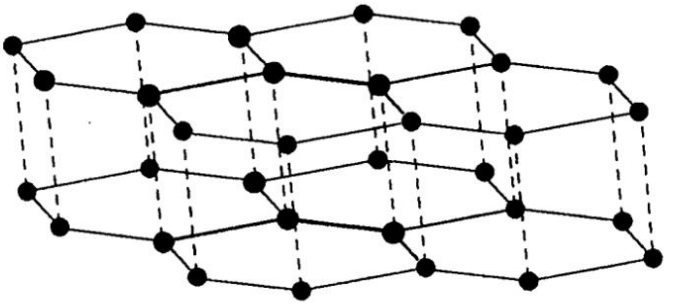


Figure 1.12.4. Graphite is covalently bonded carbon in hexagonal sheets.

strations, is a salt of the copper ion and the sulfate ion. The bonding is covalent within the carbonate and the sulfate ions, but between the positive ion (sodium or copper) and the polyatomic ion, the bonding is ionic. These crystalline salts of polyatomic ions were used in the mid-1800s to answer an age-old question: How do you weigh an atom?

The question is obviously a very difficult one, but it has always been a very important one, too. Its significance arises from the fact that atoms react one to one. So if you want to do any kind of accounting for their actions you are going to have to be able to count them—but they are so darned tiny that you cannot. What you can do is weigh a big collection of atoms, such as a spoonful or a cupful, and calculate how many atoms are in the spoonful or cupful, but in order to know how many atoms you have in that spoonful or cupful, you have to know the mass of one atom. Scientists began to get a handle on this when they realized that there are many different metals that form sulfate salts, and all of these crystallize in approximately the same way. How does this help? It has to do with density.

Density, as you may recall, is the amount of mass of a substance per unit volume. Density varies from substance to substance; for instance, the density of a bag of feathers is considerably different from that same bag filled with bricks. As a characteristic, density is very useful because you don't need a specific amount to measure it. The density of bricks is going to be the same if you are looking at one brick or a brick wall. A spoonful of table salt will have the same density as a cupful of table salt because density does not depend on sample size. To measure the density, you need only to measure the mass of a specific volume.

For sulfate crystals, it was assumed that each "brick" of crystals contained the same number of sulfate units and metal units whether the metal

was copper, magnesium, or whatever. So any difference in density had to be due to a difference in the mass of the metal. When a mass was assigned to one of these metals, then the relative weights of the others could be determined. The idea was clever and useful for its time, but has been improved upon since. Today, x-rays are used to determine the arrangement of atoms and the number of atoms in a given volume of a crystal, and the results are much more precise.

The x-ray technique for crystals, however, is not the same as that of a medical or dental x-ray. In the case of a medical or dental x-ray, the x-rays are allowed to pass through the body and the images are of the shadow cast by the dense tissue—bones or teeth—that the x-rays could not penetrate. X-ray studies of crystals (called x-ray *crystallography*) look at reflected x-rays, rather than transmitted x-rays, and analyze the patterns in the reflected rays.

Crystals reflect x-rays somewhat as CDs reflect visible light. The visible light bounces off the grooves in a CD in such a way that the light separates into its various colors, giving the CD a rainbow cast. The various layers in a three-dimensional crystal act somewhat like a miniscule groove pattern in a CD. X-rays bounce off microscopic crystal structures and produce a pattern on an x-ray film. From the particulars of the pattern it is possible to discern the size and structure of a single unit of the crystal. The position of the pieces—atoms, ions, or molecules—that make up the crystal can be extracted from this information. Once the volume of the smallest unit of a crystal and the number of atoms that it holds is known, the mass of just one piece—an atom or a molecule—can be determined from the density.

Of course, all that glitters is not gold, and not all solids are crystalline. The solids that are not crystalline are generally referred to as amorphous. These solids include rubber, some plastics, waxes, and glass, though there may be some debate over the actual assignment. The label, amorphous solid, is a human attempt at classification that nature does not have to obey. Amorphous solids can be distinguished from crystalline solids in that amorphous solids do not have a clear, distinct melting point. Crystalline solids exhibit very sharp melting points if they are pure, and therefore, a sharp, abrupt melting point is used as evidence of purity.

Water is a most interesting solid for a couple of reasons. First, it is

one of the few solids that expands when it freezes rather than contracts. This expansion explains why ice floats in our drinks. The expanded solid water is less dense than the liquid water—it has fewer molecules per unit volume. The reason for the expansion is hydrogen bonding. When water freezes, it is happiest when its oxygen aligns with neighboring hydrogens, sort of like Tinker toys. Tinker toys are wooden sticks that can be joined together by connectors and made into various structures (windmills and houses are some universal favorites). Taken apart, as pieces lying in the box, the pieces don't take up that much space. But in a rigid structure, connected together, they take up far more space. Because of its **V** shape and need to align for optimum hydrogen bonding, water solidifies with large gaps that are normally filled in the freely moving liquid state. (See figure 1.12.5.)

Because of the gaps, water expands when it freezes. The expansion of water as it freezes is responsible for the cracking of sidewalks in the winter and is part of nature's plan for breaking up rocks into soil. Water is also intriguing insofar as it can satisfy the demand for hydrogen bonding with several different crystalline shapes. One of the most famous is the hexagonal structure that gives rise to the six-sided symmetry of snowflakes.

Snowflakes develop when new water molecules strike the surface of a seed crystal. They grow into six-armed structures because the molecules that strike at the tips of the crystal are more likely to stick: the point projects into space and snags molecules floating by, just as debris catches on a branch jutting into a stream.

In general, surfaces are different creatures than the bulk that spawns them. For instance, a water drop forms itself into a sphere because the water molecules inside the water drop have all their opportunities of hydrogen bonding met and are content. The water molecules at the surface have some unhappy hydrogen ends without their oxygen mate on an adjacent molecule and vice versa. This situation creates a tension, called *surface tension*, and the natural response of the system to minimize this tension

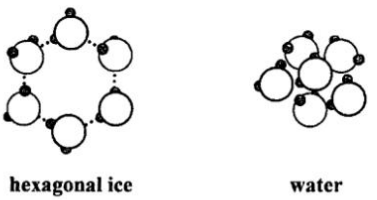



Figure 1.12.5. Hexagonal ice is the foundation on which six-sided snowflakes are built.

is to form itself into a sphere. A sphere presents the minimum surface area and thereby minimizes the number of molecules exposed to air and thus the surface tension. Solids aren't able to roll themselves up into balls, so the unique situation at the surface of solids is usually not so dramatically expressed, but the surfaces of solids are also different than the bulk material and have a special reactivity nonetheless.

The two most common concerns with surfaces in everyday experience are making things stick to surfaces when you want them to and getting them to unstick when you don't want them to. To get materials to stick to surfaces, bonding agents, or glues, are normally used. And these wonderful materials, without which we would not have essentials as diverse as plywood or sticky memo notes, have a chemistry that dates back to antiquity. Glues were originally made from animal proteins, which means they really did send old horses to the glue factory. The word *glue* has ties to the words *gluten*, which is the gooey mess derived from wheat and flour that makes dough sticky enough to form balls, and *gluteus*, which is the ball of muscle on which you sit. The ability of a particular glue to stick may be due to chemical bonding, intermolecular attraction, or both. Depending on the origin of the material—animal, mineral, or vegetable—some glues work better than others because of the type of bonding or attraction being exploited. Sometimes it is desirable to reverse the effects of glue, or unglue things, in which case it is a good idea to use a material that will insinuate itself between the glue and the glued, to break the surface bonds. Oil, such as cooking oil, is often useful in this regard. Oil can be used to remove chewing gum from most surfaces because oil can form a film on the surfaces and in effect alter the bonding properties of the surface. Because of these surface interactions, oil can be grouped with a class of materials called *surfactants*.

A commonly used surfactant is soap. Soap has a long carbon chain that is attracted to organic material, such as dirt and grease, and an ionic end that is attracted to water. Soap can interfere with the surface attractions and is useful for unsticking things such as wedged on wedding rings or corks stuck in bottles. Machine part lubricants are also surfactants because the lubricants interfere with the attractions between bare metal parts.

Porous surfaces present a different problem because the actual surface area, including the interior of the pores, is many multiples of the apparent surface area. Therefore, a porous surface is much more difficult

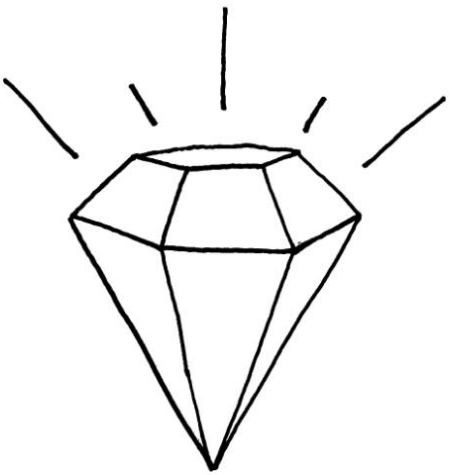
to clean and may resist heroic efforts by surfactant detergents. This intractability of porous surfaces is why natural materials such as wood, bone, and teeth are so prone to staining. Recent methods for removing stains from teeth involve using surfactants to hold a mild bleaching agent against the teeth. Because bones, teeth, and ivory are similar in composition, these same teeth-whitening products have been used to clean aged, stained (and, thankfully, irreplaceable) natural ivory piano keys.

The special properties of surfaces also account for the action of solid-state catalysts. The action of a catalyst often depends on its ability to hold molecules in a particular orientation that will facilitate the reaction. In the gas or liquid phase, a collision at just the right orientation is a function of chance. If the target molecule is held in a favorable orientation on a surface, the chances of a productive encounter are improved.

A solid-state *substrate* is a type of catalyst that allows many reactions or layers of product to grow on its surface. In our discussion of gas-phase reactions we mentioned that a substrate could be used to grow long-chain organic molecules for waxes and oils. Substrates have also been used to grow crystalline products, such as diamonds.

## For Example: Diamonds Are (Almost) Forever

Over the eons there have been many materials, from sea shells to spices, that have been used as a medium of exchange, but the most popular have been materials that are durable and gain as much value from their scarcity as their utility. Gold is an example of the latter, as well as gemstones, in particular, diamonds. The durability of gold, its resistance to corrosion, has contributed to its usefulness for applications such as dental prostheses and electrical contacts. Likewise, the durability of diamonds has con-



tributed to the usefulness of this particular mineral in cutting tools, drill bits, and abrasives.

Demand for gold during the European Middle Ages led to many curious and creative attempts to manufacture gold from more common metals such as lead or copper. As noted, this enterprise, called alchemy, did not succeed, but fostered enough new knowledge of chemical reactions to stand as an important phase in the history of chemistry. To date, the only way to create gold artificially is via a nuclear reaction, but the process is many times more expensive than the gold it produces. Since the mid-1900s, there have been, however, methods for producing synthetic diamonds that are economically viable.

One method involves the microwave-induced removal of hydrogen from methane ($CH_4$, swamp gas) in a very sparse gas phase so that carbon atoms, stripped of most of their hydrogen, can settle out on the substrate and start building diamond crystals. In the past, the diamonds formed in this process were tiny and only suitable for industrial applications, but lately gem-quality crystals have been grown. The artificial diamond is virtually indistinguishable from the natural diamond because they are both just a crystalline form of carbon.

If diamonds are manufactured rather than mined, will that dim their sparkle in lovers' eyes? Probably somewhat. But it is hoped that someday semiconductor materials with important properties can be routinely made from the less expensive and more perfectly pure synthetic diamonds. If diamonds find use in semiconductor devices, this could give a whole new meaning to "a diamond chip."

The interest in diamonds, artificial and real, is due to their unique properties, one of which is their extreme durability. But are diamonds indestructible? Not at all. As may be recalled from our discussion of Lavoisier's proof of the conservation of mass, diamonds will burn in oxygen, if heated enough. As we shall see next, in science as in social situations, strange things can happen when matters heat up.

## Demonstration 13: Hot Packs and Cold Packs

*The fields of Nature long prepared and fallow—the silent, cyclic chemistry;*
*The slow and steady ages plodding—the unoccupied surface ripening—the rich ores forming beneath.*

—Walt Whitman, *Leaves of Grass*, ca. 1900

Citric acid undergoes many chemical and biochemical reactions, and it also displays a property that holds particular interest for us. When citric acid dissolves in water the solution cools. Citric acid requires thermal energy to dissolve; and it draws this energy from its surroundings. A process that requires thermal energy to proceed is called *endothermic*.

To demonstrate this effect, put on your safety glasses then take a plastic sandwich bag and put in about two teaspoons (10 milliliters) of the sour salt (citric acid) suggested for purchase in the "Shopping List and Solutions." Then put one tablespoon (15 milliliters) of water into the bag and seal it up. The bag will feel cold to the touch as the sour salt dissolves. The effect is most pronounced at the beginning of the dissolution. To give

yourself a good comparison, take a second bag and place just a tablespoon of water into it. The bag containing the sour salt will be clearly colder. If you have difficulty locating sour salt, try using baking soda. The cooling is not so dramatic, but still quite noticeable. Citric acid is used in some novelty self-cooling drink mixes.

There are also many processes that release thermal energy. One such reaction involves dissolving lye in water. Be aware that this process releases a great deal of heat, so you should use a lot of water with only a few crystals of lye. Also be certain your safety glasses are in place. Fill a glass that holds at least two cups (480 milliliters) with one cup (240 milliliters) of water. Don't use the bag for this demonstration because the process releases heat, which, you will recall from our discussion of the gas phase, will cause the air trapped in the bag to expand. If the reaction were in a closed bag, then the buildup of gas pressure could cause the bag to spring a leak.

Extract one half a plastic spoonful of lye from its container and introduce these crystals slowly into the glass of water. Swirl the contents slightly. The quantity of thermal energy transferred to the glass container by the process creates a warmth in the glass that can be sensed by touching the outside of the glass. Again, the effect is greatest at the beginning of the process. A process that generates thermal energy is called an *exothermic* process.

Hot packs and cold packs are sold in various sports supply stores and pharmacies for the treatment of muscle ache and sports injuries. Although usually made with different salts, the basic principles of operation are the same as the preceding demonstration.

# CHAPTER 13

## When Matters Heat Up

*You are well aware that chemical preparations exist . . . by means of which it is possible to write on . . . paper . . . so that the characters shall become visible only when subjected to the action of fire. Zaire, digested in aqua regia, and diluted with four times its weight of water, is sometimes employed; a green tint results. The regulus of cobalt, dissolved in spirit of nitre, gives a red. These colors disappear at longer or shorter intervals after the material written on cools, but again become apparent upon the re-application of heat. . . . I now scrutinized the death's-head with care. Its outer edges—the edges of the drawing nearest the edge of the vellum—were far more distinct than the others. It was clear that the action of the caloric had been imperfect or unequal.*

—Edgar Allan Poe, *Gold-Bug*, ca. 1840

*The bit of practical teaching he afterwards reviewed with most curiosity was the course in Chemistry, which taught him a number of theories that befogged his mind for a lifetime.*

—Henry Adams, *The Education of Henry Adams*, 1920

The quote from Poe is included because it refers to *caloric*, the name that was given to heat when it was still thought to be a substance, and the quote also alludes to "the action of fire." The second citation is included because *thermodynamics*, which concerns itself with the understanding and application of the action of fire, has a bad reputation for befogging the mind. But understanding it is well worth the effort: thermodynamics embodies a powerful theory that enables chemists to predict whether a chemical reaction will take place, the extent to which it will take place, and the amount of energy that will be generated or consumed in the process—all before mixing chemicals together. Because some reactions release enough energy to weld metals, it is a good idea to know how much energy to expect in advance of experimentation. Other reactions may look good on paper but react only to a limited extent in the lab—and this information, too, is good to know before investing too heavily in a project.

Given the predictive power of thermodynamics, the theory holds a prominent place in the study of chemistry. The machinery of thermodynamics really boils down to three concepts: energy, entropy, and free energy. We will start with energy and build from there.

Our understanding of the energy of molecules is based on a molecular model of matter that assumes that all matter is in constant motion. This idea may seem a bit implausible at first, given that there are ample observations in our everyday experience that tell us some materials are solid, stable, and immobile. It is a bit difficult to acknowledge that at the molecular level a cement sidewalk is actually wriggling around like a can of anxious worms, but it is. The model of molecules in motion works well for explaining why gases and liquids behave as they do and still allows cement to behave the way it does.

Actually, the model works well only if we admit to at least three different modes of motion. These modes of motion are *rotation*, *vibration*, and *translation*. Translational motion is straight-line motion, such as walking across the room. Vibrational motion is the molecular equivalent of waving your arms up and down. Rotational motion is the molecular equivalent of spinning around in place, perhaps as an ice skater might. Vibrational and rotational motions are only available to molecules, not atoms, because the rotations and vibrations are with respect to some center defined by the bonded elements.

For instance, water has both vibrational and rotational modes. One vibrational mode is the scissor movement of the hydrogens toward and away from each other. A rotational mode is the spinning of the hydrogens about an imaginary axis through oxygen. Both these modes of motion are shown in figure 1.13.1.

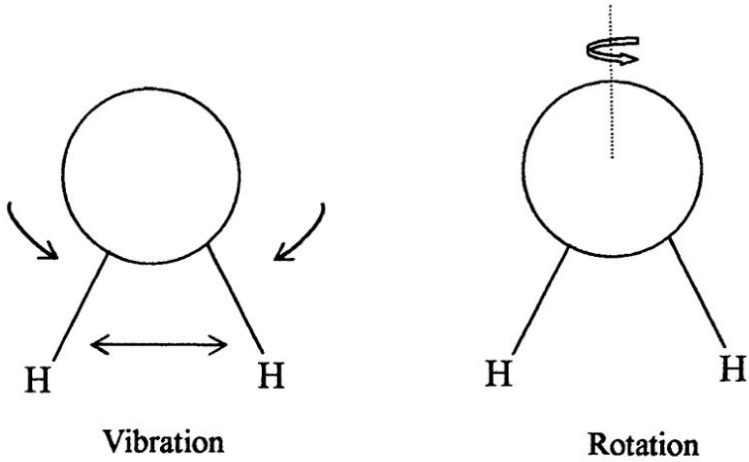



Figure 1.13.1. Water molecules are in constant motion. They vibrate, rotate, and move in a straight-line motion called translational motion. Shown here are a vibrational and a rotational mode of motion for water.

The significance of these modes of motion is that energy added to a collection of molecules will distribute itself between the various modes. An analogy might be made to a jellyfish. Poking a jellyfish will make it not only move forward but also wobble and roll about, too. In a given sample, the sum of the average energy expressed in each mode is called the *internal energy*. Every bit of matter has some internal energy, even if it is very cold. Recall that the Kelvin temperature scale defines a point of absolutely zero energy, called *absolute zero*, but this point is merely a theoretical limit and in actuality can never be reached.

Temperature is a measure of the internal energy of an object. Using temperature as a gauge of internal energy, however, assumes that the energy is uniformly distributed among the various modes of motion. This assumption is necessary because temperature is really only the measure of one mode of motion: translational motion. A thermometer registers

energy transferred to it by molecules striking its surface. There are situations in which added energy does not add equally to all modes of motion, and in these cases it is possible to add energy without changing the temperature. Boiling water is a case in point. Energy is added, but the energy goes into breaking the molecules free of their intermolecular attractions so that they can go into the gas phase. A thermometer inserted into a pot of room-temperature water registers a change in temperature as energy is added from the burner—until the boiling point is reached. Then added energy continues to boil the water, but the temperature stays constant at 212°F (100°C).

When two materials are put in thermal contact, energy will flow from the high-energy material to the low-energy material until they are both at the same energy. It is the flow of energy that is technically termed *heat*, though in casual speech, the term can be used rather loosely. For instance, when we are cold, we ask to turn up the heat when technically we should ask to turn up the thermal energy. Heat is energy being exchanged, flowing from one material into another or being transferred to a material via radiation such as microwaves or sunlight. So we are correct when we say we feel the heat from the sun or a hot water bottle because this is energy being transferred to our skin.

Work is also a form of energy transfer. When you do work on a system you give that system energy at the expense of your own energy. Work can come in many different forms: you can squeeze on the system (pumping a bicycle pump can cause its temperature to rise); you can run an electric current through the system (computers have to be cooled so that their temperatures don't rise too much); and you can also use chemistry to do work. Some examples of using chemistry to do work might be burning gasoline to power a car or digesting the chemicals we call food to do all the work of our bodies.

When we use chemistry to do work or transfer energy, where does the energy come from? It comes from the breaking and forming of chemical bonds.

A bond can start to form as two atoms come together. If conditions are favorable for bonding—conditions that include the desire of each atom for additional electrons or the ability to provide electrons—electrons can rearrange into a molecular orbital instead of individual atomic orbitals. When this happens, the energy of the system is lowered. A pretty

fitting analogy can be made with magnets. If the opposite poles of two magnets come close together, it requires energy to keep them apart. It is a less demanding energy situation to go ahead and let them come together. So it is with atoms that want to bond. It is a lower energy situation when they come together.

Bonding can lower the energy of two atoms, but it does not reduce the energy to zero. Each nucleus may be attracted to the electrons of the atom, but the two nuclei are repulsed by each other because each nucleus has a positive charge. So the analogy with opposite poles of magnets fails at this point. The two nuclei may settle into a bonding situation, but there is always a tension between them. When a more favorable situation presents itself, the bond can break and a new bond can form. Sometimes there is a net energy release and sometimes there is a net energy requirement. When energy is released, the reaction is termed *exothermic*. When energy is required, the reaction is termed *endothermic*.

Let's take a moment to recap. Basically, we're saying that the internal energy of a collection of molecules or atoms is the sum of their (1) rotational, (2) translational, and (3) vibrational energy. The amount of internal energy that a system contains can be changed by heat. Heat can be added to or subtracted from a system in many ways, but the method of primary interest to us is by chemical reaction. When a chemical reaction gives off heat, it is termed exothermic. When a chemical reaction absorbs heat, it is termed endothermic.

Now we add an additional item of information: molecules and atoms are lazy. Atoms and molecules like to lower their energy whenever they can. Bowling balls roll downhill, boats float downstream, and molecules settle in the lowest energy arrangement that they can manage.

But there is a catch: molecules like to be in the lowest energy configuration they can manage, but this may not be the lowest energy configuration *possible*. In the demonstration at the beginning of this chapter, we illustrated two different types of reactions, ones that give off heat and ones that absorb heat. When a chemical system goes to its lowest energy configuration, it gives off heat. Only when it goes to a higher energy configuration is energy required and only when energy is required does the system absorb heat from its surroundings. But the reaction that absorbed heat occurred freely, on its own, without any incentive other than mixing. Now we have a question to pose: Why? Do chemical systems obey dif-

ferent laws than bowling balls and boats? Are chemicals free to hop up hills and swim upstream?

The question is not a simple one, and indeed, there was a good deal of discussion on the nature of heat throughout the 1700s, the 1800s, and into the opening days of the 1900s. The answer has to do with something called *entropy*. Entropy is the tendency of systems to move toward a state of maximum disorder.

Drinks mix; office desks clutter; decks of cards shuffle: entropy is the natural tendency toward disorder. Entropy has also been called the tax that nature charges. Entropy has also been called the universal death sentence. But entropy is not just a philosophical construct or a pessimistic outlook. It is a real driver for physical processes and does indeed weigh in as a determinant in the fate of the universe.

All other considerations being equal, a system will move toward the state that has the maximum disorder. Molecules and atoms are not only lazy, they are messy. Why should systems seek a state of maximum disorder? The answer, though it was a long time coming and quite a struggle to discover, is that the disordered state is by far and away the most probable.

The idea is usually explained by analogy with a deck of cards. There is only one way to deal a perfectly ordered hand in bridge: thirteen cards of the same suit. But there are some 640 billion other, disordered, hands one can be dealt. Disorder is amazingly more probable than order. In a way, this fact can be seen in a positive light: anything is possible—just not very probable. On a molecular level, it is possible that all the molecules of a chair might move in the same direction at the same time and the chair might defy gravity and jump up off the floor—but it is highly, highly unlikely. It is *extremely* likely that the motions of the molecules will remain disordered and any movement of a molecule up will be countered by movement of a molecule down, and the chair will stay put. This tendency of systems to become disordered and stay disordered is strong enough that it explains, along with considerations of energy, the outcome of chemical reactions.

In physical as well as chemical processes, the effect of entropy is to motivate reactions, even those where an input of energy may be required. A classical example is the evaporation of a liquid such as water or alcohol. The indication that the process requires energy is the cool feeling of the skin when water or alcohol evaporates. The water or alcohol

absorbs some energy from the body. However, the process occurs quite readily. Using a term that had been adopted by science and fitted with special, narrow meaning, the reaction occurs *spontaneously*. Spontaneity gains a more precise meaning in thermodynamics because, with the machinery of thermodynamics, the tendency of a reaction to occur spontaneously can be calculated and assigned a number. The number it is assigned is called the *free energy*.

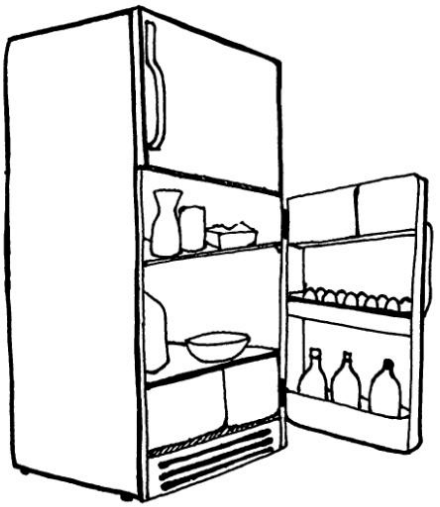
What is free energy? It is the energy that results from the difference between the energy gained or lost in a chemical reaction and the amount borrowed or expended because of entropy. Just like a checkbook or a balance sheet, nature tallies how much energy is lost or gained and subtracts the taxes due to entropy. The energy left over is the available capital, or as we say in thermodynamics, the free energy: the energy free to do work. We said that all this reshuffling of energy occurs when chemical bonds are made or broken, but the same considerations come into play when intermolecular attractions are made or broken. Evaporation, the change of a liquid into a gas, is an example of a process that requires energy but can still be spontaneous because so much entropy is gained. Does gas expansion do work? It certainly does in the cylinder of an internal combustion engine.

A liquid might be viewed as a school of fish or a flock of birds: all moving, but in unison, heading first one way and then another, together, with positions in the group seemingly assigned and varying only slightly as the entire group moves. Gas, however, is a swarm of gnats, flitting about individually and in random directions, the group being carried by air current rather than purposeful direction. It is much easier to predict the movement of one fish in a school than it is one gnat in a swarm, and a liquid is more ordered than a gas. Alcohol evaporates from skin, disrupting intermolecular attractions, which requires energy, because it is able to gain entropy by turning into a gas.

Thus a process that absorbs heat can be spontaneous if it creates enough disorder at the same time. On the other hand, if enough energy is expended, reactions that create order can be driven forward. An orderly solid of cake can be created from a disorderly liquid batter with the addition of heat.

In refrigeration, cooling occurs when compressed refrigerant absorbs heat and expands, which disrupts intermolecular attractions. We are all

familiar with the sound of refrigerant flowing through the coils at the back of the refrigerator and the compression pump running. But how do they get refrigerators to run off the cigarette lighter outlet in cars? Itty bitty coils and a miniature compression pump? Not quite. But some of the fundamental principles are the same.



## For Example: Refrigeration on the Road

Before we address refrigeration on the road, let's look at the principles behind good old-fashioned household refrigeration. When a fluid is allowed to evaporate on the skin, the skin feels cooler. Try it with rubbing alcohol. Sweating is the body's attempt to cool itself by producing a fluid that will evaporate and cool the skin. Sweat absorbs heat from the skin and uses this heat to break the intermolecular attractions that are holding the materials in the liquid state. A pot of water boiling on your range top and the refrigerant in your refrigerator are experiencing the same effect. The pot of water stays at a steady 212°F (100°C) (assuming you are at sea level) because the heat added from the burner is going into breaking intermolecular attractions between water molecules, not increasing the translational energy. In effect, the pot of water is refrigerating the stove burner by dissipating the heat. Driving this process forward is the need for the ordered liquid to disorder by becoming a vapor.

As an aside, wart removal by liquid nitrogen exploits the same principle. As may be recalled from our discussion of intermolecular forces, the attractions of induced dipoles, dispersion forces, are caused by temporarily uneven distributions in the electron clouds, which produce momentary positive and negative regions. Nitrogen is formed from two nitrogen nuclei bonded together—the electrons have no reason to prefer one nitrogen in the molecule over the other—so dipoles, a permanent separa-

tion of positive and negative charge, are not a feature of nitrogen molecules. Cooled and put under pressure, nitrogen liquefies because of the attraction of dispersion forces alone. But for anyone who has felt the cooling of liquid nitrogen, the pain can leave no doubt as to the strength of these forces. The energy absorbed from the skin when liquid nitrogen evaporates causes frost bite severe enough to kill that portion of the skin. If this is the portion of skin that is hosting a wart, then the wart is removed.

The fluid that flows through the coils in the back of a refrigerator removes heat from the interior by the same process. In fact, the refrigerant used in freezers will absorb so much heat that it can freeze skin. The fluid is compressed by the compressor, then allowed to expand through the coils. The compression is driven by an electric motor, and the expansion is driven by entropy: the gas phase is a more disordered state than the liquid phase.

Though the evaporation process is driven by entropy, it still requires energy to happen, so it draws its energy from its surroundings, thus cooling the surroundings in the process. The refrigerant is collected and recompressed into a liquid. The recompressed liquid releases the energy drawn from the refrigerator, which is the heat that can be felt at the back of a refrigerator. After compression, the cycle starts over.

But there is no compressor noise associated with an automobile refrigerator, so what is happening here? Something called the *thermoelectric Peltier effect*, which can also be explained in terms of thermodynamics, as follows.

Some semiconductors allow the passage of electrons more readily than other semiconductors do; therefore, when any two dissimilar semiconductors are joined in a circuit, the electrons experience a change in energy as they go from one semiconductor to the other. When the electrons jump from one semiconductor to a new semiconductor—and then back to the first semiconductor—one of those jumps will be uphill, and the other will be downhill. One of the jumps will require energy, and one of them will release energy. Where do the electrons get this energy? Why not down the road at the junction where it is being given off? That is essentially what happens: heat flows, and one junction gets warm while the other cools. If the warm junction is outside an insulated box and the cool junction is inside, then voilà, you have a refrigerator.

The applications of thermodynamics are many in chemistry, as well

as refrigerators, but are singularly useful in understanding phase equilibrium as well as the important concept of chemical equilibrium. Because chemical equilibrium involves phase equilibrium, we will look at phase equilibrium first. The phase before equilibrium.

## Demonstration 14: Zoned-Out Ice

*What Youth deemed crystal, Age finds out was dew.*
—Robert Browning, *Jochanan Hakkadosh*, ca. 1840

We have now discussed the solid phase of matter as well as the gas phase and the solution phase. We have encountered interesting chemistry in each, but this is just the tip of the iceberg, as it were. The next topic for discussion will be the change from one phase to another. Though the physics of phase changes experienced by pure materials—such as melting, freezing, and boiling—has a fascination of its own, the situation becomes even more intriguing when a bit of chemistry is added to the mix. As an illustration of a phase change with a little chemical color, try the following demonstration.

After carefully donning your safety glasses, take up the bottle of freshwater aquarium indicator suggested for purchase in the "Shopping List and Solutions." Add three drops of the indicator to a half cup (120 milliliters) of water in a see-through glass or plastic cup, noting as you do the color of the drops as they exit the container and the color of the drops as they diffuse through the water. The drops will be yellowish-orange coming out of the dispenser and greenish-blue in tap water. The reason for

the color change is that the indicator is a mild acid. In water it loses a hydrogen ion to water and in the process changes color. Swirl the solution a bit to mix in the indicator then cover the cup with plastic wrap. Secure the plastic wrap in place with a rubber band or adhesive tape. Wipe the outside of the container clean with a paper towel, and then put the glass in your freezer on a paper towel. Take precautions to keep it away from any food and label it carefully as something not to be consumed. Allow the mixture to freeze solid.

After the mixture is frozen, take it out and look at it closely. You should see that the ice cube formed is clear on the outside and all of the indicator has been pushed together in the middle. The indicator sequestered in the middle will have reverted to a yellow color.

In industry, a technique known as *zone refining* is used to purify metals. In zone refining, the metals are cooled slowly starting on one end of a molten metal rod. The impurities are squeezed to the end of the material where they can be removed. In the ice cube, the water started freezing slowly from the sides of the glass, and as it did, it pushed the indicator out of the mixture and to the center of the ice. Concentrated at the center, the indicator has reverted to the color it was when it was concentrated in its bottle. Zone refining of ice can be seen in regular ice cubes, too. The outside of the ice is clear, but the inside is opaque to solid white. This dense white area in the middle is formed when gases dissolved in the tap water are pushed to the center of the ice cube by freezing.

# CHAPTER 14

## A Whole New Phase

*In the weeks we were together, Hooper became a symbol to me of young England, so that whenever I read some public utterance proclaiming what youth demanded in the future and what the world owed to youth, I would test these general statements by substituting Hooper and seeing if they still seemed as plausible. Thus, in the dark hour before revelry, I sometimes pondered Hooper rallies, Hooper hostels, international Hooper cooperation, and the religion of Hooper. He was the acid test of all these alloys.*

—Evelyn Waugh, *Brideshead Revisited*, ca. 1945

One of the most important concepts in chemistry is that of chemical equilibrium. Unfortunately, it is also one of the more complex and can be confounding. To avoid this dilemma, we will approach the topic incrementally. We have already taken a major step by delving into the subject of thermodynamics. We now take the second step by discussing phase equilibrium, a less complicated and more familiar phenom-

enon. In fact, we are all so familiar with the different phases of one chemical, $H_2O$, that we have a pet name for each phase—water for the liquid phase, ice for the solid phase, and steam for the gas phase—though the phase we commonly call steam, the stuff you can see, is actually an aerosol of condensed water. True steam is invisible, scalding hot, and rather dangerous. The aerosol you can see is formed when hot invisible steam cools and condenses in midair. What we commonly call steam could more appropriately be called *fog*. Phase change is what happens when ice melts, water boils, and steam condenses to fog.

Phase change is caused by heat: heat flows in for some changes, and heat flows out for others. Heat flowing into a system normally shows up as increased rotational, vibrational, and translational energy, giving rise to temperature increases. However, at a certain temperature (a different temperature for each different substance), so much energy has been added to the system that the molecules are able to break free of their intermolecular entanglements and transpose themselves into the next phase. The rigid structure of a solid eases into the loose state of a liquid, or the loose state of a liquid eases into the free state of a gas. When heat flows out of a system, molecular motion slows, and intermolecular forces become important again. Gas turns to liquid, and liquid turns to solid. However, materials do not have to go through all three stages in order. Depending on the pressure, it is possible for a material to go directly from a solid to a gas or vice versa. An example of a material that goes directly from a solid to a gas at room temperature and under normal atmospheric pressure is dry ice, solid carbon dioxide, $CO_2$. This property of dry ice, and the fact that carbon dioxide is denser than air, leads to its use on the theatrical stage to produce fog effects.

The process of going directly from solid to gas phase is called sublimation. Deposition is the process of going from the gas phase directly to a solid. An example of deposition might be frost: under certain conditions, water vapor in the air will deposit as frost without condensing to a liquid first. Sublimation and its companion process, deposition, are shown in figure 1.14.1 along with the common phases of matter and the processes that connect them.

In figure 1.14.1, the lighter arrows on the inside of the triangle indicate changes for which energy is required, changes termed *endothermic* changes. The heavier arrows on the outside of the triangle indicate changes for which energy is given off, changes termed *exothermic* changes. An endothermic

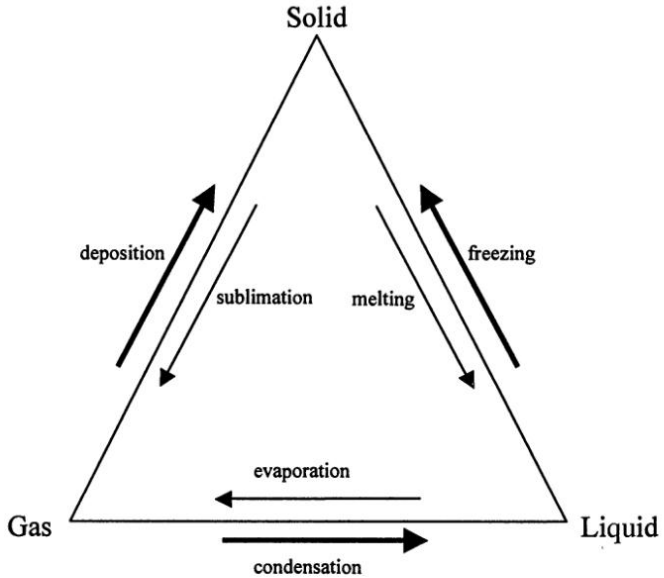



Figure 1.14.1. The normal phases of matter and the physical changes that connect them.

change is one that would take place on a stovetop: melting, evaporation, sublimation. An exothermic change is one that would take place in a freezer: condensation, deposition, and, of course, freezing. The fact that condensation is an exothermic process can be evident in rainstorms: when the gas-phase molecules in the atmosphere condense to rain, heat is given off, which may be sensed as a slight warming of the ambient air.

If that were all there were to the story, this would be a short chapter and chemistry would be considerably less rich. But as we mentioned above, pressure plays an integral role in the wide-ranging behaviors of various materials, which adds another dimension to the discussion. In a mixture, composition also has to be considered, which adds one more factor. Pressure accounts for why ice skating is fun but dry-ice skating is not, and the composition consideration addresses why good pizza goes bad. We'll start with ice skating and have pizza later.

When water boils on the stove, it undergoes a phase change: from liquid to vapor. Bubbles are pockets of vapor that form in the water as it evaporates. The pressure inside the bubbles is the same as the pressure pushing down on the water, otherwise they could not rise and the water would not boil. When pressure is reduced over a liquid, the liquid can boil

at a lower temperature because the vapor pressure inside the bubble does not have to be so great. A slight lowering of the boiling point of water is observed at higher altitudes, which means that the maximum temperature of water at a full boil will be less than 212°F (100°C). At this lower temperature, food can take longer to cook thoroughly, which is why some recipes recommend longer cooking times for foods at high elevations.

The way that pressure affects phase change can be demonstrated with the basting syringe described in the "Shopping List and Solutions." Heat a small cloth in hot water, wringing out excess moisture. Remove the needle from the syringe and draw a small amount of rubbing alcohol up into the syringe. With one finger, cover the end where the needle was attached. Wrap the warm cloth around the top of the barrel of the syringe, but leave the end stoppered by your finger uncovered so you can watch the phase change. Draw up gently on the plunger of the syringe, which will create a vacuum over the alcohol and lower the pressure. You should be able to observe the rubbing alcohol start to boil with just the heat from the warm cloth.

We experience phase changes every day with the weather. Even if it doesn't rain or snow, there is often morning dew. The dew point, the temperature at which the moisture from the air will condense on the ground, depends on the ambient pressure. As such, in the past, dew was used as a sort of primitive barometer for weather prediction. The temperature at which water freezes also depends on the pressure. So when we say the freezing point of water is 32°F (0°C), we should really qualify this by saying this is the freezing point under normal atmospheric conditions. But the slight variations we experience in atmospheric pressure are not enough to change the freezing point significantly, so it is justifiable to neglect this qualification in casual conversation. Saying that 32°F (0°C) is the freezing point is also really indicating that this is the point at which water just begins to solidify, so at this temperature there is also some water present, too, which makes ice skating possible. The thin water layer on the ice allows the skates to slide easily. And although ice skating could obviously be accomplished while wearing boots because of the slippery water layer present on the ice at normal temperatures and pressures, ice skating with skates is more fun because it is one of the peculiar properties of water that increasing the pressure lowers the melting point. The design of the skate focuses the weight of the skater on the narrow blade,

thereby increasing the pressure for an even more slippery ride. Dry-ice skating would not be fun because, as the name implies, dry ice is dry; that is to say, there is virtually no liquid layer present at normal temperatures and pressures.

Because each substance displays unique behaviors with changing temperature and/or pressure—wax goes from a solid to a liquid when it is heated, egg white goes from a liquid to a solid—it would require columns upon columns of data to describe the temperature/pressure behavior of each substance. It would also require a different table for each substance. In the late 1800s, Josiah Willard Gibbs, a gifted mathematician and physical scientist in the United States invented a device, called a phase diagram, that allows all the data to be displayed on a convenient graph.[1] For example, the phase diagram for $H_2O$ is shown in figure 1.14.2.

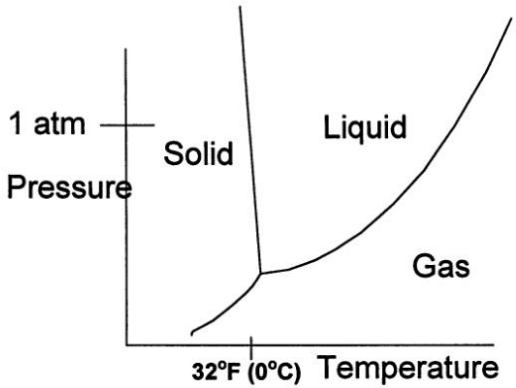


Figure 1.14.2. The phase diagram for $H_2O$.

The phase diagram displays those regions of temperature and pressure that result in the various phases of water: gas, solid, and liquid. The lines between the phases represent the conditions under which the material is in *equilibrium*; that is, it could just as happily be in either phase, so some amount will be in one phase and some amount will be in the other. The diagram shows that under one atmosphere of pressure, which is our "normal" condition, solid $H_2O$ is in equilibrium with liquid $H_2O$—that is to say, it will begin to freeze or melt—at its normal freezing temperature (32°F, 0°C). If the temperature is higher, if we moved to the right on the phase diagram, we would find that water would be in the liquid phase under normal pressure. If the temperature increases to 100°C while we're still level at one atmosphere, then water would be transitioning into the gas phase.

But not unlike the periodic table, there are other layers of meaning in a phase diagram. If, say, the temperature were 100°C and pressure were

higher, then we can tell from the diagram that we would have $H_2O$ in the liquid phase, even though we are at the "normal" boiling point. Also, if the pressure were to go down, the temperature at which the material transitioned from the liquid phase to the gas phase would decrease. This is what happened to the alcohol in our syringe. We can also see from the phase diagram that at lower temperatures water can still be in equilibrium with its vapor, but the vapor pressure will be much lower than at boiling temperatures.

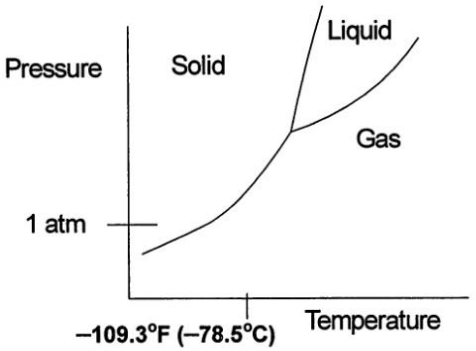


Figure 1.14.3. The phase diagram for carbon dioxide.

The phase diagram of carbon dioxide is shown in figure 1.14.3. From this diagram, we see that at one atmosphere of pressure, carbon dioxide, $CO_2$, is solid only at very low temperatures, and at any temperature above –109.3°F (–78.5°C) it is in the gas phase. So as solid carbon dioxide warms at one atmosphere, it turns directly into a gas (the phase transition called sublimation), which is why solid carbon dioxide is used to simulate fog and why it would be difficult to go skating on it at normal temperatures and pressures: there is no slippery film of liquid, only gas.

It is also possible for a pure material to have several different solid phases. Tin, a material that was once used for organ pipes, can change from a uniformly solid white tin to a powdery gray tin at low temperatures. This phase transition has been termed *tin disease*, or *tin pest.*[2] Ice can solidify into several distinct forms, including ice IX. Reportedly, Kurt Vonnegut, a chemist by training, was unaware of the actual existence of ice IX when he used the name in the plot for his novel *Cat's Cradle.*[3]

The phase changes that occur in mixtures can also be represented by phase diagrams; however, these diagrams tend to be much more complex. A phase is any uniform and stable state of matter, pure or mixture, so each of the different states that a mixture can find itself in qualifies as a separate phase on the phase diagram. There is also the possibility of several phases existing together in equilibrium, and this must be represented, too. Alloys are a class of mixtures that can have distinct phases

and serve to illustrate how complicated these phase changes can become. If you have copper, it is possible to have liquid copper or solid copper, depending on the temperature. If you have zinc, it is possible to have liquid zinc or solid zinc, depending on the temperature. But if you have an alloy of copper and zinc, it is possible to have liquid copper and liquid zinc, liquid copper with solid zinc in it, liquid zinc with solid copper in it, or solid copper mixed with solid zinc, each of which is a separate phase. Which situation will be stable depends on temperature, pressure, and the relative amounts of zinc and copper in the mixture—and that's just for two ingredients. If one counts the number of ingredients listed on the label of a bottle of shampoo, it is easy to see how complex a phase diagram can quickly become. In an attempt to simplify the situation, pressure is usually assumed to be constant, at one atmosphere, and the two variables that are tracked are temperature and composition.

Take the simple system of baking soda in water. As baking soda is added to water, the first few pinches go into solution, but as more is added, the mixture becomes saturated, and a solid is present as well as a solution. In other words, solubility depends on composition: if you have a system composed of mostly water and a pinch of soda, the soda goes into solution; if you have a system composed of mostly water but a lot of soda, the soda comes out of solution. If you keep the composition constant, that is, stick with a glass of water that is saturated with baking soda, then you can see how solubility depends on temperature. If you gently heat the solution in a microwave oven, the baking soda will go into solution as the system heats up and the solution will appear clear. If the solution is allowed to cool, the baking soda will come back out of solution.

Another instance in which solubility changes with temperature and composition is in the fine art of distillation. Distillation takes advantage of the fact that the vapor over a solution will generally have a different composition than the solution from which it came. This difference in composition between a liquid and its vapor can be demonstrated with a glass of water that has food coloring in it. If a glass with just an inch or two of water with food coloring is covered with a thin film of plastic wrap held in place by a rubber band and gently warmed on low power for a short time (fifteen to twenty seconds) in a microwave oven, the inside of the glass will be seen to be covered with condensation. The condensation, however, is clear. It is not colored by the food coloring. This color differ-

ence is because the composition of the vapor phase differs from the composition of the liquid. The vapor phase is pure water, not the mixture of food coloring and water. The water has a lower boiling point than the food coloring, so it enters the vapor phase more readily, leaving the food coloring behind. There may be some food colorings that are able to vaporize with the water, but most will not and the effect is nice to see. If the experiment doesn't work with your food coloring, get different food coloring (old-fashioned food-coloring drops seem to work best) and try again.

Distillation is used to purify water when necessary and has also been employed for a more nefarious purpose. Ethanol, grain alcohol, can be separated from water by heating up the mixture until the ethanol goes into the vapor phase and the water stays behind. However, not all the water can be removed from ethanol in this manner because of the strong intermolecular forces between water and ethanol. There will always be some water in the ethanol. The best you can get with ordinary methods is 95 percent ethanol (190 proof)—more than adequate for most casual applications.

The general observation that solubility usually increases with temperature can also be illustrated with a sugar-water mixture, but this time with a bit of a twist. While it may be true that a tablespoon of sugar is not soluble in a tablespoon of water at room temperature, gentle heating can cause the sugar to go into solution. This transition, from phase to phase, can again be represented on a phase diagram, such as the one shown in figure 1.14.4.

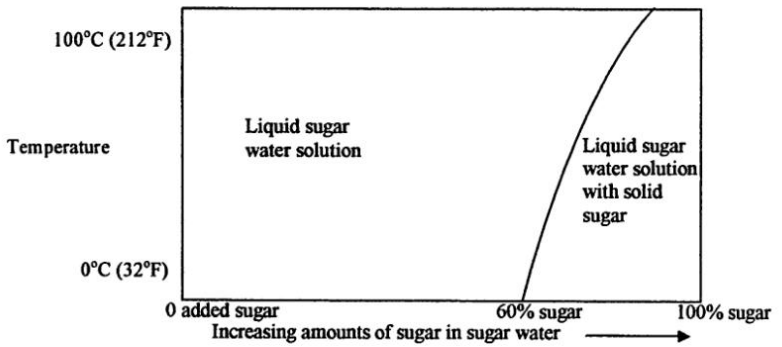



Figure 1.14.4. Phase diagram for the solubility of sugar in water. Note that when we were drawing a phase diagram for a *pure* substance, water or dry ice, the parameters that were varied were temperature and pressure. In this diagram, however, the phase diagram for a *mixture*, temperature and composition are the parameters being varied. Pressure is assumed to be constant.

This diagram tells us that if we have a mixture in which some of the sugar won't go into solution, and the mixture is heated, without changing the composition, the mixture will change phases from a solid-sugar/sugar-water mixture to an all sugar-water solution. In other words, heat up sugar in water and more sugar will go into solution.

This fact may seem a poorly kept secret. The method for forcing more sugar into solution has been known to cooks and bartenders for eons and may hardly seem worth a detailed separate treatment. Hollandaise sauce might also seem a mundane topic for a book on chemistry, but we're going to discuss it here, too, for the following reason: hollandaise sauce is different from sugar water. It displays a behavior that has far-reaching implications—from the London Bridge to Limburger. The difference is in what happens when the hollandaise sauce cools down again.

Hollandaise sauce is a tasty suspension of butter in egg, and when it is warm and freshly prepared, hollandaise pours as a smooth, one-phase mixture. Hot sugar water is a uniform mixture of sugar and water. When sugar water cools down, it remains a uniform mixture of sugar and water. But when hollandaise sauce cools down, something else happens. It separates. Cool hollandaise sauce does not stay together because hot hollandaise is in a *metastable state*, that is, not its lowest energy state but a stable state above the lowest energy state.

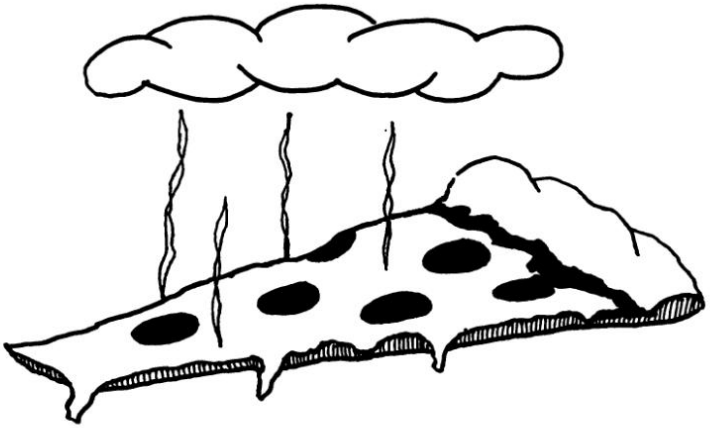
A bowling ball balanced atop a stepladder might be an example of a metastable state. The bowling ball is stable, but not at its lowest energy state, which would be on the ground. At the slightest provocation it will seek its lowest energy state and will come tumbling off the ladder. A system that is proceeding to its most stable state so slowly that it is virtually at rest can also be considered metastable. Hot hollandaise sauce is in a metastable state, but the oils will seek to rejoin each other if they can find a route, which is why hollandaise separates.

Metastable states are not confined to sauce. Metastable states can also occur in systems as diverse as medicines and alloys. Many medicines are *suspensions*, a metastable state of solids disbursed in liquid. Metal alloys are mixtures of metals that normally have to be heated to very high temperature in order to mix. If the mixture is cooled slowly enough, separation, such as the zone-refining described above, would probably occur. But if the cooling is done quickly, a metastable solid mixture can result. Of course, a metastable state implies that there is another state, a stable

state, toward which the mixture can proceed with time. So metal alloys can change their properties, albeit slowly, with time. In other words, structures composed of alloys, such as bridges, can age. It is not only surface corrosion that must be considered when deciding if a bridge is safe but also the age and nature of the material from which it was made.

But there is no reason for immediate concern on the homeward commute. Not only are bridges carefully monitored for the effects of age, their return to their most stable state from their metastable state can be too slow to observe in several human lifetimes, and most bridges are built to last.

But not so with our next concern: cheese.



## For Example: When Good Pizza Goes Bad

Many materials we deal with every day are in a metastable state. Medicinal emulsions and suspensions, shampoos, salad dressings, sauces, and condiments like catsup, mayonnaise, and mustard. But of all the metastable mixtures that have been used for foods, perhaps the oldest and most celebrated is cheese.

It is believed that cheese making was discovered by accident when someone tried to store milk in a bag made out of an animal's stomach and as a result, the enzymes in the stomach curdled the milk.[4] It must have been a very brave or very hungry person who tasted that first cheese, but since then, as a species, we have acquired a liking for the stuff, to the tune of about thirty pounds of cheese per person per year in the United States alone. Cheese, a metastable mixture of oil, water, fats, calcium com-

pounds, and milk, is produced when enzymes harvested from the stomach of calves slowly coagulate proteins into solids. The enzymes that start the process of digesting proteins are in all mammalian stomachs, but in the cheese-making process, the enzymes are allowed to carry out their digestion slowly enough that metastable lumps of solid are formed, surrounded by a liquid containing fats and sugars.

The solids are the *curds*. *Whey* is the more liquid part. Cheese can be thought of as a metastable suspension of curds in whey. The texture of a particular cheese is determined by how the curds are chopped and separated from the whey and the amount of time the cheese is cured or aged. When the curds are not separated from the whey and the cheese is not aged, the result is a mushy mixture called unripened cheese, something like cottage cheese. When all the whey possible is squeezed from the curds and the cheese allowed to age, the result is a solid brick called hard cheese, something like parmesan. Aging consists of allowing bacteria time to complete the coagulating process that the enzymes started, which explains why hard cheese keeps well: it has already been attacked by bacteria and has survived. Soft cheeses, like cottage cheese, which have not been aged, have to be kept in the refrigerator.

The action of the bacteria also serves to break down any remaining *lactose*, a sugar found in milk. Cheese has been much maligned as a difficult food to digest, but in fact, hard cheese that has been made using live bacterial cultures should be easier to digest because it does not contain lactose. Adults that are lactose intolerant are often advised to eat cheese as an alternate source of calcium and protein. It has been speculated that cheese's bad reputation for being "binding" may arise from the experience of long-time sufferers of food sensitivities and loose stools who find the normal digestion of cheese "binding" by contrast! There are, however, many cheese products that have milk added back in, so read the label carefully.[5]

Of the thirty pounds per person per year of cheese consumed in the United States, a good deal of it is in the form of melted cheese found atop our new national food: pizza. Pizza has its own yellow-pages heading in most phone directories, a privilege not accorded to apples, artichokes, or spinach. And although the crust and the sauce may be important to good pizza, it must be acknowledged that without the cheese, pizza would just be an open-faced tomato sauce sandwich. The quality and proper properties of pizza cheese is a topic that preoccupies pizza entrepreneurs.

What is the most important property of a good pizza cheese? Taste, of course. But also the ability to melt smoothly, uniformly, and without separating back into curds and whey—which is why pizza is not topped with an unripened cheese like cottage cheese, or a hard cheese like parmesan, but a semisoft cheese: mozzarella.

As we have said, the degree of softness or hardness of a cheese depends on the amount of curds and whey, so we may be able to illustrate the problem with a stylized phase diagram that we could call Little Miss Muffet (LMM): a phase diagram for mixtures of curds and whey.

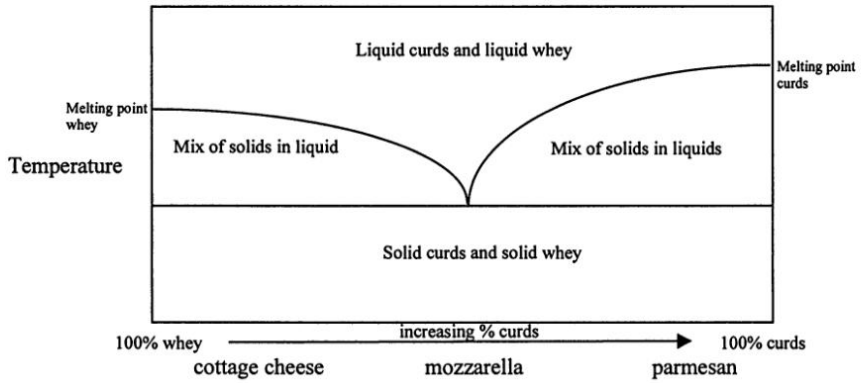



Figure 1.14.5. The LMM hypothetical phase diagram for cheese.

Before interpreting our LMM diagram, we must first acknowledge that LMM is not a real phase diagram. A true phase diagram for a real cheese would be much more complicated. The purpose of this phase diagram is to show how melting and freezing behavior can depend on composition, not to explain the chemistry of cheese. For instance, if a very liquid cheese, such as cottage cheese, is heated in the microwave it will gradually become a uniform mush of curds and whey, and when it is cooled, it will eventually separate into layers of clear liquid whey and white liquid curds. The stuff we call cottage cheese is a metastable suspension of solid curds in liquid curds and whey. A hard cheese might have to be heated to a much higher temperature before it will melt, and it may very well burn before it melts, but if heated gently to a temperature below the melting point, it will start to "sweat" and exude an oily liquid. Because hard cheese, as purchased, is in a carefully crafted metastable

state, the cheese will not return to its original state when cooled. After temperature-induced phase separation, the texture of the cheese will have changed when it is cooled; it will have become more brittle or stringy. What is needed for good pizza, however, is a cheese that will not separate like an unripened cheese or sweat like hard cheese. When it came to choosing the best cheese for pizza, people gravitated toward a semisoft cheese, mozzarella, because mozzarella melts smoothly and evenly. We have come to believe that mozzarella is the best-tasting cheese for pizza because that is what we are used to. Actually, another cheese might have done just as well if its phase-change behavior would have been more accommodating.

Another advantage to using mozzarella is that even as a mixture it melts quickly and uniformly at its melting point. For most solid mixtures, the mixture melts over a range of temperatures; that is, the mixture will begin to melt at one temperature, but the entire mixture will not be liquid until it has been heated to some final temperature.

There can be, however, some interim mixture that has just the right composition to show an abrupt, decisive melting point. In chemistry, this single-melting-point mixture is called the *eutectic* mixture. In cheese, it's called mozzarella. Solder is a eutectic mixture.

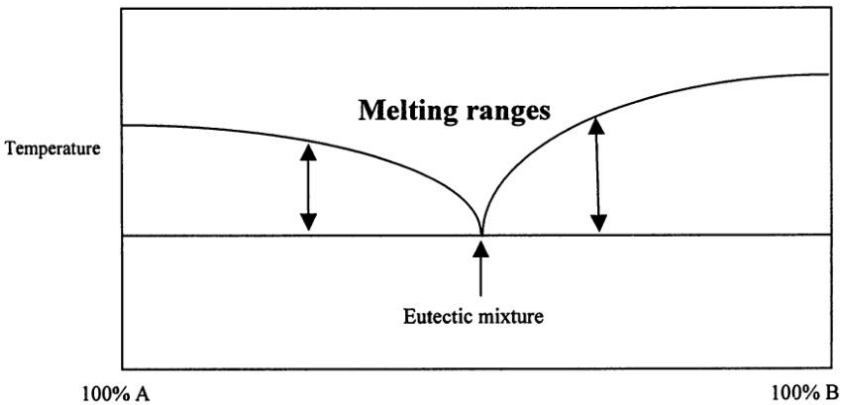



Figure 1.14.6. A generic phase diagram for a mixture showing the melting behavior of a eutectic mixture such as solder.

However, the problem facing the pizza entrepreneurs of America is not just melting cheese but freezing it as well. Pizza lovers of America

demand immediate access to their favorite food, which means a form that can be frozen and then quickly prepared in a microwave or convection oven. But cheeses can fare badly when undergoing quick phase changes such as freezing in a freezer and heating in a microwave. Freezing followed by quick heating can result in a crumbly, stringy, tough texture, or burned cheese. The solution has been to use processed cheese, which is a mixture of ground cheese, emulsifying salts, and other stabilizers. Processed cheese allows pizza to be frozen and reheated or even sit out on a table for a fairly extended period of time. The best phase transitions from frozen to melted, however, are achieved by imitation cheese formulated from soybean oil and curds.

To demonstrate the difference in phase change behavior, purchase some shredded real mozzarella and shredded imitation mozzarella topping. Given the existing labeling laws, imitation mozzarella will be clearly marked as imitation, but if there is doubt, a look at the ingredients list should make the difference clear. Place a pinch of each on either side of a paper plate and write "real" and "imitation" on the paper plate near the respective piles. Heat the plate with the cheese samples in a microwave for twenty to thirty seconds. You should see the imitation mozzarella melt smoothly and retain its color and pliability. The real mozzarella will likely turn brown and become brittle and unpleasantly hard. Leaving fresh piles of the real mozzarella and imitation mozzarella out on the counter for two days should result in the real mozzarella's becoming brittle and dry, but the imitation topping should appear as fresh as when it came out of the package.

So if your goal is to defeat the physics of phase change, imitation mozzarella is the way to go. But not if you want to preserve the wonderful aroma. The chemistry is just not the same. Unfortunately, our many experiences with processed cheese have led to an expectation of robustness in our pizza that will not be there if the pizza is made of unprocessed ingredients. So if you invest in a really good pizza, and there is enough left over to store, you may want to do so cautiously. Treated respectfully, true mozzarella may fair just fine; frozen pizza should be thawed before reheating, and it should be reheated on low in the microwave, or perhaps better yet, in a warm oven. But even with these precautions, there may be changes in the texture and taste. So the best

idea is to enjoy—eat the pizza when it is fresh and good. If you must, then freeze, but do not be disappointed if that good pizza goes bad.

There remains, however, an additional problem that no amount of stabilizer will fix. And that is that frozen pizza will inevitably dry out in the freezer if it is not properly sealed. For those uninitiated in phase diagrams, the drying out of food in freezers may seem strange. But by looking at the phase diagram for water, it can be seen that at about 32°F (0°C), the temperature of most freezers, solid ice is in equilibrium with a water vapor, though the vapor pressure is much less than one atmosphere. So water vaporizes in a freezer, but because the freezer is sealed most of the time, we might still expect the water loss to be minimal. The difficulty, however, is that frostfree freezers maintain their freedom from frost by circulating air and collecting vaporized water before it has a chance to deposit on the side of the walls as frost. In other words, because water is constantly being removed from circulating air, the water in the freezer is not in equilibrium—it is not in its happy, balanced state with some in the liquid phase and some in the gas phase. More water vapor will be produced from the food as the system tries to restore equilibrium. This drive to establish equilibrium accounts for the fact that ice cubes slowly get smaller in the freezer and poorly sealed frozen pizza can suffer freezer "burn" and will not remain pristine forever. An interesting extension of this manifestation of physical equilibrium is to consider what happens when one hangs one's laundry out to dry in Antarctica. Does it dry? Yes. As long as the air is removing the water vapor from the immediate vicinity of the frozen laundry, the icicles in the underwear will keep evaporating to try to restore equilibrium.

The other kind of equilibrium we now consider, chemical equilibrium, is every bit as common but not always as easily recognized as such and certainly more complex. But complicated or not, it is where we are headed next.

## Demonstration 15: All Things Being Equal

*Without any objective change whatever, variety had taken the place of monotonousness. His host and his host's household . . . began to differentiate themselves as in a chemical process.*
—Thomas Hardy, *Tess of the d'Urbervilles*, ca. 1890

Put on the old safety glasses. Take the copper sulfate solution, prepared as suggested in the "Shopping List and Solutions," and pour about two inches into a clear glass or see-through plastic cup. Take a clear soda bottle, add a half cup (120 milliliters) of water, and then use your funnel to add two tablespoons of baking soda to the water. Shake this solution. While waiting for it to settle, pour two to three inches (5 centimeters) of vinegar into a second clear soda bottle.

Add three or four drops of the baking soda solution to the copper sulfate, making certain no undissolved baking soda is transferred over when you add the drops. You can avoid transferring over undissolved baking soda by using an eyedropper or a straw covered by your finger to pick up drops from the top of the baking soda solution and by being careful not to stir up the sediment on the bottom.

As soon as you add the baking soda solution to the copper sulfate

solution, a lightly colored, fluffy precipitate should form and sink to the bottom of the glass. Because you have been careful to add no other solid, this precipitate must be a product of the reaction of the copper sulfate and the baking soda and is, in fact, copper carbonate.

copper ion + carbonate ion → copper carbonate (solid)

If you add a few more drops of baking soda solution, you should see the volume of precipitate increase. The solution above the precipitate should remain blue, which indicates the presence of copper sulfate that has not reacted.

Now add several drops of vinegar to the glass and watch the fizzing that shows the removal of carbonate from the solution. Recall that vinegar is an acid and baking soda is a base. They react to form carbonic acid, which immediately dissociates into water and bubbles of carbon dioxide.

vinegar + baking soda → carbon dioxide + water

If you watch carefully, you will see that the fizzing occurs at the surface of the solution just as the drop of vinegar enters. Keep adding drops of vinegar until the solution stops fizzing. You may need to stir the solution in the glass a little after each addition. As vinegar is added and carbonate ion removed, the precipitate in the bottom should start disappearing.

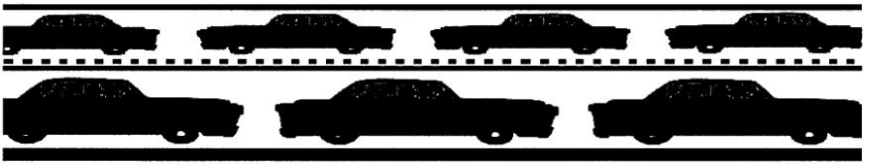
copper carbonate + vinegar → copper ion + carbon dioxide + water

When the fizzing has stopped and the precipitate has disappeared, add baking soda solution again until precipitate forms again. Then remove the precipitate again with drops of vinegar. This back-and-forth process will continue as long as you keep disturbing the situation by adding carbonate ion or removing carbonate ion by adding vinegar. (Or until the solution becomes too dilute, but the cup would probably overflow before this happened.)

When the baking soda is added initially, copper carbonate comes out of solution until the system is in *equilibrium*; that is, the system is stable and balanced with tolerable amounts of copper carbonate as precipitate and tolerable amounts of copper and carbonate ions in solution. Chemical reactions, however, are not one-way streets; the traffic flows both ways.

So when this equilibrium was upset by removing some of the carbonate ions by allowing them to react with vinegar, the reverse reaction occurred. The system restored its equilibrium by shifting some of the precipitate back into solution. When more carbonate ion was added, the system responded by forming more precipitate again.

Understanding the back-and-forth of chemical equilibrium is of paramount importance to the art of manipulating chemical reactions and is the subject of our next discussion.



# CHAPTER 15

## Equilibrium—Chemistry's Two-Way Street

*Lily sat gazing absently through the blue rings of her cigarette-smoke.*

*"It seems to me," she said at length, "that you spend a good deal of your time in the element you disapprove of."*

*Selden received this thrust without discomposure. "Yes; but (t)he real alchemy consists in being able to turn gold back again into something else; and that's the secret that most of your friends have lost."*

—Edith Wharton, *House of Mirth*, ca. 1905

The preceding demonstration, "All Things Being Equal," was intended to illustrate three significant subtleties concerning chemical reactions. The first is that although we often symbolize chemical reactions with neat little arrows pointing from reactants to products,

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

the truth, as suggested several times in previous discussions, is that chemical reactions are really two-way streets. That is, chemical reactions are reversible. If a reactant can become product, then product can become reactant. So although we haven't emphasized this aspect of chemical reactions thus far, whenever a chemical reaction is "done," we are normally left with a mixture of reactants and products, called an *equilibrium mixture.*

Granted, sometimes a reaction will go essentially all to products. When gunpowder explodes, it turns almost entirely into products. "Almost" is an important qualifier here, as gunpowder residue has undone many a miscreant. Other times a reaction mixture may remain virtually unreacted starting material. This problem was faced by Haber in the manufacture of ammonia, as may be recalled from our discussion of gas-phase reactions. Hydrogen and nitrogen gases were all around him, but he had to struggle mightily to bring them together to make ammonia. Many other reactions, however, are like clabbered milk. Clabbered milk is milk in which curds have formed and can be made by pouring vinegar in milk. The curds form immediately when the vinegar is added, but some vinegar and milk remain. The reaction occurs very quickly, but once it is over, the final ratio of curds to uncurdled milk and vinegar stays the same over time. The reaction has reached equilibrium.

The second point we wished to illustrate with "All Things Being Equal" is that saying a reaction has reached equilibrium is *not* the same as saying there are no more reactions taking place. In fact, equilibrium mixtures tend to be very active—with reactants continuously turning into products and products turning back into reactants. This dynamic quality of chemical systems can be illustrated in a straightforward way. Cut a strip from a paper towel and lay it over the edge of a glass containing a little water so that the end of the paper towel just dangles in the water. The water will rise up in the towel only so high and no higher because the water and the towel will eventually establish an equilibrium between the attractions of the towel for the water, the attractions of the water for itself, and gravity pulling the water down. Wait ten minutes to let the towel soak up as much as it will, and then add a drop of food coloring to the water at a spot that is well away from the dangling paper towel. The food dye will disperse by entropy (as we established in our chapter on thermodynamics) and eventually the color will creep up the paper towel, too. The

color can creep up the towel because the water molecules in equilibrium are always changing places: some towel molecules are becoming puddle molecules and some puddle molecules are becoming towel molecules. When the dye is added, the new puddle molecules that replace the old ones bring the dye along, too.

But even with all this activity, equilibrium is maintained because reactants change into products and products change into reactants at rates that maintain the same relative amounts of reactant and product. We call this type of equilibrium a *dynamic equilibrium*. Although the net effect may appear constant, it is maintained by steady rates of change. An analogy may be found in a traffic situation. Viewed from a traffic helicopter, the density of cars on a congested freeway may appear fairly constant, but it is the result of constant change: there are new cars entering and exiting all the time.

Which brings us to the third point being illustrated in "All Things Being Equal": as a result of all this activity—products turning to reactants and reactants to products—chemical reactions are flexible. They can respond and adjust to change. If products are removed, the system responds to produce more products until the equilibrium ratio is reestablished. If reactants are added, the system responds to produce more products. In our traffic analogy, this might correspond to the equilibrium between cars on side streets to cars on the freeway:

cars on side streets ↔ cars on freeway

Here cars on the side streets represent our reactants and cars on the freeway represent our products. Our arrow points both ways because cars are getting onto the freeway and off of the freeway. The equilibrium is dynamic and it is reversible.

Early in the morning, there may be a few cars on side streets and a few cars on the freeway, but at 7:30 the number of cars on side streets may suddenly increase.

cars on side streets ↔ cars on freeway

The system will soon respond, and the number of cars on the freeway will increase until equilibrium is reestablished.

# cars on side streets ↔ cars on freeway

In our above chemical demonstration, we also had a dynamic, reversible situation: copper carbonate precipitate formed, but it also redissolved. When we added vinegar, we removed some of the carbonate from the equilibrium. The solid redissolved in an effort to reestablish equilibrium concentrations of both reactant and product.

The ability of chemical systems to respond to stress is captured in *Le Châtelier's principle*, named after Henry Le Châtelier, an influential French chemist of the early 1900s.[1] According to Le Châtelier, whenever a chemical system at equilibrium is stressed, the system will shift in a manner that relieves that stress. This stress can be induced by a change in the quantities of products or reactants, which means we can coax a reaction to produce more of the product we desire. For instance, let's look at a generic reaction:

$$A + B \leftrightarrow C$$

where A and B are reactants and C is a product.

The classic analogy to use at this point is a seesaw, and we will not shy from it because the picture works quite well. When the system is in equilibrium, the seesaw is balanced. This situation is represented by figure 1.15.1a.

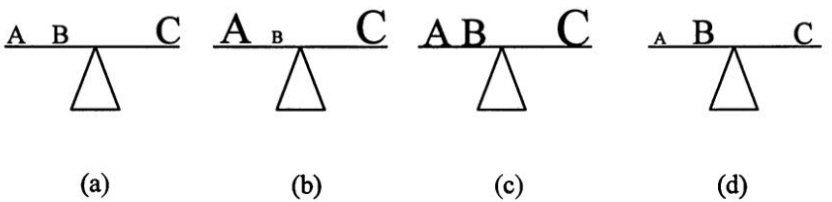



Figure 1.15.1. An equilibrium can be seen as a balanced seesaw. When one side changes, the other adjusts to restore the balance.

If we increase A, the system responds by consuming B to produce more C and reestablish equilibrium. This situation is represented in figure 1.15.1b.

This trick could certainly come in handy if you were in the business of producing C. If, however, your business was to produce B, then there

are two tricks you could try. You could increase C to force an increase in B, which would also increase A. This situation is shown in figure 1.15.1c. In our discussion of water softeners, we said that after the water softener is saturated with calcium ions, these ions can be removed by backwashing with large amounts of sodium. This backwashing is an example of increasing the product to shift the equilibrium back toward the reactants.

Alternatively, you could remove some A, which would cause the reaction to shift toward the reactants in an effort to restore equilibrium. As A is replenished, more B is formed and C is depleted. This situation is shown in figure 1.15.1d. All of these techniques have been used at various times in industrial applications. Pretty handy.

The stress on the equilibrium could come from a change in the amount of available energy, too. If a reaction requires energy, energy can be thought of as a reactant. When we dissolved baking soda in water, we noticed the solution became cool. We also saw that warming a baking soda solution increased the solubility of the baking soda.

$$\text{heat} + \text{baking soda} + \text{water} \leftrightarrow \text{baking soda solution}$$

Combining this observation with Le Châtelier's principle gives us a handle on manipulating reactions with heat. If a reaction requires heat, adding heat will cause the reaction to shift to the product side.

$$\text{heat} + \text{baking soda} + \text{water} \leftrightarrow \text{baking soda solution}$$

We can shift the balance the other way by cooling the solution, which, in essence, is removing heat. When we allowed our warm baking soda solution to cool, more baking soda came out of solution.

$$\text{heat} + \text{baking soda} + \text{water} \leftrightarrow \text{baking soda solution}$$

So now we have established that chemical reactions are dynamic and reversible, and, as a result, chemical reactions are an equilibrium mixture of reactants and products. We have also seen that sometimes the reaction strongly favors the products (as in reacting gunpowder) and sometimes the reaction strongly favors the reactants (as in Haber's ammonia synthesis from nitrogen and hydrogen). We haven't answered one question,

though, and that is, Why? Why are reactants sometimes favored, and why is it sometimes the products? What determines to which side the equilibrium will lie?

One deciding factor is energy. The natural tendency of chemical systems, as with other physical systems, is to move to a state of lower energy. Acids neutralize base. Batteries run down. When all other factors are equal, a reaction will spontaneously adjust to lower its energy and discharge excess energy in the process. But we saw citric acid very spontaneously go into solution, and this mixture *cooled*—it *absorbed* energy—so lower energy can't be the only consideration. To understand the second factor involved, consider the examples we gave at the beginning of this discussion. One reaction went nearly completely to products, gunpowder, and one that stayed nearly completely as reactants—the synthesis of ammonia from nitrogen and hydrogen. The reaction that went to products produced gas-phase products. The reaction that stayed reactants had more reactants in the gas phase. What is the attraction of the gas phase? What does the gas phase have that other phases don't? Entropy. More entropy. What finally determines the position of equilibrium, either favoring the reactants or favoring the products or somewhere in between, is the trade-off between energy and entropy: a situation again best illustrated by analogy. The analogy we choose this time is a trade show.

Trade shows have become so prevalent in our modern world that there are now trade shows for everything and everybody, from computer lovers to campers and from chemists to corrections officers. At a trade show, typically held in a large convention center, people who have items or services to sell that target a trade or special interest group can set up booths to hawk their wares. Because the purpose of the trade show is actually more to advertise than to make sales, the people who staff the booths count their success by the number of people who visit their booths. To attract visitors, the salespeople may offer free goodies for visiting their booth, such as pens, pocket knives, binders, or such. At our equilibrium trade show, we will imagine a very enterprising firm that has decided to offer free vacation giveaways to anyone who visits its booth. Now let's see what the consequences of that action might be.

To begin with, we'll let the booth with the free vacations represent our low-energy state, and we'll set that booth on the products side of the

auditorium. We'll now imagine another booth that is charging a five-dollar entrance fee to its booth. We'll call that our high-energy state, and we'll set it up on the reactants side of the auditorium. In between and all around are other booths that are not charging or offering free vacations. Now we'll open the door and allow in the conventioneers. As may be imagined, many will immediately gravitate to the low-energy booth to get their free vacation. This is the situation shown in figure 1.15.2. The reaction being represented here would favor the products because going over to the product side lowers energy in the form of a relaxing, energy-lowering free vacation.

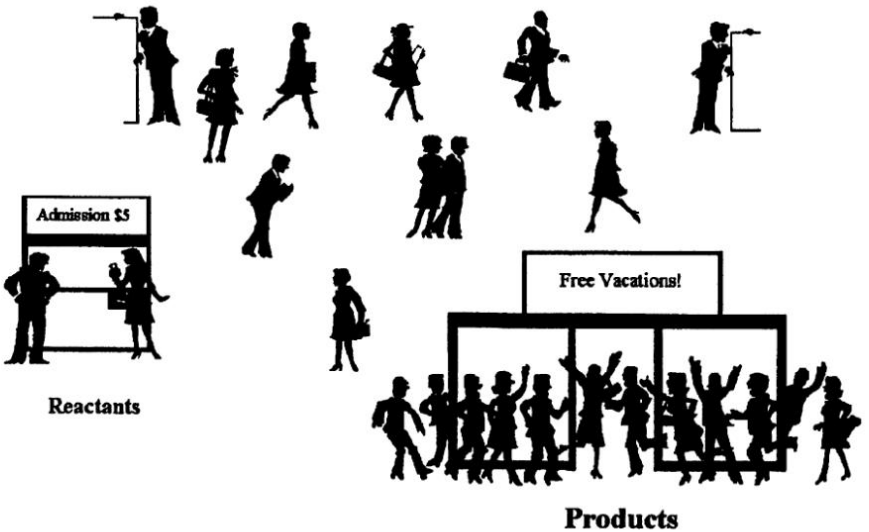



Figure 1.15.2. Attendees at a trade show will tend to gather at the big booth that is offering free vacations because this booth promises a relaxing, low-energy vacation.

However, not everybody will be able to go to the booth with the free vacation because there just isn't enough room around the booth to fit everyone in. Some of the people will be crowded out and will find themselves wandering to the other booths. People will spread over the auditorium because people don't like to be crowded together. We will call this desire to spread out *entropy*.

A molecule of sugar is fairly well located in a handful of sugar. But

if that handful is tossed into the ocean, the molecules will spread to the four corners of the globe. This urging by entropy to spread out can cause at least some reactants to take a little heat and go uphill in energy. Because of their desire to spread out, some people will even make their way to the high-energy booth. One or two may even pay the five-dollar charge. The final equilibrium ratio established between the people at the products booth and the people at the reactants booth will be controlled by the desire of the trade show attendees to lower their energy *and* spread out, but in this case will favor the products.

Let's now change the situation a bit. Let's make the free-vacation booth very small and the five-dollar fee booth very large. Fewer people will go to the free-vacation booth because people hate to be squeezed together. They will want to spread out. More people will find themselves at the huge five-dollar booth—even at the five-dollar cost. The equilibrium ratio for this situation will be reversed. The equilibrium will favor the reactants. This situation is illustrated in figure 1.15.3.

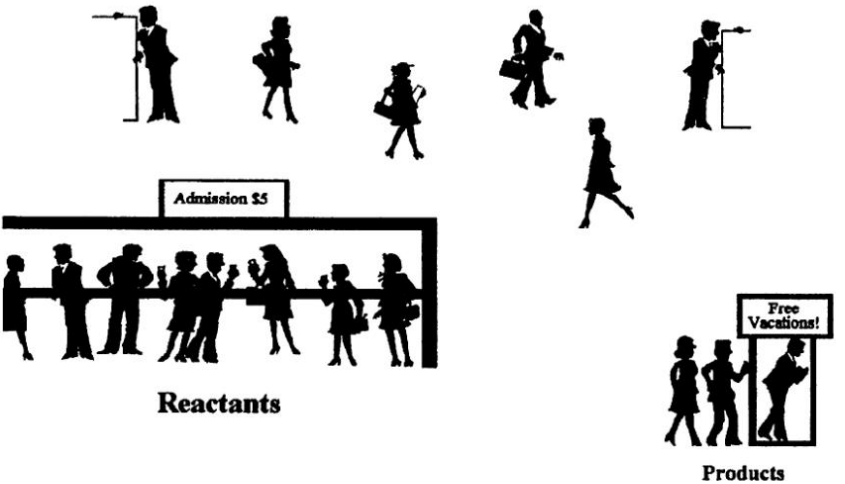



Figure 1.15.3. If the free-vacation booth becomes too cramped, people will gravitate to the booth that allows them to spread out, even if the cost is higher.

Chemical reactions can behave in this manner, too. At equilibrium the molecules will distribute themselves between products and reactants in a manner that allows them to minimize their energy and maximize their entropy. But it is always a trade-off. So if there is little to be gained either way for entropy, lower energy will carry the day. But if there is a lot of

entropy to be gained, even reactions that require an input of energy can happen spontaneously.

Of course, some reactions have it all—in the explosions in a car engine, gasoline lowers energy by giving off heat and increases its entropy by turning into gases. The heat generated causes the gases to expand, further increasing the entropy.

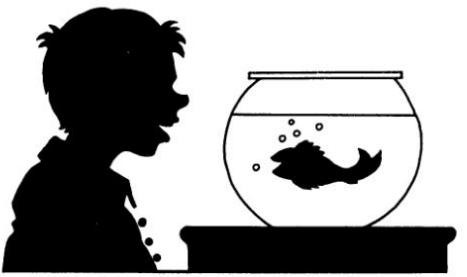
$$\text{gasoline} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$$

So the stuff that comes out the tailpipe is basically carbon dioxide and water—with a little soot and NOx mixed in, as previously noted.

So there we have it. The final position for an equilibrium will be determined by the desire to lower energy and maximize entropy: maximum stability. The trade-off is between energy and entropy. In our discussion of thermodynamics, you may recall, we gave this trade-off a name: free energy. Where there is no more free energy to be given off, when there is no more energy free to do work, we have reached a pleasant state of quiescent equilibrium.

And equilibrium always carries the day. Equilibrium may be held at bay for a time, and systems may even enter a metastable state, but ultimately, equilibrium rules. Chemical reactions are able to respond to and adjust to lower energy and maximize entropy because chemical reactions are reversible and dynamic. Being reversible and dynamic means that chemical reactions can be quite pliable and can be coaxed into producing more products or reverting to reactants. Such manipulations are obligatory in chemical industry and the chemical lab, but they are more important than that. Equilibrium concerns us all, every day. As we live and breathe.

## For Example: Breathing Out and Breathing In



In biological systems, equilibrium plays many roles. The one we are perhaps most familiar with is the one

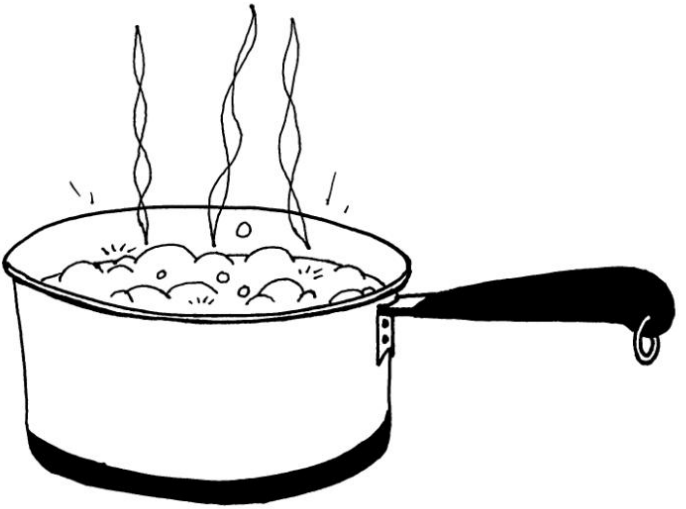
we experience some one thousand to three thousand times an hour, twenty-four hours a day, rain or snow, asleep or awake—and that is the equilibrium established by breathing. Free hemoglobin and oxygen are the reactants, and the bound oxygen-hemoglobin complex is the product. We can represent this reaction as

$$Hb + O_2 \leftrightarrow HbO_2$$

In the lungs, the excess of oxygen in the oxygen-rich air forces the formation of more oxygen-hemoglobin complex, $HbO_2$. The blood containing $HbO_2$ then travels to the cells where oxygen has been depleted. If there is relatively little oxygen in a particular cell, oxygen flows into the oxygen-poor cell.

When the atmosphere contains less oxygen, as in the case at high altitudes, there may not be enough oxygen brought into the lungs. When the cells do not get enough oxygen, a person may experience hypoxia, or oxygen deprivation, which can cause headache, fatigue, dizziness, clumsiness, and nausea. The balance has been tipped, and for the body, that is not good. The body, however, operates on the principles of equilibrium, so if there is a deficiency somewhere, the body shifts to make up for the deficit. Obviously, the body cannot make more oxygen, so it does the next-best thing, it makes more of the other reactant: hemoglobin. A person inhabiting the mountains can have half again as many red blood cells as someone habitually at sea level. Of course, making more hemoglobin creates a deficit in the proteins used to make hemoglobin, so this creates pressure on the cells to make more of these proteins, which sets up a whole cascade of equilibrium-restoring reactions, all triggered by the drive to lower energy and maximize entropy.

Can there be a chemical reaction that does not involve a change of energy and entropy? No. If a new material is forming—the definition of a chemical reaction—then there will be making and breaking of bonds, which means there will be an energy and entropy change. In fact, it is difficult to imagine any process, physical or chemical, that involves energy but does not involve entropy. However, there are physical processes that are driven by entropy and involve virtually no energy change. The spontaneous mixing of food dye and water is an example of an entropy-driven process. There is, in fact, another entire class of reactions driven by entropy, and this is what we will explore next.



## Demonstration 16: Antifreeze and Antiboil

*Everybody's youth is a dream, a form of chemical madness.*
*How pleasant then to be insane!*
—F. Scott Fitzgerald, *The Diamond as Big as the Ritz*, ca. 1922

In this set of four demonstrations, we will illustrate the four *colligative properties of solutions*. The colligative properties of a solution describe how the presence of solute alters the phase-change behavior of the solvent. The properties are intriguing in that they depend only on how many solute particles are present, not the identity of the particles. An analogy might be made with crowd behavior: crowds tend to behave in ways that depend on the size of the crowd, not the individual natures of the people that make up the crowd. Of course, on some level, the individuality of the people will assert itself, and on some level the nature of our particles is important. But the gross effect, the crowd behavior, is what we will concern ourselves with here.

The colligative properties we will be observing are *freezing-point depression*, *boiling-point elevation*, *vapor-pressure lowering*, and *osmosis*. Put on your safety glasses for all four demonstrations.

To demonstrate freezing-point depression, take two old plastic soda or water bottles that still have their caps and rinse them out. Add a cup (240 milliliters) of water to each and screw the cap on one. Into the other, pour a tablespoon (15 milliliters) of table salt, screw on the cap, and shake the contents. If all of the salt dissolves, pour in a little more and shake the contents again. Keep adding small amounts of salt until no more dissolves and, after shaking, there is some salt remaining on the bottom of the bottle. Identify the saltwater bottle with a permanent marker or a strip of tape, tighten the caps of each bottle, and place them both in your freezer. Check back through the day. You will find that the regular water freezes as you would expect, but the saturated salt solution has such a low freezing point that it will not freeze at home-freezer temperatures, which demonstrates freezing-point depression. You can leave both bottles in the freezer to convince yourself that the salt solution will not freeze.

You may be familiar with the property illustrated in the first demonstration, freezing-point depression, if you have ever used an ice cream maker. In ice cream making, the cream mixture is poured into a container and the container is placed in a bath of salted ice. The salt-ice mixture cools to a point below the freezing point of water, so when the water in the cream comes into contact with the sides of the container, it freezes. A paddle to scrape ice crystals off the sides of the container is turned constantly until the cream and ice form a uniform semisolid. The freezing point of the salt-ice mixture is lowered because of the presence of a dissolved solute (salt) in the solvent (water). Antifreeze works on the same principle. Chosen to be noncorrosive, antifreeze is a material added to radiator water to lower the freezing point so the radiator water will not readily freeze.

A second colligative effect, called *boiling-point elevation*, can be demonstrated with vinegar. Vinegar displays colligative effects because it is a solution of acetic acid in water. You can measure the temperature of boiling vinegar with the large-range thermometer suggested for purchase in the "Shopping List and Solutions." These thermometers are not always that accurate, so to see the difference you may have to compare the temperature of boiling vinegar to the temperature of boiling water by putting the thermometer first in one and then in the other. You should find that vinegar boils at around 216°F (102°C) instead of 212°F (100°C), the tem-

perature at which pure water boils. While your thermometer may not read this exactly, the vinegar should still show a higher boiling point than the water does. The boiling point of the solution is higher with the solute than without the solute, which is an example of boiling-point elevation.

Our third demonstration involves the decreased ability for a solution to evaporate when compared to the plain solvent. Once again, this property, called *vapor-pressure lowering*, does not depend on the chemical nature of the solute but simply on how much of the solute is dissolved in the solvent. Take two spoons and crush three aspirin tablets. Take two small, clear cups and add the crushed aspirin to one of the cups. Pour a half cup (120 milliliters) of rubbing alcohol into each. It is necessary to have the solution levels the same. Swirl the aspirin-alcohol cup to mix the contents. (Some may remain undissolved.) Label the cups to show which one contains the aspirin and then set both cups in a similar environment so that they both get the same amount of heat, air currents, and so forth. Side by side on a counter works well. In about an hour, you should observe an obvious difference in the levels in the cups. Although solvent is evaporating from both cups, it is evaporating more slowly from the aspirin cup. The same effect can be observed for vitamin pills or iron tablets dissolved in alcohol. Thus, it is the presence of the solute that causes the effect, not the nature of the solute.

To show that the number of solute particles makes the difference, try the above aspirin demonstration again, but this time set up three or four cups and vary the number of aspirin in each cup. After allowing them to evaporate for about an hour, you should end up with three or four distinctly different solvent levels, ranging from a low with the cup containing the fewest aspirin to a high containing the cup with the greatest number of aspirin.

The last colligative property to demonstrate is *osmosis*. The process of osmosis is rather specialized in that it requires a *semipermeable membrane*: a material that will allow solvent molecules to pass through but not solute molecules. In osmosis, solvent flows from one solution to the other through the semipermeable membrane. If both containers are open to the same atmospheric pressure, the direction of the flow is from the more dilute solution and into the more concentrated solution.

To demonstrate solvent flowing into a concentrated solution, drop a raisin or other piece of dried fruit into water and check it after about an

hour. The raisin will have swollen up as the pure solvent, water, traveled through the semipermeable membrane—the raisin's skin—and into the raisin's cells in an effort to dilute the concentrated contents of the cells. To demonstrate the flow of solvent from the less salty solution of the cells into a salty brine, cut two slices of raw potato as thinly as you can. Even a very thin slice of raw potato will feel stiff and crisp because the cells that make up the potato are completely filled with water. Put one slice in a strong saltwater solution made from one tablespoon (15 milliliters) of salt in one half cup (120 milliliters) of water. Put the other slice in pure water. Wait half an hour and then pull out the potato slices and examine them. The one that was soaking in pure water will still be crisp. The slice that was soaking in salt water will be limp. Compare it to a freshly cut slice of potato. It is limp because some of the water left the cells and went into the more salty brine.

The seemingly effortless movement of the solvent in osmosis is captured by the expression "learning by osmosis." Learning by osmosis implies that the knowledge can be absorbed by proximity alone and does not require effort by the learner. But learning is never truly effortless. Whether in learning or chemistry, there are forces behind osmosis, as well as the other colligative properties, as we will discover in the pages that follow.

# CHAPTER 16

## Colligative Properties—Strength in Numbers

*In the experimental sciences what we know we call the laws of inevitability, what is unknown to us we call vital force. Vital force is only an expression for the unknown remainder over and above what we know of the essence of life.*

—Leo Tolstoy, *War and Peace*, 1866

When dealing with chemical reactions, the first questions usually have to do with the identity of the material. What's the reactant? What's the product? What's that smell? When it comes to the *colligative* properties of solutions, however, the question is how much, not what kind, of solute is in the solution. In other words, it may matter to you whether you put sugar or brandy in your tea, but as long as it is the same number of molecules from sugar as from brandy, it would not matter a whit to the colligative properties of the tea.

The colligative properties of solutions are physical properties, not chemical properties, because the chemical nature of the solute and the solvent remain unchanged. In truth, in solutions where there are significant intermolecular forces between particles, different solutes may

behave a bit differently, but the general effect will be the same. These effects are germane to many chemical processes and control circumstances as diverse as the functioning of the living cell to the preservation of life on the highway.

The colligative properties of solutions are phase-change properties and include an odd collection of effects. Freezing-point depression refers to the observation that solutions have a lower freezing point than the pure solvent. The more particles of solute added, the lower the freezing point. Road crews make use of this effect in the winter when they spread salt on the roads to dissolve the ice. As we mentioned in our discussion of phase changes, a sample of ice will be coated with a thin film of water because of the equilibrium among the phases. Salt sprinkled on ice will dissolve in this water film and make a very concentrated solution. Equilibrium, as we have pointed out, is dynamic, meaning that the molecules in the solid phase are constantly trading places with the molecules in the liquid phase. In this instance, however, the situation is a bit different. When the solid molecules venture into the solution, they create a solution that is no longer at its freezing point, so they do not turn back into a solid. The balance has been tipped toward the liquid phase, and gradually more and more molecules find themselves in solution. Sand is also sometimes used on slippery roads, but sand is apt to be used in situations involving snow or slush, where traction is more of the problem. When the goal is to melt ice, the salt trucks are called out.

Boiling-point elevation refers to the fact that solutions boil at a higher temperature than the pure solvent. The more solute, the higher the boiling point. A solute, such as antifreeze, added to a solvent, such as radiator water, will lower the freezing point of the solution in the radiator so that it won't freeze quite so readily. It turns out the antifreeze could also be called *antiboil* because the same substance that helps to keep radiators from freezing helps to keep radiators from boiling over, too. Two cautions need to be added here. First, *antifreeze* and *antiboil* do not imply radiators won't ever freeze or won't ever boil, just that a lower or higher temperature must be attained to achieve freezing or boiling. Second, the antifreeze one adds to a radiator is a poisonous brew, so it is *not* a substance with which to experiment.

When we talk about vapor-pressure lowering, we are talking about

the behavior of fumes. Any volatile solvent is going to have fumes associated with it, such as the pungent fumes of gasoline or alcohol. In the parlance of chemistry, these fumes are referred to as the vapor above the solvent. The amount of vapor associated with a solvent will depend on the temperature of the solvent, which is why many people associate gasoline fumes with hot summer days more than with chilly winter mornings. The vapor pressure also depends on the amount of solute that is dissolved in the solvent.

Osmosis is the tendency for solvent to flow into salty solutions to dilute them. Osmosis is responsible for the revival of wilted celery when soaked in pure water: water flows into the celery to dilute the salty cells. Osmosis is responsible for pickles pickling: water flows out of the pickles in an attempt to dilute the salty brine. How does the taste get into the pickle? Osmosis is also striving for equilibrium, and equilibrium situations in chemistry are dynamic. At equilibrium, the flavorful molecules will be redistributed between pickle and brine. Recall the demonstration with the paper towel and the food dye: the paper towel was allowed to take on its equilibrium load of water from a puddle, and then food dye was added to the puddle. Because equilibrium is dynamic, some food dye eventually found its way into the towel. At equilibrium there will be more water outside the pickle cell than inside, but the flavoring in the brine will have found its way into the pickle.

Cells exist, and enable life to exist, because the cell membrane is semipermeable: it allows in what the cell needs, allows out what the cell doesn't need, and keeps the contents of the cell from spilling out or drizzling away. An example of the action of a cell's semipermeable membrane can be found by anyone who takes the time to soak in a bath: skin puckering. When asked, most people will say that bathtub skin puckering is caused by water flowing out of the skin. In truth, the folding and bunching of the skin is caused by the skin swelling up with the water it has absorbed. The fluid in the cells is a very concentrated concoction of solutes: proteins, salts, sugars, and other specialized molecules, so the water in the bathtub flows into the cell in an attempt to dilute the cell's contents.

But bathtub amusements are not the only use the body has for osmosis. The body uses the presence or absence of certain solutes to stimulate or inhibit various processes that are necessary for cell growth, reproduction, and repair. Around the turn of the nineteenth century, the German

scientist Jacques Loeb managed to stimulate unfertilized sea urchin eggs to develop to the larval stage by changing the salt concentration of their surrounding solution, thereby establishing life as a physico-chemical process rather than the result of a mysterious vital force.[1]

Nonetheless, colligative properties of solutions still remain a bit mysterious in and of themselves. The current consensus seems to be that there are two major factors driving the observed colligative behaviors. One is that the physical presence of the solute in solution interferes with the normal function of the solvent particles. For instance, the vapor pressure is lower because solute particles take up some of the surface sites from which the solvent would depart into the gas phase. This inhibition of evaporation causes vapor-pressure lowering—and thus boiling-point elevation—because boiling occurs when the vapor pressure of the solvent is equal to the ambient pressure and bubbles of vapor can escape. Solute molecules can also interfere with the intermolecular attractions that facilitate freezing and thereby lower the freezing point. But with these effects accounted for, the major driver for the observed colligative properties is entropy.

As you may recall, systems tend toward a state of maximum disorder, that is, maximum entropy, and a dilute solution is more disordered than a concentrated solution. Now consider two extremes: one in which there are only two particles—one solute particle and one solvent particle—and one in which there is one solute particle in a sea of solvent. The first situation, the one with one particle of solute and one particle of solvent, is considered very ordered because it would be easy to locate the solute particle. The other situation, the one with one solute molecule in a sea of solvent, is considered very disordered because it would be impossible to locate the solute particle. The more dilute a solution is, the more it is disordered.

As we affirmed in our discussion of thermodynamics, systems naturally tend toward a state of maximum entropy. Physical and chemical systems alike favor disorder. It is their natural state. Gases expand. Dyes distribute. Mixtures do whatever they can to dilute. Solutions do not want to lose solvent and become concentrated because there is more entropy in being dilute. The vapor pressure of a solution is lowered so the solution will not lose solvent and become more concentrated. The boiling point is elevated for the same reason. There is also more entropy for a liquid solution than for a solid, so solution freezing is anti-entropic. Hence, solutions experience

freezing-point depression. In osmosis, the motivation is to seek a uniform, dilute solution as a means of increasing entropy.

From pickles to celery to cells: if there is a vital force, it is entropy.

## For Example: Kidneys and Chemistry

What do kidneys have to do with pickles and celery? As it happens, quite a bit. Colligative properties of solutions figure into body chemistry in a big way because the body is just one big salt solution partitioned into cells by semipermeable membranes. The semipermeable membranes of the cells, however, have a much bigger job to do than letting water into limp celery or pulling water out of pickles. Blood bathes the cells in a solution of many particles beside water, and the cells themselves contain a soup of many particles in water. Some of these particles are relatively large, some are relatively small. Some are ions, some are neutral. Some are polar, some are nonpolar. Some are supposed to be there, some are not. To regulate the composition of cell contents, the blood must be rich in what the cells need and deficient in whatever the cells consider waste. The tricky part is deciding what is waste and what is not: what stays and what goes.

For instance, urea, the product of protein digestion from which the term *urine* is derived, must be removed. Other waste products of metabolism must be removed. Any toxins produced by bacteria must be removed. Any drug residue or other unusable material must be removed. Any excess hormone must be removed. Glucose, on the other hand, should not be eliminated and proteins should not be secreted. Vitamins need to be saved, as does calcium and a certain amount of sodium and other minerals. However, water must be regulated. Too much water in the blood would be bad because if blood were too dilute, then not enough nutrients would be transported to the cell. If blood had too little water, then the physical process of pumping the blood around would be

impaired. The job of the kidneys is to sort among the various materials that come floating by and choose what to keep and what to flush.

One straightforward mechanism employed by the kidneys is good old-fashioned filtration. Water and small molecules are squeezed out of the blood by applying pressure, as in an espresso machine. The solution that comes through the filter (the coffee, as opposed to the grounds, in our espresso example) is called the *filtrate*. Red blood cells are too large to be filtered at this point and should stay out of the filtrate. Any red blood cells visible in urine indicate a possible leak in the lines and should be brought to the attention of a physician.

However, a filter isn't very discriminate, and some of the materials small enough to pass through the filter actually need to be retained. The kidneys compensate by having special proteins called *transporters* on the kidney membranes that recognize and reabsorb molecules such as certain sugars and proteins. Of course, the body has developed transporters only for those substances that it has manufactured itself or routinely takes in from the environment. Human-developed drugs are categorized by the body as waste and, as such, are eliminated. Therefore, drug dosage has to be timed and regulated to keep adequate quantities in the blood.

The blood must not be allowed to become too acidic or too basic—the pH of the blood must not be allowed to go too high or too low—so the carbonate and bicarbonate ions must be carefully regulated. If there is too much carbonate, it will be skimmed off and removed, and if there is too little, there is a mechanism for restoring this equilibrium, too.

A product of kidney cell metabolism, like the metabolism of all cells, is carbon dioxide. As we have noted before, carbon dioxide reacts with water to form carbonic acid, some of which becomes carbonate in the blood. Under other circumstances, carbon dioxide would be transported to the lungs and exhaled. But if it is needed by the blood to restore pH, this carbon dioxide can be retained.

Of all these intricate and specialized mechanisms for partitioning materials between the blood and the waste stream, osmosis is extremely important. However, if osmosis were allowed to proceed without regulation, our cells might swell or collapse like ungoverned celery and pickles. Luckily, there are hormones produced by the body that affect the permeability of the membranes across which osmosis takes place. One such hormone is the antidiuretic hormone, ADH.

ADH is secreted by the pituitary gland, a gland located at the base of the brain. The pituitary gland is also responsible for secreting other hormones that regulate growth and metabolism. When the pituitary gland detects high levels of sodium in the blood, ADH is released so that water will be retained by the kidneys, the blood will be more dilute, and there will be less water loss by the cells—a mechanism that no doubt worked quite well when we were running across the savannah and eating the diet that we had evolved to eat. Unfortunately, we no longer run as much as we used to, and we tend to have much more sodium in our diets than would have ever been available to us on the savannah. Therefore, water retention can be abnormally high, which can upset many body systems. Certainly weight-loss regimens can be defeated by either eating diet meals made tasty with too much sodium or by refraining from drinking water in the belief that excess water will be retained. In truth, extra water dilutes the blood and convinces the body that it is okay to shed water rather than retain it. In addition, dehydration brings about fatigue (when the body senses a lack of water, it attempts to conserve what it has), which makes exercise less likely. So while drinking extra water on a diet may seem counterintuitive, it could help increase the metabolic rate.

Metabolic rates are not the only rates that can be manipulated. The rates of all chemical reactions, from the most explosive to the most sluggish, are described by a set of basic principles, and it is these that we will look at next.

## Demonstration 17: Kick It up a Notch

*I saw a telegram handed to a two hundred pound man at a desk. . . . He gave the boy a nickel, tore the envelope and read. Then he yelled "Good God," jumped for his hat and raincoat, ran for the elevator and took a taxi to a railroad depot. . . . (I)t was like a set of crystals in a chemist's tube and a whispering pinch of salt. . . . I know a shoemaker who works in a cellar slamming half-soles onto shoes, and when I told him, he said: "I pay my bills, I love my wife, and I am not afraid of anybody."*

—Carl Sandburg, *Smoke and Steel*, ca. 1922

*Syme sprang to his feet, stepping backwards a little, like a chemical lecturer from a successful explosion.*

—G. K. Chesterton, *The Man Who Was Thursday*, ca. 1908

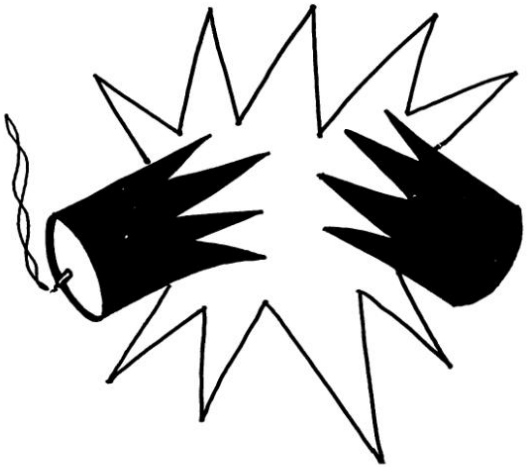
Two major factors that affect the rate of a chemical reaction—the *kinetics* of the reaction—are concentration and temperature. The effects of both are easily demonstrated using items from our "Shopping List and Solutions."

For the first demonstration, put on your safety goggles and pour a half cup (120 milliliters) of household bleach straight into each of two small clear cups. Be careful that the bleach doesn't splatter, just as when doing the laundry. You may want to wear gloves to protect your hands. Place both cups on a sheet of white paper so the color is easy to observe. Make sure you have a watch or clock in a convenient viewing location.

Add two drops of methyl red indicator (found in the swimming pool test kit) to the first cup. Immediately after the addition to the first cup, add four drops of methyl red indicator to the second cup. Swirl both cups gently to ensure mixing. Set both cups down on the white paper and note on the paper the time at which the drops were added. The red color present in each cup will fade slowly over the next five to ten minutes as the bleach attacks the dye molecules that are coloring the solutions. When the red color is gone from the cup with two drops, note the time on the paper and turn your attention to the cup with four drops. Note the completion time for that reaction on the sheet of paper. You can empty everything down the toilet bowl, but make sure to avoid splattering the bleach.

You can watch the color fade because chemical reactions take time. Some reactions are extremely fast and some are extremely slow, but they all take time. The bleach reaction is paced so that we can observe the process without growing old ourselves. You should have observed that the cup with four drops of dye takes longer to react than the cup with two drops. However, it is not twice as long, even though there is twice as much dye to attack. The rate of reaction is affected by varying the concentration, but not always in a direct way.

The effect of temperature on reaction rates can be demonstrated with two tablets of effervescent antacid, two cups, and tap water. Into one cup, place a half cup (120 milliliters) of cool tap water from the faucet. In the other cup, place an equal amount of hot tap water from the faucet. Drop one tablet into each cup at the same time. The fizzing action is clearly more vigorous in the hot water than in the cool water. In this case, the higher temperature helps in two ways. It forces more bubbles out of solution (which is the same reason you're cautious about opening a warm can of soda), and it increases the reaction rate because molecules at a higher temperature move around faster, find each other more often, and hit each other harder when they do. This effect and other principles concerning chemical kinetics is the subject of the following discussion.



# CHAPTER 17

## Chemical Kinetics—A Veritable Explosion

*Roger, you blessed innocent! . . . Life will no longer be tranquil with a girl of nineteen round the place. You may fool yourself, but you can't fool me. A girl of nineteen doesn't REACT toward things. She explodes. Things don't "react" anywhere but in Boston and in chemical laboratories. I suppose you know you're taking a human bombshell into the arsenal?*

—Christopher Morley, *The Haunted Bookshop*, ca. 1940

Thermodynamics, as noted earlier, deals with the effects of heat and entropy on equilibrium and is useful for predicting the extent to which a reaction will occur. But like an obstreperous child avoiding chores, thermodynamics may tell you the reaction *will* take place, but not *when*. For example, thermodynamics predicts that graphite is a more stable form of pure carbon than diamond, so all diamonds will eventually turn to graphite. But before you start adjusting your investment portfolio, be advised that this transition may take billions of years.

Thermodynamics should not be blamed. There are many pursuits in which it is easier to predict that an event will occur than when it will occur. For instance, we can predict our own deaths with absolute certainly, but imagine how differently we would behave if we could predict when! But regardless of predictability, it is critical to know reaction rates when manipulating chemical reactions. It may not come up in everyday conversation that diamonds are gradually turning into carbon dust, but explosions make the nightly news. The goal of the study of reaction rates—chemical kinetics—is to measure and study the rates of chemical reactions with an eye to predicting how fast or slow a given chemical reaction will proceed and how to speed it up, or slow it down, as needed.

The word *kinetics* implies movement—as in kinetic art or kinesiology, the study of human muscles and motion. The word *kinetics* was chosen to describe the study of reaction rates because reaction rates rely on the movement of molecules. Scientists have been measuring reaction rates since at least the mid-1800s in Europe, but the explanations of the observed rates had to wait for the general acceptance of a theory of molecular motion. The kinetic theory of molecular motion states that molecules and atoms are always in motion, though the motion may be as subtle as the vibrations of ions in a crystal lattice or as frenzied as gas-phase molecules clocking around 1,640 feet (500 meters) in one second.

At normal atmospheric pressures, however, the distance traveled by a gas molecule in one second would not be in a straight line: the density of atmospheric molecules under normal terrestrial conditions is such that one molecule in the gas phase will experience some seven billion collisions in each second. All these collisions are good news for chemists who study reaction rates because the rate of collision is related to the rate of reaction: before anything else can happen in a reaction, molecules must first come together. They must collide.

The idea that reaction rates are tied to the rate of collision is aptly called the *collision theory of reaction rates.* But nature's mysteries are not so easily solved. During a chemical reaction, the electron orbitals (that is, the electron clouds) on individual reactants overlap and coalesce, the way two bubbles come together and merge into one. Once the conditions are right, it takes about a quadrillionth of a second for the electrons in the individual orbitals to readjust themselves into the orbitals around the products. But if all reactions took place as fast as collisions, then food would cook before

you could blink; paint would dry before it was spread; and we would have died as soon as we were born because the metabolic reactions in our body would have burned us up. So why don't all reactions happen in fractions of seconds? The answer is in the phrase "once the conditions are right."

To begin with, gas-phase reactants may encounter each other billions of times per second, but solution-phase reactants can be held apart by a sea of solvent and encounter each other far less often. Dropping some food dye in water and dropping some food dye in glycerin should serve to convince you that the rate of diffusion—the movement of solute in a solution—can vary significantly from solvent to solvent. (For a better show, view these diffusions from the side.) But then again, viscosity does not always inhibit a reaction. Sometimes viscosity can enhance the reaction rate by holding the reactants together.

But even when the reactants are able to collide, not all collisions result in a reaction, just as not all dates end in marriage. Once again, the conditions have to be right. For one, the orbitals have to be aligned just so and the collision has to occur with sufficient energy. A bumper-to-bumper, two-car encounter at five miles per hour may not even cause a dented fender. But a side-on collision at forty miles per hour could crush in the side of a car. So in order for a reaction to occur, the reactants have to come together, and they have to have a specific orientation. They have to have the right energy, too.

Given what we know about molecules and their motion, we can do certain things to manipulate reaction rates. For one, we can control concentration. The idea is straightforward—the bigger the crowd, the greater the chance for reaction. But as noted in the directions for the first demonstration given above, the increase in rate is not always directly proportional to the increase in concentration. If the reaction, for instance, is not just one step but a series of steps (as most reactions are), then there can be a complex response to concentration increases. For some reactions, higher concentrations of some reactants can actually impede a reaction.

Another factor that can influence the rate of a reaction is the physical state of the reactants. Ground-up chalk will dissolve much more quickly in vinegar than a solid stick of chalk. The phase of the reactants can also influence the rate of the reaction: liquid gasoline burns; gasoline vapor explodes. Foreign surfaces are always present in a reaction, even if it is just the surface of the container, so they have to be considered, too. Sometimes these surfaces increase the rate of reaction by holding one reactant

in an advantageous orientation. Sometimes surfaces impede the reaction by promoting a reverse reaction or by cooling the reactants on collision.

Temperature is virtually always a major factor because it is important on so many levels. The vast majority of reactions speed up as the temperature increases because raising the temperature increases the speed at which the molecules are zooming around, which increases the number of collisions and the energy of the collisions. One of the mammalian responses to infection or injury is to raise the body's temperature so that (among other effects) the immune system reactions and repair reactions will occur more quickly. Increasing the temperature usually increases a reaction rate, but not always. If a certain step in a reaction produces heat, then increasing the temperature, adding *more* heat, can drive this reaction step backwards and end up slowing the reaction down. Predicting and manipulating reaction rates is rarely straightforward.

The state that is halfway between reactants and products, called the *intermediate*, or *activated complex* must also be considered. The intermediate might be thought of as the batter when making a cake. You start with shortening, eggs, flour, sugar, and milk (the reactants), but before they become the cake (the product) they have to go through an intermediate state, the batter.

Every reaction goes through an intermediate, however short lived. The reactants have to come together and form a complex in which the orbitals are rearranged and the product formed. It always requires energy to form this activated complex, this intermediate, though the amount of energy may be very small or very large. Chemists speak of an *activation barrier*, meaning the minimum amount of energy that is required to form the intermediate and then kick it down the hill to the product side. This activation barrier can be understood in terms of any human endeavor: it takes energy to go from idea to finished product, no matter how desirable the finished product may be. In chemical reactions, it requires energy to get over the initial hump in going from reactants to products, even if energy is given off by the overall reaction.

At other times, however, the situation can be helped (finally some good news); sometimes a catalyst can be found that will speed up the desired reaction. A catalyst is a substance that lowers the activation energy required for the reaction. A catalyst does not change the amount of product produced; it just makes the reaction faster. A catalyst would be like a moving sidewalk at an airport: it doesn't bring the terminals any closer together, but it does reduce the amount of energy required to move

from terminal to terminal and it speeds up the rate at which you can walk there. To further extend our analogy, the moving sidewalk conveys travelers from terminal to terminal but doesn't leave the airport itself. A true catalyst enters into the reaction, but it is not used up in the reaction.

Enzymes are catalysts. The dietary supplements that help the body digest dairy products or roughage such as beans are, in fact, enzymes. Enzymes are sometimes added to detergent to speed the breakdown of stains. A catalytic converter in a car speeds the breakdown of nitrogen-oxygen and carbon-hydrogen compounds into more innocuous nitrogen gas, oxygen gas, water, and carbon dioxide. Catalytic converters have to make these reactions very fast to keep up with the exhaust of a standard automobile.

For some catalysts, the mechanism for the catalytic action is fairly well understood. Biological enzyme catalysts, for instance, may be structured so that intermolecular forces will hold reactants together in an optimum position for reaction. These enzymes act like hands screwing a lid on a jar. To screw a lid on a jar, a jar and the lid could be tossed together in a bag until they eventually found each other, and the lid landed just right and twisted. But if this were the only way a jar could gain a lid, it would take a very long time to screw lids on jars. Two hands can bring the jar and the lid together and get the job done a lot faster. A sketch of an enzyme acting in this manner is shown in figure 1.17.1.

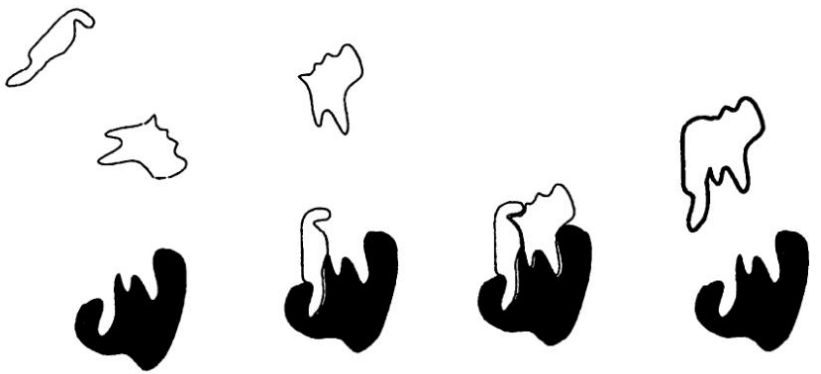
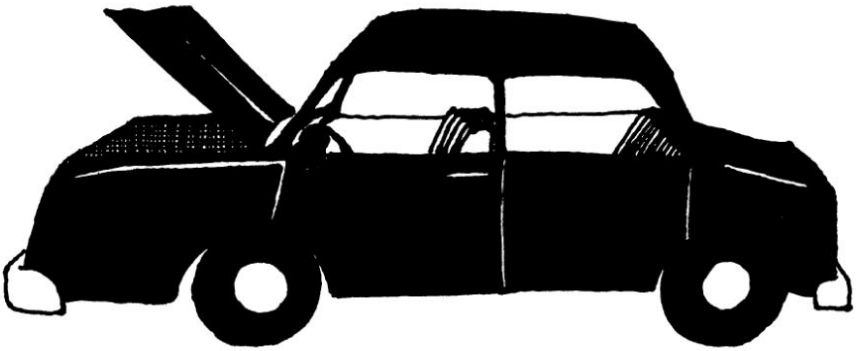


Figure 1.17.1. Some enzymes speed up reactions by holding the reactants together in the right orientation. The reaction is shown in four steps going from left to right. First the reactants (white) are floating freely in solution. Then they attach to the enzyme (black). Held together, they react. The finished product leaves the enzyme and the enzyme is free to catalyze another reaction.

For other catalysts, the mechanism is less well understood, and the basis for choosing a catalyst for a particular reaction is still something of an art. For instance, a copper wire will catalyze the decomposition of hydrogen peroxide much better than a similar strand of steel wool. This difference can be demonstrated satisfactorily by putting on safety glasses and then dropping a copper wire in a half cup (120 milliliters) of drugstore hydrogen peroxide and a few strands of steel wool in a similar hydrogen peroxide sample. Along the copper wire there will be bubbles as the hydrogen peroxide breaks down into oxygen gas and water.

Because of the many factors that influence reaction rate—concentration, temperature, catalyst—and the fact that the reactants come together randomly and not always in the right orientation or with the right energy, there is no straightforward recipe for predicting reaction rates. Chemists are making good progress, and maybe some day we will know enough to control reaction rates completely, but for right now, for most reactions, we are stuck with the speed limits that nature has posted.



## For Example: When Your Car Comes Knocking

The word *explosion* is often associated with devastation, but it really means just a very rapid reaction—so rapid that the surroundings don't have time to accommodate the change. In our modern world, explosions are as common as breathing. The internal combustion engine can generate some several thousand explosions per minute.

It seems odd that the internal combustion engine has only been around for a century or so while humankind has been making explosions for several thousand years. The explanation, of course, has to do with all

the engineering that was necessary to harness the explosions, including how to make several explosions operate at once and have them all work together. In other words, it's all in the timing.

In an internal combustion engine, gasoline and air are mixed in a sealed cylinder that houses a movable piston. The piston moves up and compresses the gasoline-air mixture, which is then ignited with a spark. The resulting explosion pushes the piston down, and the downward motion moves a lever that turns the driveshaft. The explosions are timed so that when one piston is pushing down, part of its downward force is being used to move another piston up, seesaw fashion—or at least that's what happens when things are going right. One of the things that can go wrong is a condition called "engine knock," an imperfect explosion that can result in "pinging," or sudden loss of power. The cause of engine knock can be understood in terms of chemical reaction rates.

In a simple picture of an engine operating, it may appear that a piston moves up, compressing the gasoline-air mixture, until it reaches the top of its upward stroke, and then the spark plug fires, the gasoline explodes, and the piston moves down. But this simple picture neglects the fact that the burning of gasoline is a chemical reaction and like all other chemical reactions, including explosions, does not happen instantaneously. The explosion takes time to propagate though the gasoline-air mixture.

To account for the fact that the explosion takes time, the spark is usually set to occur right before the piston reaches the top of its upstroke. This way the piston will receive the shove from the explosion of gas just as it is ready to start moving down, and it will benefit from the full impact of the explosion. If the explosion were to start right at the top of the piston's stroke, then the piston would already be moving away as the full force of the exploding gases were moving toward it, and the impact of the force would be lessened. If the spark were to occur too far in advance of the piston, then the full explosion could meet the piston on its way up and work against the power stroke of the other pistons down the line.

The benefit of all this intricate timing can be destroyed, however, by unauthorized ignition. If something happens to cause the gasoline-air mixture to ignite before the spark plug has a chance to spark or causes the mixture to start burning at several places at once, the result will be shock waves. These uneven and unaccounted for pressures can seriously interfere with the functioning of the piston.

Temperature, as we've seen, is an important factor in reaction rates. Increasing the pressure, as you may recall from our discussion of the gas phase, can cause an increase in temperature. It is possible to heat the gasoline-air mixture to its ignition point by pressure alone, and, in fact, diesel engines are based on this concept. Diesel engines do not have a spark plug but rely on compression to ignite the fuel-air mixture. If this occurs in a nondiesel engine, however, it spells uncontrolled burning and trouble. The gasoline-air mixture has to be carefully regulated in a well-tuned engine to prevent knocking.

Another factor is fuel. If the gasoline is of a grade that is better able to withstand the temperatures and pressures within the cylinder without spontaneously igniting, then knock is less likely. A fuel with a high "octane" rating is formulated to resist burning until it is sparked.

The name *octane* denotes a compound with eight carbon nuclei in its structure. The *octane rating* of gasoline originally meant the ratio of a particular type of octane (there are several ways to arrange eight carbons in a chain) to a particular seven-carbon chain. Since its inception, however, the term has evolved to describe the burning characteristics of a fuel more than its exact composition. For instance, when it was found that certain lead compounds could improve the burning behavior of gas and thereby avoid knocking, lead additives were said to raise the "octane" level of the gasoline.

Fortunately, engine design is also a factor in preventing knock, so when it was found that lead in the fuel became lead in the environment, cars were redesigned to accommodate a lower octane-rated fuel. But shouldn't all cars routinely use a high-octane fuel anyway, just to be on the safe side? Not necessarily. Some cars run better with a lower octane fuel. The benefit from a high-octane fuel will depend on engine design, age, condition, location, tuning, and time of the year. Experience is probably your best guide. If your car is running well, don't knock it.

## Demonstration 18: Black-Light Chemistry, Paper-Clip Chemistry

*The persons who constitute the natural aristocracy are not found in the actual aristocracy, or, only on its edge: as the chemical energy of the spectrum is found to be greatest just outside of the spectrum.*

—Ralph Waldo Emerson, *Essays*, ca. 1830

In our catalog of the many factors that influence engine performance, one we did not list was intensity of sunlight because the reactions in engines take place where the sun doesn't shine. But sunlight does affect cars. The chemicals in car paint, tires, and plastic fixtures can be degraded by the sun. In fact, light can be a factor for many reactions. Light can also be a mysterious factor because many times it is not just light, but the type of light, that matters. To demonstrate the effects of light on a chemical reaction, revisit the demonstration of the last chapter in which we measured the rate of bleaching of an indicator solution.

Put on your safety glasses, then set up the cups with bleach as before, but this time expose one of the solutions to the black light suggested for purchase in the "Shopping List and Solutions." The black light should be moved to within an inch of the solution's surface for maximum effect. The

light should shine directly on the surface, not through the glass or plastic of the container. The exposure should be for about fifteen minutes. Take care that the other solution is not exposed to the black light. Now add equal drops of indicator to the cups of bleach and time how long it takes for the color to fade. The reaction should run significantly faster for the solution that has been exposed to the black light because the bleach has been *photochemically degraded*; that is, the black light has caused the bleach to be chemically broken down into more reactive species.

Now, with safety glasses still in place, pour about a half inch (1 centimeter) of copper sulfate solution (made as directed in the "Shopping List and Solutions") into a disposable glass or plastic cup. Unbend a paper clip and allow one end to dangle in solution. Put one end of a galvanized nail into the solution, taking care not to touch the paper clip. Put one end of a length of aluminum wire into the solution, making certain it doesn't touch either of the other metals. Wait about an hour and then take the metals out and examine them. The paper clip should have a nice copper coating, the galvanized nail should be darker where it has touched the solution, and the aluminum wire should be unchanged. With the paper clip and the galvanized nail, electrons at the surface of the metal have been transferred to the copper ions in solution. Metallic copper formed when the ions accepted the electrons. Copper deposited on the paper clip and nail surface as iron in the paper clip and the nail ionized and dissolved. The electrons, however, have a harder time leaving aluminum. An exchange of electrons through solution or through metal is termed *electrochemistry.* We'll investigate more of these reactions—and their causes and consequences—next.

# CHAPTER 18

## Electrons and Photons: Turning on the Light

*The lightning that preceded it*
*Struck no one but myself,*
*But I would not exchange the bolt*
*For all the rest of life.*
*Indebtedness to oxygen*
*The chemist may repay,*
*But not the obligation*
*To electricity.*

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

What do fireworks and fall foliage have in common? Photochemistry: chemistry in which light is a product or reactant. In fireworks light is a product and evident to the eye. In producing fall foliage, light is a reactant: placing a paper bag over a clump of deciduous tree leaves will prevent them from turning colors. Light is a reactant in fall's most famous reaction.

What do batteries and bumpers have in common? Electrochemistry: chemistry in which electricity is a product or reactant. Batteries produce electricity via chemical reactions and create enough electrons to light up

a lightbulb. Electroplating employs a stream of electrons to reduce a metal, such as chromium, onto a surface, such as the bumper of a 1956 Crown Victoria. What do photochemistry and electrochemistry have in common? Both are types of reactions that involve small particles that are not atoms but that do chemistry. In electrochemistry the particles are electrons, with which we are now familiar. In photochemistry the small particles are photons, which beg a bit of explanation.

We begin with the nature of light. Light can be characterized as an *oscillating electromagnetic field*, a term that wants dissecting on its own. In the physical sciences, a *field* is an effect that extends out over a region of space. For instance, if there is a bonfire in the middle of a back yard it will create a temperature field: the temperature will be highest where the fire is centered, then extend out and gradually diminish with distance from the fire. An *oscillating field* is a field that varies regularly with time. An oscillating fan blowing over a block of ice could serve as an example of an oscillating temperature field. An *oscillating electromagnetic field* is an oscillating electric field accompanied by an oscillating magnetic field.

You can demonstrate the relationship between electricity and magnetism by using a nail, a length of wire, a D-cell 1.5-volt battery, and a battery holder (the last item being optional). The wire is wrapped around the nail in a series of tight coils and then the ends are attached to (or held to) the ends of the battery. As a result, the nail becomes an electromagnet that will pick up paper clips. The magnet can be switched on and off by connecting and disconnecting the battery. The wire may become hot, so don't keep it attached longer than necessary. Never store a battery with wires attached, as they may come in contact and become hot enough to ignite flammable material.

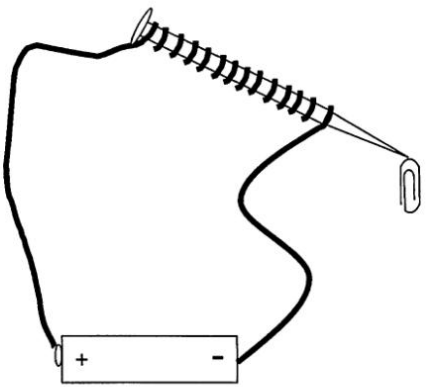


Figure 1.18.1. A homemade electromagnet can pick up paper clips.

Why does a moving current create a magnetic field? To be perfectly honest, no one has completely explained it yet, so we won't try here. Suffice it to say that the effect is well established and makes for some interesting chemistry, too.

Why would an oscillating electromagnetic field have anything to do with chemistry? As may be recalled from our discussion of atomic structure, the atom itself has an electric field, as we illustrated with our "Water Witch" demonstration. The electron has a negative charge and the proton has a positive charge, and the two are separated, so there is a field—an attraction—between the electron and the proton. The molecule may absorb energy from the oscillating electromagnetic field of light as the electrons are pushed and pulled from their normal positions, as a child in a swing will absorb energy from the parent as the child is pushed from the equilibrium position in the swing. All of chemistry boils down to a rearrangement of electrons, so electrons pushed around in this manner may find themselves in new situations, which may result in new materials.

But why did we say that light *may* interact with atoms? If light is an oscillating electromagnetic field and the atom contains an electric field, shouldn't light *always* interact with atoms? The answer may be found in another question you may have asked yourself during the demonstration for this chapter: Do I have to buy a black-light lamp? Those things are expensive! Can't I just use a regular lightbulb or just set the solution out in the sun?

The answer is that the black light provides extra ultraviolet light (UV light), the type of light needed for the reaction. The action of UV light also explains why chlorine levels in swimming pools have to be monitored. They cannot be counted on to change by the same amount every day because there is not the same amount of sunlight every day. But if the sun gives off ultraviolet radiation, why don't we just set the reaction outside and save the expense of a black-light lamp? The answer is that ultraviolet light isn't the only light emitted by the sun, and the presence of other types of light would confuse our experimental results. The sun also gives off visible light and infrared light, and the latter is capable of heating the solution. As we mentioned in our discussion of chemical kinetics, heat can speed up a reaction. So if we set our solution in the sun, we would not be certain if it were the UV light or the heat causing the breakdown of the bleach. The type of light needed for a reaction is very specific because the type of electric field surrounding a molecule is very specific. The field depends on the nature of the elements that make up the molecule and their positions in the molecule.

The energy carried by light depends on the type of light. The type of

light that would heat our solution if we put it in the sun (infrared) is relatively low-energy light; the visible light that our eyes respond to is a moderate-energy light; and the UV radiation that caused the chemical reaction is relatively high-energy light. UV is the type of light that can cause skin damage if we stay out in the sun too long. The light required for a chemical reaction can be so specific that the light can be thought of as a stream of energy packets, each particle causing one chemical change. These energy packets are called photons, and they can be counted, just as we count electrons, molecules, and atoms.

How can light be a particle *and* a wave? This question has confounded generations of chemistry and physics students, especially because the answer is that it is neither—and it is both. Light can be modeled as a particle when the particle model is convenient, and it can be modeled as a wave when the wave model is convenient. Neither model captures the true essence of light, just one aspect.

An analogy might be found in the common house cat. Is a house cat a domestic animal or a wild animal? A cat behaves as a domestic animal when it comes when called for food or for affection, but it behaves as a wild animal as soon as a spider has the bad fortune to scuttle across its path. So is the cat domestic or wild? Sometimes one description works, sometimes the other. The cat is neither and it is both. Our light is sometimes described well as a particle and sometimes as a wave.

We've already seen that light is able to induce chemical reactions, but how can we show that chemical reactions are able to produce light? Probably the easiest way is to go to a county fair or a circus or a novelty store and buy a glow stick. These plastic-encased elongated tubes are activated by bending and/or twisting until a membrane separating two solutions is broken and the solutions mix and react. These solutions contain materials that phosphoresce when they react, and the observed effect can be quite pleasing. Another example can be found in fireworks. The metal salts in the fireworks are heated by a gunpowder explosion to the point where the electrons are disturbed in their orbitals. As the atoms relax back to their more comfortable, stable state, they emit excess energy in the form of light.

Photochemistry, chemistry caused by light, is responsible for many of the atmospheric reactions that determine the quality of our air. Photochemical smog is the name given to the red-brown haze that can form over cities under certain weather conditions. Nitrogen (as $N_2$) and oxygen

(as $O_2$) are natural components of the atmosphere and can form NO in lightning strikes. NO reacts with $O_2$ to form $NO_2$, which dissolves in rainwater and falls to the ground. Here the nitrogen can be latched onto by bacteria and, through a series of reactions, make proteins for plant and animal life forms. Unfortunately, there is another not-so-natural source of atmospheric $NO_2$, and that is from the cylinders of automobiles. The resulting $NO_2$ would not be a problem if it were present in small amounts, but in large quantities it can cause damage. Released into the atmosphere, $NO_2$ can absorb UV light from the sun and break down into NO and O again. The difficulty is that O can then react with $O_2$ to form $O_3$, commonly called *ozone*. While ozone in the upper atmosphere is a good thing—it shields Earth's surface from the full force of the sun—down at street level, it isn't so good. Ozone damages rubber, plastic, plants, and animals and reacts with car exhaust to form irritating pollutants.

So energy from light causes some chemical reactions. But why do some reactions give off light? Because a chemical reaction consists of a rearrangement of electrons, and depending on the reagents and products, these electrons may find themselves in product molecular orbitals that are not at the lowest energy. Just like the electrons in our fireworks, as they work their way back to a stable ground state, they may emit light.

There is another way in which electrons can be rearranged in a chemical reaction, and that is through a wire. Electrochemistry is redox chemistry wherein the site for oxidation is separated from the site for reduction. Electrochemical setups basically come in two flavors: electrolytic and voltaic (also known as galvanic) cells. Voltaic cells are cells that produce electricity, so a battery would be classed as a voltaic cell. The principles that drive voltaic cells are the same that drive all other chemical reactions, except the electrons are exchanged though a wire rather than direct contact. The reactions are redox reactions (which is why they produce an electron current); the reactions obey the laws of thermodynamics and move toward equilibrium (which is why batteries run down); and the reactions have defined rates (which is why some batteries have to be warmed to room temperature before they produce optimum output).

But electrochemical reactions have to obey the laws of electronics as well as the laws of chemistry, so even if the solutions are connected by a wire, the circuit has to be completed or the electrons will travel only so far and no farther. Contact is normally achieved by an ion-containing

solution called an *electrolyte*. Because ions are charged particles that move in the electrolyte, they are able to conduct charge from the oxidation site to the reduction site as the electrons move through the wire. In batteries that you buy from a store, the electrolyte is usually in the form of a moist paste rather than a liquid. But in high current-producing car batteries, the electrolyte is usually sulfuric acid.

A lemon is acidic, so lemon juice actually makes a fair electrolyte, too. While wearing safety glasses, stick a zinc-coated nail (a galvanized nail) in one end of a lemon and a penny into a narrow slit on the other end. Now measure the voltage between the nail and the penny with a hardware store voltmeter, attaching the negative lead to the galvanized nail and the positive lead to the copper. The actual voltage measured will depend on the lemon and other factors.

The reaction in the lemon battery is the reduction of copper ions (a little bit of copper dissolves from the copper penny in the acidic lemon juice) and the oxidation of zinc into zinc ions—the thermodynamically more stable state. Because the reaction is moving toward a more stable state, it can produce electricity as a voltaic cell. An electrolytic cell is the antithesis of the voltaic cell. In the voltaic cell, a chemical reaction is used to produce electricity. In an electrolytic cell, electricity is used to produce chemistry. A demonstration electrolytic cell can be set up as follows.

Make certain you are still wearing safety glasses and then take your copper-coated iron nail from the first demonstration and dangle it in a glass with about an inch of the freshwater aquarium pH-lowering solution suggested for purchase in the "Shopping List and Solutions." Hook it via a wire to the positive end of a D-cell battery in a battery holder. Add a companion iron nail to the solution and hook it to the negative end of the same battery. The copper will gradually leave the first iron nail and plate out on the second. This process, called electroplating, has been used to add metal coating to everything from furniture to jewelry. The purpose of electroplating can be decorative, but is usually more practical. Electroplating can successfully seal a reactive metal, such as iron or iron alloy, from the corrosive affects of moisture. Why is moisture damaging to iron? One would think that a steel bridge that can withstand the weight of tons of traffic every day would be able to withstand a few drops of water. But water drops on iron form an electrochemical cell just as an iron wire

connecting two solutions. In the rust-forming reaction, iron is oxidized to iron oxide, which is rust, and oxygen from the air is reduced to water. To demonstrate that this reaction happens at two different sites—one for oxidation and one for reduction—unwind a paper clip and set it half in and half out of a glass of vinegar for a couple of days. Then take it out and look at it under a magnifying glass. You should see the rust piled up at one specific location and below this spot a small clean-looking area. Rust forms above the solution because the reaction requires oxygen.

So now we have demonstrated that fireworks and fall foliage have something in common, and batteries and bumpers have something in common. But in this chapter, we have grouped all four together, so what do fireworks, fall foliage, batteries, and bumpers *all* have in common? The answer? Solar energy.

## For Example: Photon Meets Electron—Solar Energy

Basking lizards and sunflowers were taking advantage of solar energy long before intelligent life came along. Broadly speaking, we could say that all life is based on solar energy. But we have added a little technology over the years. To begin with, we have borrowed from the lizard idea and developed solar collectors that absorb energy from the sun and store it. We have also developed photovoltaic cells that turn light from the sun into an electric current. Photovoltaic cells are being used successfully to power small devices such as calculators and even for large-scale energy production in areas where the sunshine is abundant. Scientists are also

working on other creative technologies that will tap into the abundant energy from the sun. One of these is use of solar energy for the electrolytic degradation of pollutants.

Some of the more difficult pollutants to deal with are the organic pollutants that derive from fertilizers and insecticides. Organic compounds are the types of materials that make up oils, waxes, and plastics and can be very resistant to attack by water, simple salts, or even acids and bases. However, organic materials can be broken up by putting them in an electrolytic cell and driving electrons through them or removing electrons from them. But the electrons have to come from somewhere. If the current is produced in an oil-burning plant, then the process of breaking down pollutants creates pollutants, and we're back to square one. Fortunately, there are materials such as titanium oxide particles.

Titanium dioxide is used in paints because of its pure white color. When the sun is out, the titanium oxide particles can absorb the solar radiation and use this energy to promote its electrons to an excited, more reactive state. These electrons then act like tiny electron sources on diminutive batteries to break down organic pollutants, molecule by molecule. So as in the Aesop tale—the quarrel between the sun and the wind as to which was the stronger—that which resists force can often be conquered by gentle persuasion. The warm, welcome light of the sun.

# PART 2

# INTRODUCTION

## Playing the Tunes

*"I am happy," said M. Waldman, "to have gained a disciple; and if your application equals your ability, I have no doubt of your success. Chemistry is that branch of natural philosophy in which the greatest improvements have been and may be made: it is on that account that I have made it my peculiar study."*

—Mary Shelley, *Frankenstein*, ca. 1820

We have covered a great deal of territory. We discussed the nature of chemistry, the structure of atoms and chemical compounds, and the properties of elements as reflected in the periodic table. We explored fundamental classes of chemical reactions such as redox reactions, acid-base reactions, and displacement reactions. We laid out the theory that describes the nature of the chemical bond and the principles of chemical reactions. We discussed the practical considerations of intermolecular forces and concentration and considered the rarefied properties and reactions of gases. We contrasted the slippery properties of solutions with the concrete properties of solids. We delved into thermo-

dynamics and explored phase equilibrium. We examined the important concept of chemical equilibrium, and we saw how the principles of thermodynamics predicted the observed colligative properties of solutions. We looked at the precepts of chemical kinetics, and we wrapped up our survey of the principles of chemistry with a look at chemistry induced by electricity and light.

Whew!

A lot of head scratching and page turning, but now we are ready for a payoff: seeing how these basic principles come together in some of the remarkable specialized fields of chemistry—organic chemistry, inorganic chemistry, biochemistry, and analytical chemistry—and a look ahead to an intriguing future.

Before we begin, let us indulge in a bit of an overview.

Organic chemistry and inorganic chemistry are not *applications* of chemistry so much as they are *explorations* of chemistry, but explorations with specific goals in mind. The organic chemist is interested in the chemistry of hydrocarbons: materials made from covalently bonded carbon and hydrogen. The objective of organic chemistry is to synthesize and understand the properties and reactions of the interconnected, looping chains of hydrocarbons in all their infinite variety. These materials are found throughout our oily, waxy world and in the materials from which our bodies are made.

The inorganic chemist investigates the materials made from the other one hundred and some elements on the periodic table, an enormous undertaking. But while these compounds are rich and intricate in their behaviors, they do not form long, interconnected chains like the hydrocarbons do, so their diversity is in their elemental composition. Inorganic materials form the rock and salty solutions of Earth, the planets, and all the materials of the stars. Inorganic chemists devise syntheses for semiconductors, superconductors, alloys, and many other new materials.

The biochemist studies the identity, properties, and interactions of the materials that are the foundation of life. This important, exceedingly complicated endeavor draws from all disciplines of chemistry and employs all the principles of chemistry to understand the chemical reactions that drive the rhythms of life.

The analytical chemist draws from all of the above. The objective of

the analytical chemist is to identify and quantify materials—be they organic, inorganic, or biochemical—sometimes by separating them from the soup and sometimes as they sit in their murky matrix. Each chemist must have some command of the art of analyzing chemicals for their composition and concentration. The analytical chemist finds employment as an integral part of academic, industrial, and governmental laboratories. We will gain some appreciation for the virtuosity of the analytical chemist by following some of the adventures of a special breed of analytical chemist—the forensic chemist—during the course of an interesting day.

And so, to the lab. . . .

# Organic Chemistry Demonstration: Aspirin to Acid

*It was in their undergraduate days, however, in the midst of their profoundest plunges into the mysteries of organic chemistry, that Doris Van Benschoten entered into their lives.*

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

*When I had succeeded in dissolving the hydrocarbon which I was at work at, I came back to our problem of the Sholtos, and thought the whole matter out again.*

—Arthur Conan Doyle, *Sign of the Four*, ca. 1890

Owing to several unique properties of carbon, such as its ability to form long chains, organic compounds—carbon compounds—come in virtually infinite variety. Organic chemists spend their time studying the ways that carbon reacts with itself and other compounds and